DEPARTMENT OF URBAN INNOVATION
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EVALUATION OF IRON APPLICATION METHOD TO REMEDIATE COASTAL MARINE SEDIMENT

By

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ABSTRACT

Sediment is the important habitat for organisms and act as a store house for nutrients in aquatic ecosystems. Hydrogen sulfide is produced by microorganisms in the water columns and sediments, which is highly toxic and fatal to benthic organisms. However, the irons have capacity to regulate the formation of sulfide by poising the redox sequence and to form insoluble iron sulfide and pyrite compounds. Therefore, we conducted two experiments aimed to evaluate the remediation efficiency of iron application to organically enrich and improve sediments environment. Experiments carried out in the laboratory using intact sediment cores taken from Mikawa Bay, Japan at every month from June to September 2017 and October 2018.

In Experiment 1, after cores were collected, the iron powder or iron hydroxide were applied to the surface sediment with 5 g/ m2, or 5.6 g/ m2, respectively.

In Experiment 2 we experimentally investigated the removal of hydrogen sulfide using (2mm or less and 2 to 5mm) of the steelmaking slag.

Experiments are conducted both in the laboratory with the same boundary conditions. The overlying water were replaced with deoxygenated filtered seawater and cores were sealed a top cap to keep anoxic condition with a stirrer to circulate the overlying water gently. The incubation experiments have been set in three treatments included the control and each treatment replicated and were conducted with the same temperature of the in-situ conditions. Water samples were collected to measure the dissolved sulfide concentrations in the overlying water at appropriate time intervals by the methylene blue method. Sediment quality was also analyzed after completion of the experiment.

After the 21 days incubation, experimental results using iron powder and ferric hydroxide revealed that application of these iron containing materials significantly reduced sulfide release flux from the sediment into the overlying water, the average dissolved sulfides concentration in the overlying water of treatment group was significantly decrease ($p = .0001$). While, no significant difference was observed between the control group after 21‑day incubation. Therefore, the application of iron to the sediment is a promising method to remediate contaminated sediments in eutrophic water body, although ferric hydroxide has better hydrogen sulfide removal effects.

Experiments using the steelmaking slag also clarified the fact that capping with (2mm or less and 2 to 5mm) of slag steelmaking is an effective technique for remediation of bottom sediments enriched organic containing hydrogen sulfide because it leads to the induction of chemical reaction between Fe and sulfides occur in sediments which did not occur in conditions naturally. Although (2mm or less) of slag steelmaking has better hydrogen sulfide removal effects. Because of the economic reasons, the application of steelmaking slag to the sediment is a promising method to remediate contaminated sediments in eutrophic water body.

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I.   INTRODUCTION

1.1   Sources of pollution overview

Pollution is the introduction of harmful materials into the environment. Environmental pollution refers to any physical, chemical or biological alteration in the quality of air, water or soil to a degree that is harmful to living organisms. These harmful materials directly or indirectly change in any component of the biosphere that is harmful to the living components and on particular undesirable for human. There are various types of environmental pollution namely but, the three major types of pollution are land pollution, air pollution, acid rain and water pollution (Coker, 1990; Flower, 2006).

Over two thirds of Earth's surface are covered by water; less than a third is taken up by land. As earth's population continues to grow, people are putting ever-increasing pressure on the planet's water resources. It was once popularly believed that the oceans were far too big to pollute. Today, with around seven billion people on the planet, it has become apparent that there are limits. Marine pollution is one of the signs that humans have exceeded those limits. Water pollution happens when toxic substances enter water bodies such as lakes, rivers, oceans, aquifers, groundwater and so on, getting dissolved in them, lying suspended in the water or depositing on the bed. This degrades the quality of water. Although, pollutants can be natural, such as volcanic ash, they can also be created by human activity, because, it's a matter of fact that, the majority of pollutants going into the ocean come from activities on land. Since water is the basis of life, water pollution is a global challenge that has increased in both developed and developing countries, undermining economic growth as well as the physical and environmental health of billions of people. Therefore, management of water quality increasingly requires an integrated approach to pollution control at the lakes and oceans, and bottom marine sediments are sensitive indicators for monitoring pollutants as they act as a sink and a carrier for contaminations in aquatic environment. Water clarity is a measure of the amount of particles in the water, as particles that settle on the beds of waterbodies slowly build up the sediment compartment of the aquatic ecosystem. Sediments can become contaminated either by the settling of contaminated particles or by precipitation of soluble contaminants out of the water column. Moreover, sediments in suspension in the water

column in significant concentrations may cause physical effects that are hazardous to aquatic life, even if they are not contaminated by pollutants (Rome, 2000; "Sediment," n.d.; Richmondvale Blog," n.d.; Pengra, 2012; Flower, 2006; Klein & Bartnicki, 2018).

Besides, various organisms in both marine and freshwater environments rely on replenishment of sediment for their reproductive habitat, changes to sediment (either too much or too little) can change substrates. As well as freshwater sediments, marine sediments can keep high levels of biodiversity and support biogeochemical processes that are pivotal to life on Earth. Sediments can cause water to become cloudy, or "turbid", making it difficult for fish to see and feed properly. Sediments can also damage fish gills and impair the feeding and breathing processes in aquatic. So, this proves that, sediment is the important habitat for organisms and act as a store house for nutrients in aquatic ecosystems.

While freshwater and marine ecosystems are experiencing numerous anthropogenic stressors that threaten ecosystem stability and the organisms that live in marine sediments, one of the major shortcomings of marine is low oxygen levels in the water there have led to reproductive problems for fish and shrimp. So, it's called dead zones that are areas of large bodies of water typically in the ocean but also occasionally in lakes and even rivers that do not have enough oxygen to support marine life (Problem, 2014; Amita Bhaduri, 2019;Carstensen, et al., 2014; Krumins et al., 2013).
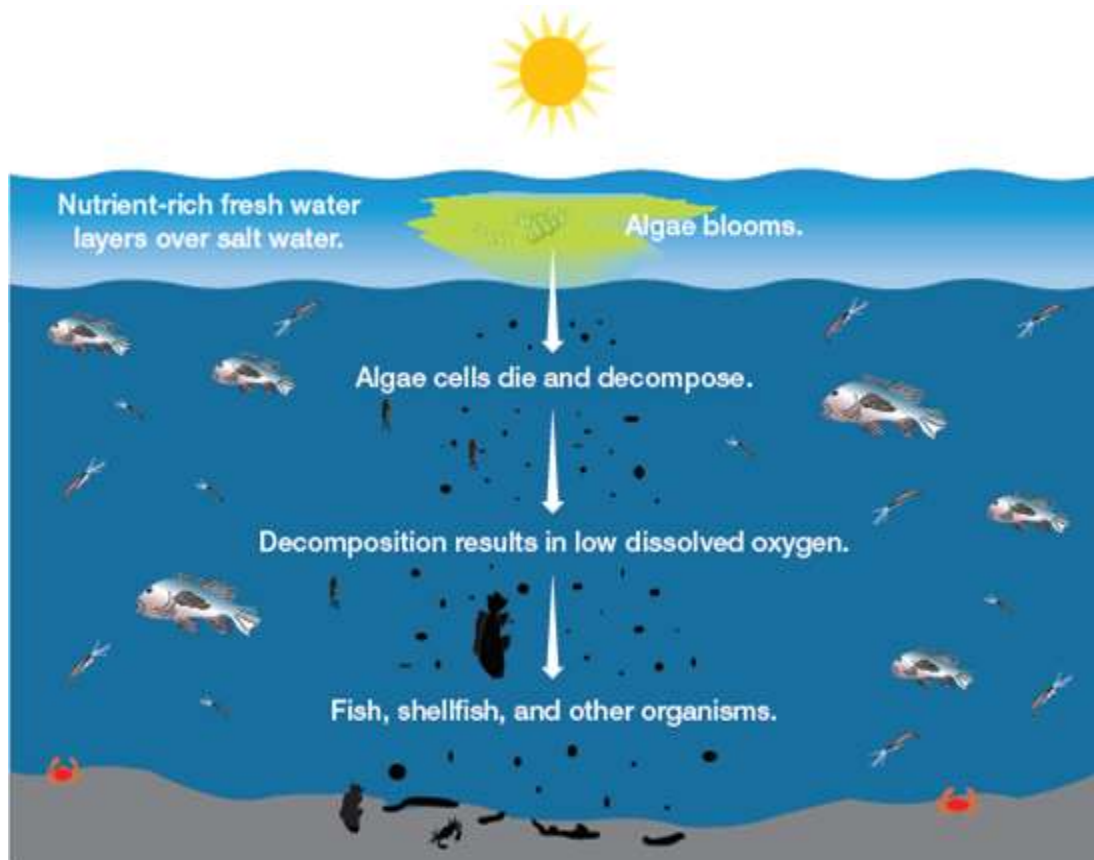
Figure 1.1.1 Factors that lead to dead zone formation in Gulf of Mexico ((Problem, 2014).

As mentioned above, aquatic organisms need a certain amount of dissolved oxygen (DO) in order to survive, therefore, dissolved oxygen (DO) is a key element in water and sediment quality that is necessary to support aquatic life. There are two ways that dissolved oxygen (DO) enters water, diffusion from the atmosphere and photosynthesis by aquatic plants. Since oxygen is a byproduct of photosynthesis, when aquatic plants and algae are exposed to sunlight they produce oxygen as a waste product of photosynthesis. Therefore, water with lots of aquatic plants have higher levels of dissolved oxygen, since submerged plants produce oxygen through photosynthesis. Typically, dissolved oxygen (DO) concentrations of surface water are highest around midday due to photosynthetic activity of aquatic plants. While, the lowest levels of dissolved oxygen (DO) usually occur in the morning, because photosynthesis stops at night while respiration continues. From the air, oxygen can slowly diffuse across the water's surface from the surrounding atmosphere, or be mixed in quickly through aeration, the mixing of surface waters by wind and waves increases the rate at which oxygen from the air can be dissolved or absorbed into the water.

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Likewise, fast moving water generally has more oxygen than still water, because the movement mixes the air into the water. Thus, oxygen from the atmosphere as well as that produced as a byproduct of photosynthesis may increase the dissolved oxygen (DO) concentration in water. It is then available in the water for consumption by aquatic organisms (Smith, Delorme, & American, 2017; Manual, n.d.; "Photosynthesis in Aquatic Plants," n.d.; Deacutis, 2016; "Instructor's Manual - Dissolved Oxygen - Robert B. Annis Water Resources Institute (AWRI) - Education & Outreach - Grand Valley State University," n.d.).

However, there are some processes that reduce dissolved oxygen (DO) levels in water. The solubility of oxygen, or its ability to dissolve oxygen in water, decreases as the water temperature or salinity increase. aquatic respiration and decomposition. First, the solubility of oxygen decreases as temperature increases. As temperature increases, water tends to hold less dissolved oxygen (DO) so dissolved oxygen (DO) levels in water tend to decrease when it is warmer, and when it is cooler dissolved oxygen (DO) levels tend to increase. Similarly, lower dissolved oxygen (DO) concentrations are expected during the summer, since warm water cannot hold as much dissolved oxygen (DO) as cold water. Also, as barometric pressure increases, the solubility of oxygen increases so levels of dissolved oxygen (DO)tend to increase. Likewise, the solubility of oxygen in water is dependent on salinity, while the partial pressure and the percentage saturation of oxygen is not affected by changes in salinity. This means that in absolute concentration a seawater sample will contain less oxygen than a freshwater sample at the same temperature although the partial pressure is the same. As brackish water lakes often exhibit different salinity levels along the salinity gradients, it is important to properly assess the interaction between the salinity and the release of chemicals representing water quality variables. Accordingly, as salinity increases, less oxygen can be dissolved into the water (Smith et al., 2017;"Dissolved Oxygen - Environmental Measurement Systems," n.d.; "Water Temperature - Environmental Measurement Systems," n.d.; "ＪＷＧ ジャパン・ウォーター・ガード," n.d.; Focus, Understandings, Performance, Addressed, & Level, n.d.; Kim et al., 2017) .

Oxygen is also consumed in the water by respiration of aquatic animals and plants, decomposition of organic matter (OM) by microorganisms, and different chemical reactions. The combined oxygen consumed by all of the biological processes is called 'Biochemical Oxygen Demand (BOD). If more oxygen is being used than is being introduced, organisms may weaken,

move away, or die. In deeper waters, dissolved oxygen (DO) can remain below 100% due to the respiration of aquatic organisms and microbial decomposition. These deeper levels of water often do not reach 100% air saturation equilibrium because they are not shallow enough to be affected by the waves and photosynthesis at the surface (US EPA, n.d.; Muralikrishna, Manickam, & Management, 2017; "Dissolved Oxygen - Environmental Measurement Systems," n.d.).

Organic matter deposited on the seafloor provides food for the benthic communities, either at the sediment surface or upon burial into the sediment layers below, which breakdown of organic matter (OM) is an important process in aquatic food webs. It also has the greatest potential to decrease dissolved oxygen (DO)levels. This is because microorganisms, such as bacteria, rapidly break down available organic matter (OM), consuming oxygen in the process. As the amount of dead organic material increases in water more oxygen is used by bacteria to decompose that material. Generally, marine sediments accumulated on the bottom of enclosed or semi-enclosed water bodies located adjacent to large metropolitan areas are affected by significant terrigenous organic matter loads. Since the oxidative decomposition of organic matter consumes dissolved oxygen within the water column, and high respiratory oxygen demand that quickly leads to the depletion of oxygen in the lower water column, therefore, the result of hypoxic and anoxic conditions arises from an imbalance in the transport rates of organic matter (OM) and oxygen into deeper layers.

As excess organic material is left to be decomposed, and if the amount of oxygen is insufficient, decomposition processes continue due to bacterial activities employing electron acceptors other than oxygen. In some cases, this results in the reduction of sulfate, a major constituent of seawater, because, in the absence of dissolved oxygen (DO) and in the presence of soluble Biological Oxygen Demand (BOD). Under such anaerobic environments, anaerobic microorganisms, dominate the redox reaction between the "organic" and "other than oxygen oxidant". When DO oxidizing power is strongest component is lost, an oxidizing agent such as the following are successively used, the redox reaction proceeds. Among the anaerobic microorganisms, sulfate reducing bacteria (SRB: Sulfate Reducing Bacteria) is a general term for bacteria that oxidize organic matter using sulfate ion (SO4 2-) as an oxidizing agent, thus, in restricted coastal brackish water bodies hypolimnion waters often becomes anoxic due to stratification by a halocline, that allows dwell to below the oxygen penetration depth (generally 10

mm or less) anoxic conditions prevail and bacteria use other oxidants such as sulfate to breakdown organic matter (OM), which by the bacteria catalysed reduction of sulfate releases hydrogen sulfide (Zopfi, Ferdelman, & Fossing, 2004; Yakushev et al., 2007; Ayangbenro, Olanrewaju, & Babalola, 2018).
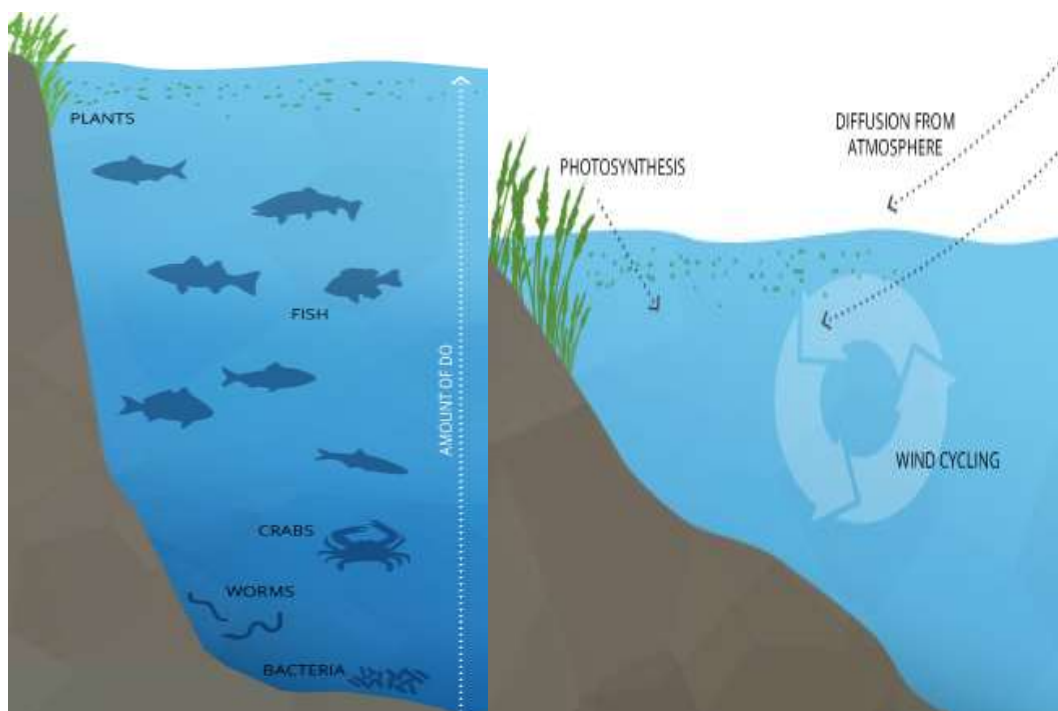
Figure 1.1.2. Dissolved oxygen is important to many forms of aquatic life, it can enter the water as a byproduct of photosynthesis (URL:https://images.app.goo.gl/P7ktwq1Fx6qX1N5X7).

There are three forms of sulfide (H_2S, HS^- and $S2^-$), and they exist in a pH- and temperature-dependent equilibrium. At pH 6, 90% of the sulfide will be present as hydrogen sulfide (H_2S), and the higher the H_2S concentration the greater the tendency for it to volatilize. Conversely, at pH 10, 100% of the sulfide will be present as $S2^-$. However, environments rich in naturally occurring hydrogen sulfide (H_2S) are one form of extreme habitat found in aquatic systems throughout the world. Hydrogen sulfide (H_2S) is highly toxic for aerobic organisms even in micromolar concentrations because it interferes with reoxidation of cytochrome A3 in respiration. In addition, the reduction of species richness in sulfidic habitats is likely directly related to the toxic properties of hydrogen sulfide (H_2S). The toxicity of sulfide to aquatic organisms has been linked with the low levels of dissolved oxygen in water and hydrogen sulfide (H_2S) toxicity increases with lower pH in sediment and water. Toxicity is most likely when this

phenomenon occurs in ponds with water of pH < 7, because the proportion of sulfide in the form of toxic hydrogen sulfide (H_2S) is greatest at lower pH. Sulfide has been viewed as more toxic than ammonia under certain conditions. The USEPA fresh- and saltwater quality criterion for hydrogen sulfide (H_2S) is 2 µg/L, whereas that for unionized ammonia (NH_3) is 35 µg/L. Thus, sulfide, may well be more important than ammonia in determining sediment toxicity. In addition to killing many fish and contaminating shellfish, can kill marine animals including dolphins and endangered manatees. Moreover, anoxic conditions with sulfide may have different consequences because of the toxicity of sulfides are different for many organisms. Consuming contaminated fish can be a major exposure route for humans and it may take months or years of regularly eating contaminated fish to build up amounts that are a health concern. Mothers who eat highly contaminated fish for many years before becoming pregnant may have children who are slower to develop and learn (Lapota, Duckworth, & Word, 2000; Kumar, 2017; Zhao, Biggs, & Xian, 2014; Szabo et al., 2014; Topics, n.d.).

There are a significant number of methods that can be employed to suppress the dissolved sulfide dissolution of the sediment underwater area which depending on the system design and treatment goals, in general, there are two basic ways to control hydrogen sulfide (H2S) (Lochrane, 1977). Regardless of the mentioned method,

First, prevent sulfide formation: Inhibiting bacterial action or moderating the variables affecting hydrogen sulfide (H_2S) generation is often the basis for controlling hydrogen sulfide (H_2S) in wastewater treatment systems (OxyChem, 2014; Thomas, 2007). Treatment options include the following: Figure 1.1.3.

Second, removing the sulfide after it has been formed can be achieved using a variety of chemicals either alone or in combination. The treatment mechanism generally employed is oxidation of the hydrogen sulfide (H_2S) to either sulfur or the sulfate ion. In some cases, the chemical treatment program also promotes bio-oxidation of organic odors (OxyChem, 2014;Thomas, 2007;Zhang et al., 2008). Treatment options include all of the following: Figure 1.1.3.

But, among the often-applied chemical treatment technologies, addition of chemical oxidants gains a great deal of popularity because it is a quick and effective approach in hydrogen

sulfide (H_2S) control.
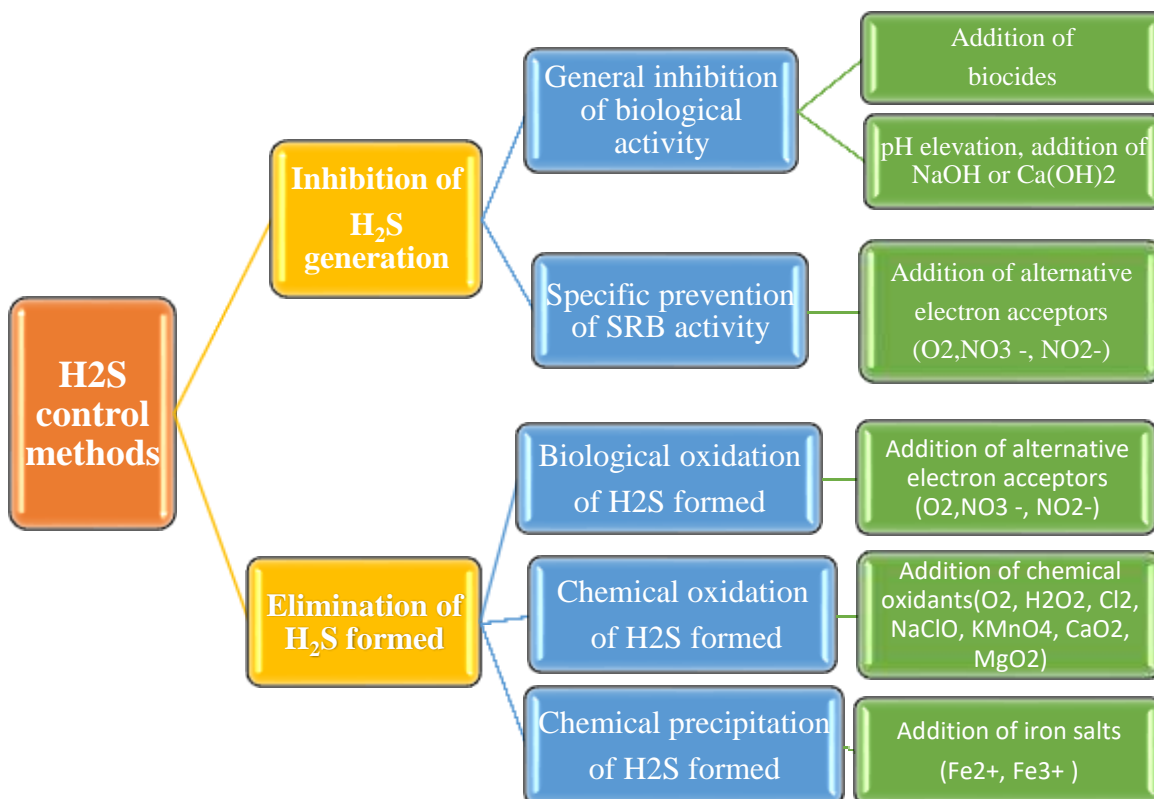
Figure 1.1.3 The techniques available to control hydrogen sulfide

Regardless of the mentioned method, there are a few different methods for suppressing the dissolution of dissolved sulfide from the sediment in these waters, as described below:

1. *Oxygen supply*: oxygen supply to the aeration is a suitable method for very small lake and moats. However, it is practically difficult to implement the supply of oxygen to aeration for large lakes and sea (non-patent document).

2. *Sediment dredging*: dredging of sediment is the method to remove sediment as a source of pollution of the sea and lakes and is widely applied as environmental improvement measures. However, when dredged soil is widely contaminated with various harmful organochlorine compounds, we must take action against pollution, and how to dispose of dredged soil becomes an issue. Moreover, dredging of bottom sediments cannot be applied

to the depression that has been dredged (non-patent document).

3. *Sediment coating*: Coating the bottom sediment is a coating method of bottom sediments with a coating material such as high-quality sand or clay and is generally called the sand cover. It is reported that it is a very effective method for reducing the consumption of dissolved oxygen (DO) near the seabed and suppresses the formation of anoxic water mass when the coating of good quality is available. In addition, it has been reported that the use of marine stone has an effect of suppressing elution of hydrogen sulfide (Yasuhito, *et al*., 2018). However, as a result of investigations by the present inventors, it is considered that there is a problem in the suppression of the generation of dissolved sulfide in the conventional method using a coating material, in fact, sand and the like with high quality and high safety are being exhausted, and it is becoming difficult to obtain large quantities.

4. *Sulfide ion absorption by steelmaking slag:* The sulfide reduction effect of steelmaking slag has been evaluated by measuring the sulfides in artificial seawater after addition of slag to artificial seawater. Both laboratory and field experiments showed that steel-making slag is removed the hydrogen sulfide from the seawater and reduce the concentration of hydrogen sulfide in the sediment. Field experiments also showed that steelmaking slag changed the anaerobic condition of sediment into an aerobic condition (Hayashi et al., 2013). However, some steelmaking slags have a high percentage of single oxide CaO, and when the bottom sediment in a narrow environmental region is coated, there is one that rapidly raises the pH in water. Such a steelmaking slag may be subjected to carbonation treatment so that single oxide CaO is changed to $CaCO_3$. That is, a steelmaking slag that has been subjected to carbonation treatment (carbonated steelmaking slag) may be used as the alkali supply material. Carbonation treatment of steelmaking slag can be carried out by bringing the steelmaking slag into contact with carbon dioxide or carbonic acid-containing water (non-patent document).

5. *Pure iron powder*: Potential iron hydroxide to remove dissolved hydrogen sulfide from the seawater has been examined and rates of sulfide removal were determined under laboratory conditions at pH 8.5. The concentrations of dissolved sulfide and Fe2+ were plotted versus time for four representative laboratory runs, and the experiments were performed under the

same conditions. The results highlight the initial rapid removal of dissolved sulfide, with a gradual increase in outflow concentrations as the availability of reactive ferric oxide surface sites decreases, maximum Fe^{2+} concentrations were observed 2–4 min after the initial maximum removal rate for dissolved sulfide (Poulton, *et al.*, 2002). Kanaya and Kikuchi (2009) examine a method that controlled sediment hydrogen sulfide amount by forming insoluble FeS after the addition of pure iron powder. In a lab environment, the additive-free treatment contained much more of hydrogen sulfide and lost the sulfide-reactive Fe^{2+} pool after 20 days of incubation, against, treatment of iron addition to significantly increase levels of Fe^{2+} (including iron sulfide), pH, and recovering sulfide-reactive Fe^{2+} in the sediment. Field experiment has also shown that iron can remove hydrogen sulfide toxins from sediment, without negative effects on macrozoobenthos (Kanaya and Kikuch, 2009). Therefore, the irons have capacity to regulate the formation of sulfide by poising the redox sequence and to form insoluble iron sulfide and pyrite compounds. The chemical equation showing this process is

$$H_2S + Fe^{2+} \longrightarrow FeS + 2H^+ , \quad FeS + S^0 \longrightarrow FeS_2$$
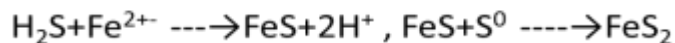
Keeping these points in view, for marine environmental remediation, we aim to propose a method for improving the sediment environment and conduct an elution experiment using an undisturbed bottom mud core added with various iron materials in laboratory experiments to precipitate hydrogen sulfide (H_2S) over a long period of time.

2 Review of literatures

As already mentioned in the introduction, hydrogen sulfide (H_2S) is a highly toxic compound that can form in any aqueous system which contains both organic matter and sulfate. Likewise, Sediment is recognized as a major repository for persistent contaminants in aquatic ecosystems. However, three techniques that have been developed and applied to prevent or control hydrogen sulfide (H_2S) generation for the remediation of these contaminated sediments. There were some sediment management-specific techniques, that is used to suppress and remove hydrogen sulfide (H_2S) from sediment within a small area it is known the following method (Barton, Fardeau, & Fauque, 2014).

Dredging is the process of removing the contaminated-sediment and debris from the bottom of lakes, rivers, harbors, and other water bodies. It has been widely implemented as environmental improvement to prevent the spread of contaminants to other areas of the water body. However, if the sediment is dredged has been widely contaminated with heavy toxic organic substances and other harmful chemicals, pollution measures are required, disposal of dredging the soil becomes a problem. Furthermore, dredging sediment cannot be applied, such as the depression that has already been dredged (Mahmood, Kovacs, Gibbons, & Paradis, 2010).

Oxygen supply by aeration is a common method of removing hydrogen sulfide (H_2S) from the water. with this method, when oxygen is injected into water, the oxidation-reduction potential (ORP) of water is increased, which inhibits the activity of sulfate reducing bacteria (SRB), hence, less hydrogen sulfide (H_2S) will be produced. In addition to that, hydrogen sulfide (H_2S) can also be oxidized by oxygen after formation. However, aeration is a method suitable such as a very small lakes region and moat. Also, applying the oxygen supply by aerating for large lakes and seas, practically it is difficult (Khanal & Huang, 2006; S. A. Smith, Knauer, & Wirth, 1975).

Coating of sediment, the sediment in this method of coating with a coating material such as high-quality sand and clay, not the most economical and effective method for suppressing the elution of dissolved sulfide from sediment it is considered one. However, in practice, such as high quality a safety sand is being depleted, it is becoming difficult to large quantities available (García De Lomas et al., 2006; Hobson & Yang, 2000).

But generally, sediment remediation techniques refer to the use of physical, chemical or biological treatment technologies to prevent hydrogen sulfide (H_2S) contaminated water within the sediment in order to resolve environmental problems and cleanup goals. While, conventional techniques such as physical and chemical method most applied for hydrogen sulfide (H2S) removal from the liquid phase in an anaerobic process has been precipitation with irons and showed the best performance for the sulfide control (Kijjanapanich, Annachhatre, & Lens, 2014).

In response to the risk that contaminated sediments pose, new methods for the remediation of contaminated sediment problems have developed rapidly during the last few years. Which, it should be pointed out that the investigated methods in the compare results are not at equal stages of development, because where more than one technology is feasible and capable of meeting remedial objectives, a comparative approach is better understand contaminated sediment sites and identify and design remedial approaches that are more efficient and effective, likewise, contaminated sediment management is a difficult and costly exercise that is rarely addressed with easily identified and implemented remedies. Hence, the review of literature on processes assessment and contaminated sediment management can help identify and implement management approaches that provide an optimal, if not entirely satisfactory, solution to sediment contaminant problems. Following a brief consideration of methodological problems, studies will be reviewed under the following headings:

- ❖ Inhibition of hydrogen sulfide (H_2S) generation.
- ❖ Elimination of hydrogen sulfide (H_2S) formed.

2.1 Inhibition of hydrogen sulfide (H_2S) generation:

Sulfate reducing bacteria (SRB) gain energy for growth by reduction of sulfate to hydrogen sulfide (H_2S) with electrons usually derived from the degradation of organic matter. However, there are several chemicals inhibiting hydrogen sulfide (H_2S) formation or can inhibit hydrogen sulfide (H_2S) production by sulfate reducing bacteria (SRB), such as, addition of oxidizing agents using nitrate, oxygen, or air; supplying ions to produce insoluble sulfide compound, addition of oxidizing chemicals such as hydrogen peroxide (H_2O_2), chlorine, and potassium permanganate and increasing pH above 9, it can be inferred that as pH values approach 6, the ionized form predominates, so the pH value plays a fundamental role in the degree of inhibition. Biological

solutions are also available, such under oxidative conditions, sulfur oxidizing bacteria (SOB) remove sulfide from high sulfate or oxidize reductive sulfur products to sulfate (Oh, Kim, Choi, Cho, & Kim, 2000; Moon, Ahn, Lee, Nam, & Kim, 2004; Sublette, Kolhatkar, & Raterman, 1998; Kimura, Nakamura, & Watanabe, 2002; Gu, Qiu, Koenig, & Fan, 2004; Park et al., 2014).

2.1.1 Addition of nitrate

Nitrates can be used in certain applications where hydrogen sulfide (H_2S) odor is already present (curative) or to prevent the formation of hydrogen sulfide (H_2S) (preventative) odor. The possibility of biological sulfide oxidation using nitrate as the electron acceptor has also been investigated in sewer systems. Because, nitrates react mostly in the water column supplying electrons for oxidation. According to (Heukelekian, 1943), nitrate was reduced preferentially over sulfate, thus diminishing hydrogen sulfide (H_2S) formation. While, all these methods have a problem with the high cost.

Allen, (1949), discovered that the addition of ($1.0g / L^1$) of nitrate to sewage sludge can prevent sulfide production for at least 29 days. This was due to the increase in redox potential by the presence of nitrate.

According to Poduska & Anderson (1981) the nitrate could regulate the production of sulfide in the wastewater lagoon if enough nitrate was injected to raise the redox potential of the lagoon to above 300 mV. In a full implementation of nitrate to prevent the development of sulfides where the sulfide concentration of 29 mg/L and an ORP of -370 mV before nitrate addition were recordred, the sulfide concentration of 1.7 mg/L was achieved and the ORP increased to +140 mV after three days. It is a preventative measure, however, and frequent chemical transport to the stage of injection and chemical dosing are needed. In addition, it may increase the nitrate load to negatively affect wastewater treatment and deteriorate the performance of obtaining water.

Bentzen et al., (1995) reported that dose of nitrate was significantly suppressed the hydrogen sulfide (H_2S) in a rising main, as the results showed that nitrate dosing at the concentration range of 10 to 40 mg N/L was reduce the sulfide concentration to 0.2–3 mg S/L in main sewers with lengths from 2.4 to 5 km.

Mohapatra, Panda, & Kar, (2012) compared the effect of various concentrations (20, 40

and 60 mM) of three nitrates (NaNO3, NH4NO3 and KNO3) on a marine SRBs consortium. Inhibition of sulfide production was remarkable after 28 and 14 days of incubation. The result indicated that with both concentrations 40 and 60 mM, the effectiveness started from 14th day and increased up to 27.82 to 30.86 % of inhibition in maximum incubation time. However, with 60 mM concentration decrease in sulfide production occurred gradually till 63 days reaching maximum 46.79 to 48.86 % of inhibition. Similarly, 60 mM concentration of various nitrates, potassium nitrate had significant effectiveness to control sulfide production than sodium and ammonium. While, lower concentration (20 mM), ammonium nitrate shows the better efficiency in controlling sulfide over a long period of incubation.

To avoid the emission of hydrogen sulfide (H_2S) and deal with microbially concrete corrosion, it is essential to remove sulfide from anaerobic sewage as quickly as possible. According to De Gusseme et al., (2009) reported that inhibition of net sulfide production occurs through the activation of a pre-existing metabolic pathway in the biofilms (NR-SOB activity) rather than a change in the composition of the microbial community. Metabolic changes in these biofilms induced by sulfate and nitrate amendments were not reflected as major changes in the wastewater biofilm bacterial communities as confirmed by 16S cDNA fingerprinting.

The methods for achieved the production of nitrite and then using the urine- generated nitrite (forming FNA along with acid dosage) for sulfide control was investigated scientifically, the pee collected from men toilet urinal was fed to laboratory-scale sequencing batch reactors. The stable nitrite production was achieved at both relatively high (1.0–2.0 mg/L) and low (0.2–0.3 mg/L) dissolved oxygen concentrations. Test dosage in laboratory-scale sewer systems confirmed the sulfide control effectiveness of free nitrous acid generated from urine. Which this method is proposed a cost effective and environmentally attractive approach to sewer sulfide control through urine separation Zheng et al., (2017).

Montgomery, Mclnerney, & Sublette, (1990) has investigated that, addition of nitrate and nitrite may also favor biological oxidation of sulfide by means of nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB). Park *et al.* (2014) similarly reported that, nitrate addition can effectively control sulfide production. Nevertheless, the addition of nitrate seems a very attractive option due its high solubility, low consumption rate and low operational costs compared to those

of the other chemicals. Moreover, Jiang, Sharma, Guisasola, Keller, & Yuan, (2009) reported that the anoxic conditions in wastewater stimulate nitrate reducing and sulfide oxidizing-bacteria to convert dissolved sulfide formed by Sulfate Reducing Bacteria (SRB) back to sulphate. Because, the expansion of nitrate in wastewater oxidizes naturally broken-down sulfide, by means of autotrophic denitrification by sulfur denitrifying microscopic organisms and furthermore advances the improvement of heterotrophic denitrifying microbes, rivaling Sulfate Reducing Bacteria (SRB) for natural issue.

According to the results of a review paper by Jiang, Gutierrez, Sharma, & Yuan, (2010), it ought to be noticed that addition of nitrate does not inhibit the activity of the Sulfate Reducing Bacteria (SRB), and like oxygen as soon as the nitrate is depleted, anaerobic conditions would return, and disintegrated sulfide creation would recommence. Similar results were reported earlier by Jobbagy, Szanto, Varga, & Simon, (1994) that, the short-term efficacy of nitrate injection was demonstrated in a field study carried out in a sewer network in the Hungarian catchment Lake Balaton.

Can-Dogan, Turker, Dagasan, & Arslan, (2010) found that the formation of elemental sulfur beneath nitrate limiting situations and indicated that the end product of sulfide oxidation depended on the ratio of the nitrogen source to sulfide. Their results showed that, sulfide was eliminated more than 90% at the loading rates between 0.055 and 2.004 kg S^{-2} /m^3 d, when the influent sulfide concentration level was kept around 0.163 kg/m^3 and the HRT reduced from 86.4 to 2 h. But, according to a previous field experiment Cai, Zheng, & Mahmood, (2008) that the sulfide volumetric loading rate in the biological treatment was between 0.042–0.294 kg/m^3 d while the maximum nitrate loading rate varied between 0.175–0.594 kg/m^3 d.

Vaiopoulou, (2018) reported that, nitrates can serve as a final electron acceptor in place of sulfates. According to the result flooding the wastewater with nitrates, forces the bacteria to utilize nitrate instead of sulfates which minimizes the hydrogen sulfide (H_2S) fermentation byproduct and inhibits sulfide production, since sulfide concentration remains below detectable levels until complete denitrification.

García De Lomas et al., (2006) investigated the effectiveness of nitrate addition for controlling sulfide generation in wastewater treatment, according to the study, pre-dosing

investigation within the water line of the WWTP indicated that the in a sharp decrease of sulfide, both in the air and in the bulk water, reached maximum decreases of 98.7% and 94.7%, respectively. Resulted definition, that the development of the nitrate-reducing, sulfide-oxidizing bacterium *Thiomicrospira denitrificans* instead of the direct inhibition of the SRB community.

Gonzalez, et al., (2003) have studied the efficiency of concentrated calcium nitrate (Nutriox^{TM}) on hydrogen sulfide (H_2S) generation in wastewater. This estimation is valuable to evaluate the genuine proficiency of techniques for sulfide control in situ, since an exceedingly complex microbial community happens in this sort of frameworks. Moreover, molecular microbiology techniques permitted the culture independent identification of the main organisms responsible for the efficient use of nitrate for preventing hydrogen sulfide (H_2S) generation.

2.1.2 Oxygen Injection

Nitrate and oxygen are electron acceptors in the oxidation of sulfides. The oxidation of S^{-2} in the presence of oxygen is thermodynamically greater favorable than the oxidation using the nitrate, because, dissolved oxygen levels above 0.5 mg/L can generally prevent sulfide formation. One of the main advantages of air injection include no need of chemical transport; no chemical addition and no undesired byproduct formation, furthermore, oxygen injection is often an attractive choice because it is relatively inexpensive and targets rising mains, where sulfate reducing bacteria (SRB) activity is highest. (Sublette et al., 1998; (Firer, Friedler, & Lahav, 2008) Hvitved-Jacobsen, 2002). Therefore, oxygen has been injected into force mains in wastewater collection system for many years and pure oxygen is normally injected into the flowing wastewater. That is, just in case of the intermittent flow as within the case of rising main, oxygen is injected only when the pump is running. In this process, has been demonstrated to convert hydrogen sulfide (H_2S) to elemental sulfur, as per following formula:

$$2\ H_2S + O_2 \text{------}\rightarrow 2S + 2\ H_2O$$
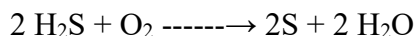
Which produced elemental sulfur ($2\ S^0$) is an insoluble colloidal particle and must be removed by filtration. Various oxygen injection techniques are accessible, can be mentioned following methods applied:

Direct injection of compressed air

Pressure tank air/oxygen injection

Side stream oxygen injection

Use of Venturi aspirators

Although these methods might be able to minimize hydrogen sulfide (H_2S) to some extent, the disadvantages outperformed their beneficial aspects. However, various operational constraints can reduce the effectiveness of oxygen injection in practice and the complete assessment of this strategy with detailed investigations of the impact of oxygen injection on anaerobic biofilm activities is still lacking. in addition, disadvantage consist of low solubility of oxygen in water, high power input and maintenance requirement. For example, high chemical and energy inputs are usually needed and they are not economical, impractical and unsustainable due to the fact that oxidants in dissolved form are easily carried and discharged with treated water. Likewise, different authors have found evidence to support the possibility of no inhibitory effects of oxygen on anaerobic microorganisms. Also, it can be mentioned that the oxygen injection to sewers can negatively impact on downstream biological nutrient removal due to the consumption of valuable and often limiting volatile fatty acids (VFA) and this ideally should be minimized (Firer et al., 2008 a; Botheju, 2011; Hvitved-Jacobsen, Raunkjaer, & Nielsen, 1995). Several major challenges need to be overcome to successfully implement oxygen injection as a sulfide control strategy. First, to maximize transfer through the ascending main pipe, oxygen can only be injected when the wastewater pump is working. And the solubility of pure oxygen in water is limited to 45-50 mg O2 / L at the pressure source (Hvitved-Jacobsen, 2002).

According to the results of a review paper by Boon and Lister., (1975) the use of oxygen to maintain aerobic conditions in a rising-main sewer, to prevent sulfide being formed and hence causing corrosion of concrete or steel in a subsequent length of gravity sewer or causing odor nuisance at the point of discharge, has recently been described. Among alternative factors, the oxygen demand of the sewage and the area of internal level of the rising main which becomes coated with a slime of microorganisms. Typically, for sewage at 15 $^\circ$C it is necessary to inject oxygen at a rate equivalent to 14 mg oxygen / 1 sewage h and 700 mg oxygen / m^2 wall surface h.

Pure oxygen has been used for odor control at a wastewater system and in receiving streams

to boost oxygen concentrations during critical low-flow periods. Total liquid sulfide result showed an average decrease of 13% between the influent pump station and the aerated grit basin influent box. With the injection of oxygen, the average decrease went to more than 60% reduction of the total sulfide, and the dissolved liquid sulfide showed a slight 5% decrease between the influent pump station and the aerated grit basin influent box. With oxygen injection, the average decrease was greater than 68% (reduction of dissolved sulfide), reported by McMillen, *et al*., (2008).

Tzvi and Paz, (2019) suggested that those results shown a very efficient way for the removal of hydrogen sulfide (H_2S) from water. The method was based on the combination of short (254 nm) UV light and oxygen. The method was tested with hydrogen sulfide (H_2S) enriched water, which containing up to 20 mg/L of hydrogen sulfide (H_2S). The change of up to 90% was obtained within a residence time of no more than a few minutes. The quantum effectiveness, defined as the proportion between the number of removed hydrogen sulfide (H_2S) molecules to the number of impinging photons, was found to be as high as 70%, depending on conditions. Besides, the primary item was observed to be sulfate, without the presence of essential sulfur i.e. with no major change in turbidity.

Gutierrez et al., (2008) suggested that the sulfate reducing bacteria (SRB) are only active without oxygen and nitrate, and the addition of these compounds to widely used to control the generation and emission of hydrogen sulfide (H_2S) in waste water. Therefore, their method aimed to keep aerobic conditions in wastewater in order to avoid sulfide generation and favor a decrease of Biochemical Organic Demand (BOD). The results of the qualification tests undertaken on laboratory scale. Oxygen injection (15–25 mg O2/L per pump event) to the inlet of the system decreased the overall sulfide discharge levels by 65%. And the main effect of the oxygen injection was found to be direct oxidation of the hydrogen sulfide (H_2S) in the waste water and outer layers of biofilms rather than removing the cause of the problem by removing the hydrogen sulfide (H_2S) -producing bacteria. However, they also mentioned that, Oxygen, which is an important chemical for sulfide control, does not have a long-lasting inhibitory effect on sulfide production by sulfate reducing bacteria (SRB), and the sulfate reducing bacteria (SRB) activity resumes immediately after depletion of oxygen.

Tanaka *et al.,* (2000) conducted an experiment in Kawasaki (Japan) on the process of forced injection of aerial oxygen within a penstock, length and internal diameter were 3500 m and 349 mm, respectively, and slope was about 0.3%. Air–water ratio was from 7% to 47%, wastewater speeded up from 0.18 to 0.26 m/s, and oxygen transfer velocity in the interphase at 20 °C, KL (20), between 0.19 and 0.32 m/h for wastewater velocities of 0.3 and 0.6 m/s, respectively. In these conditions, concentrations of dissolved oxygen of 0.2–1.0 mg/L were recorded. Measurements verified that the process of sulfide formation was slowed down or suppressed completely. However, forced injection of air into a penstock requires considerable expenses of electric power due to work of a compressor installation. In this regard, they were offered to apply the method of saturation of exhaust fluid with air oxygen through natural discharges to the pipe, which can be executed in the pressure suppression chamber. A similar experiment was carried out by

In an experiment performed by Vasiliev and Stolbikhin (2016) were conducted to determine the stability of the protective layer in the pressure suppressing chamber in Novosibirsk. Researchers say their findings suggest that, dissolved oxygen concentrations higher than 0.5 mg / L can prevent sulfide formation in general. Likewise, the authors offer a new alternative method for corrosion prevention based on aeration of waste liquid in pressure suppressing chambers, which has proven efficiency. However, the pressure suppressing chambers itself also needs protection, and in this case, it is best to use the surface layer with polyethylene sheets or concrete surface layers with the composition.

Study was to investigate the removal of hydrogen sulfide using air (Moussavi *et al.,* 2007) in this work, the performance of a bench scale activated sludge system used to remove hydrogen sulfide (H_2S) from dirty air, and the effects of hydrogen sulfide concentration (5 to 50 ppm) on chemical oxygen demand reduction (COD) and biomass settleability were studied. After biomass acclimation, the reactor showed excellent removal (>93%) for both chemical oxygen demand (COD) and hydrogen sulfide (H_2S), and efficient removal can be done within a few days after starting the reactor. In addition, the results of analyzing liquid samples for total sulfide and sulfate showed absence of sulfide and presence of sulfate accumulation in the mixed liquor. The results also shown that the concentration of hydrogen sulfide (H_2S) commonly found in wastewater treatment facilities is low enough to avoid damaging and toxic effects on activated sludge biomass.

A new technique for sulfide control was investigated in upflow-anaerobic (UAF) filters that handle high-strength, sulfate-rich waste. This technique used periodic oxygen injection using oxidation reduction potential (ORP) as a control parameter to regulate oxygen injection. Khanal and Huang, (2006) reported that oxidation reduction potential (ORP) control by aeration was effective to control sulfide and to regulate oxygen dosing in an up-flow anaerobic filter (UAF) process. The oxidation reduction potential (ORP) based oxygenation was able of achieving reliable online sulfide oxidation at all influent sulfate levels. The oxidation-reduction potential requirements (ORP) elevation was dependent on the influent-sulfate level. However, during oxygenation, the water-sulfide content is almost eliminated.

Zitomer and Shrout (2000) observed a decrease in sulfide in water, from 60 to 5% of fluent sulfate during aeration, but there was a concurrent increase in sulfide gas from 4 to 30% of smooth sulfate resulting from stripping. So, in their case, sulfide is only transferred from water to the gas phase. Fox and Venkatasubbiah (1996) also reported an efficiency of removing sulfides in water by 95% in a confusing anaerobic reactor that was combined with an aerobic sulfide oxidizing unit.

A study was conducted on the elimination of hydrogen sulfide (H_2S) by ECO_2 super oxygenation in Laguna Beach, California. Over the past ten years, City has tried many methods and spent a lot of money to reduce the smell of production. This problem is more likely to occur in long force mains and slow-cycled residential lift stations due to high microbial oxygen uptake rates, long detention times, and low dissolved oxygen levels. This anaerobic condition produces a large amount of hydrogen sulfide (H_2S) which is both odorous and highly corrosive. Since anaerobic conditions are precursors of hydrogen sulfide (H_2S) formation, the logical solution for hydrogen sulfide (H_2S) removal is to induce aerobic or oxic conditions. The ECO_2 super oxygenation system is a technology designed to dissolve pure oxygen into raw wastewater to maintain aerobic conditions to prevent the formation of hydrogen sulfide (H_2S). The high oxidation reduction potential (ORP) created in aerobic conditions prevents the conversion of hydrogen sulfide (H_2S) into sulfuric acid, thus avoiding the possibility of corrosion (Clidence & Shissler, 2012).

This method avoids hydrogen sulfide (H_2S) production by dissolving pure oxygen in the sewage and has been found to reduce the production of hydrogen sulfide (H_2S) gas in in amounts

exceeding 300 ppm to an average of under 2 ppm at the force main discharge ~ 1.5 miles downstream. ECO_2 super oxygenation also reduces the potential for corrosion and extend the usefulness of collection systems for many years (Clidence & Shissler, 2012)
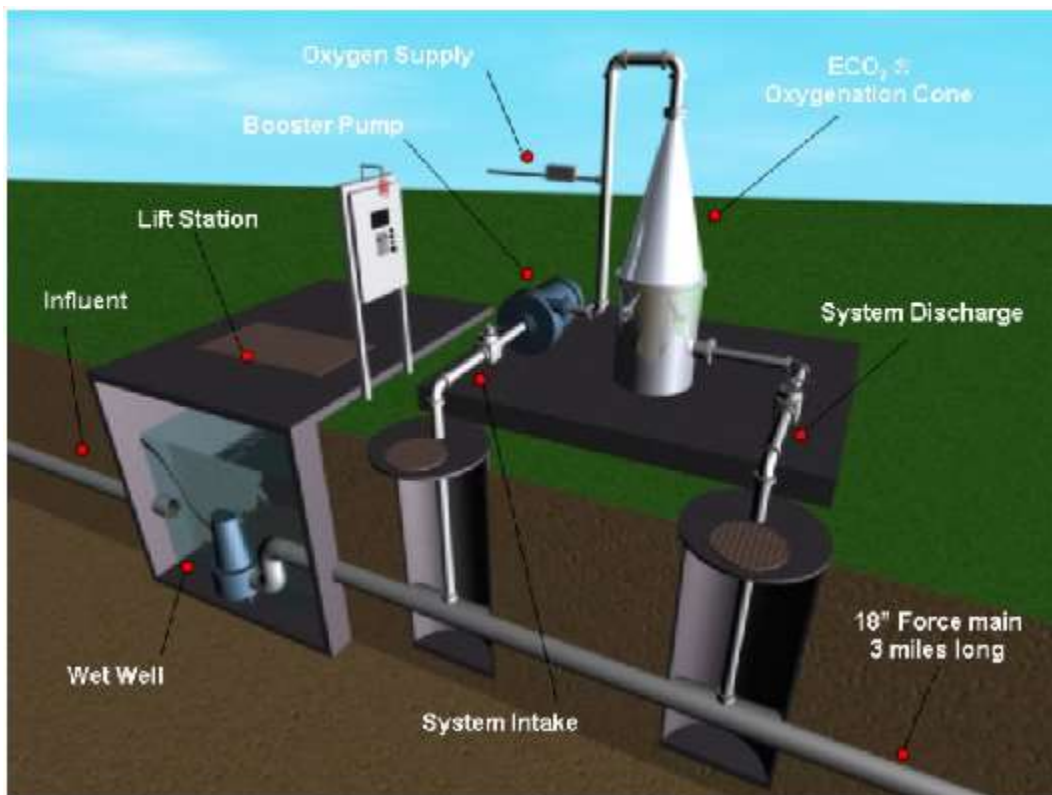

Figure 2.1.1. Schematic of an ECO2 Super Oxygenation System Installed on a Force Main.

2.1.3   Elevation of pH

The main chemical parameters that affects the generation of hydrogen sulfide are pH and oxidation reduction potential (ORP). pH has a role to ensure the development of Sulfate reducing bacteria (SRB), which prefer mostly acidic condition, the sulfides present in the solution can be classified as molecular form (H_2S aqueous) and ionized form (HS^- and S^{2-}) based on pH (Andriamanohiarisoamanana Fetra, 2016). As the pH increases, the H_2S dissociates into its ions HS^- (bisulfide) and S^{2-} (sulfide), which are not measured by a typical H_2S sensor. At pH 6, 90% of the sulfide will be present as H_2S, and the higher the H_2S concentration the greater the tendency for it to volatilize. Because the lower pH values are considered to have a more aqueous H_2S the

rate of hydrogen sulfide will increase with lower pH values. Conversely, at pH 10, 100% of the sulfide will be present as S^{2-} (Palmer, Lagasse, & Ross, 2000). So, the method for controlling the H2S without any negative effect on the wastewater treatment facility would be to consider a pH adjustment. To control hydrogen sulfide production by pH adjustment. The pH should be increased in a range of 9 to 10 standard units. All the pH adjustments below is a viable option. When adjusting the pH of sodium carbonate, note that it is temperature sensitive and should be applied at room temperature (Environment & Climate Change, 2017;pH-Independent Measurement," n.d.).
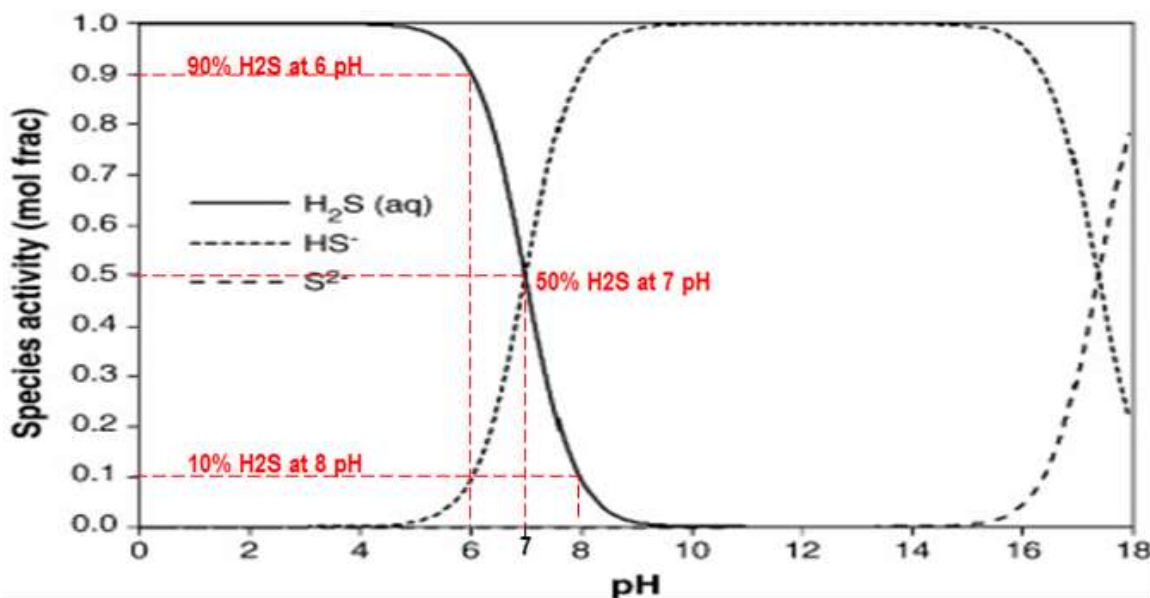

Figure 2.1.2. Effect of pH on hydrogen sulfide generation.

The following are a few effective methods for hydrogen sulfide control and reduction through alkalinity /pH adjustments.

a) Quick Lime (CaO)
b) Lime (Ca (OH)$_2$)
c) Soda Ash (Na2CO$_3$)
d) Caustic Soda (NaOH)
e) Caustic Pot Ash (KOH)
f) Calcium Nitrate (Ca(NO$_3$)$_2$)
g) Potassium Nitrate (KNO$_3$)
h) Sodium Nitrate (NaNO$_3$)

All of the above-mentioned worked equally well, but each have their own advantages and disadvantages.

Treatment Method	Advantages	Disadvantages
Quick Lime (CaO)	- Raise PH - Increase Alkalinity	- High cost - High dosage rates - May require Neutralization of PH - Hazardous- Storage/Handling - Corrosive - Scaling
Lime (Ca(OH)$_2$)	- Raise PH - Increase Alkalinity	- Requires slacking facilities = high installation cost - High dosage rates - scaling - Hazardous –Storage/Handling
Soda Ash (Na2CO$_3$)	- Raise PH - Less dangerous than other lime processes - Reduce Scaling - Increase alkalinity	- High cost - High dosage rates - Corrosive
Caustic Soda (NaOH)	- Side Benefit is Alkalinity Addition - Cost is fixed not subject to increased Sulfides - Most commonly used at treatment facilities	- Costly when treating High Flows - May require neutralization - Hazard –Handling/Storage - Corrosive
Caustic Pot Ash (KOH)	- Strong Alkali - Raise Ph - Increase Alkalinity	Moderately caustic
Magnesium Hydroxide Mg(OH2)	- Better PH Control - Non Hazardous-Safe handling/Storage - Non Corrosive - Long Lasting Alkalinity - Better when insufficient Alkalinity	- Not cost Effective when treating over10 mg/l of H2S - Does not destroy H2S but rather neutralizes. - Slurry can cause solids build in wet wells - May change or worsen odors - Will freeze at 32f

An alkaline agent such as Quick Lime (CaO) is used to increase the pH , which react and form complexes with odorous sulfur species such as hydrogen sulfide and organic mercaptans. Therefore, the odors of biological waste are not covered, but are destroyed (Sheet, n.d.). as also mentioned by (Zhang et al., 2008) sulfate reducing bacteria (SRB) activity can also be inhibited by pH elevation, because, at a pH above 9.0, the amount of hydrogen sulfide H_2S (aq) in solution is negligible since the sulfide present is nearly entirely in its ionic form (HS). Similarly, (Gutierrez et al., 2009) reported, increasing the pH to 8.6-9.0 greatly reduces Sulfate reducing bacteria (SRB) activity from sewer biofilms and prevents release to the gas phase. The level of hydrogen sulfide H_2S production from biofilms was reduced by 30% at pH 8.6 and 50% at pH 9.0, compared to without pH control.

Sodium hydroxide (NaOH) to increase sewer pH, used to reduce hydrogen sulfide H_2S emissions to the gas phase of the sewer system (Hvitved-Jacobsen et al., 2013). According to Nag1, (1999) In a caustic scrubber, which is kept higher pH of 9 by continuously adding sodium hydroxide (NaOH). The flow of the cleaning should be added to prevent the precipitation of salts. However, if the purge stream is added back to the other flow processes, the reaction is driven to the left and Hydrogen sulfide is released. For this reason, the spent caustic must be carefully disposed of.

Hydrogen sulfide gas can also be removed by adsorption. An adsorbent can attract hydrogen sulfide molecules in a gas stream introduced to its surface. Adsorption can continue till the area of the material is covered and then the materials should either be regenerated (undergo desorption) or replaced. Which activated carbon is also often applied for the elimination of hydrogen sulfide by adsorption. the activated carbon can be impregnated via sodium hydroxide (NaOH) or potassium hydroxide (KOH), which can be reused to remove hydrogen sulfide (Feng et al., 2005)

Adjusting the pH to 8 by about 7.6 in reactor 1 on the 72nd day by adding 45 mg of lime (Ca (OH)2) per liter of reactor wastewater significantly reduced the sulfide concentration in the liquid compared to reactor 2. likewise, a further adjustment to pH 8.4 with a similar amount of lime (Ca (OH)2) on the 77th day further reduced the aqueous sulfide concentration in reactor 1. (Rathnayake, Kastl, & Sathasivan, 2017).

Sodium carbonate (Na_2CO_3) or sodium carbonate is a widely used chemical to increase the pH of water from a more acidic level to a neutral range. It is also known as a water softener. Slightly alkaline, it is produced from inexpensive and abundant raw materials. Sodium hydroxide (NaOH) is another substance that can be added to water to the raise ph. whereas, the addition of sodium bicarbonate ($NaHCO3$) is a way to increase the alkalinity or the ability of the acid to neutralize water. When using salt coagulants (no polymers), this alkalinity is necessary for flocculation because it is the reaction between the coagulants and the bicarbonate (alkalinity) that binds to the colloidal particles to form the flocs that trap the suspended matter. (Brennan, 2003).

Laboratory research shows that increasing the pH from 6.7 to 8.2 through the addition of phosphate buffer reduces sulfide gas emissions from 2900 to 100 ppm, while increasing the concentration of soluble sulfide from 18 to 61 mg / l (Zicari, 2003). Alternatively, the sulfate reducing bacteria (SRB) activity can also be inhibited by the elevation of pH or inhibitors such as biocides and molybdate (Nemati et al., 2001)

Metal salt dosing at 24–105 mg FeCl3/L, with and without alkali (NaOH) addition, to the anaerobic digesters (AD) feed flows was the method chosen to reduce hydrogen sulfide in the anaerobic digesters (ADs). Additional NaOH dosing at 60 mg/L in the feed to anaerobic digesters $(ADs)_2$ did not produce any significant effect on either the hydrogen sulfide level or pH during this period (Stra-S3) (Erdirencelebi & Kucukhemek, 2018).

A pH gradient seven pH units is observed downwardly through the tower and absorber effluent is pH 2. As CI_2 to release the NaOH ratio is reduced below 4.5, the KGO strongly decreases until to a minimum of 3.4 or 42 percent sulfur removal. The chlorine required for the oxidation of sulfide also decreases become 2.0 mole of Cl_2 per mole of hydrogen sulfide oxidized in a Cl_2 respect to NaOH of 2.0. An asymptotic increase in the mass transfer coefficient is then regarded as the chlorine feed to hydroxide ratio is reduced to 1.5(Jensen, Adams, & Stern, 1966).

Activated carbon is often used to remove hydrogen sulfide by adsorption. Activated carbon can be impregnated with sodium hydroxide (NaOH) or potassium hydroxide (KOH), which acts as a catalyst to remove hydrogen sulfide (Nag1, 1999).

2.2 Elimination of hydrogen sulfide (H₂S) formed:

Often, the better way to eliminate or reduce odors and corrosion is to prevent them from occurring. Theia offers the most effective and efficient way to remove hydrogen sulfide (H2S), the main cause of odor and corrosion in wastewater collection systems. However, as mentioned in the previous section, inhibition of hydrogen sulfide generation is among the best methods to prevent hydrogen sulfide generation. It consists of a modification of the diet, an inhibition of the biological activity and a prevention of the activity of the sulfate reducing bacteria (SRB) such as the ventilation, which chemical oxidation of sulfide and biotic inhibition of SRB are two major mechanisms by which slow release solid phase oxygen may be able to decrease sulfide concentration in water. By providing long-term inhibition of sulfate reducing bacteria (SRB) activity, slow-phase oxygen release provides a good alternative way to control the formation of hydrogen sulfide in water. In anaerobic digestion, elimination of hydrogen sulfide formed is often applied to control the hydrogen sulfide production, another approach has been used by the authors, focused on the elimination of hydrogen sulfide once produced, rather than preventing its formation (Andriamanohiarisoamanana Fetra, 2016; Chang et al., 2007).

In general, there are three strategies for reducing hydrogen sulfide under anaerobic conditions:

2.2.1 Biological oxidation

The biological oxidation of hydrogen sulfide can occur on the sewer surfaces exposed to the sewer atmosphere. The aerobic and autotrophic *Thiobacillus sp*. which grows in moist surfaces can oxidize hydrogen sulfide to sulfuric acid. Therefore, biological oxidation are the best means to control sulfur in the water. Recently, it has been shown that sulfide emission control after addition of nitrate and nitrite may also favor biological oxidation of sulfide by means of nitrate-reducing, sulfide-oxidizing bacteria. (Devereux et al., 1989; Gadekar, Nemati, & Hill, 2006; Islander et al., 1991; Zheng et al., 2017) .

But researchers reported that oxidation of hydrogen sulfide in seawater consisted of a series of complicated processes which dependent upon the composition and conditions of coastal water. Various seawater conditions; that include physical, chemical, and biological parameters is

interacting and will influent hydrogen sulfide breakdown in the coastal water (Hidrogen, Laut, & Terlarut, 2017).

Improving the biological oxidation of sulfide produced by the addition of nitrate is found by Okabe et al., (2003), their results clearly revealed that the addition of $500\mu M$ $NO3^-$ did not kill SRB but due to the interspecies competition for common carbon source between nitrate reducing bacteria and sulfate reducing bacteria (SRB) and increase oxidation of sulfide produced, which were possible main causes of the suppression of in situ sulfide production in the agar gel.

maximum sulfur production ($73 \pm 10\%$) took place in an oxygen atom sulfur ratio of 0.6 to 1.0 mol L-1 h-1 / mol L-1 h-1. At lower oxygen to sulfide ratios, the lower biological oxidation capacity has resulted in production of more thiosulfate. At higher oxygen to sulfide ratio, the more sulfate produced because more energy is consumed for the growth of bacteria rather than to the formation of elemental sulfur (Janssen et al., 1995).

The physical, chemical, and biological methods used method for hydrogen removal. Among them, the biological processes for the treatment of hydrogen sulfide has been researched and developed because of the relatively low operating costs and minimal generation of undesirable byproducts (Dasgupta & Mondal, 2012).

Khoshnevisan et al., (2017) also reported that the physical, thermal, chemical, and biological treatments are the most valued methods; each has its own advantages and disadvantages. Since the physical and chemical treatments have proven to be more disadvantageous compared to biological treatment, most researchers have focused on biological treatment.

Klok et al., (2013) reported that the hydrogen sulfide concentration as a determinant factor for sulfide biological oxidation. According to their results, hydrogen sulfide at concentrations from 0 to 0.15 mmol L-1 and 0.3 to 1.0 mmol L -1 increased and decreased of the biological sulfide oxidation, respectively. Likewise, biological oxidation increased again when the sulfide concentration was in the range of 1.0 to 5.0 mmol L-1.

Since no biological oxidation was provided in the reactor A, while removal of hydrogen sulfide to these conditions has been due to chemical oxidation by oxygen gas. The results indicate that the oxidation by the cells in suspension approximately 22%, and that the cells immobilized

30%. Thus, the biological oxidation of *T. Novellus* SRM played an important role in removing hydrogen sulfide (Cha et al., 2007).

According to (Myung Cha, *et al.*, 1999) the microorganism was isolated from wastewater and characterized as *Thiobacillus novellus* SRM. To effectively remove hydrogen sulfide by a biological method, they have identified and isolated a new sulfide oxidizing strain of bacteria that satisfies growth and reactor operation conditions.

Using a most probable number (MPN) method, 8-30 000 cells of sulphate-reducing bacteria per ml were found in groundwater. The content of lytic phages infecting the indigenous bacterium *Desulfovibrio aespoeensis* in Aspö groundwater was analysed using the MPN technique for phages. The lytic efficiency of a bacteriophage in *Desulfovibrio aespoensis* has been tested in SRB in laboratory scale with inspiring results. It has to be demonstrated that the phage will not have any adverse effect on bacteria in activated sludge systems (Eydal et al., 2009).

The biological method for controlling odor problems caused by hydrogen sulfide originating from sewer networks was investigated under aerobic conditions. The proposed method is based on the continuous addition of nitrate oxidizes the dissolved sulfide according to an auxotrophic bioprocess by the sulfate reducing bacteria, until the complete denitrification. Based on their results from experiment, with the addition of 10 kg of NH4NO3 h-1 is proposed for practical implementation as the optimal dose, given sufficient odor control and improvement of the load of ammonia tolerated (Mathioudakis et al., 2018).

2.2.2 Chemical oxidation

The effectiveness of chemical oxidation of hydrogen sulfide is affected by pH, oxidation potential of an oxidizer, and the temperature of the water source. Typical oxidants include oxygen, chlorine, potassium permanganate, hydrogen peroxide, and ozone, as already several of the research mechanisms discussed in the previous sections (Cotrino, 2006).

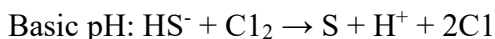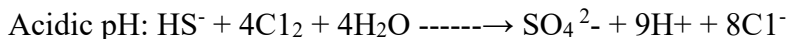### 2.2.3 Oxidation of Sulfide by Chlorine

As mentioned above, oxidation of sulfides can be accomplished with oxygen, chlorine, hydrogen peroxide, ozone, potassium permanganate, and dipotassium ferrate. According to reports

(Apgar et al., 2007), the chlorine application reported was first described by Melbourne Water (1989) whose text reported that in 1854, lime chloride was used by the United Kingdom's first waste disposal commission to remove the odor of London wastewater. Today, wastewater chlorination is widely practiced to reduce microbial contamination and potential disease risks to exposed populations, simplicity and use of chlorine a relatively inexpensive chemical that is also used for disinfection. In general, the chemical response for direct free chlorine oxidation of hydrogen sulfide (H_2S) is shown below:

$$H_2S + Cl_2 \text{------}\rightarrow S^0 + 2Cl^- + 2H^+$$
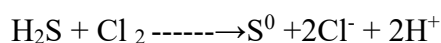
This reaction works well between pH 6.5 to 8.5.

Chlorine is also very reactive with many compounds found in raw domestic wastewater, including hydrogen sulfide (H_2S). Chlorine and sulfide react as shown below:

$$\text{Acidic pH: } HS^- + 4Cl_2 + 4H_2O \text{------}\rightarrow SO_4{}^{2-} + 9H^+ + 8Cl^-$$

$$\text{Basic pH: } HS^- + Cl_2 \rightarrow S + H^+ + 2Cl$$

Stoichiometrically, 8.57 parts by weight of chlorine are needed to oxidize each part of sulfide under acidic pH conditions, while 2.14 parts of chlorine per part of sulfide are needed for basic conditions. Theoretical amount of chlorine to oxidize 1 mg / l Hydrogen sulfide (H_2S) into element Sulfur requires about 2 mg / l chlorine, but the oxidation of chlorine from hydrogen sulfide (H_2S) to elemental sulfur produces undesirable chemical turbidity consisting of very fine particles that must be removed. This shows the oxidation of hydrogen sulfide (H_2S) to sulfur can take place simultaneously or takes place more slowly depending on the pH and reactant concentration, to completely oxidize hydrogen sulfide (H_2S) to sulphate, 8.32 mg /L of chlorine is required for each mg / l of oxidized hydrogen sulfide (H_2S), as in all chemical reactions. However, because chlorine indiscriminately oxidizes reduced compounds in wastewater, competing side reactions also affect the effective dose required, which the excess of oxidant will force the reaction to complete more quickly (McVay, 2017).

Advantages and disadvantages of using chlorine for hydrogen sulfide (H_2S) control ("Removal of Hydrogen Sulfide and Sulfate | UGA Cooperative Extension," n.d.).

2.2.3.1 *Advantages*

Important benefits of chlorine for wastewater treatment are listed below:

Disinfection: chlorine is a good bacterial disinfectant that kills iron and manganese bacteria, sulfur- and sulfate-reducing bacteria, and other harmful bacteria, chlorine requires short to moderate contact times. Iron and manganese bacteria can foul a water softener or oxidizing filter.

Chlorine is effective in oxidizing certain organic and inorganic compounds.

Chlorine accomplishes BOD reduction by oxidation of organic compounds present in wastewaters.

Suppresses hydrogen sulfide (H_2S) generation.

Chlorine has flexible dose control.

Chlorine can eliminate certain harmful odors during disinfection.

Helps to eliminate bubbles and fats.

Controlling activated sludge bulking

Control the foam and fly filter.

Stabilize the activated sludge waste before disposal.

Destroys cyanide and phenol.

Removal of ammonia.

2.2.3.2 *Disadvantages*

Residual chlorine, even at low concentrations, is toxic to aquatic life and I need chlorination.

All forms of chlorine are very corrosive and poisonous. Thus, shipping and handling storage poses risks, requiring increased safety regulations.

Chlorine is consumed by ammonia, which can increase the dose requirement.

Chlorine may inhibit downstream biological treatment.

Storage and use of sufficient amounts of chlorine can create reporting requirements under the risk management plan program and represent potential security challenges (Brik *et al.,* 2004; Rajkumar & Kim, 2006;Strokatova *et al.,* 2000).

2.2.4 Types of chlorine used in water treatment

Today chlorine is still used in a variety of forms. Chlorine treatment can come from several source. The four most common chlorine-containing substances used in water treatment are Chlorine dioxide (ClO_2), Sodium chlorite (NaClO2), Sodium hypochlorite (NaClO), and Calcium hypochlorite ($CaClO_2$). The decision of the chlorine type to be utilized regularly relies upon expense, on the accessible stockpiling choices and on the pH conditions required (Biard et al., 2009; Thomas, 2007).

Chlorine dioxide (ClO_2) is a neutral chlorine compound, it is an unstable gas that dissociates into chlorine gas. Chlorine dioxide has been widely used as a disinfectant in water supply and wastewater treatment. Chlorine dioxide (ClO_2) is practical at or near the source of hydrogen. Chlorine dioxide responds more quickly and totally than other accessible oxidizers and does not form colloidal sulfur. the following reaction takes place:

$$2 \, H_2S + 2 \, ClO_2 \text{------}\rightarrow 2 \, HCl + H_2SO^4 + S$$
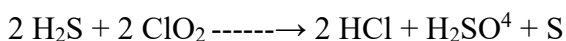
Sodium chlorite ($NaClO_2$) is also being applied at or near the source of hydrogen sulfide (H_2S). it is likewise utilized for the treatment of waste-water. Typical field applications require a minimum of 3 mg/L of sodium chlorite per 1 mg/L of sulfide. According to the following reaction:

$$2H_2S + NaClO_2 \text{------}\rightarrow 2S^0 + 2H_2O + NaCl$$
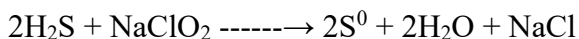
Calcium hypochlorite ($CaClO_2$): This compound is relatively stable, has disinfecting properties similar to those of sodium hypochlorite and contains more available chlorine than sodium hypochlorite. The commercial value of Calcium hypochlorite ($CaClO_2$) generally contains about 70% available chlorine making it suitable for drinking and wastewater applications.

Although that the, wastewater treatment systems using calcium hypochlorite ($CaClO_2$) generally require dechlorination after disinfection to reduce chlorine discharges into receiving waters (Takeshita, Higuchi, & Hanashima, 2003). The reaction of hydrogen sulfide(H_2S) degradation by calcium hypochlorite (CaClO2):

$$2Ca (ClO)_2 + H2S \longrightarrow CaCl_2 + CaSO_4 + 2HCl$$
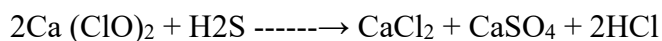
Chlorine, potassium permanganate and hydrogen peroxide are common washing solutions used to remove sulfur compounds in a second step. Amongst them, the most commonly used scouring chemical is chlorine in various forms (hypochlorite, chlorite, or even chloride dioxide). On the contrary, chlorine-based systems involve the formation of hazardous by-products such as chloroform (Myslinski, et al., 2000).

The effects of calcium hypochlorite/ sodium, hydrogen peroxide / and ferric / ferric salts on hydrogen sulfide ($H2S$) dissolved in wastewater have been described in evaluation of chemicals to control the generation of malodorus hydrogen sulfide (H_2S) in waste water (Tomar & Abdullah, 1994), the reaction time is 30 minutes and the optimum concentration of this chemical was estimated at 13.3 mg / L. The authors reported the advantages for calcium hypochlorite ($CaClO_2$) as a strong oxidizer such as high removal efficiency for hydrogen sulfide (H_2S) and other organic compounds in addition odor control.

Based in part on reported effort to use hypochlorite shocking in Arizona, where hypochlorite dosing was maintained on the (3.2-kilometer) reach. In this instance sulfide also dropped during the shock dosing, but once the dose was stopped, the system quickly returned to the liquid and gas phase hydrogen sulfide (H_2S) (Apgar et al., 2007).

Six out of nine wastewater treatment plants in Virginia are classified as a source of odor. Waltrip and Snyder, (1985) have described continuous dosing evaluations of forced main chlorine injection in Virginia. Although not enough information has been provided to determine the level of dosage used, as per their reports that chlorine was dosed in a main force that carried 12 to 20 mg / L of dissolved sulfide. Doses effectively increase oxidation reduction potential (ORP) to +200 and eliminate sulfides, but within 1 to 2 miles downstream of the point of application, the sulfide started to rise again, and within 5 miles, the sulfide returned to the initial background levels of 15

to 18 mg / L. This shows that chlorine may be effective but only for relatively limited periods and intermediate dosing stations may be needed.

A field experiment was conducted using ferrous chloride to control dissolved sulfides in interceptor sewers (Jameel, 1989) treatment success rates were reported down to 0.5 mg/L dissolved sulfides on collection systems in Arizona. The required dose is used 6 gallons per hour from 40 percent ferrous chloride $FeCl_2$ dose to 9.5 mgd, equivalent to about 23 mg / L. This was also reported as 4.3 lb. iron chloride per lb. of sulfide removed. On the contrary, the increase in hydrogen sulfide (H_2S) emissions is related to the acidic conditions generated during the conditioning of iron chloride (pH = 3.8) which keeps the sulfides contained in the sludge in their non-ionized form (Gostelow, Parsons, & Stuetz, 2001).

Charron et al., (2004) investigated the use of hydrogen peroxide H_2O_2 as a replacement for sodium hypochlorite (NaOCl) in a chemical scrubbing tower for the purpose of removing hydrogen sulfide (H_2S). The study concluded that regardless of the packaging and the scrubbing pH used during the experiment, hydrogen peroxide was efficient in removing hydrogen sulfide (H_2S) (removal > 90%).

Several chemical oxidants, such as, (ferric chloride, sodium hypochlorite, potassium permanganate, hydrogen peroxide and potassium nitrate) have been proposed for controlling hydrogen sulfide (H_2S) emissions (Devai & Delaune, 2002). The sludge was treated with 0, 30, 300 and 1000 ppm of each chemical oxidants and the changes in the emission of the various reduced sulfur gases were monitored over a 24-hour period. Potassium permanganate and hydrogen peroxide are proven to be the best chemicals for reducing hydrogen sulfide (H_2S), sodium hypochlorite has also been shown to be effective in reducing hydrogen sulfide (H_2S) emissions, followed by the addition of ferric chloride. But, the effect of various chemical additions was not as significant as the observed reductions in hydrogen sulfide (H_2S) emissions. While, potassium nitrate application had no significant effect on the reduction of hydrogen sulfide (H_2S) or one of the reduced sulfur gases during the 24-hour test period.

Chlorite was injected instead to control the activity of sulfate reducing bacteria (SRB). Supplementation with 1 mM chlorite in the influent medium had a slight effect on sulfide production. After injection 5 PV, the sulfide decreased from 1.89 mM to 1.56 mM. However, an

increase in chlorite concentration to 2 mM induced complete inhibition of sulfide production by sulfate reducing bacteria (SRB) in the bioreactor (Gloria, N.O., 2017).

Perchlorate treatment is a technology that appears as a specific inhibitor of biological sulfate reduction and has been proven to be effective in batch and continuous flow systems. Perchlorate is a direct and indirect inhibitor of sulfate reduction. This is a direct inhibitor of the enzyme needed for sulfate reduction and is an indirect inhibitor in that regard, such as nitrate reduction, energetic reduction of perchlorate is more beneficial than sulfate reduction. In addition, Perchlorate is effective at lower concentrations compared to nitrate, and seems to be more predictable and more consistent in its effects than nitrate (Engelbrektson et al., 2014; Gregoire et al., 2014; Carlson et al., 2015).

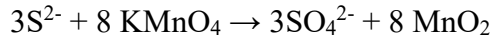### 2.2.5   Uses of Potassium Permanganate

Potassium permanganate ($KMnO_4$) is an oxidizing agent that has been used for many years in aquaculture. Chemical oxidants such as permanganate have been used for more than 50 years to treat contaminants in drinking water and wastewater. Potassium permanganate (KMnO4) was first used as an oxidizing agent in 1910 for water treatment in London (Chritensen, 2003). Potassium permanganate ($KMnO_4$) has been used for more than 30 years in hydrogen sulfide (H_2S) control applications and is a well-understood technology. Because chemicals cannot distinguish between desirable and undesirable organic matter, it is up to individuals to use chemicals in a way that produces maximum benefits and minimum harm to the fish being processed. Potassium Permanganate (KMnO4) is specialty technology for the short-term control of hydrogen sulfide (H_2S) in the gravity of the collection system and force main discharge, which the oxidation treatment of potassium permanganate (KMnO4) quickly destroys hydrogen sulfide (H_2S) in wastewater. The chemistry of hydrogen sulfide (H_2S) oxidation is very complex, and the reaction can follow different pathways depending on the conditions encountered. In anaerobic systems, potassium permanganate (KMnO4) directly oxidizes hydrogen sulfide (H_2S)(USP-Technologies, 2018;CARUS, n.d.). But end points can vary based on temperature, time, and pH of the treatment system.

As an example, under acidic conditions, the following reactions occur:

Neutral-Acid pH:

$$3H_2S + 2\ KMnO_4 \rightarrow 3S + 2\ MnO_2$$

Alkaline pH:

$$3S^{2-} + 8\ KMnO_4 \rightarrow 3SO_4^{2-} + 8\ MnO_2$$
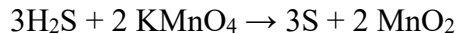
Under conditions between acidic and alkaline pHs, various reactions occur, yielding final products of sulfur, sulfate, thionates, dithionite and elemental manganese sulfide. Potassium permanganate (KMnO4) has been quite effective when added to sludge dewatering operations. The theoretical dose ratio of potassium permanganate (KMnO4) depends on the pH of the solution being treated. Under neutral pH, the theoretical dose ratio is 3.1pounds (lbs.) potassium permanganate (KMnO4): pound (lb.) hydrogen sulfide (H_2S) with practical dose rates anywhere from 3.5 to 5 depending on the application. While, under alkaline pH conditions, the theoretical dose ratio is 12.4 pounds (lbs.) of potassium permanganate (KMnO4): pounds (lb.) of hydrogen sulfide (H_2S) with a practical dosage rate anywhere from 12.5 to 15 depending on the application (Thomas, 2007; Francis-floyd & Klinger, 2006).

1. Under aerobic conditions, oxidation of the hydrogen sulfide (H_2S) by potassium permanganate (KMnO4) takes place in two ways.
2. This results in direct oxidation of the sulfide by potassium permanganate (KMnO4) and various non-odorous sulfur compounds.
3. Importantly, this reaction also produces newly produced manganese dioxide (MnO_2) and MnO2 acting as a catalyst for oxygen transfer which results in further oxidation of sulfides.
4. Through these pathways, the amount of permanganate needed for sulfide oxidation is minimized.

There are advantages and disadvantages in using potassium permanganate.

2.2.5.1 *ADVANTAGES:*

Strong oxidizer which has gained considerable acceptance as an odor control agent. Also oxidizes other odorous compounds as well as other organic/inorganic compounds. $H_2S + 2KMnO_4 \rightarrow 2MnO_2 + H_2SO_4 + 2K$ Oxidizes primarily hydrogen sulfide (H_2S).

(a) Potassium permanganate is emerging as a chemical oxidant that can be used to destroy organic compounds.

(b) Potassium permanganate controls nuisance organisms.

(c) Quick reaction.

(d) Works well in high solids waste streams.

(e) Removes grease build-up in lines and wet wells.

(f) Overdosing may provide small amounts of additional dissolved oxygen.

(g) Potassium permanganate may oxidize organic compounds through several reaction pathways, including electron exchange, hydrogen abstraction or direct donation of oxygen.

(h) Potassium permanganate will produce insoluble environmental reduction products (MnO_2) which can dissolve, which can increase coagulation and simultaneously adsorb trace metals before being removed by sedimentation / filtration.

(i) Potassium permanganate is easy to transport, store, and apply.

(j) Potassium permanganate is useful in controlling the formation of THMs and other DBPs.

(k) The use of potassium permanganate has little impact on other treatment processes at the water treatment facility.

(l) permanganate is effective over a wide pH range and can control the formation of and other disinfection by-products.

Potassium permanganate has been shown to be effective against some viruses.

2.2.5.2 *DISADVANTAGES:*

Doses are difficult to predict and control in most liquid applications. The high cost and high dosage, 6 or 7 parts of potassium permanganate required for each part of hydrogen sulfide (H_2S), are disappointing. Safety precautions are needed for handling and storage.

1) Potassium permanganate provided in its dry or liquid form creates a messy handling situation or requires a labor intensive-feeding system. In addition, potassium permanganate is unable to control residual hydrogen sulfide (H_2S).

2) The slow reaction of permanganate with organic contaminants in bench-scale studies can lead to estimation of excessive oxidant demand because complete mixed conditions are available in the laboratory but not in the field.

3) Expensive equipment and maintenance required.

4) Expensive equipment and maintenance required.

5) Expensive equipment and maintenance required.

6) Long contact time is required.

7) Potassium permanganate tends to give water a pink color.

8) Potassium permanganate is toxic and irritating to the skin and mucous membranes, could have adverse effects on aquatic.

9) No by-products are produced when preparing feed solutions, but these dark purple / black crystalline solids can cause serious eye injury, are skin irritation and inhalation, and can be fatal if swallowed.

10) Application in ground water produces a deep purple color; therefore, special precautions, such as hydraulic containment, may be needed if the location is near a receptor such as a water recovery well and a surface water body.

11) Over-dosing is dangerous and resulting in higher adverse effects on aquatic animals.

In locations that contain very acidic (low pH) groundwater, manganese ions (Mn2 +) can last for a long time in aquifers, which can lead to exceedances of secondary groundwater standards for manganese (Ma and Graham, 1996; Sugihara & Keating, 2009; Korshin, *et al*, 2007; Dash, Patel, & Mishra, 2009; Rodríguez *et al*, 2007; Thomas, 2007).

Automatic systems for adding potassium permanganate and removing hydrogen sulfide (H2S) from ground water have been developed and tested. The current system uses on / off control for adding chemicals. This system successfully removes hydrogen sulfide (H2S) in the range of 1-30 ppm. The amount of potassium permanganate required as a percentage of the amount used was between 5 and 28%. They concluded that, photocells and circuits can be used to add an amount of chemicals that are constantly proportional to the amount of hydrogen sulfide (H2S) in water and positive displacement chemical feed pump control would be an ideal application for this system. Furthermore, the speed of the pump can be controlled in such a way as to allow a very small amount of excess potassium permanganate to be maintained in the system (Edwards, Alharthi, & Ghaly, 2011).

According to Cadena and Peters, (1988) interactions between oxidizing agents such as

potassium permanganate (KMnO4) and hydrogen sulfide (H_2S) are very fast and produce solids in the form of manganese oxide (MnO_2) flocculant particles and elemental sulfur (S^0) which can be removed with sand filters. That these reactions take place in accordance with the following equation:

$$3H_2S + 2KMnO_4 \text{------} \rightarrow 3S^0 + 2H_2O + 2MnO_2 + 2KOH \text{ If pH } <7.5$$
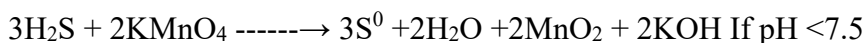
Potassium permanganate (KMnO4) is a strong oxidizing agent that converts sulfide to sulphate. It is normally supplied in the dry state, but it is fed as a six percent solution in water (Ali *et al*, 2019). Potassium permanganate (KMnO4) has also been reported as a potential alternative TEA in the MFCs. Potassium permanganate (KMnO4) as an oxidant has the capacity to accept three electrons under acidic and alkaline conditions (Wei, Han, & Shen, 2012).

Potassium permanganate (KMnO4) was used as pre-oxidant in the reverse osmosis water plant of Marbella (Spain) during the summer of 1997. Water samples were analyzed according to the standard methods, 1989 and Marín Galvín, 1995. the organic materials were analyzed by the heat acidic medium permanganate method (COD-Mn), and the total phosphorus by the ascorbic-molybdate method. The use of potassium permanganate (KMnO4) as a concern in doses of approximately 0.45 to 0.8 g / m3 has greatly improved the process by removing algae and organic matter in the water (Galvín & Rodríguez Mellado, 1998).

Potassium permanganate (KMnO4) can have toxic effects on microorganisms because phospholipids in cell membranes are susceptible to oxidation of permanganate to carbon-carbon double bonds and can cause cell death (Waddell & Mayer, 2003).

Hendratna (2011), examined the usage of manganese dioxide (MnO2) and potassium permanganate (KMnO4) as strong oxidants to remove specific recalcitrant organic compounds and chemical oxygen demand (COD) from wastewater. The results showed that manganese dioxide (MnO2) was effective in removing COD of wastewater and was not affected by the high content of suspended solids. He also mentioned that, manganese dioxide (MnO2) oxidation was negatively influenced by consulate compounds, such as metal ions and natural organic compounds which inhibit the chemical reaction by occupying the reactive surface site of manganese dioxide (MnO2). He stated that the permanganate (MnO_4) can be used to remove drugs

and other micropollutants that contain electron-rich groups.

Liang et al., (2018) presented the first comprehensive study of a combined potassium permanganate (KMnO$_4$) and ozone (O$_3$) technique to treat different kinds of textile dyeing wastewater. Follow the procedure described below in image.

According to Bowker et al., (1985) preventing the formation of odorous compounds, it is achieved by adding chemicals to the liquid stream, maintaining aerobic conditions and good cleaning. chemicals added to biosolids liquid to reduce odors include hydrogen peroxide and potassium permanganate, these chemicals are strong oxidizers which react with hydrogen sulfide to form the non-odorous compound. While according to (Waltrip & Snyder, 1985) potassium permanganate in the bulk water might not be cost-effective and durable way to control hydrogen sulfide dissolved chemicals added tend to be flushed into receiving water bodies before they can exert positive effects.
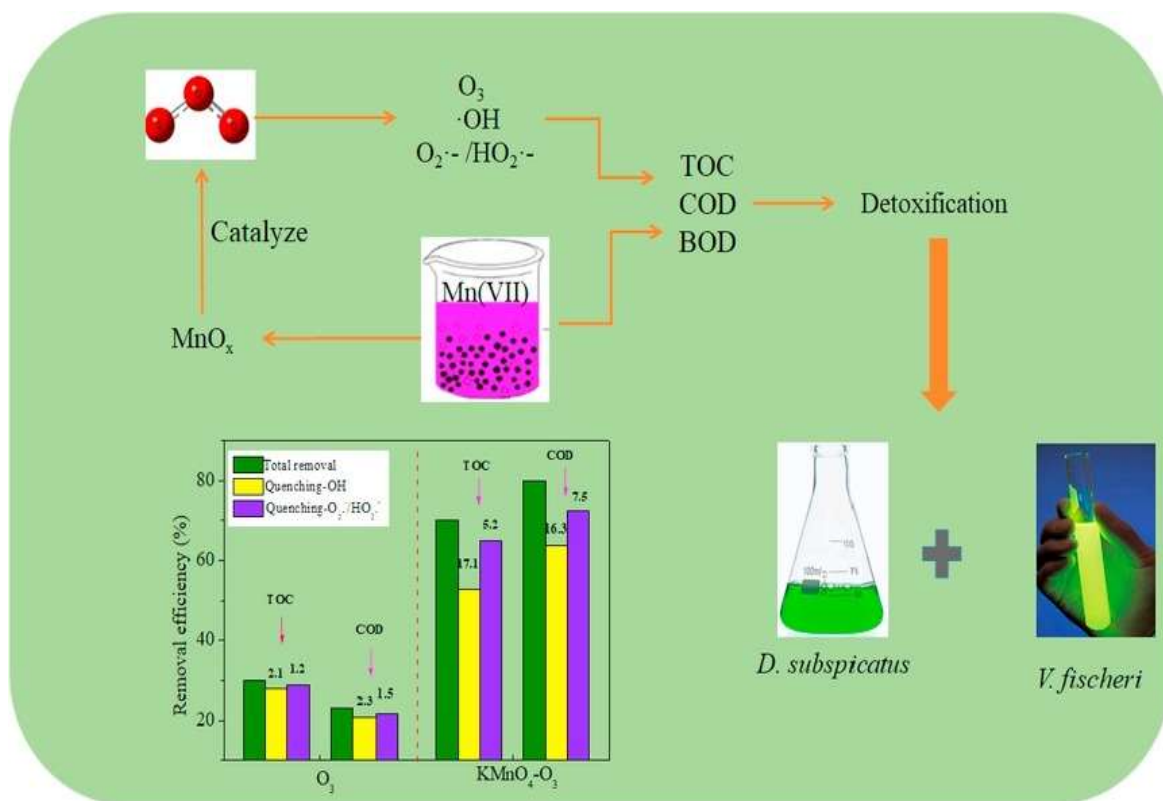
Figure 2.2.1. Method for preventing hydrogen sulfide.

The total organic carbon (TOC), chemical oxygen demand (COD), and toxicity decreased by about 70%, 80%, and 34.4 to 95.5%, respectively, using a 1.5 mM potassium permanganate (KMnO4) dose, ozone (O3) dose of 10 mg / L, a pH value of 7, and a reaction time of 30 minutes.

Aquifer sediments are treated with a 0.02 M potassium permanganate (KMnO4) solution. The abundant resaturation of the columns treated with permanganate with the native groundwater, simulation of a potential scenario during a period of unavailability of ASR in operation or prolonged recovery resulted in a substantial reduction of the Mn oxides previously formed by the release of high concentrations of Mn (II) from ferrous iron into the underground waters. During the next recovery cycle, this concentration of Mn (II) was not successfully isolated due to the absence of sufficient Mn-oxide, which had an adverse effect on the quality of the recovered water. Thus, care must be taken to avoid this situation; if not, repeated treatment of permanganate may be needed (Antoniou *et al*., 2014).

2.2.6 Hydrogen Sulfide Oxidation with Hydrogen Peroxide (H2O2)

Hydrogen peroxide (H2O2) is an inorganic peroxide consisting of two hydroxyl groups which combine with a single bond of covalent oxygen. It has a role as an oxidizing agent. Hydrogen peroxide (H2O2) is a colorless liquid at room temperature with a bitter taste. Historically, that hydrogen peroxide (H2O2) has been efficient in oxidizing hydrogen sulfide (H2S) for odor control in wastewater treatment systems. Hydrogen peroxide (H2O2) can control sulfide in two ways, depending on the application (Hoffmann, 1977; Takenaka et al., 2003; Kaczorowska, et al., 2005; Ksibi, 2006; Gutierrez et al., 2008).

Inhibition: by providing dissolved oxygen which inhibits the septic conditions which that lead to biological sulfide formation.

Destruction: by oxidizing sulfide to elemental sulfur or sulfate ion.

as it is applied to industrial wastewaters containing moderate to high levels of sulfide (50 - 10,000 mg/L). But, Oxidation of sulfides with hydrogen peroxide (H2O2) produces different depending mainly on the pH of the wastewater.

Based on the following responses, hydrogen peroxide (H2O2) is used to chemically oxidize

hydrogen sulfide (H_2S):

pH < 8.5: $H_2O_2 + H_2S$ ------→ $S + 2H_2O$

pH > 8.5: $4H_2O_2 + S^{-2}$ ------→ $SO_4^{-2} + 2H_2O$
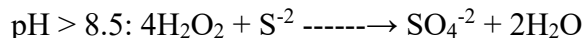
Hydrogen peroxide (H_2O_2) Dosage: The stoichiometry calls for 1.0 pound. hydrogen peroxide per pound. hydrogen sulfide (H_2S). Hydrogen peroxide (H_2O_2) 50% is a strong oxidizer that effectively controls odor causing sulfides and related oxidized compounds in municipal and industrial wastewater systems. During treatment, it breaks down into oxygen and water, thereby adding dissolved oxygen to the system which reduces Biological Oxygen Demand (BOD). But excess hydrogen peroxide (H_2O_2) breaks down to release oxygen and water, thereby increasing dissolved oxygen in the flow. Generally, 90% of the reaction among hydrogen peroxide (H_2O_2) and hydrogen sulfide (H_2S) takes place in 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes (Charron et al., 2004; Stephens, Hill, & Phelps, 1980).

2.2.6.1   *APPLICABLE TREATMENT PROCESSES:*

(a) Hydrogen peroxide (H_2O_2) oxidizes hydrogen sulfide (H_2S) and various sulfides, while simultaneously suppressing backtrail activity which tends to cause the formation of hydrogen sulfide (H_2S).

(b) Hydrogen peroxide (H_2O_2) supplies dissolved oxygen to the drainage system, avoiding the anaerobic conditions required by sulfate reducing bacteria that lead to initial sulfide formation, as mentioned above formal.

(c) Hydrogen peroxide (H_2O_2) reacts with hydrogen sulfide (H_2S) under acid, neutral and alkaline conditions.

(d) Hydrogen peroxide(H_2O_2) force mains and gravity sewers.

(e) Hydrogen peroxide (H_2O_2) Upstream of WWTP headworks facilities

(f) Application of Hydrogen Peroxide to the Control of Eutrophic Lake Systems.

(g) Hydrogen peroxide (H_2O_2) can be used as a biocide for SRBs and iron bacteria and a dechlorinate. Furthermore, Hydrogen peroxide (H_2O_2) helping to prevent future production of sulfides and other undesirable chemicals by anaerobic bacteria ("Hydrogen Peroxide - Webster Environmental Associates, Inc.," n.d.;"In Reply: BEHAVIOUR THERAPY," 1966).

Advantages and disadvantages of using hydrogen peroxide for hydrogen sulfide (H_2S) control("H2O2 | SSWM - Find tools for sustainable sanitation and water management!," n.d.).

2.2.6.2 *ADVANTAGES:*

- ✓ Controllable process.
- ✓ Safety and security precautions required.
- ✓ Inexpensive capital installation.
- ✓ Inexpensive chemical cost.
- ✓ Quick and easy installation.
- ✓ Suppresses hydrogen sulfide (H_2S) generation for 3 to 4 hours after hydrogen peroxide (H_2O_2) addition.
- ✓ Effective removes 90% of odors.
- ✓ Fast reaction time.
- ✓ May increase dissolved oxygen level of wastewater.

2.2.6.3 *DISADVANTAGES:*

- ➢ Optimum mixing and long reaction / contact times.
- ➢ Incomplete oxidation.
- ➢ Large dosages needed.
- ➢ Turbidity – requires filtration.
- ➢ Secondary containment required.
- ➢ Special operator training.
- ➢ Special safety handling measures are needed.
- ➢ Adversely affected by high O2 uptake rates.
- ➢ Control for > 1-2 hours is costly.

The oxidation of the sulfide in aqueous solution by hydrogen peroxide has been studied in the presence of hydrated ferric oxide catalyst. The catalyst was effective enough to oxidize the sulfide with hydrogen peroxide. Based on the conclusions, total removal of sulfides in aqueous solutions was achieved by a catalytic chemical oxidation process. Such that, sulfide oxidation rates were found to be higher at lower initial sulfide concentrations indicating an unusual negative reaction sequence with respect to sulfides, besides that, the rate of sulfide oxidation was found to

be directly proportional to the catalyst loading and the addition of hydrogen peroxide, furthermore, at higher temperature levels the oxidation of sulfides by hydrogen peroxide in the presence of an iron oxide catalyst increased mostly (Ahmad *et al*., (2009).

(Takenaka et al., (2003) studied sulfide oxidation using hydrogen peroxide at low temperatures. They found that the decomposition rate of sulfide by hydrogen peroxide in freezing at 15∘C was about five times faster at 258 K than the maximum decomposition rate in solution at 25∘C (room temperature). Thiosulfate, sulfite, and unknown sulfur compounds were also observed as intermediates in freezing reactions, thiosulfate, and sulfite consumed after 90 minutes. But unknown sulfur compounds are not oxidized and are preserved for a long time even in the presence of excess hydrogen peroxide.

Laboratory experiment have been carried out to evaluate the performance of chemicals to control the generation and emission of odor in Kuwait sanitation (Tomar & Abdullah, 1994). They found that the minimum concentration of hydrogen peroxide needed to remove 100% dissolved sulfide was 1.0 g oxidizer per g sulfide in wastewater at pH 7.6. They mentioned that is in accordance with the following reaction takes place.

$$H_2S + H_2O_2 \text{ ------} \longrightarrow S + 2H_2O$$
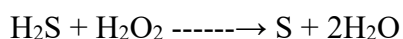
The most commonly applied methodology for the modification is the use of oxidizing agents. that treatment with hydrogen peroxide causes a slight increase in oxygenated function groups and this fixation depends on hydrogen peroxide concentration used in treatment (Domingo *et al*., 2002). While, the results are explained by an excessive hydrogen peroxide concentration, that the highest concentration of hydrogen peroxide (4 mM) did not cause a significant increase in either the oxidation level or the percentage of oxidation at the end of the treatment. However, it must be emphasized that at high concentrations, hydrogen peroxide can act as a scavenger and therefore, reduce the possibility of oxidation (Andreozzi *et al*., 1999).

The oxidation process was investigated at different levels of hydrogen peroxide (H_2O_2) addition (F. Ahmad, 2012), he found that at the addition of higher hydrogen peroxide (H_2O_2), thiosulfate oxidation becomes faster. The higher concentration of hydrogen peroxide (H_2O_2) in the water will allow more reaction with thiosulfate ions excited in the water, and with

increasing the reaction will shorten the time to oxidize thiosulfate in the water. The results of this study showed that when the addition of hydrogen peroxide (H_2O_2) was increased from 0.1 M to 0.5 M, the oxidation of thiosulfate increased, and the duration of treatment became shorter, which, that oxidation of 800 ppm of sulfide took 50 minutes, and the complete elimination of thiosulphate from wastewater has been achieved by oxidation in the presence of ultrasonic vibrations with the aid of hydrogen peroxide(H_2O_2).

Chemical oxidation of sulfides and biotic inhibition of sulfate reducing bacteria (SRB) are the two main mechanisms by which the release of solid phase oxygen might reduce the concentration of sulfides in water. The hydrogen sulfide (H_2S) concentration was reduced from 20 mg S / L to 0.05 mg S / L immediately after 0.1% hydrogen peroxide was added but began to recover only four days later. So, hydrogen peroxide doesn't seem to be able to inhibit sulfide production for a long time. By providing long-term inhibition of the sulfate reducing bacteria (SRB) population, ORC is a good alternative way of controlling the production of hydrogen sulfide (H_2S) in water (Chang et al., 2007).

sulfate reducing bacteria (SRB) belong to strict anaerobic bacteria that often encounter oxic conditions in their different natural biotopes, and some sulfate reducing bacteria (SRBs) even have protective aerobic respiration. As such they represent the organism of choice to study various antioxidant defense systems in anaerobes that provide competitive advantage and survival in a changing environment. Therefore, the regulation of its antioxidant defense system was investigated in detail at the transcriptome and proteome levels for the cases of oxygen (Brioukhanov, Pieulle, & Dolla, 2010) the molecular oxygen was able to directly inactivate key enzymes of sulfate reduction metabolism. According to the results, the concentrations of injected oxidizers in sulfate reducing bacteria (SRB) cultures decreased steadily with time due to their uptake by the cells and interaction with sulfide, a product of sulfate reducing bacteria (SRB) metabolism.

### 2.2.7 Hydrogen Sulfide Oxidation with Calcium peroxide (CaO_2)

Different chemicals and their combinations are added to the waste at various concentrations for inhibition of dissolved hydrogen sulfide in the sewer system. The results obtained from the application of chemical combinations showed that 2 mg / L iron (III) chloride

plus 2.5 mg / L Magnesium hydroxide and 2 mg / L iron (III) chloride is added 5 mg / L Calcium hypochlorite, resulting in a safe range of oxidation reduction potential (ORP) and pH with lower operating costs than using chemicals individually in a reaction time of 30 minutes. Furthermore, the reduction of dissolved hydrogen sulfide in the effluent at a rate higher than 95% is obtained through the application of chemical combinations (Faridah et al., 2011).

2.2.8 Chemical precipitation (Iron)

The irons have capacity to regulate the formation of sulfide by poisoning the redox sequence and to form insoluble iron sulfide and pyrite compounds. The irons have capacity to regulate the formation of sulfide by poisoning the redox sequence and to form insoluble iron sulfide and pyrite compounds.

The chemical equation showing this process is:

$$H_2S + Fe^{2+} \text{------}\rightarrow FeS + 2H^+ \quad , \quad FeS + S^0 \text{-------}\rightarrow FeS_2 \quad (1)$$
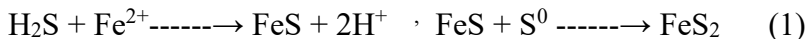
Accordingly, the two dissolved iron species (ferric iron and ferrous iron) that have been typically used for sulfide elimination react with sulfide species in two different ways: ferrous iron (Fe2+) can remove sulfide by precipitation as ferrous sulfide (FeS) according to Eq. (1). while ferric iron (Fe3+) can remove sulfide by oxidizing it chemically to elemental sulfur while being reduced to Fe (II), which can subsequently produce FeS (Eq. (2) and (3).

$$Fe^{2+} + HS^- \text{------}\rightarrow FeS + H^+ \quad (2)$$

$$2Fe^{3+} + HS^- \text{------}\rightarrow 2Fe^{2+} + S^0 + H^+ \quad (3)$$
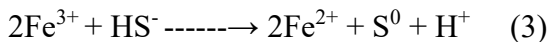
Either ferrous or ferric iron is more effective in controlling the concentration of dissolved sulfide is not clear from the literature (Tomar & Abdullah, 1994). Conversely, two other possible mechanisms for the precipitation of pyrite were suggested by Padival et al., (1995):

$$Fe^{2+} + 2HS^- + 0.5O_2 \text{------}\rightarrow FeS_{2(s)} \downarrow + H_2O + H^+ \quad (4)$$

$$FeS + S^0_{(s)} \text{------}\rightarrow FeS_{2(s)} \downarrow. \quad (5)$$
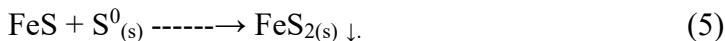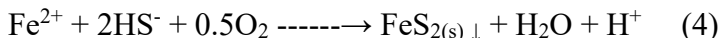
The actual incidence of reactions described in the Eqs. (8) and (9) in the sewages also be

considered questionable because under typical pH range encountered in municipal sewage dissolved oxygen, if it exists, is more likely to oxidize sulfide rather than to take part in a precipitation reaction. Moreover, iron sulfide precipitation has been proven as the process is generally fast, cost-effective methods and well-studied.

Although, sulfide dissolution creates iron sulfide is not very soluble in water which that can interfere in downstream processes, but oxidized metals such as Fe (III), Mn (IV) and Mn (III), for example, are efficient catalysts to overcome the kinetic barrier for the chemical oxidation of sulfides. (Nielsen et al., 2005).

Iron and steelmaking slag is a by-product of the iron and steelmaking process, considering Japanese manufacturing facilities, It is classified into two categories: blast furnace slag and steel slag. The former comes from the process of converting iron ore into pig iron, while the latter is produced from the refining of pig iron into steel. Japan produces about 40 million tons of slag making steel and iron each year and reached a slag recycling rate close to 100%. The iron manufacturing process produces 25 million tons / year blast furnace slag, which is already used in applications with high added value. The steelmaking process produces about 15 million tons / year of steelmaking slag. Although 60% of this is used in building materials and civil roadbed, technologies that allow intensive use of the added value while taking advantage of the physical properties and chemical composition of the slag are not sufficiently implemented (Yao & Millero, 1996 ; Asaoka et al., 2013; Miyata et al., 2016).

The precipitation and oxidation of hydrogen sulfide were investigated in Torquay Canal and Bald Eagle Creek. The highest concentration of Fe^{+2} (Ferrous) ($\sim 30 \mu M$) was measured at the oxic - anoxic interface. Under stable weather conditions, hydrogen sulfide was maintained at or below the interface. The catalytic iron cycle prevents the hydrogen sulfide to be released to the surface water during seasonal anoxia. But, when storms came, the water column was reversed, and hydrogen sulfide was released into surface water. Therefore, storms cause hydrogen sulfide to reach the surface water and the possibility of fish kills occurring. In the absence of storms, Fe^{+2} (Ferrous) can oxidize hydrogen sulfide to S^2_{x-} S_8 and S_8 but has been demonstrated that the predominant oxidation product in this search (Shufen Ma, et al., 2006).

The experiments were performed in anaerobic wastewater laced with sulfide and carried

out under different pH and with various ratios of iron-to-sulfide. sulfide precipitation levels are shown to be faster with Fe^{+3} (Ferric) as compared with Fe^{+2} (Ferrous). Subsequent experiments showed that for Fe^{+3} (Ferric), pH is the controlling parameter, while for Fe^{+2} (Ferrous) both pH and the iron-to-sulfide ratio were important (Kiilerich, Nielsen, & Vollertsen, 2018).

The study was conducted by (Kiilerich et al., 2017) on the sulfide precipitation with ferric iron, found that the stoichiometric ratio of the precipitation process and conversion, sulfide becomes poor with a decrease in pH. the result showed that the precipitation of dissolved sulfide by ferrous iron was not as instantaneous as commonly assumed. Correspondingly, the highest sulfide conversion only reached 60%.

Experiments were performed in anaerobic conditions enriched with sulfide, iron (III) (iron) chloride was applied to a wide range of 24-105 mg $FeCl_3$ / L with and without solution using different strategies. introduction points were performed in the feed line and the sludge thickener unit. Iron (III) chloride dosage 24-50 mg / L FeCl3 four digesters provided a significant reduction but was not enough. the reduction of hydrogen sulfide of 3360 mg / L or 39% (up to 4170 mg / L) occurred gradually over a period of 12 days (STRA-S1). Since each feed stream was mixed with the digester sludge to the reactor inlet, iron chloride added to a digestion was distributed to all anaerobic digesters (ADs) gradually, and consequently the hydrogen sulfide has been reduced to a certain degree (1345 ug / L of 16%) in non-dosed digesters (Erdirencelebi and Kucukhemek, 2018).

Carbonated steel slag 0.8 to 5 mm in diameter were used in this research was provided by Kobe Steel, Ltd. (Asaoka et al., 2013) the purpose of the study was to reveal the mechanism of elimination of hydrogen sulfide using carbonated steel slag produced through the carbonation process to alleviate the impact of alkaline. The chemical composition of the carbonated steel slag they used in the study included mainly calcium carbonate, iron, and calcium oxide compounds, etc. Which, around 47% of the calcium in the carbonated steel slag was carbonated. The adsorption and oxidation conduct of hydrogen sulfide on carbonated steel slag were revealed in their investigation. Hydrogen sulfide was adsorbed on the slag carbonated steel with a maximum adsorption 7.5mg g / g[1]. Hydrogen sulfide has been removed by the two processes.

Sulfur oxidation coupled with the reduction of manganese oxide in carbonated steel slag.

The formation of pyrite.

Hayashi et al., (2013) investigated the adsorption of hydrogen sulfide H_2S ion by using steelmaking slag. Their research aimed to evaluate and demonstrate the effects of removal of hydrogen sulfide in seawater by steelmaking slag. Steelmaking slag was filled with metal gabions 2 m long, 1 m wide and 0.5 m in height. laboratory experiment on the removal of slag with steelmaking sulfides was performed, and this method demonstration experiment was conducted in a closed sea. As per the results obtained, both laboratory and field experiments have shown that the steel slag eliminates hydrogen sulfide from sea water and reduces the concentration of hydrogen sulfide in the sediments. The laboratory experiment has clarified the fact that the steel-making slag is effective to reduce the sulfide content in artificial seawater. Field experiments also showed that the steel-making slag reduces the sulfide concentration in interstitial water in the steelmaking slag and sludge under contact with the slag and increase the anaerobic atmosphere in bottom sediments in contact with slag. EPMA analysis results and XAFS suggested the possibility that Fe in the slag of steelmaking absorbed sulfides in seawater.

To evaluate the sulfide reduction effect of steelmaking slag (Miyata et al., 2016 b) carried out field experiments in Fukuyama inner harbor. The first steel slag construction was carried out at a test site A (area: 432 m^2), and the construction of the second slag carried performed at test sites B and C (total area: 3510 m2). The first, steel-making slag with a small particle size of 5 –10 mm was deposited to a thickness of 35 cm. On the test site C, Slag 1 was used as the base material, while Slag 2 was used with a size of 30-50 mm on top. Gas, water quality and benthos were investigated after the construction of the first and second slag, likewise, monitoring was carried out at 2, 8, 20 and 42 weeks after the first construction, and at 2, 12, 19, 21, 30, 37, 41 and 46 weeks after the second construct. The best results were obtained over a period of about two years. Sulfide dissolved in the sediment pore water in the slag treatment zone was remarkably reduced compared with that in the control plots. Oxidation-reduction potential (ORP) and dissolved oxygen were also improved, and the effect lasted for at least two years, and the concentration of hydrogen sulfide gas was also diminished. These results indicated that capping with steel-making slag was an effective method for repair of bottom sediments containing hydrogen sulfide enriched organic.

The previous research work of the same authors (Miyata *et al.,* 2015a) on multi-objective

were conducted in the laboratory using steelmaking slag to recover sediment quality in terms of the elimination of hydrogen sulfide in different application modes, as they the steelmaking slag was placed on or mixed with the sediments, which the bottom sediment for the experiments have been collected from Fukuyama inner harbor and the sediment was muddy and rich in organic matter and total sediment sulfide concentrations more than 10 times the water quality standards. The main components of the slag were Fe, CaO, SiO_2, and Al_2O_3, of which Fe and Ca contents were particularly high compared with those of natural stone (granite) size (5-10 mm). Black polyethylene container with a volume of 30L was placed in large volume (500L) black polyethylene containers, it had been used to minimize the water temperature fluctuation between each container experiment, and each container of 30L was capped with a tight lid to air. Samples were taken at 15, 27, 40, 68, 122 and 172 days. The overlying water samples collected at 80 mm above the surface of the sediment using 50-ml syringe, Sediment samples were taken at 10 mm and 80 mm below the surface of the sediment. The results revealed that the reduction of dissolved sulfide by the steelmaking slag was confirmed in treatments, both uses of the steelmaking slag significantly suppressed hydrogen sulfide gas through the reduction of the dissolved sulfide in sediment pore waters. With the mixing method, the concentration of sulfide dissolved in interstitial water is significantly lower than the capping. This was clearly more effective than the results obtained by capping with natural stones, which was conducted as a method of control.

The reaction between synthetic ferrihydrite and dissolved sulfide in artificial seawater was investigated. All solutions of [Fe $(NO_3)_3$. $9H2O$ to pH 6.5 with 1 M KOH] were prepared using Milli-Q purified water and all chemicals were analytical reagent grade. After hydrolysis, ferrihydrite washed thoroughly to remove traces of nitrates and then freeze-dried. Experiments were carried out in constantly stirred (using glass-coated magnetic stirrer) artificial sea water or 0.42 M NaCl over a range of pH 4.0 to 8.2. The temperature was maintained at 25 °C with a water bath and Techne light was excluded from all experiments. Dissolved Fe (II) and Fe (III) in 1-ml samples measured by the method of revision ferrozine. The combined evaluation of Fe (II) oxidation kinetics of dissolution and sulfides indicates that reductive dissolution of ferrihydrite by the dissolved sulfide is about 15 times slower than the rate of oxidation of sulfides at pH 7.5. They mentioned that, the reaction between the dissolved sulfide and oxides (oxyhydr) iron was controlled by complex formation sulfide surface and the availability of sites reactive surface (Poulton, 2003).

Potential uses iron-rich soil for controlling the concentration of hydrogen sulfide in the aquaculture system was investigated (Lahav et al., 2004). Four sources of iron oxide obtained commercially, including hematite and magnetite ores were tested, with the addition of two local soils rich in iron and two magnetite ores and two magnetite ores. Sulfide was measured by the method of iodide and ferrous iron concentration was measured by the method of phenanthroline. Elimination of sulfide capacity assessment of various sources of iron oxide revealed that both Terre Rosse soil (iron content of 8.3 mass %) and Bazalt (iron content of 2.6 %) soil of northern Israel have much higher rates specific deletion than hematite's commercially available. Under anaerobic conditions, the elimination of sulfide was found to proceed through a redox reaction (the final product: elemental sulfur) followed by FeS precipitation. The reaction kinetics were found to be pseudo-first order to the total concentration of sulfides. Iron oxide in the soil react rapidly in the presence of reactive iron-sulfide fraction in the soil dissolve almost completely after about one day in the presence of high sulfide concentrations (>0.9 g S l^{-1}). At low concentrations, 2 g of Terre Rosse decreased the sulfide concentration from 200 to about 5 mg S l^{-1} in around 120 h. They propose that, the addition of 3 to 4 kg m $^{-2}$ sedimentary soil once a year before de-stratification is known to occur in the reservoir of freshwater fish-farming will significantly reduce the toxic effects.

Iron potential (hydr) oxides to remove the hydrogen sulfide dissolved from seawater was examined underflow-through requirements. The ferrihydrite was stabilized by precipitation on zeolite pellets, and the sulfide elimination rates were determined in laboratory conditions at a pH of 8.5. dissolved sulfide and Fe^{2+} were measured in triplicate at the port input sampling cartridge at the beginning of each experiment and measured as a time series in the output and dissolved sulfide concentration was also measured at the input port of the cartridge towards the end of each experiment. The dissolved sulfide was measured by methylene blue method and unfiltered samples originally analyzed by this method to determine whether the solid phase FeS dismissed with water flowing out. Results from laboratory experiments compared positively with sulfide elimination kinetics determined in a series of experiments conducted online in a recirculating aquaculture production system. The results showed that the rapid removal of dissolved sulfide beginning, with a gradual increase in the concentration of outflow as the availability of reactive iron oxide surface sites decreased. Nevertheless, reoxidation results in a reduction in sulfide removal rate due to the formation of more crystalline, the less reactive iron (hydr) oxides, and therefore it may be

preferable to coat the substrate with additional ferrihydrite following sulphidation (Poulton et al., 2002).

The combined use of granular ferric hydroxide (GFH)and the oxidants for aqueous hydrogen sulfide removal was evaluated (Yin, 2016). A stock solution of sodium sulfide was prepared by dissolving crystals of sodium sulfide in nitrogen gas to clean water. The filtered seawater was taken from the coastal marine laboratory to HKUST and filtered through a 0.45-µm membrane filter before use. Granular ferric (hydr)oxide (GFH) was obtained from GEH Wasserstein GmbH & Co. KG (Germany) and used without further manipulation. Sediment and water samples were collected from an odorous box culvert in Jordan Valley in Hong Kong. Concentrations of dissolved Fe (II) and Fe (III) were measured by the method phenanthroline. Methylene blue absorbance at 664 nm and Fe (II) complex -phenanthroline at 510 nm is obtained by using UV-Vis with a cuvette provides a light path of 10 mm. According to the results obtained. The combined use of granular ferric hydroxide (GFH) and common oxidizing agents was effective for removing hydrogen sulfide in aqueous systems and sediment. Recovery capacity of hydrogen sulfide removal is attributed mainly to the oxidation of Fe (II) compounds accumulated on the surface ferric (hydr)oxide (GFH) and simultaneous formation of amorphous ferric (hydr) oxides of small particle size and large surface area. Compared to conventional methods, such as frequently adding oxidants in the water / sediment systems, the integrated process comprising dosing of iron granules, adding occasionally to regenerate oxidizing the iron granules used, and reuse iron granules can be a long lasting and economical solution for the control of hydrogen sulfide. A similar result, obtained by (Berner, 1984) earlier, the responses between dissolved sulfide and ferric hydroxides are well-documented, and it arises in a variety of natural, anaerobic environments.

The reaction between the dissolved sulfide and synthetic ferric hydroxide was studied in artificial sea water, which, granular ferric hydroxide (GFH) can maintain the sediment phase with almost no loss of iron into the bulk water and continuously pressed dissolved sulfide production. The reaction between dissolved sulfide and ferric hydroxide has been recognized as a surface-controlled process. The results revealed that, the derivation of rate stabled for the oxidation of sulfide and the dissolution of Fe (II) in sea water at pH 7.5, suggests that rates of sulfide oxidation are extremely faster than rates of Fe(II) dissolution, but results in a reduced level of 65-80% for goethite, magnetite, and hematite. The decline in the reaction rate is likely to emerge from the

surface of the site blocking to sulfide complexation by adsorption solute sea water during the later stages more slowly than adsorption. Joint assessment of the effects of surface properties and competitive adsorption shown that these factors cannot explain the various observed in Fe (oxyhydr) reactivity oxide. Intrinsic factors such as the strength of the bond and the electron mobility also seems to be an important influence on the reactivity (Poulton, Krom, & Raiswell, 2004).

The steel-making slag (SMS) 2–5 mm in diameter used to investigate and reveal the mechanisms of hydrogen sulfide removal process in the in-pore water of organically enriched sediments (K. Kim et al., 2012). Steel-making slag (SMS) was mainly composed of CaO, SiO2, Fe, Al2O3, MgO, and MnO, at compositions of 45.93, 15.48, 13.75, 5.97, 5.28, and 4.85%, respectively. To assess the amount of hydrogen sulfide other than the steel slag, control experiments were carried out without the steel slag and the experiments were performed in triplicate. The initial condition of hydrogen sulfide (final steel slag making) was analyzed by the XAFS analysis. The results showed that the concentration of hydrogen sulfide decreased significantly in all experimental cases with the maximum decrease of ca. It proved that, Steelmaking slag (SMS) capable of removing hydrogen sulfide dissolved in water, and the maximum removal amount of hydrogen sulfide per unit weight of the SMS for 8 days was estimated to be 37.5 mg S/g. Chemical forms of sulfide adsorbed on the the Steel-making slag were estimated to be sulfur and manganese sulfide in the ratio of 81% and 19%, respectively. From these results, it was determined that the two processes, namely, the oxidation of hydrogen sulfide and sulfur compounds precipitate formation, simultaneously occur with the addition of steel making slag.

2.2.9 Drive Iron and Sulfur Cycling in the sediment

Zoning biogeochemical processes that occur in and around the zone of sulfidic sediments around the SMT system is dominated by a reactive metal. Pyrite is formed in the middle of the sulfidic zone. On the outskirts of the top and bottom of the sulfidic zone, the interval at which Prevails pyrite formation is limited by the zone in which the sulfurization of organic materials dominate. Polysulfides provided by free sulfide reaction with zero-valent sulfur, which in turn is supplied by oxidation of sulfides with iron hydroxide. Given the refractory nature of the organic

matter, it is interesting that the sulfidation outcompetes pyrite formation. Above and below the zone of sulfidic, elemental sulfur, and iron mono-sulfide build phase, a process driven by the oxidation of sulfides, which produces S0 and iron deposition induces mono-sulfides iron and iron by reaction with ferric iron, reported by Riedinger et al (2017).

Buongiorno et al., (2019) reported that the sulfide produced by microbial sulfate reduction can be re-oxidized by sulfur oxidizing agents, such as Thiobacillus or Sulfurimonas. However, it must microbial sulfate reduction exceeds the microbial sulfur oxidation, excess sulfide will precipitate with the reduced iron to form iron sulfide minerals, which reduces the amount of iron being transported to the shelf. The decline in overall exports reduced iron can affect primary production along the shelf, where the removal of key micronutrients can reduce phytoplankton populations that represent a large sink for carbon dioxide in the atmosphere.

The mineralization of particulate organic carbon drives the iron and sulfur cycles in marine sediments, which, sulfate reduction is the dominant method of oxidation of organic carbon in anoxic marine sediments. The products of this process, hydrogen sulfide is partially oxidized in anoxic sediments as documented by the depth profile of S^0, FeS, FeS$_2$, and porewater SO^{2-}_4 concentrations reported by Schippers and Jorgensen, (2002).

Canfield, et al., (1993) reported that the electron donors for dissimilatory sulfate and iron reduction are H2, formate, acetate or other volatile fatty acids produced by microbial fermentation of organic matter. This makes the biogeochemical cycling of carbon, iron, and sulfur inextricably linked.

3 Analysis of field survey data

3.1 Outline of Survey

As far as we know that the sulfides in the blue tidewater mass pairs are more important than low concentrations of oxygen but, the effects of hydrogen sulfide based on biological communities and the mechanism of sulfide accumulation in the environment have been rarely investigated. So, it is required to go and understand the water and sediment quality of the actual tidal flats and other ecosystems affected. To integrate these results and reduce the effects of hydrogen sulfide and hypoxia or anoxia, we propose and quantify the effects of specific measures. For the above purpose, we have conducted various surveys to collect as much information as possible, on the quality of water and sediments of Isa Bay.

Preliminary analysis of the field survey data will support our laboratory findings to identify characteristics of the horizontal and vertical distribution of hydrogen sulfide contaminated sediment and its seasonal variations, and to find out where and when the proposed method of iron application can be applied to reduce hydrogen sulfide release effectively from contaminated sediment. In this section, we looked at vertical and horizontal changes in sediments and nutrient distribution capacity in the Isa Bay and Mikawa Bay.

Field survey data were collected as part of a study to assess options for sediment information, data was collected by the Port and Airport Research Institute (PARI) during 2016 and 2017. The concept of data collection focused on anoxic water that is potentially affected by contaminated sediment, and endogenously produced hydrogen sulfide. In addition, we studied the physical-biological and chemical effects, including anoxia and sulfide (including hydrogen sulfide) avoidance behavior. To assess the effects of anoxic water masses and sulfides on the benthic marine resources in the Isa Bay, the water and sediment quality observations acid Volatile Sulfide (AVS), biochemical oxygen demand (BOD) chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen(TN), the total phosphorus (TP), total iron (T-Fe) and total manganese (T-Mn)were observed. These secondary data were collected to achieve the objectives of this study. Below is a link to the interactive Field Survey Map Figure 3.2 2.
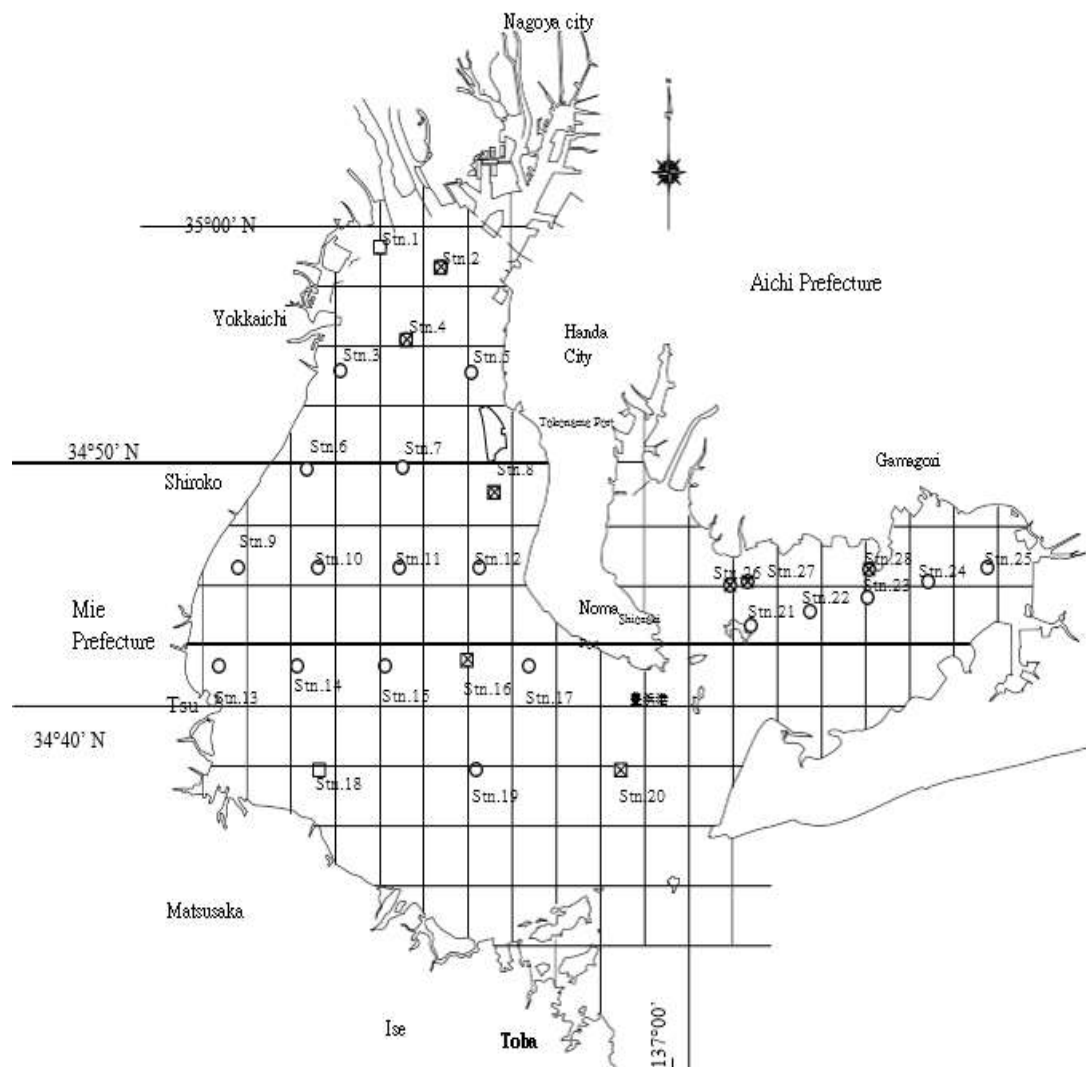
Figure 3.1.1. Sketch-map of Ise and Mikawa Bays showing survey stations.

3.1.1 Study site

Isa and Mikawa Bays are located the middle part of Japan, the (water area: 1783km2, mean depth: 20m) is the semi-enclosed structure with a narrow entrance to the Pacific Ocean, a cavity in the central portion which inhibits the exchange of seawater with the open sea, and to the relatively shallow Mikawa Bay (water area: 604 km2, mean depth: 9m) to the southeast. Isa Bay catchment area is 18 153 km2. Three major rivers, Kiso, Nagara, and Ebi, streams flow through the Inner part of Ise Bay "as shown in figure (3.1.1.1)", which contributes more than 80% of the total river discharge eight, during the spring and summer season, water is intensely stratified by

heating and large run-off. the seasonal alteration is large in summer (~ 1000m3 / s) while small in winter (~ 200m3 / s), seasonal transition is caused by both changes in input surface heat and freshwater, because it's always contributes (~85 %) of the total freshwater flows into the Bay.

Figure 3.1.1.1Three big streams, the Kiso, Nagara and Ibi Rivers

The depth of the water is equivalent to the strait inner bay, different from the fjord type

ROFI. But the tides runes very strong in the strait ensures vigorous stirring which promotes strong vertical mixing of the oceanic heavy water with relatively lighter water from the bay to produce intermediate-density water. On the top layer at bay, both temperature and salinity contribute to the density of the structure, while the dominant controller is the temperature at the bottom layer, the northwest monsoon winds of the Eurasian continent dominates in winter, and the south sea breeze is not in the warm season. Several cultural and fisheries industries are in operation there. But, due to an increasing load of nutrients from rapid industrial development since the mid-1950s, as well as from livestock farms and municipalities, the bays have become highly eutrophicated and hence have induced intense red tides and blue almost every year during summer, In excess, it leads to the development of obnoxious species, to the elimination of desirables species, and ultimately, to the development of anoxic conditions and the elimination of all higher forms of life (Kasai et al., 2002;Y. Tanaka, et al., 2014; Higashi et al., 2012; Suzuki, 2004; LU & MATSUMOTO, 2009;Sugimoto, et al., 2006). The main reason that many species are endangered is the presence of hydrogen sulfide (H2S) concentrations in the water body, which, hydrogen sulfide (H2S) is produced by an action of sulfur-reducing bacteria (SRB) in the liquid phase under anaerobic conditions, as mentioned in section 1 first paragraph, hydrogen sulfide is very toxic to aquatic organisms. Therefore, we began a study of the reduction of dissolved sulfides and suppression of the formation of hydrogen sulfide gas by placing irons compound onto the sediments with reviews from field studies.

3.1.2 Field sampling methods

Measurements were made at a total of 28 station point. At each station, the bottom mud (0-5 cm from the seabed surface) collected by an undisturbed columnar mud collector. In addition, the dissolved oxygen concentration of the seafloor water (5 cm from the seafloor surface) was measured with a fluorescent DO sensor. The temporal change and spatial distribution of hydrogen sulfide in anoxic water mass, seafloor water and sediment were investigated. The samples from each points of the survey were analyzed. The results of these analyses were important to all subsequent planning steps.

3.1.3 Physical Properties of Sediment

Sediment samples were collected from 28 different locations of Isa Bay. The selected

samples were dried to air-dry state *in vitro*. Seven primary sediment types occurred in the Isa Bay, Clay, Silt, Fine sand, Medium sand, Coarse sand, Fine gravel, and Medium gravel.

The granulometric analysis of the sediments from the Isa Bay has determined the predominance of silt and silty-clayed muds (Figure 3.1.3 .1) sediment received its name in accordance with the particle-size distribution of the sample with a semi-dispersed preparation. Coarse-grained sediments, for example, sand- and gravel-grained sediments are deposited near the bay mouth. The total content of silt with the particle size of (.002 mm to .05 mm) fraction is mainly up to 60–70% (Figure 3.1.3 .2). In clay muds, the content (less than .002 mm) fraction was mainly up to 40 %. However, slight differences were observed on the following stations (20th, 26th, 28th respectively), the fraction from fine sands (0.063-0.25mm) were approximately 70-90%. The content of the medium sand fraction (>0.25 mm) in almost all samples does not exceed 1%. The graph shows how the content ratio of the particles by a fraction of more changes to an increasing number of micro-fine particles with aggregate maximum damage in the case of dispersed sample preparation. From the results of study, the concentration of TOC was found high at the stations (1st, 2nd, 3th, 4th 6th, 7th, 8th, 9th, 10th, 11th, 12th, 13th, 14th, 15th, 16th, 18th, 23rd, 24th, and 25th) Figure 3.1.3 .3, the same tendency was also observed with the water content measurements Figure 3.1.3.4. While, there were no significant differences observed at station (5th, 17th, 20th 21st 22nd, 26th and 28th)**.** This is because the fine particle sediment provided binding sites of the greatest organic carbon for absorption. Perhaps strengthening the process of absorption and cause accumulation of TOC in the bottom of the water column.

Therefore, the particle size sediment might be playing a significant role as the controlling factor of the concentration of TOC in surficial sediments at Isa Bay. Indeed, the presence of pollutants in sediments is affected by sediment particle size and composition with fine-grained sediments associated with sulfide potentially toxic to living organisms.
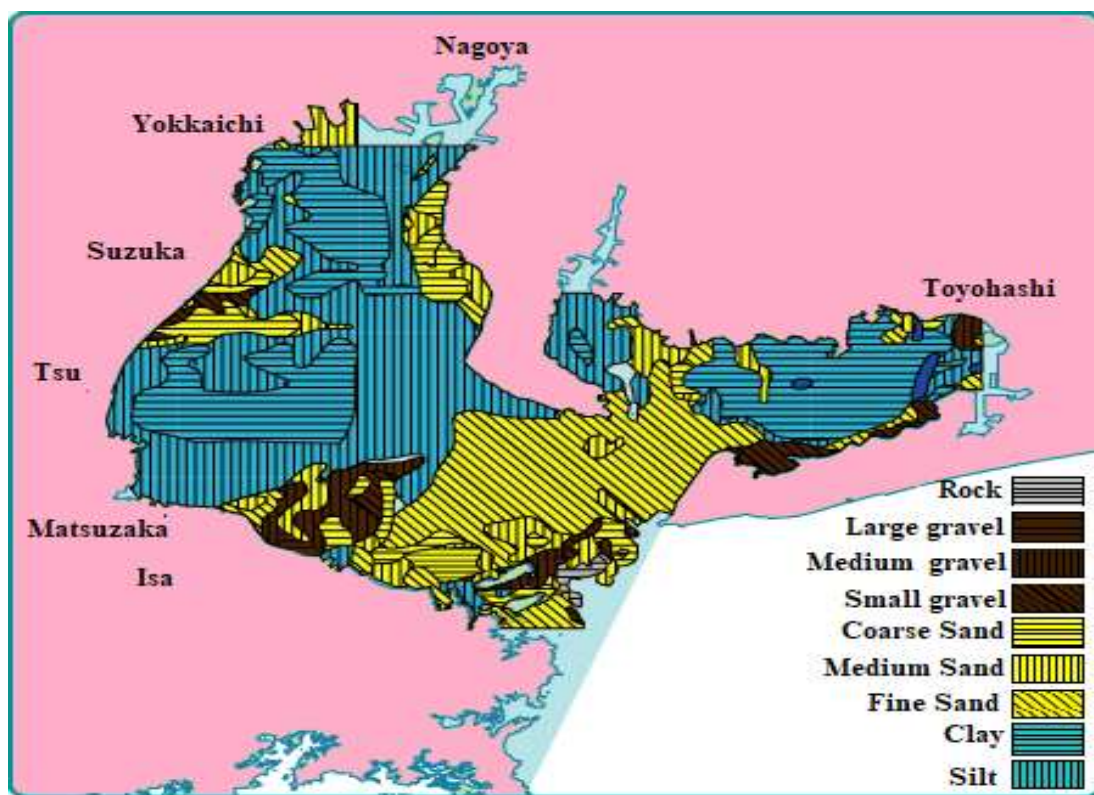
Figure 3.1.3.. 3.1*3*.Submarine geological map
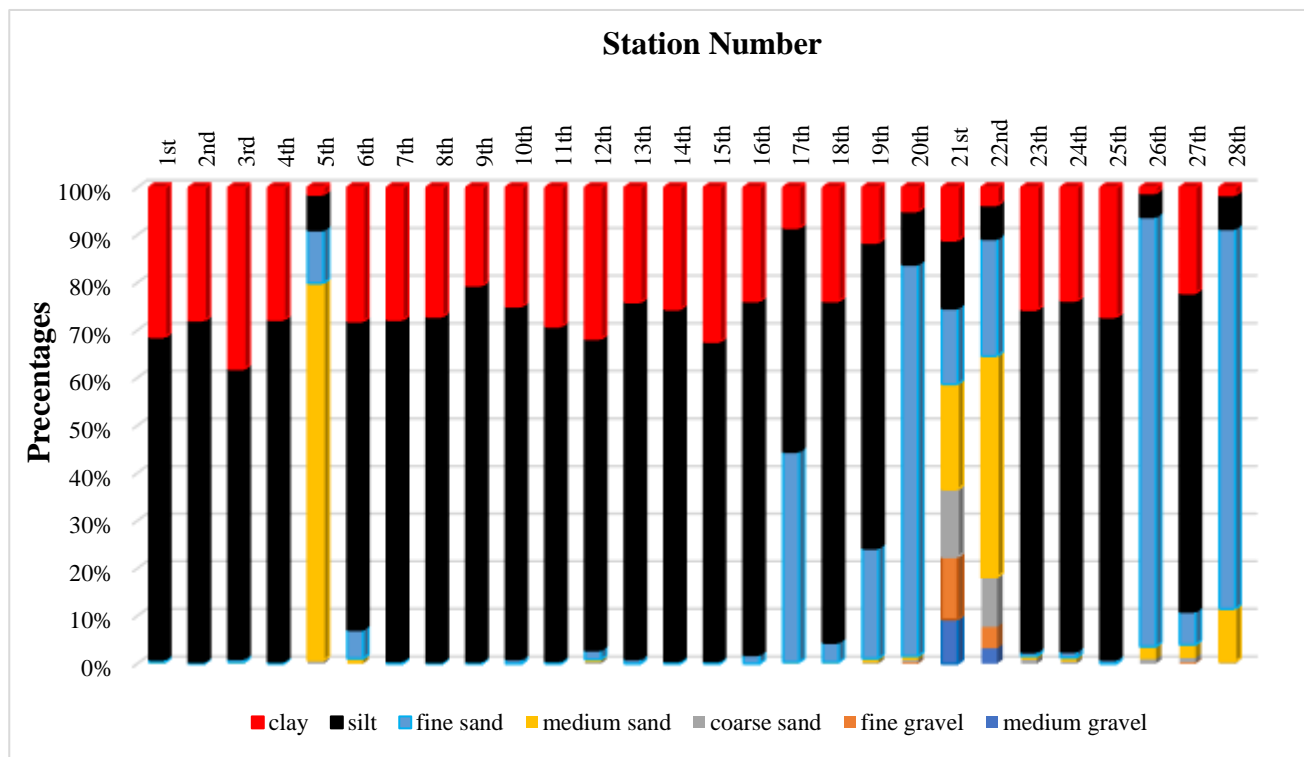
Figure 3.1.2.The particle contents in the Isa Bay sediment samples.
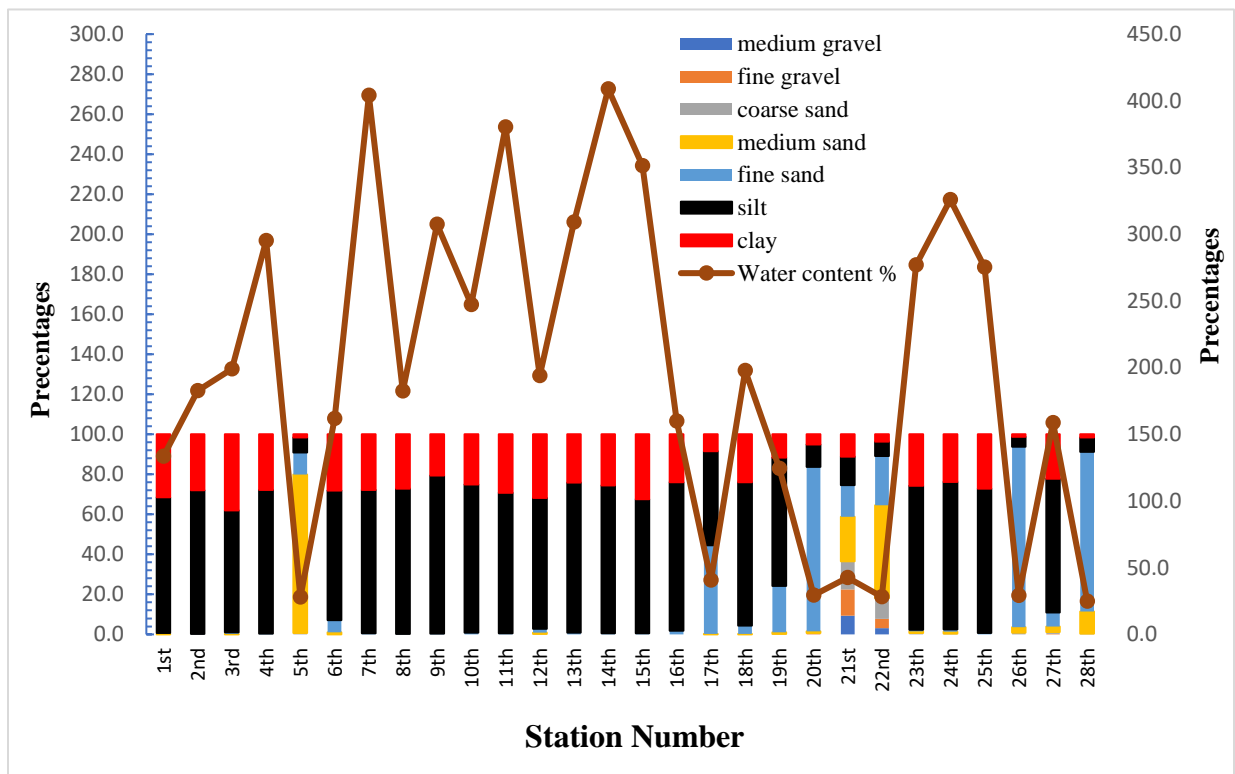
Figure 3.1.4.The particle contents and water content % in the Isa Bay sediment
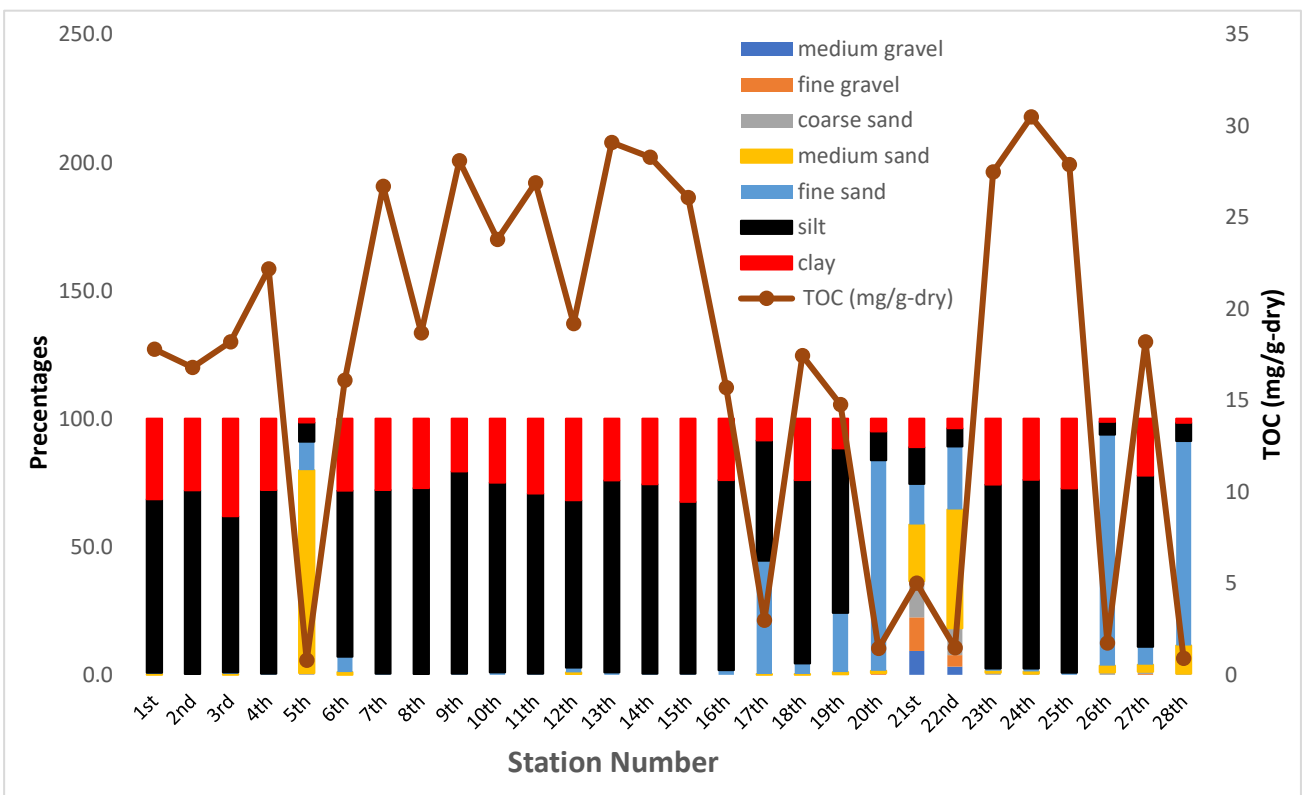
Figure 3.1.5.The particle contents % and TOC (mg/g-dry) in the Isa Bay sediment

60

3.1.4 Organic-matter content in sediments.

Based on the sediment survey result "as was shown before figure 3.1" provided by the Port and Airport Research Institute (PARI), the survey site, which is investigating 20 locations in Ise Bay and 8 locations in Mikawa Bay. Horizontal distribution of acid volatile sulfide (AVS), water content %, total organic carbon (TOC), total nitrogen (TN), the total phosphorus (TP), and biochemical oxygen demand (BOD) in surface sediment of the bays are shown in (Figure 3.1.4.1-3.1.4.8) In Ise Bay, highest concentrations of acid Volatile Sulfide (AVS), water content %, total organic carbon (TOC), total nitrogen (TN), the total phosphorus (TP), and biochemical oxygen demand (BOD) were found at stations (1st,4th, 14th, 18th and 27th), the next highest concentrations with the same parameters were observed at stations (7th, 9th, and 16th) "as shown in (Figure 3.1.4.2)". While, in Mikawa Bay, acid Volatile Sulfide (AVS), water content %, total organic carbon (TOC), total nitrogen (TN), the total phosphorus (TP), and biochemical oxygen demand (BOD) s were the highest station 27th. In general, the highest AVS contents were found in the Northern part of the Isa Bay. Indeed, TOC is one of the controlling factors in the regulation of chemicals and biological surface sediments, as can be seen in figure (3.1.4.3) the distribution of AVS in pore water is very similar to that of the TOC content of surface sediment. This is because a high number of organic matters is promoting the growth of anaerobic bacteria which allows the generation of hydrogen sulfide. Accordingly, the nutrient discharges of the ten main rivers flowing into the Isa and Mikawa bay the Kiso, Nagara, and Ibi Rivers, which contribute over 80% of the total ten river discharge, these three rivers are located on the northern coast, "shown figure 3.1.4.9". These observations suggest that for sites station where mine-waste oxidation has progressed.
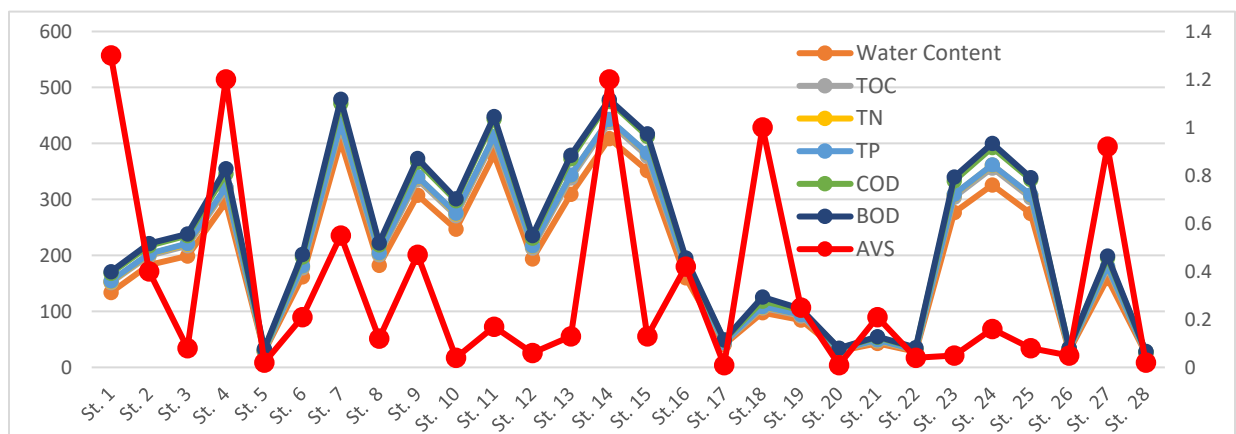
Figure 3.1.4.1.Comparison of AVS, BOD TOC, TN, and TP   concentrations measured in sediment samples at the different stations.
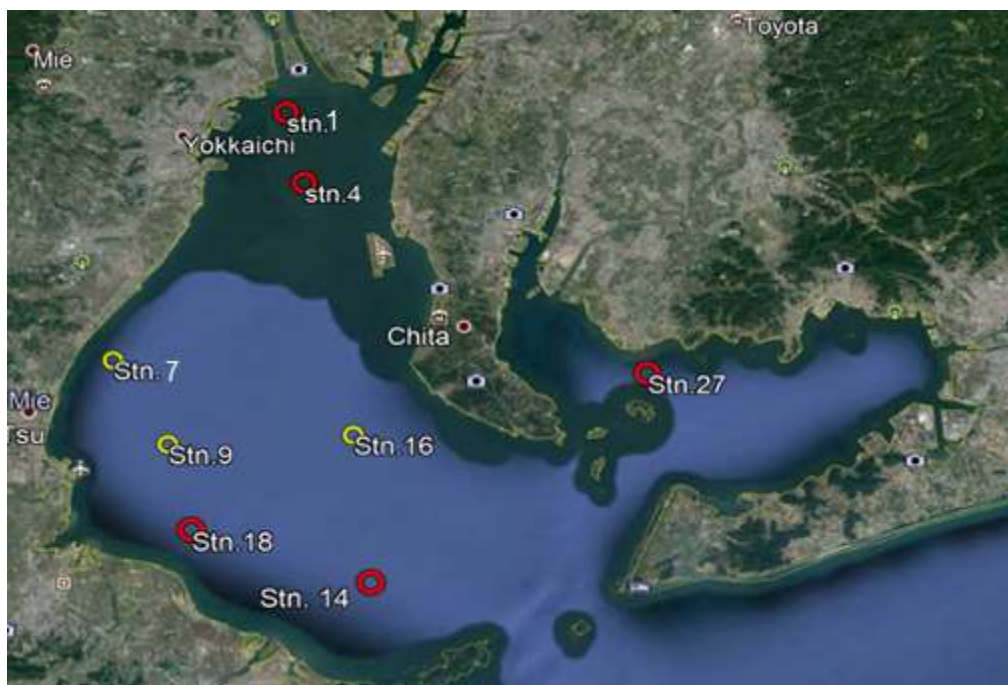
Figure 3.1.1.The horizontal intensity distribution of AVS.
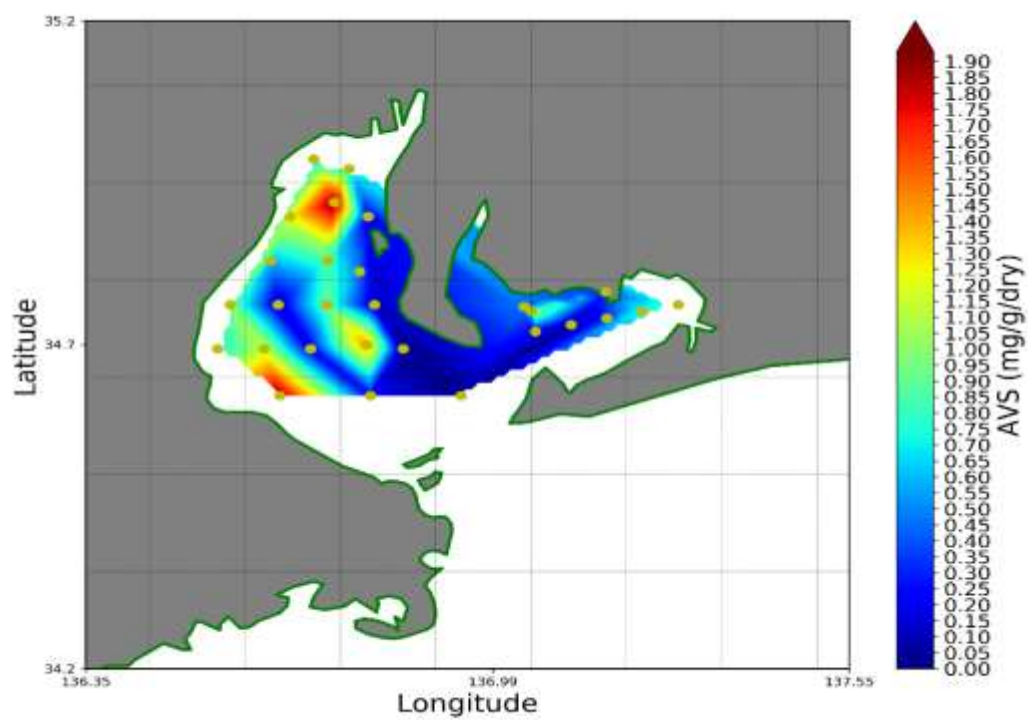
Figure 3.1.4.3. Horizontal distribution of AVS.
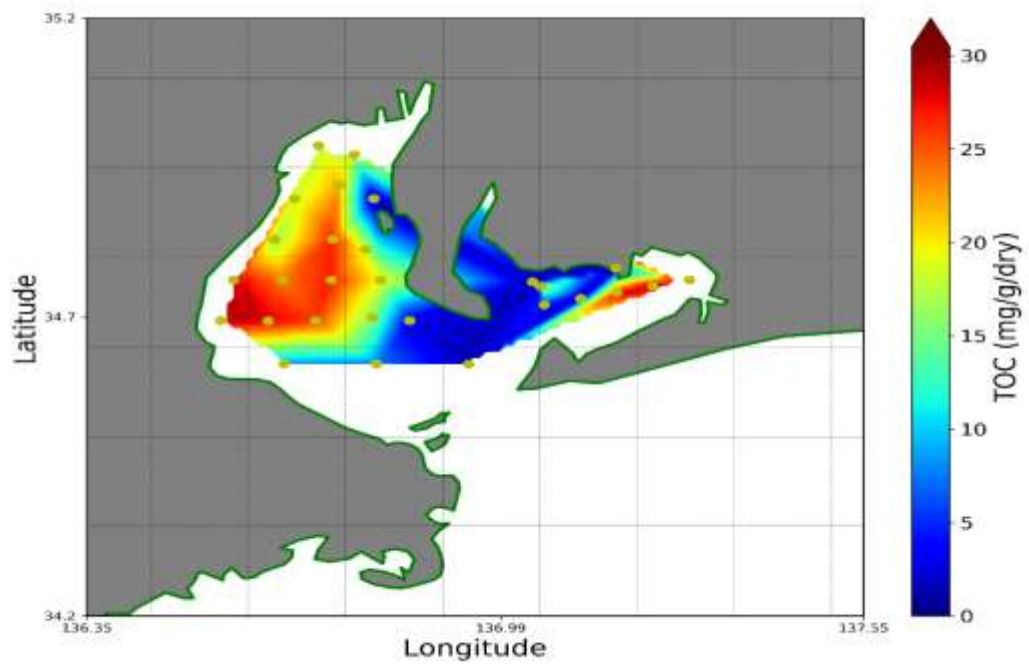
Figure 3.1.4.4.Horizontal distribution of TOC.
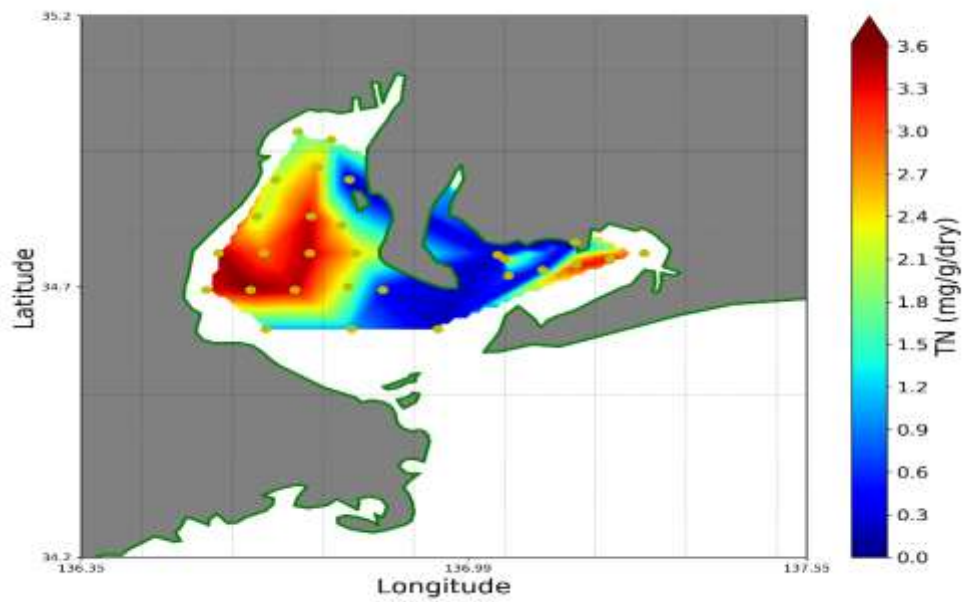
Figure 3.1.4.5..Horizontal distribution of TN.
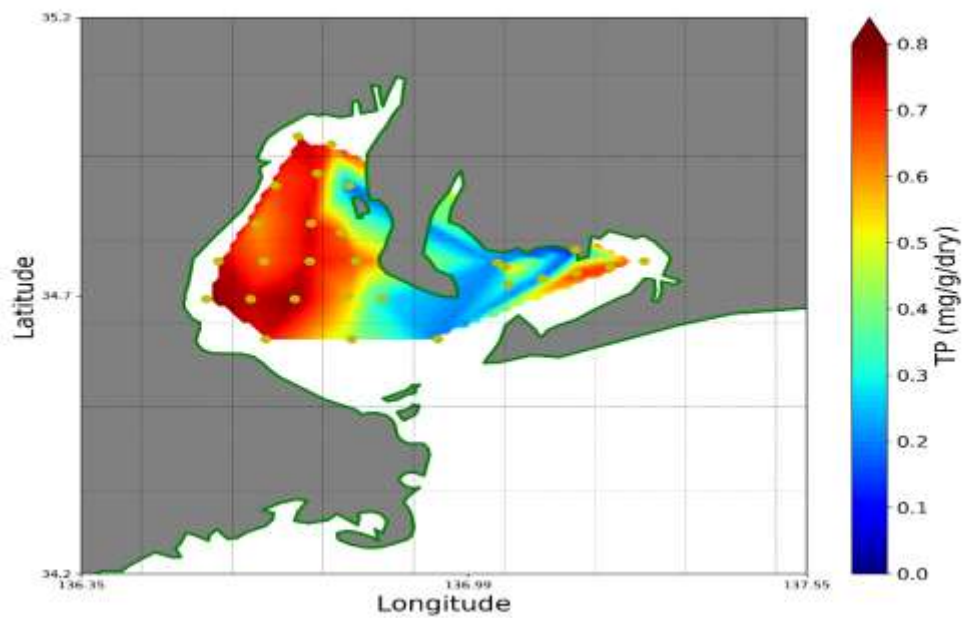
Figure 3.1.4.6..Horizontal distribution of TP
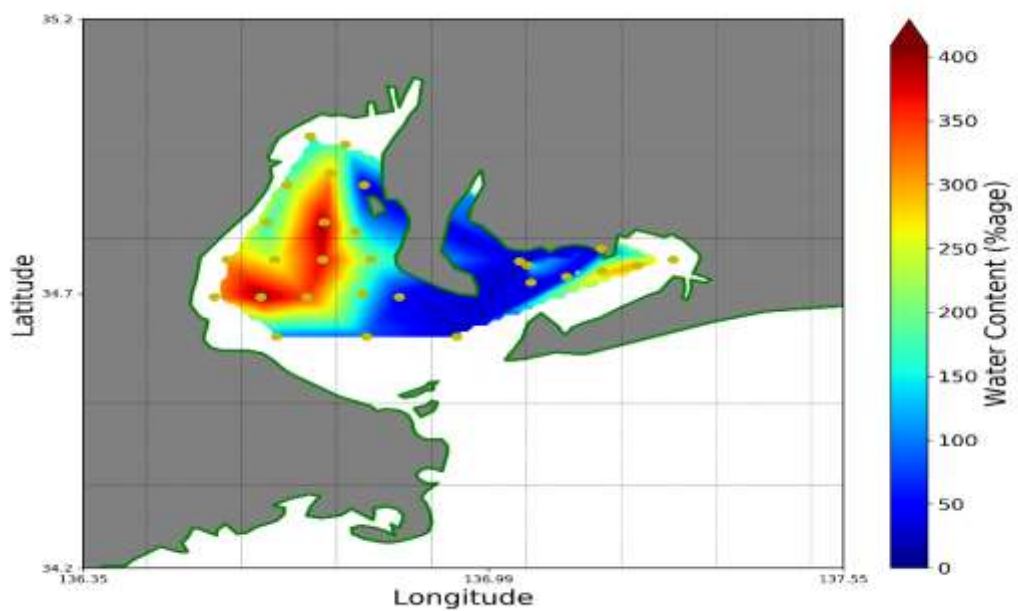
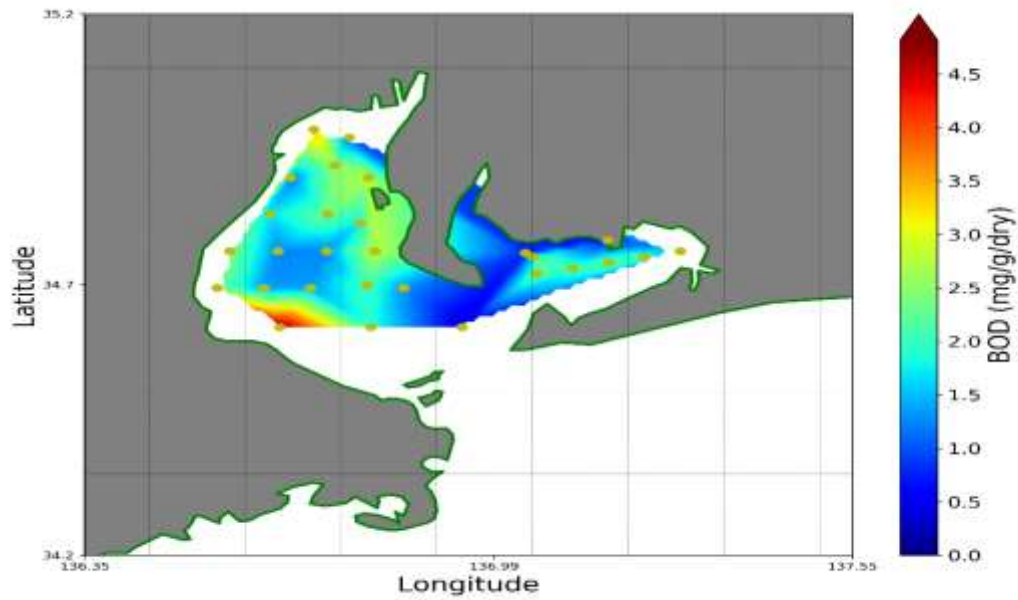

Figure 3.1.4.7..Horizontal distribution of water content.

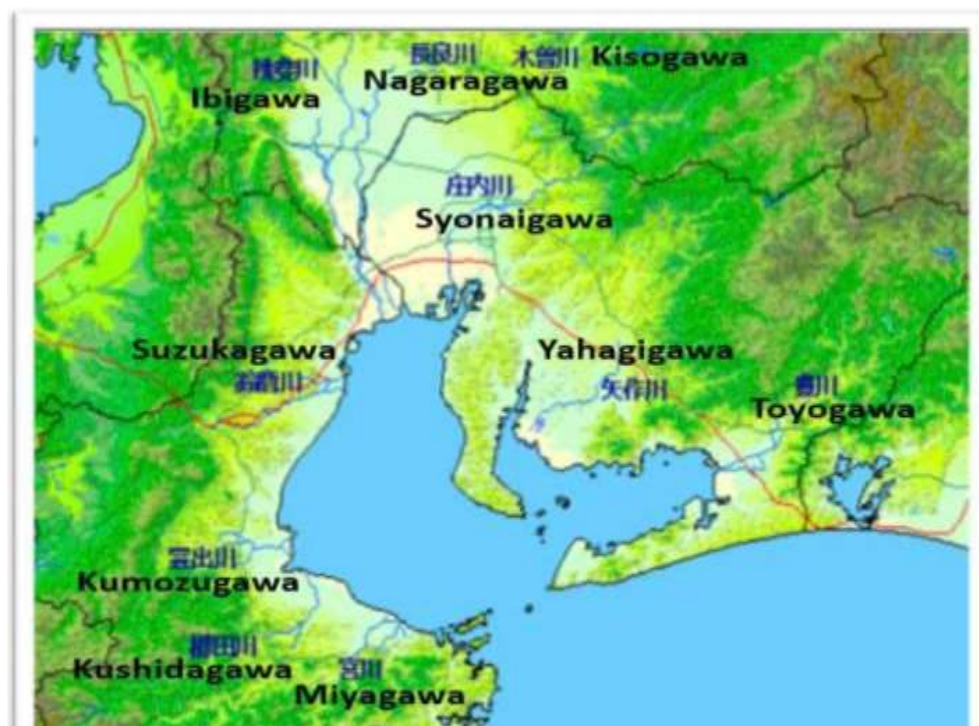Figure 3.1.4.8. Horizontal distribution of BOD.

Figure 3.1.4.9. Ten main rivers flowing into the Isa and Mikawa bay

The Multiple Regression as a Predictive Statistical Model

The results presented in the previous section have revealed some, similar distribution with (AVS), water content, (TOC), (TN), (TP), and (BOD) contents in surface sediment of the bays. Generalized linear models for regression is:

$$Y = b + m_1X_1 + m_2X_2 + m_3X_3 + \ldots + m_iX_i + \varepsilon_i$$

where Y is the expected (or predicted) value of the predicted variable for a given set of X values which serve as predictor variables; m_i is the estimated slope of the regression of Y as a function of the ith predictor variable X_i, and b is the estimated intercept. The "regression error", ε, is the amount by which the "true" value of Y differs from what is predicted by the regression equation (Zar, 2010).

Multiple regression analysis examines the effects of multiple predictor variables (Xi) on the value of a predicted variable (Y) and attempts determine a formula that can describe the functional relationships between the predicted variable and multiple predictor variables. In this study, multiple regression analysis was used to determine the combined effects of variables correlated to AVS to see the unique combination of predictors, indeed, the AVS ratio is a simple technique used to estimate sediment toxicity, and there were total of five different parameters considered for the multiple regression. All of the predictor variables (Xi) described in this study (TOC), (TN), (TP), and (BOD) served as predictor variables in a multiple regression analysis to predict AVS concentrations (Figure 3.1.5.1 and 3.1.5.2). Multiple regression analysis of AVS on the (TOC), (TN), (TP), and (BOD) have been moderately successful in establishing area correlations, as each of the four predictor variables were significantly correlated with the predicted variable, AVS, that dependent primarily upon regional estimates of site station. Results of the multiple linear regression (Table 3.1.5 1, 3.1.5 1 and 3.1.5 1) indicated that there was a collective significant effect between the AVS (calculated) and AVS (observed) $R^2 = 0.5365$. The individual predictors were examined further and indicated that between AVS and BOD ($R^2 = 0.3928$) Figure (a) water content ($R^2 = 0.3243$) Figure (b), similar, TN ($R^2 = 0.3204$) Figure (c) were significant predictors in the model. A weak relationship was found between AVS and TP ($R^2 = 0.2421$) Figure (d). it can be said that it is a very effective means to grasp various diverse bottom sediment distributions.

Table 3.1.5-1.Analysis of AVS, BOD,TN, TP and water content release rate from field data of Isa Bay (September 2017).

AVS	BOD	WATER CONTENT	TN	TP	AVS(CALCULATED)
1.3	3.48	433.5	1.59	0.757	0.8114785
0.40	1.0296	182.8	1.84	0.693	0.1569728
0.077	1.1832	199.1	0.29	0.669	0.1061323
1.2	2.496	495.2	3.67	0.920	0.7896585
0.015	2.736	28.0	0.11	0.164	0.2820532
0.55	1.6752	161.9	1.99	0.596	0.2786935
0.21	2.2968	404.0	0.342	0.739	0.4838793
0.12	1.7112	182.4	1.34	0.647	0.2600511
0.17	2.424	307.4	3.51	0.759	0.6243365
0.039	1.2336	247.1	0.295	0.641	0.1553747
0.060	1.2528	380.3	3.50	0.736	0.4557656
0.49	2.784	194.0	2.52	0.665	0.5479799
1.2	2.3520	409.1	3.34	0.801	0.6786908
0.13	1.3200	40.8	1.64	0.752	0.0860716
0.13	1.3512	351.4	3.49	0.793	0.4488717
0.42	2.052	159.9	2.04	0.574	0.3540207
0.009	1.3032	40.7	0.39	0.280	0.0269138
1.0	4.824	297.7	4.03	0.732	1.1139361
0.25	1.9224	84.5	1.03	0.444	0.2133242
0.014	0.4056	29.3	0.19	0.201	-0.164577
0.21	2.2560	42.7	0.66	0.316	0.2277727
0.036	2.0208	28.3	0.20	0.180	0.1486934
0.053	2.1840	276.9	3.28	0.707	0.5419871
0.16	2.124	32.6	0.54	0.727	0.1691786
0.082	1.5552	275.2	1.03	0.674	0.283222
0.046	0.7848	29.2	0.23	0.209	-0.089187
0.92	2.1120	158.8	3.25	0.616	0.4367148
0.017	0.6552	24.9	0.13	0.122	-0.120009

Table 3.1.5-2. Residual output.

OBSERVATION	PREDICTED AVS	RESIDUALS
1	0.811478508	0.4885215
2	0.156972797	0.2430272
3	0.106132275	-0.029132
4	0.789658468	0.4103415
5	0.282053185	-0.267053
6	0.278693493	0.2713065
7	0.48387929	-0.273879
8	0.260051081	-0.140051
9	0.624336496	-0.454336
10	0.155374654	-0.116375
11	0.455765644	-0.395766
12	0.54797987	-0.05798
13	0.678690797	0.5213092
14	0.086071586	0.0439284
15	0.448871715	-0.318872
16	0.354020738	0.0659793
17	0.026913847	-0.017914
18	1.113936066	-0.113936
19	0.213324169	0.0366758
20	-0.1645775	0.1785775
21	0.227772674	-0.017773
22	0.14869342	-0.112693
23	0.541987104	-0.488987
24	0.169178626	-0.009179
25	0.283221969	-0.201222
26	-0.08918692	0.1351869
27	0.436714804	0.4832852
28	-0.12000885	0.1370089

Table 3.1.5-3. Analysis of variance (ANOVA).

DF	SS	MS	F	SIGNIFICANCE F	
4	2.403318009	0.60083	6.6565156	0.00103451	
23	2.076022848	0.09026			
27	4.479340857				
COEFFICIENTS	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
-0.269152774	0.194143533	-1.3864	0.1789306	-0.670769271	0.132463723
0.193503083	0.07219098	2.68043	0.0133584	0.044164664	0.342841503
0.00079118	0.00066336	1.19269	0.2451521	-0.000581085	0.002163444
0.060964239	0.06224425	0.97944	0.3375555	-0.067797803	0.189726281
-0.04315597	0.434457985	-0.0993	0.9217347	-0.941900786	0.855588846

(a) BOD
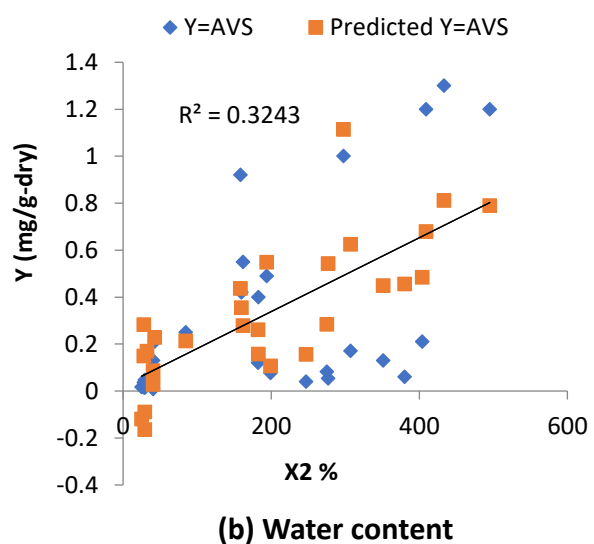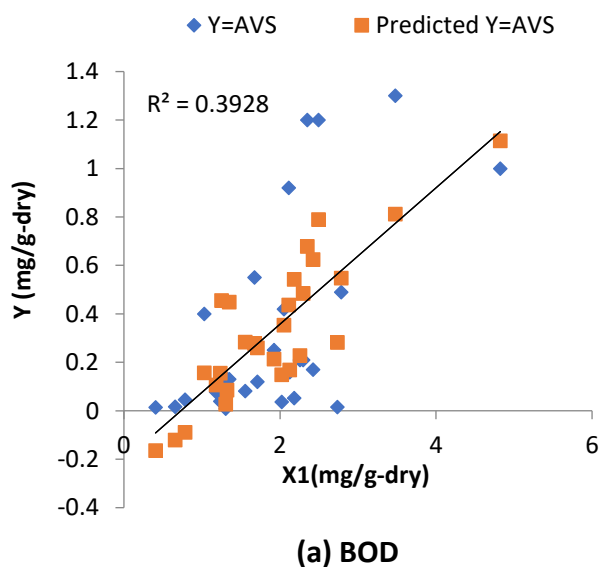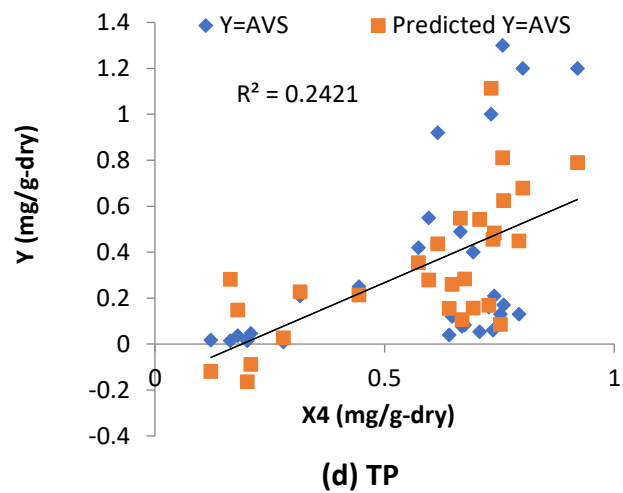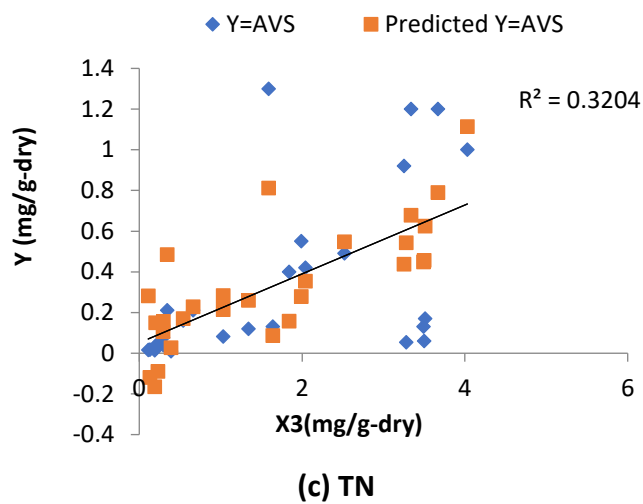
(b) Water content

Figure 3.1.2. Relationships between AVS and BOD (a) AVS and water content (b), AVS and TN (c) ANS and TP (n=28).
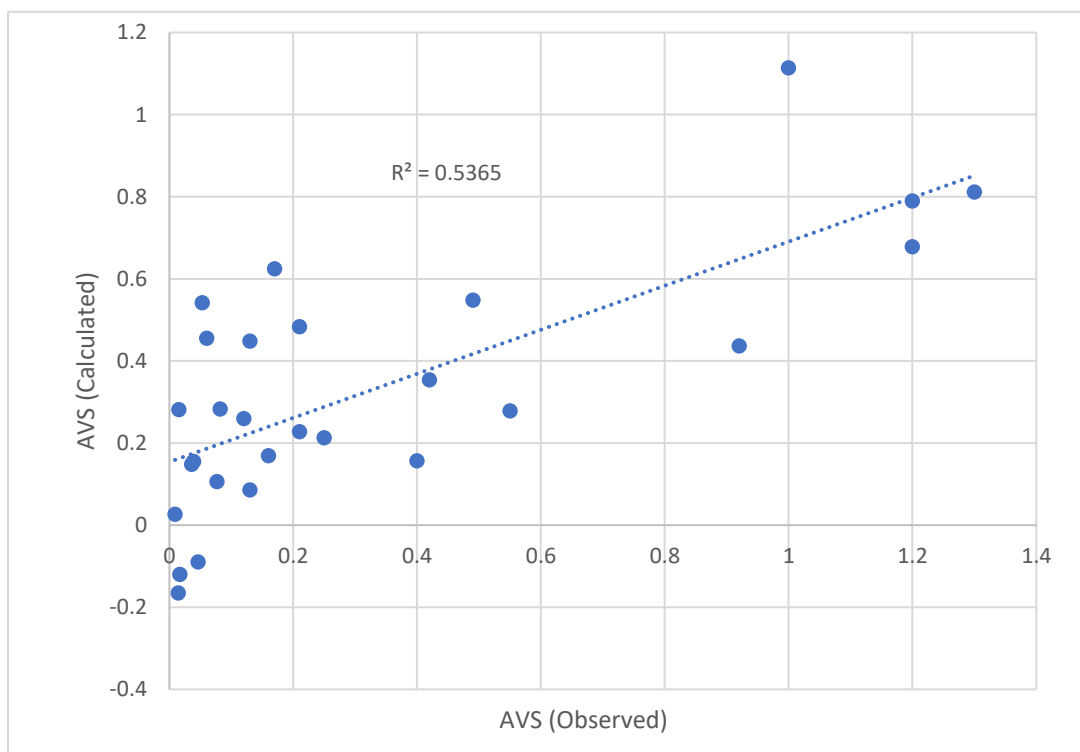
Figure 3.1.3.Multiple regression between observations between AVS (calculated) and AVS (observed)

3.1.5.1 *Relationships between water content and chemical characteristics.*

The sediment at the bottom in Isa and Mikawa Bay was found to be of very soft. the organic matter type is an important controlling factor for the activity of sulfate-reducing bacteria, and based on the results of our study, sediments with higher moisture content had higher concentration of organic content and nutrient concentration. In addition to the results, sediment quality parameters were also highly correlated with moisture content as shown in the figures and table 3.2.4.1 1.

Table 3.1.5-4. Table 2. (The Pearson correlation coefficients between water content in the Isa Bay sediment and TOC, TN, TP, TM, and COD).

Parameters	MC	TOC	TN	TP	TM	IOL	COD
MC	1.000						
TOC	.776∗∗	1.000					
TN	.813∗∗	.980∗∗	1.000				
TP	.561∗	.891∗∗	.866∗∗	1.000			
TM	.623∗∗	.865∗∗	.812∗∗	.842∗∗	1.000		
IOL	.914∗∗	.685∗∗	.756∗∗	.481∗	.460∗	1.000	
COD	.617∗∗	.797∗∗	.806∗∗	.793∗∗	.715∗∗	.540∗	1.000

∗Correlation is significant at the 0.05 level (2 tailed).

∗∗Correlation is significant at the 0.01 level (2 tailed).

In this study, simple functional relationships of the other variables in a population is a simple linear regression, defined as:

$$Y = b + mX_i$$

where Y and X represent the predicted and predictor variables, respectively; m (the slope) is the regression coefficient in the sampled population, b (the y-intercept) is the predicted value of Y in the population when X is zero, and the subscript i indicates the ith pair of X and Y data in the

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sample (Zar, 2010).

The study of data indicated that there was a significant positive correlation between TOC (total organic carbon) and water content ($R^2 = 0.776$) Figure (a), TN (total nitrogen) and water content ($R^2 = 0.813$) Figure (b), TP (total phosphorus) and water content ($R^2 = 0.561$) Figure (c), T-Mn (total manganese) and water content ($R^2 = 0.623$) Figure (d), IOL (Loss-on-ignition) and water content ($R^2 = 0.914$) Figure (e). Similarly, high correlation ($R^2 = 0.617$) Figure (f) was observed between COD (chemical oxygen demand) and water content which confirms the understanding that high organic load and water content is related to COD (chemical oxygen demand) in dry mud.

(a)

(b)

(c)

(d)
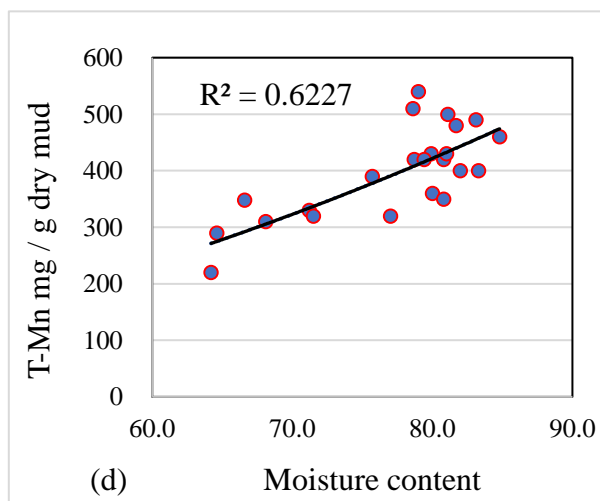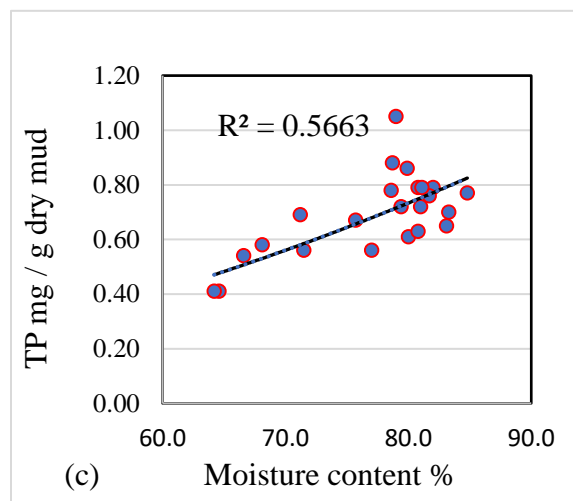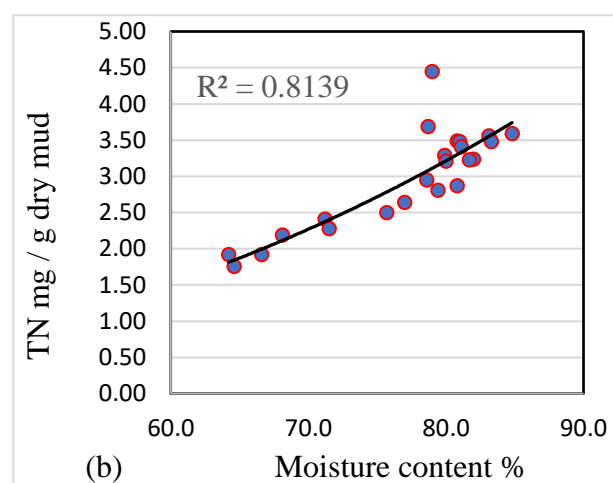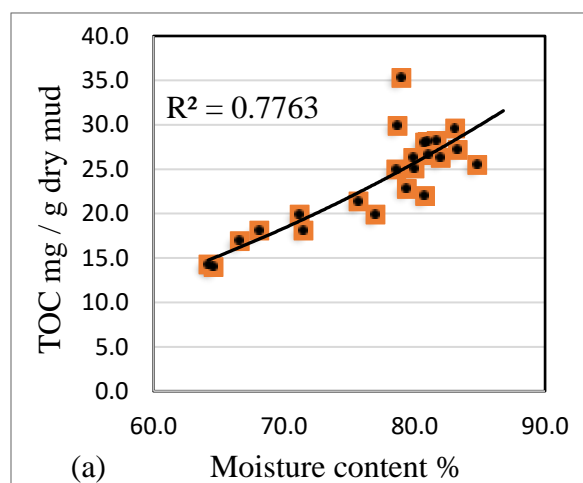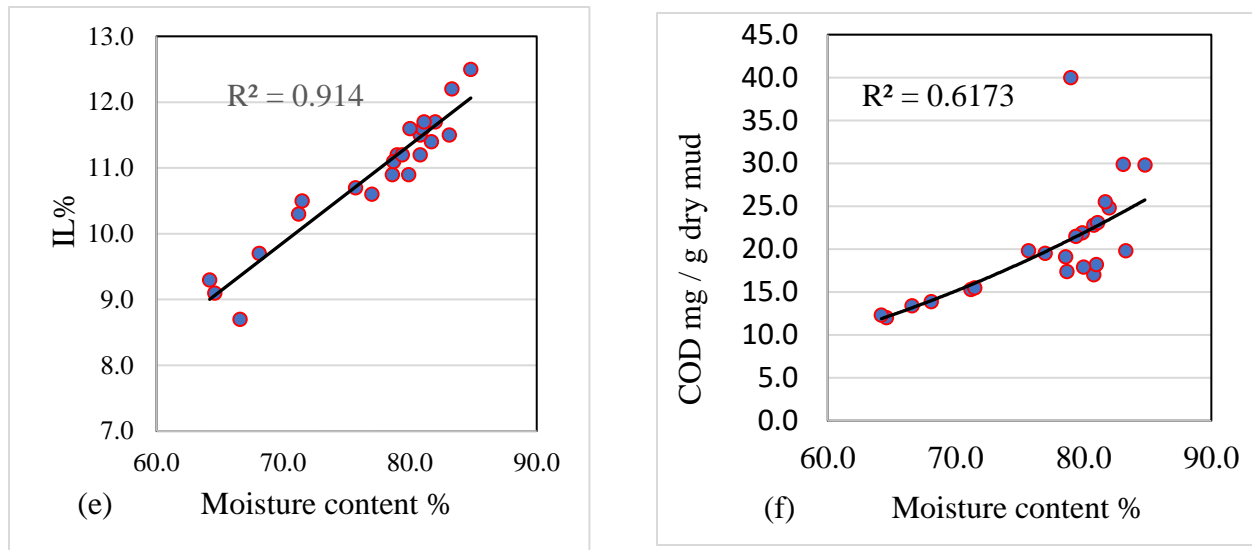
Figure 3.1.4Relationship between water content and sediment index (a) TOC, (b) TN, (c) TP, (d) T-Mn, (e) IL, and (f) COD

3.1.6 Discussion

Based on the results obtained, each index of the bottom mud was found to have a high correlation with the water content ratio, and high total organic contents were the main key to accumulate high TN and AVS contents. This work leads to a number of theoretical discussions. Based on previous research results, waste decomposition rates are known to be largely controlled by moisture content and increase moisture content to speed up the degradation, however, water content have a direct relationship to the amount of organic matter in the sediment. Hence, the organic sediment could absorb too much water inside and caused sediment particles arranged loosely, so the high organic content in the sediment, the high capability of water content absorption as well. Accordingly, the addition of organic matter (such as DOM or POM) to the marine environment has the direct effect of stimulating heterotrophic bacterial production in the water column and in sediments and these measurements were verified by comparison with sediment samples, and the field study demonstrated that sediment with a higher moisture content exists at the center of the bayhead. In Tokyo Bay, higher moisture content corresponds to smaller sediment particles, which predominantly consist of POM (Okada,et al., 2009) Examined sediment qualities in the Gulf of Santa Barbara and found that the amount of organic carbon increased 1% resulted in an increase of 9-28% of water content in the sediment. The result showed the high water content

of sediment from culture area than those of non-cultured area (Area, et al.,2015). Based on the results obtained by (Pawar, et al., 2002) it seems that the seasonal AVS contents showed significant correlations with seasonal organic carbon inputs and temperature. Multiple regression analysis showed that these two factors are explicated by 80% of the seasonal variation in the AVS content.

3.2 Dissolved sulfide vertical distribution in the Mikawa bay based on the expedition data 2015 and 2016

According to the survey, there were five stations included (0, 8, 9, 10, and 20) Figure 3.2.1, columnar mud was collected once a month from April 2015 to January 2017, and the sample was divided into 8 layers in total from the surface (0-1, 1-2, 2-3, 3-4, 4-5, 5-6, 9-10, 15-16 cm), and dissolved sulfide, iron sulfide, and dissolved iron in each layer were analyzed. Among these parameters, dissolved sulfide and dissolved iron were used as valuable data based on the requirements information for supporting our experiment hypothesis.

Results from pore-water analyses are summarized in Figure (3.1.6.2 - 7) According to data analysis, the dynamics of dissolved sulfide and iron in the bottom mud in the middle of the bay and the channel and anchorage, Dissolved sulfide increased in depth from late spring to summer at each station, Dissolved sulfide reached the bottom mud surface on August September and October 2015 at stations 0,8, and 9, similarly, in August and September 2016, at the stations 0, 9, and 20 dissolved sulfide were also increased as shown Figure (3.2.2). While, dissolved iron was distributed near the surface at each station. In general, water temperature increased from spring to summer, and the concentration of hydrogen sulfide in the sediment increased due to the depletion of dissolved iron and the predominance of anoxic water masses on the seabed. But unlike, as the temperature decreases in winter, the oxygen concentration in the seabed increases, and hydrogen sulfide is oxidized and lost. In December 2015, January, February and December 2016, at stations 0,8, 9, 10 and 20 the concentration of dissolved sulfide falls monotonically to zero, and reaches 4-5 cm below the seabed surface, while in the same depth the dissolved iron concentration high at all mentioned stations. Similarly, in January 2017, at stations 0, 9, 10 and 20, the dissolved sulfide concentration falls to zero, but dissolved iron concentration high at the same depth and all mentioned stations. According to the results of the survey, iron sulfide is gradually oxidized to

become dissolved iron and contributes to the suppression of the generation of dissolved sulfide.

Moreover, this may be understandable that the oxygen concentration in the bottom layer water increases, iron sulfide is may gradually oxidize to become dissolved iron, which that would allow it to again contributes to the suppression of the generation of dissolved sulfide
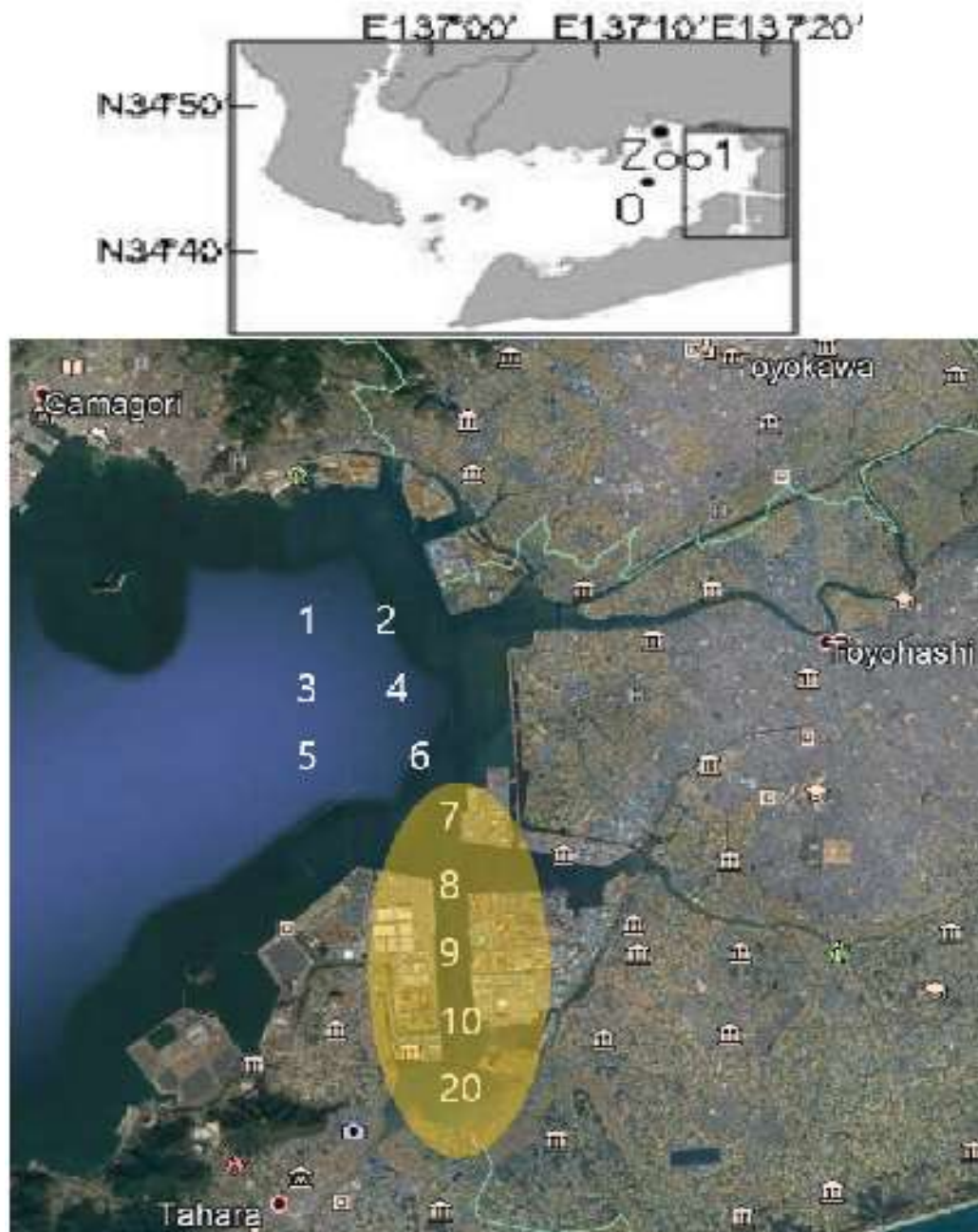
Figure 3.2.1. Sketch-map of Mikawa Bays showing survey stations.
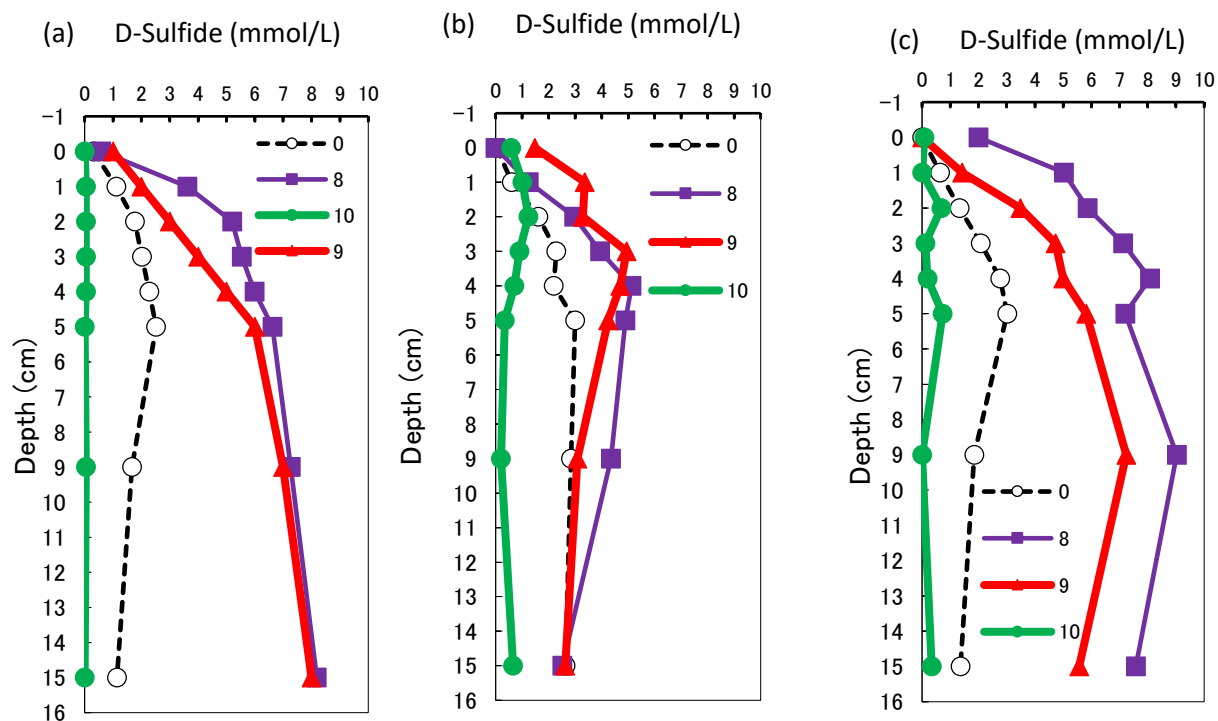
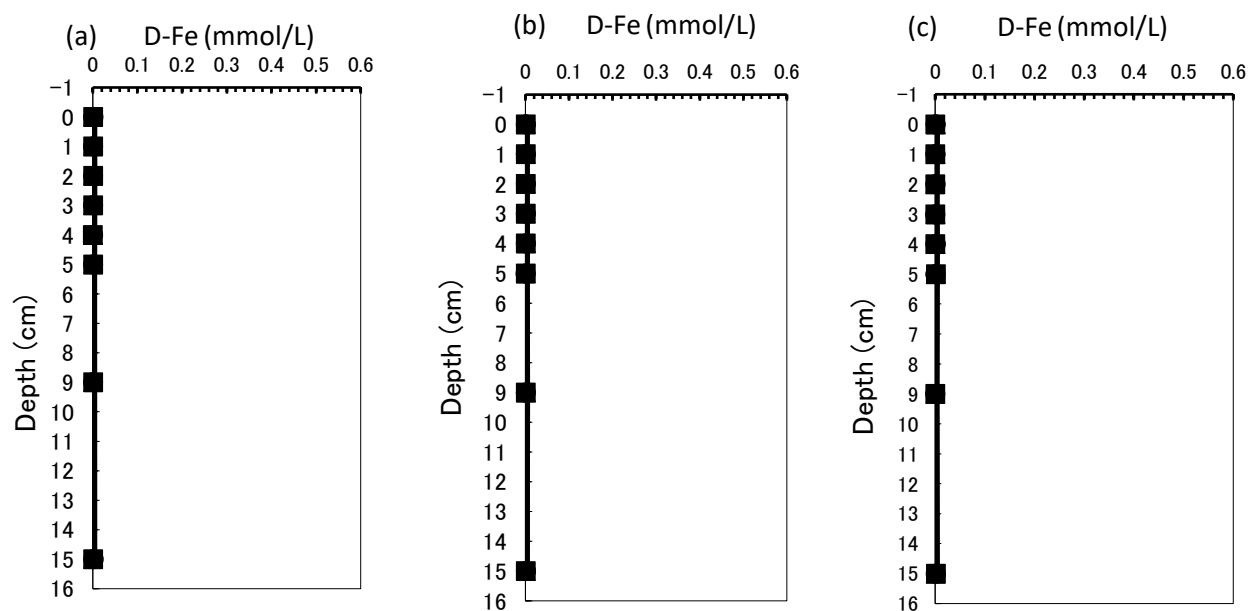Figure 3.2.2.Vertical distribution of dissolved sulfide (a) July 2015, (b) August 2015 and (c) September 2015.

Figure 3.2.3Vertical distribution of dissolved iron (a) July 2015, (b) August 2015 and (c) September 2015
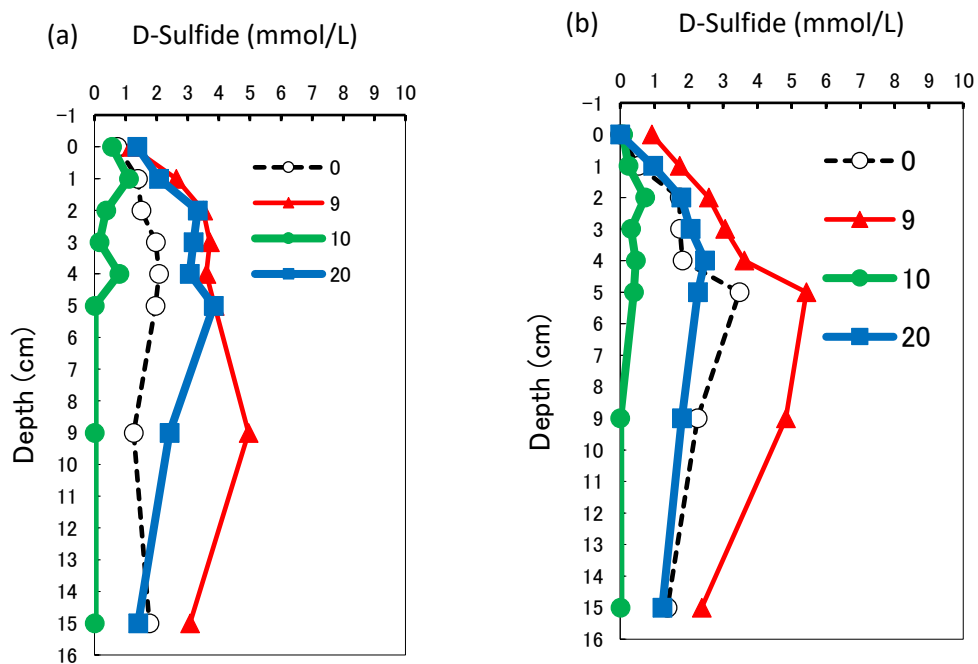
Figure 3.2.5.Vertical distribution of dissolved sulfide, (a) August 2016 and (b) September 2016.
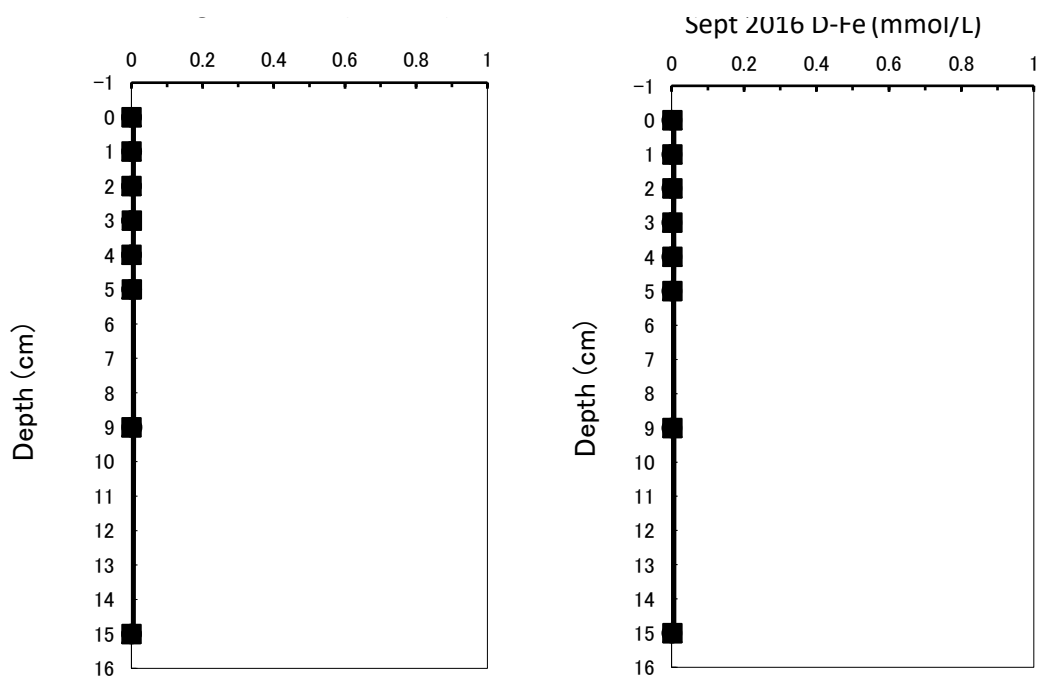
Figure 3.2.4.Vertical distribution of dissolved iron, (a) August 2016 and (b) September 2016.
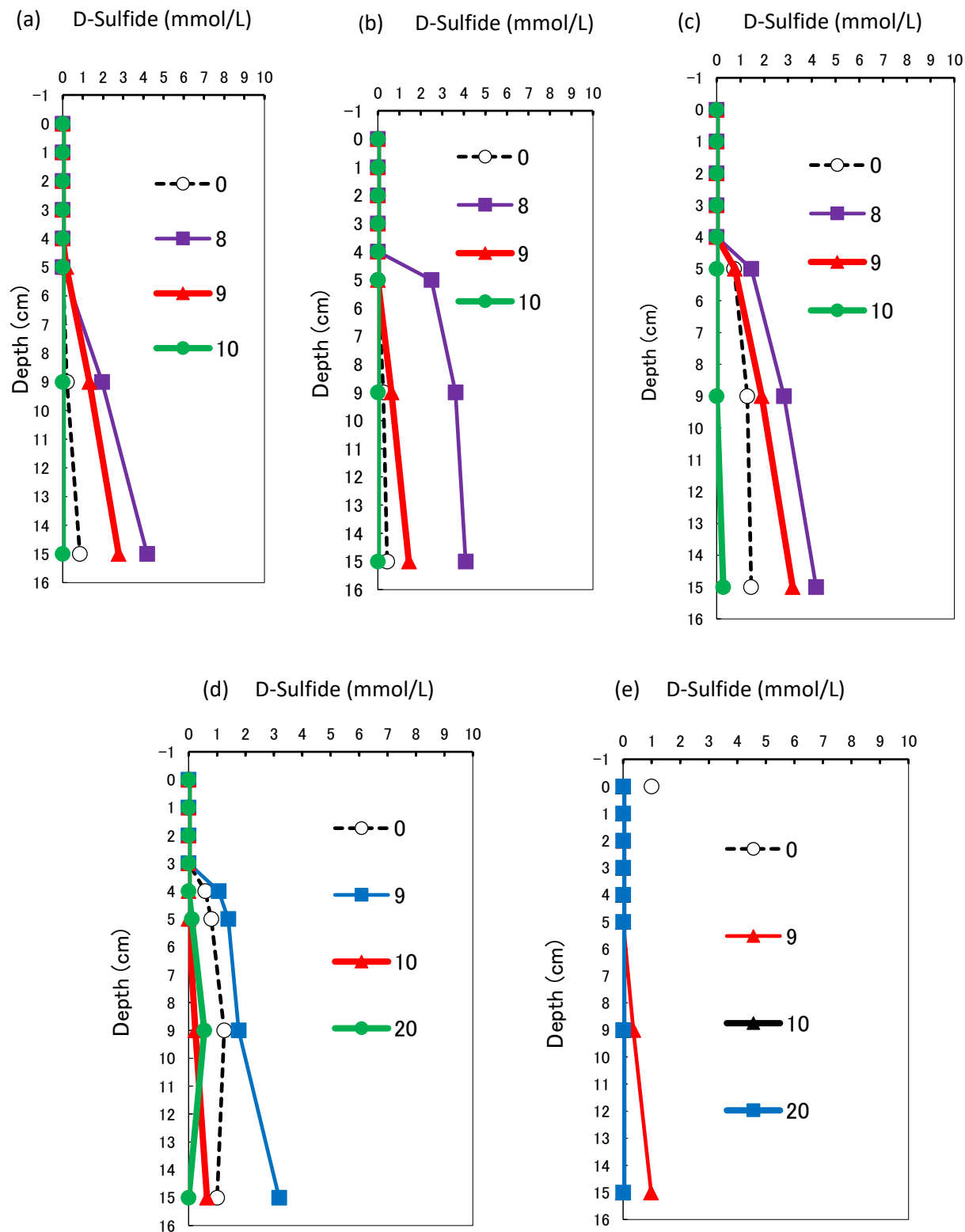
Figure 3.2.6 Vertical distribution of dissolved sulfide (a) Desember 2015, (b) January 2016, (c) February 2016, (d) December 2016 and (e) January 2017
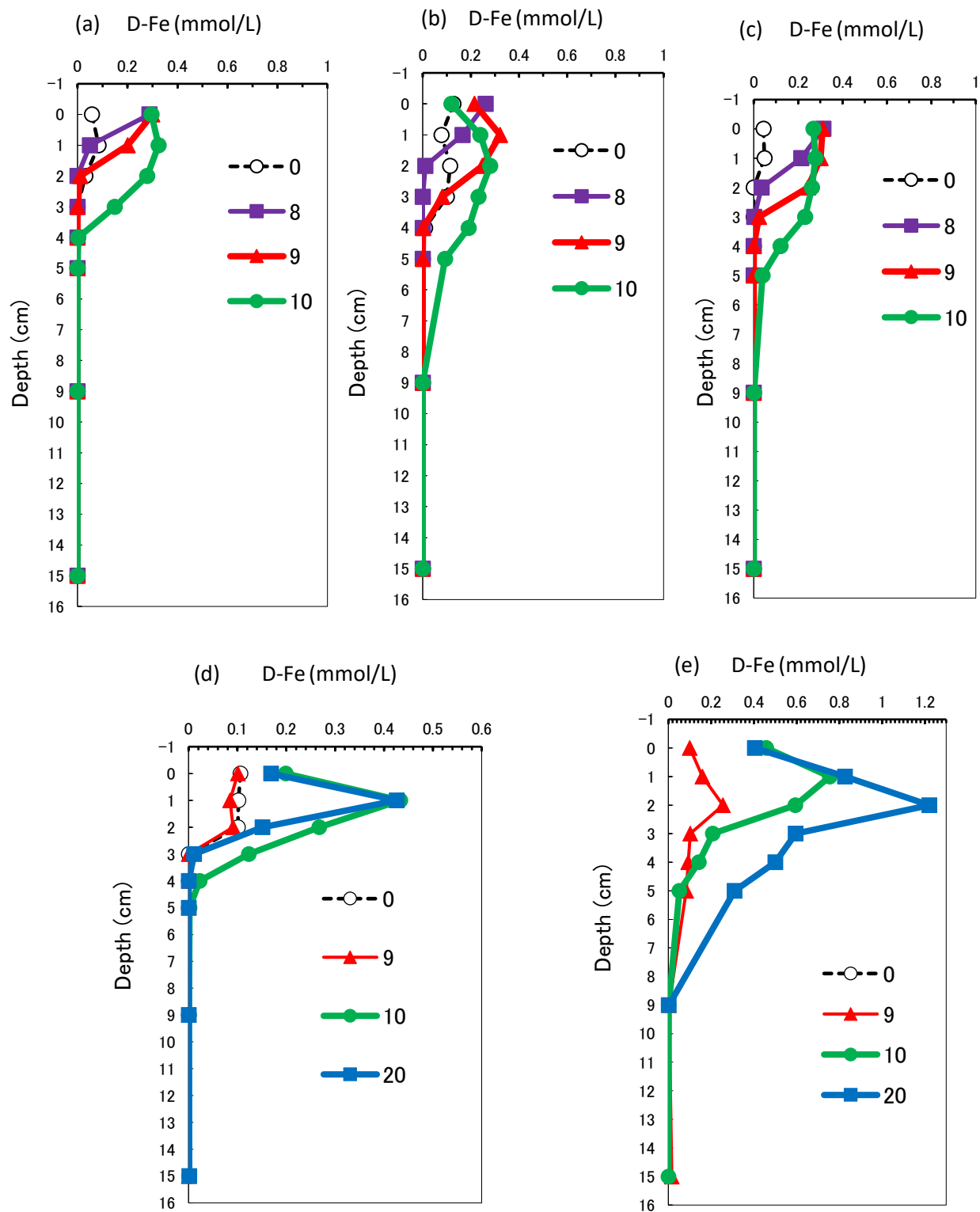
Figure 3.2.7 Vertical distribution of dissolved iron (a) December 2015, (b) January 2016, (c) February 2016, (d) December 2016 and (e) January 2017

3.2.1 Discussion

Considering the results obtained from our collected data, it seems that the analysis of field data of the sediment in the dead zone of Mikawa Bay revealed an important role of iron (Fe) in the suppression of hydrogen sulfide (H2S) release from sediment to the overlying water, as shown in the Figures (3.2.1.1. and 3.2.1.2). In the summer season, dissolved iron (Fe) is depleted in the surface sediment so that hydrogen sulfide (H2S) can release to the overlying water, while in other seasons iron (Fe) is abundant enough to suppress the hydrogen sulfide (H2S) release. These results suggest the strong possibility of sediment remediation by artificial addition of iron (Fe) containing materials to the surface sediment, especially in summer. Herlihy and Mills, (1985) also mentioned that the seasonal variation in the AVS concentration appeared to follow the same trend in both marine and freshwater sediments. For both types of systems, the optimum level of sulfate reduction occurs in summer when the water temperatures are the highest. During this time, the oxygen consumption rate can be increased to anoxic sediments at the sediment-water interface.
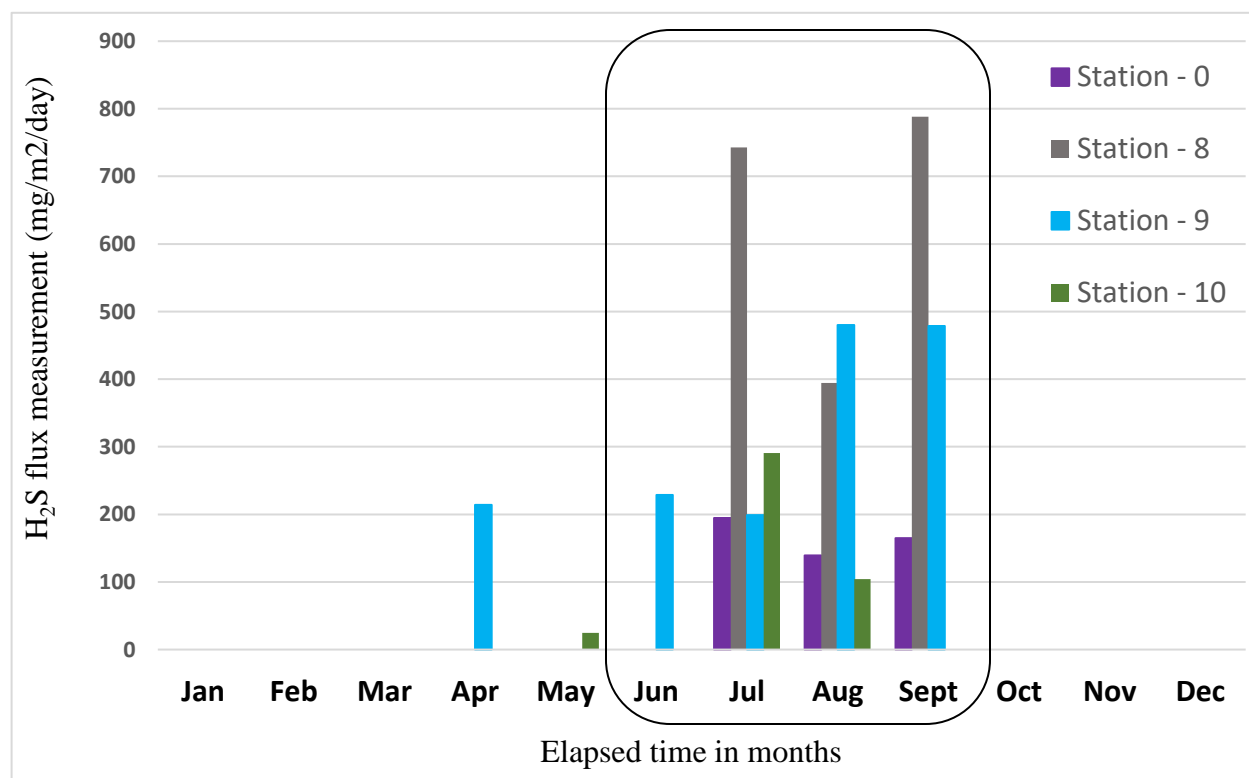
Figure 3.2.8. Analysis of H2S release rate from field data of Mikawa Bay.

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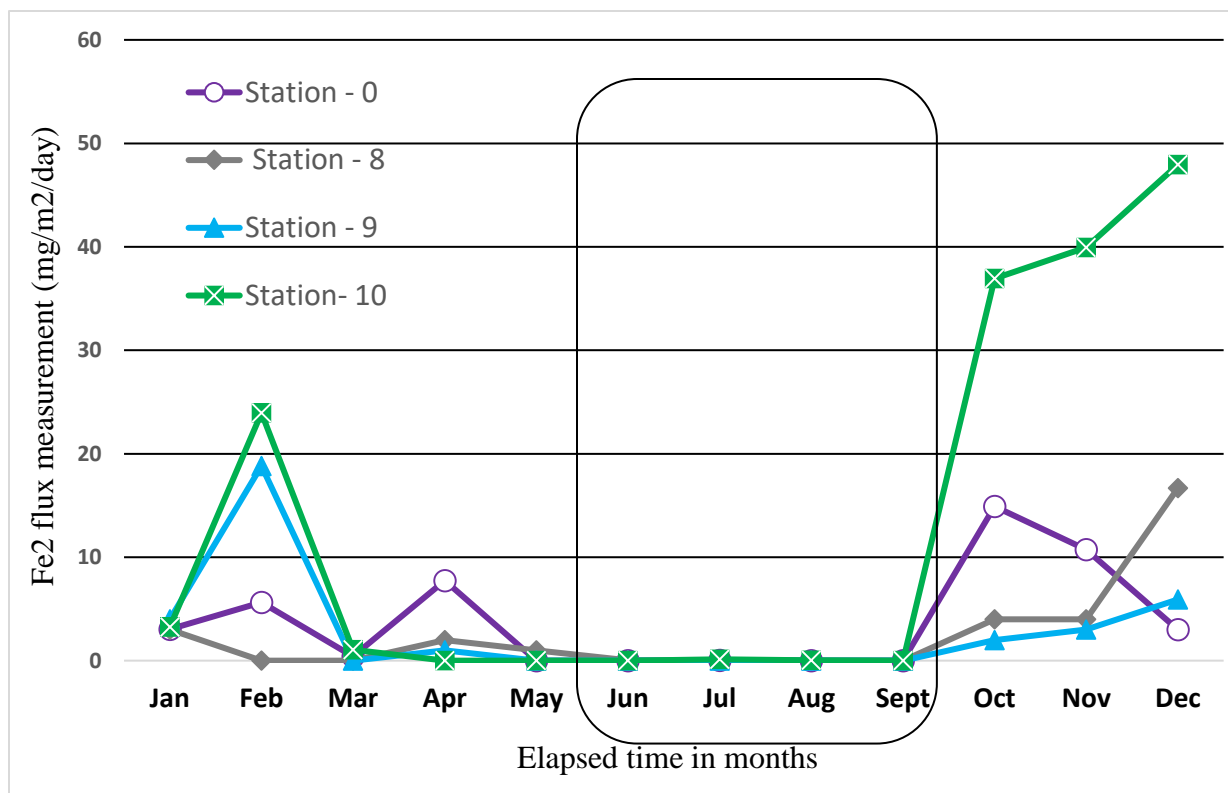
Figure 3.2.9. Seasonal variation of D-Fe release rate.

4   Laboratory experiments

The purpose of this study is to evaluate the remediation efficiency of iron and steelmaking slag application to organically enrich and improve sediments environment, therefore, we conducted laboratory experiments using intact sediment cores. The experiment namely "Evaluation of iron application method to remediate coastal marine sediment" was conducted at Regional (Toyohashi a city in Aichi Prefecture, Japan). Two experiments were performed with the same boundary conditions as:

1.   Experiment. I: Included iron and iron hydroxide.

2.   Experiment. II: Included steel making slag and pH adjustment.

Each experiment was divided into two parts.

(a)   Sulfide release experiment.

(b)   Sulfide generation rate experiment.

3.1 Experiment I.

3.1.1 Experimental Details

3.1.1 Selecting sampling sites

The purpose of this study is to achieve a better-understanding sediment cores, and the selection of sediment sampling stations should be based on a knowledge of the bottom dynamics of the study area, to represent' the major Bay Area. Thus, sampling sites (HS09) were selected based on the information from previous surveys. The sampling sites were located at (North latitude 34°, 44 minute 38.3 seconds, East longitude 137°, 13 minutes 15.8 seconds) and the water depth is C.D.L = 10.2m, as per figure 3.1. Mud sampling was conducted on June 27, 2017, July 19, August 23, September 20, and October 17, 2018. After securing the survey ship with an anchor, insert the cylindrical acrylic pipe (inner diameter 10 cm, outer diameter 11 cm, height 50 cm) into the bottom mud directly by the scuba diving, in such a way, not to disturb the sediment, so much as possible, the height of about 30 cm undisturbed sediment cores was taken from the seabed. At

the same time, the bottom layer of water is collected and used for culturing experiments which will be described later. The sampled undisturbed sediment cores were quickly brought back to the laboratory and placed in a constant temperature.
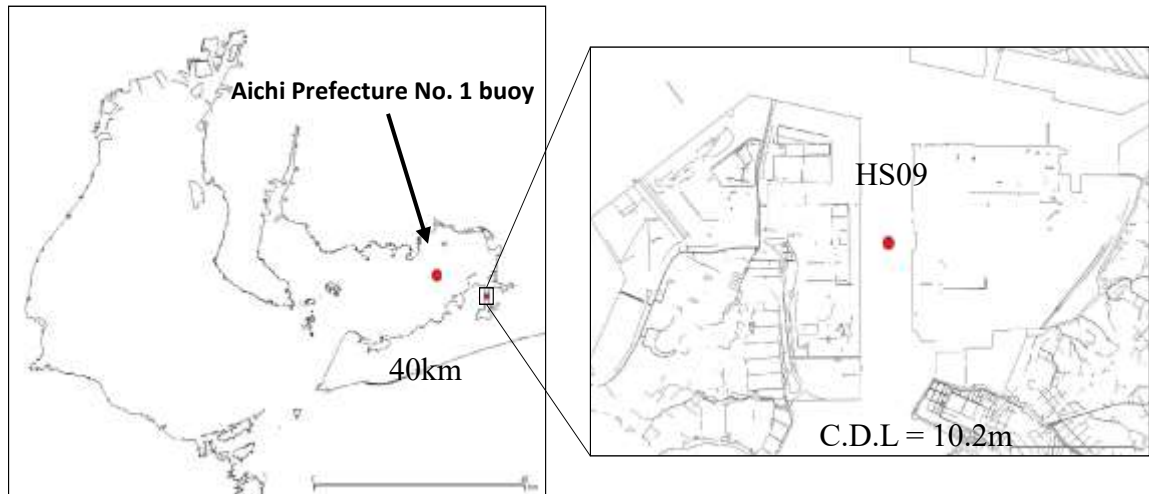

Figure 3.2.1. Survey map the true position.

4.1 Materials and methods

Flow velocity and solute concentration such as dissolved oxygen (DO) in the overlying water were controlled (Figure 3.2).
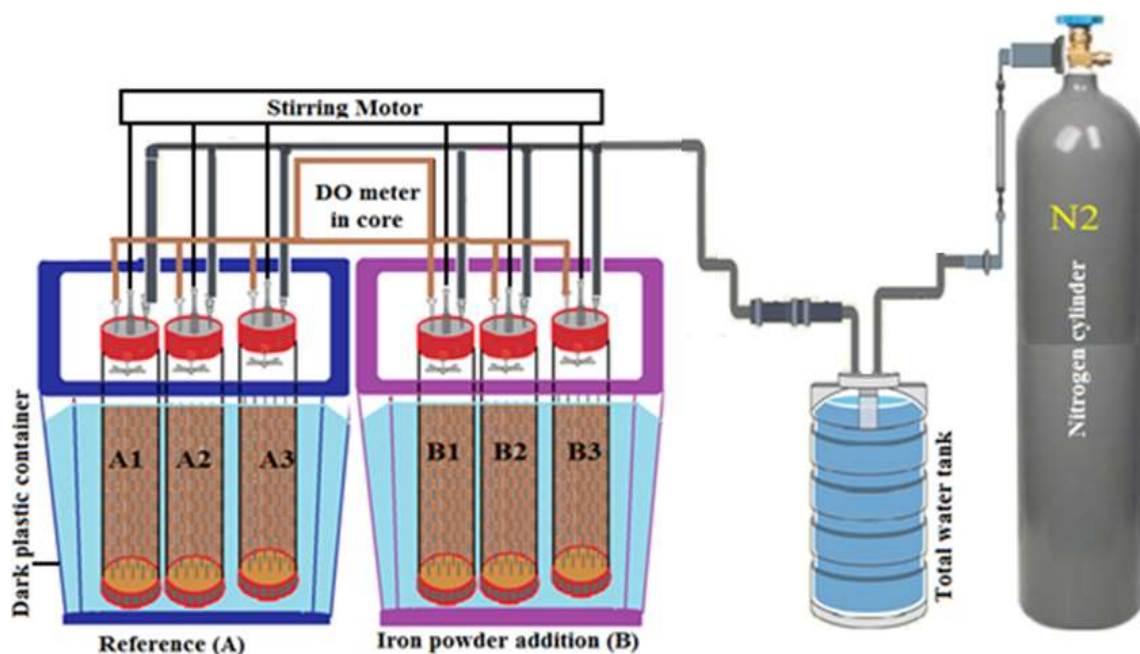

Photo 4-1. A schematic view of the experimental apparatus.

Figure 4.2. The experiment setup installed in the laboratory.

Immediately above water in the core was replaced by the on-site bottom layer water filtered with a glass fiber filter. The DO concentration of the water immediately above the sediment was set to an oxygen-free state and, DO concentration of fed water was controlled by nitrogen gas. DO meter were installed on the core lid and DO meter, sealed with a lid fitted with a stirrer, and overlying water in the sample core was agitated by a plastic propeller, whose rotation speed was controlled by a speed control motor to be rotation per minute. The water temperature was set according to the water temperature at the site at the time of sampling, In the thermostatic water tank, tap water was applied to square polypropylene and controlled to the same temperature as the bottom layer water by a heater with temperature control and a cooler. the average of the core water temperature was 20.3 °C, in June 21.7 °C, in July 25.7 °C, in August and 24.0 °C, in September. The experiment was conducted with four treatments (Additive-free core A, core B with iron oxide on iron surface added, Unused core C, core D added with iron hydroxide, performed only on September), and each experimental treatment was performed in triplicate (Table 3.1). After cores were collected, the iron powder or iron hydroxide were applied to the surface sediment with 0.637 kg /m^2, or 0.713 kg/m^2 respectively.

Table 3.2.1-1.Type and amount of iron preparation.

Treatments	Replication	Amount [kg/m^2]			
		June	July	August	September
A: Reference	Reference-1	-	-	-	-
	Reference-2	-	-	-	-
	Reference-3	-	-	-	-
B: Iron powder addition	Fe-1	0.052 kg/ m^2	0.637kg/m^2	0.637kg/m2	0.637 kg/m2
	Fe-2	0.108 kg / m^2	0.637kg/m2	0.637kg/m2	0.637 kg/m2
	Fe-3	0.205 kg/ m^2	0.637kg/m2	0.637kg/m2	0.637 kg/m2
C: Experiment unused	Only use in analysis and preparative				
D: Iron hydroxide addition	Fe (OH)2	-	-	-	0.713 kg/ m^2
	Fe (OH)2	-	-	-	0.713 kg/ m2
	Fe (OH)2	-	-	-	0.713 kg/ m2

Each of the samples was examined, and the chemical and physical characteristic analyses were performed on water samples and sediment samples. To identify the sediment sample quality and surface water parameters, sample analysis was conducted to measure total organic carbon (TOC), chemical oxygen demand (COD), total sulfur (TS), total iron (FeT), total nitrogen (TN), pH, and oxidation-reduction potential (ORP). On the 1st, 2nd, 3rd, 4th, 7th, 14th and 21st day, after the preparation of the experiment water samples were withdrawn from the sampling bottles with syringes, and the dissolved sulfide concentrations were measured by the methylene blue method. In this method, a sulfide coloring reagent comprising iron chloride III (FeCl3.6H2O) and N, N-dimethyl-p-phenylenediamine sulfate dissolved in 6 M HCl solution added into the sample for analysis. After 15 min, the absorbance of the solution was measured with a spectrophotometer at a wavelength of 667 nm with a spectrophotometer (HACH, DR 2800., T & D Co., Ltd., SP-808) within 2 hours. Typically, the glass syringes were used in this method photo 3.1.2. Samples for the determination of sulfide were drawn directly into the glass syringe, leaving no free space. Divalent iron was quantified according to the phenanthroline method, for the determination of divalent iron

by measuring the absorbance of its complex with 1,10- phenanthroline at 510 nm (λ=510 nm), followed by determination of total iron by atomic absorption spectrometer at 248.3 nm. Linear calibration ranges were 0.1-35 and 0.1-10 mg L -1 for iron (II) and total iron respectively. Sediment quality was also analyzed after completion of the experiment, the sediment core was sliced vertically from top to bottom every (0–1.5 cm, 1.5- 3 cm, 3 - 4.5 cm, 4.5-6 cm, 6- 7.5 cm until 9 cm). Sediment pore water was obtained by squeezing over a 0.45 µm filter, then dissolved-sulfide concentrations were measured in pore waters. A part of the collected sediment samples was also used to analyze the hydrogen ion concentration index (pH), oxidation-reduction potential. The data were also analyzed using one-way analysis of variance (ANOVA) at 0.05% level of significance with the SPSS package (version 23 IBM).

Photo 4-2. Sediment Sampling and Analysis.

4.2 Experimental results of dissolved sulfide concentration in the overlying water

The present investigation entitled "Evaluation of iron application method to remediate coastal marine sediment" was aimed at determining the effect of iron and steelmaking slag application to organically enrich and improve sediments environment. The chemical and physical characteristic analyses were performed on water samples and sediment samples. Dissolved sulfide concentrations were measured by the methylene blue method.

Temporal changes of dissolved sulfide concentrations in the overlying water in each treatment are shown in Figure. 4.2.1, 5.1.2 1, 5.1.3 1, and 5.1.4 1 for the experiments conducted in June, July, August, and September, respectively. For every case, the concentration of dissolved sulfide in the overlying water monotonically increased related to sediment remediation in all the cores. The concentration of hydrogen sulfide in water immediately above the sediment cores during the experimental period changes with time. As can be seen that the concentration of hydrogen sulfide monotonically increases related to sediment remediation in all the cores, data revealed that the concentration of hydrogen sulfide ranged between (0/0.40 mg/L and 87.96 mg/L) throughout the experimental periods.

4.2.1 Experimental results (June)

Result for the experiments in June shows relatively lower release of the dissolved sulfide into the overlying water even in the control cases (A1, A2, and A3). Order of the final concentration of dissolved sulfide for B-1, B-2, and B-3 did not follow the application amount of iron. Although in general, lower release of the dissolved hydrogen sulfide into the overlying water was observed with core (B-3 and B-1) ranges were (0.40 - 9.8 mg/L and 0.40 - 13.2 mg/L respectively) as against the highest (0.40 – 28.7 mg/L) core (A-2) and the next highest (0.40 – 23.6 mg/L) recorded with core (B-2) (see Figure. 5.1.1 1) but there were non-significant differences among the six sampling core at ($p < .05$) (see Table (5.1.4 1). Additionally, the final concentration for cases of the application of iron (Group B) also showed no statistically significant difference from the control case (Group A). Therefore, for later experiments we used larger amount of iron compounds for triplicate sediment cores.
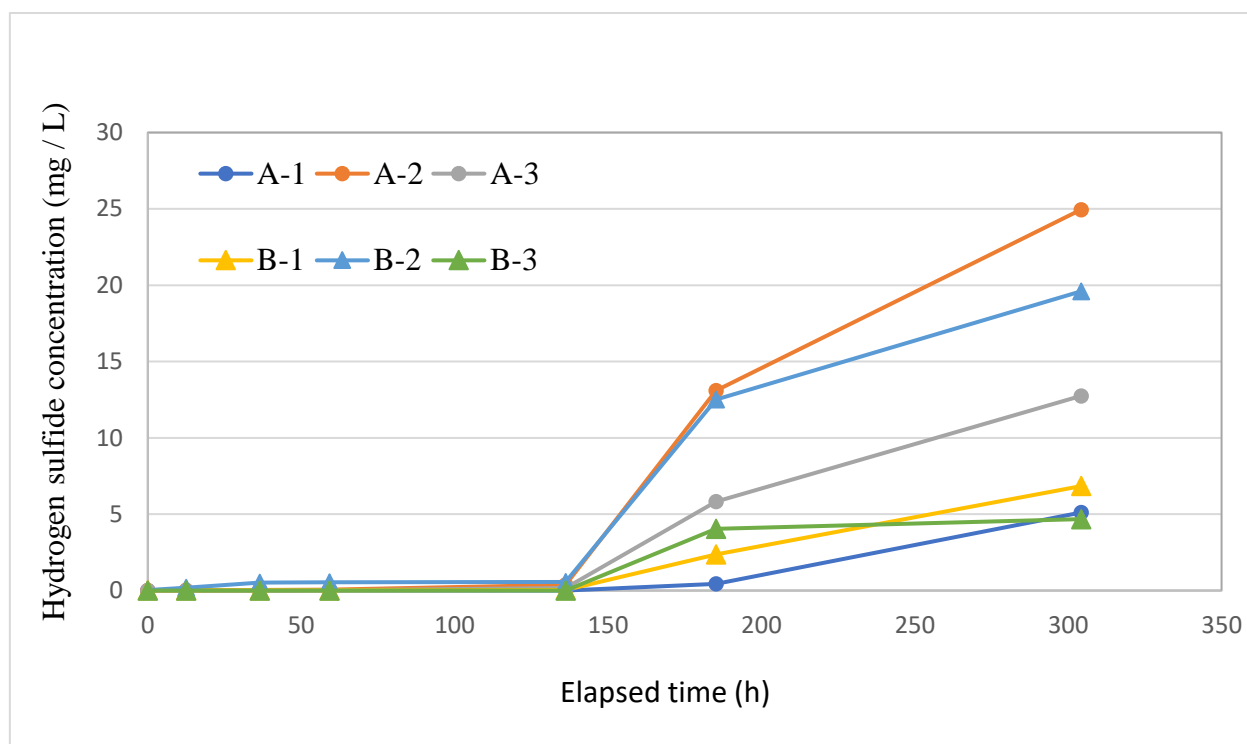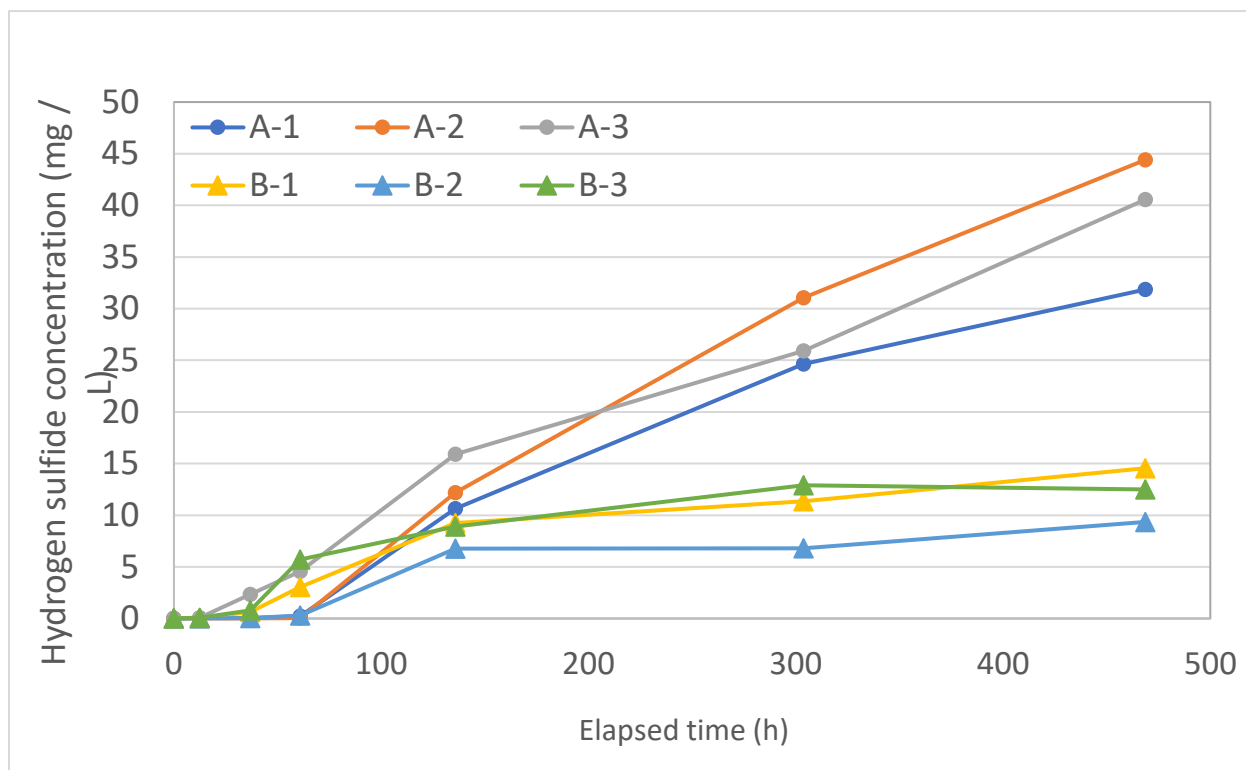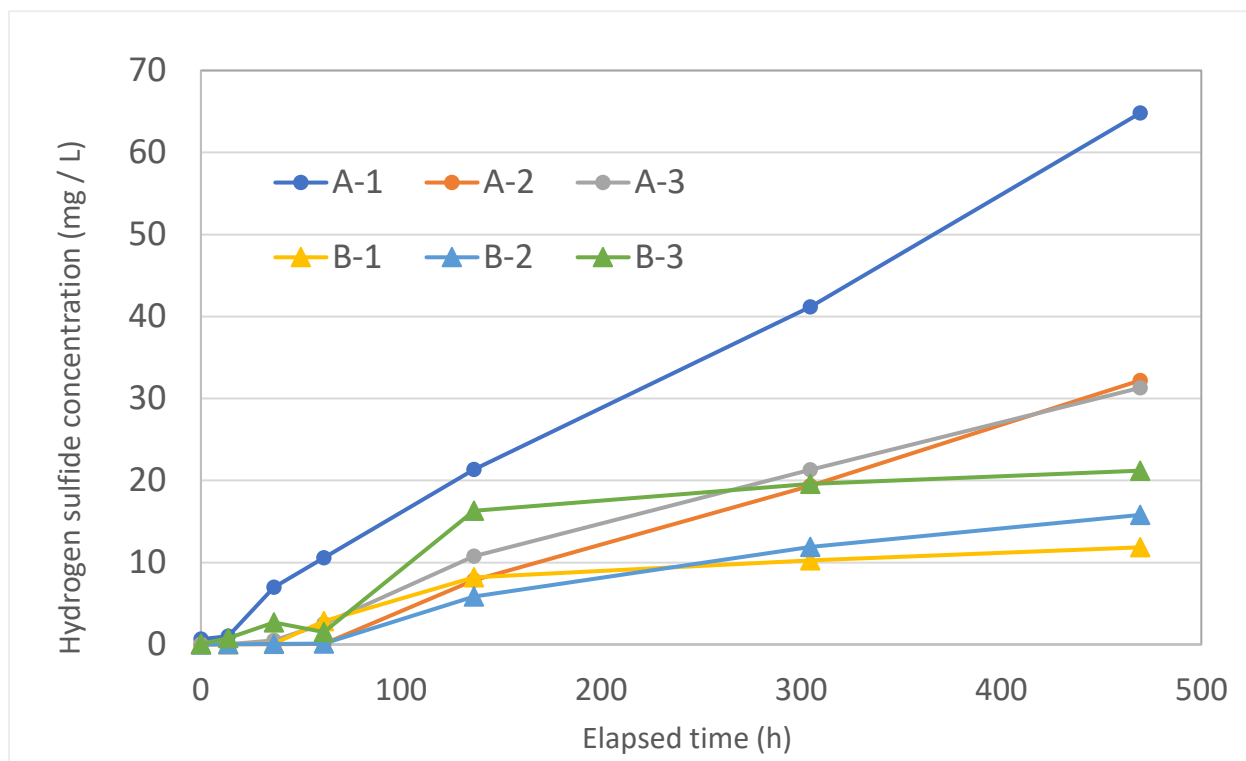
Figure 4.2.2 Temporal changes in dissolved sulfide concentration in the overlying water for the June experiment

4.2.2 Experimental results (July)

The second experiment was conducted on 20th July to 9th August 2017. A control group received no additional iron (A1, A2, and A3) and the second group who received the same dose of iron oxide 5.g followed by (B1, B2, and B3). The hydrogen sulfide concentrations in both groups started to increase in the second and third days. According to the data obtained from the experiment, for example, the final concentration of dissolved sulfide in the control cores (A-2, A-3, A-1) were 44.4, 40.6, and 31.9 mg/L, respectively. Whereas the final concentrations in the iron treatments core (B-2, B-3, B-1) indicated 9.4, 12.5, and 14.6 mg/L, respectively. These results showed remarkably lower values compared to the control cases as shown in Figure 5.1.2 1. Moreover, statistical analysis SPSS IBM 23 software was used for statistical analysis, and there were statistically significant ($p<0.05$) differences between the two groups (see Table 5.1.4 1).

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Figure 4.2.3Temporal changes in dissolved sulfide concentration in the overlying water for the July experiment

4.2.3 Experimental results (August)

In an experiment conducted on August, the second group (B1, B2, and B3) contained the same amount of iron oxide 5.0g, and iron was not added to (A1, A2, and A3). Results obtained in the third experiment shown a significant difference ($p<0.05$) between the two treatment groups. The one-way ANOVA results are shown in Table 4.2.3-1. In this experiment, it was demonstrated that the dissolved sulfide concentrations were significantly high in the undoped cores (A-1, A-2, A-3) were about (64.8 mg/L, 32.2 mg/L and 31.9 mg/L respectively), as shown in the Figure 5.1.3 1. whereas the lower dissolved sulfide concentration was observed in core (B-1, B-2, B-3) ranges were (11.9 mg/L, 15.8 mg/L and 21.2 mg/L respectively). The results indicated dissolved sulfide in the overlying water was reduced remarkably compared to that in the control groups.

Figure 4.2.4Temporal changes in dissolved sulfide concentration in the overlying water for the August experiment

4.2.4 Experimental results (September)

In the last experiment, iron hydroxide was also added to treatment groups, an equal amount (5.6 g) of iron hydroxide powder were followed by (D-1, D-2, D-3). The second group (B1, B2, and B3) contained the same amount of iron oxide 5.0g, and iron was not added to (A1, A2, and A3). The final concentration of dissolved sulfide in the overlying water for iron hydroxide core (D-2, D-1, D- 3) indicates 0.4, 3.8, and 10.7 mg/L, respectively, as shown in Figure 5.1.4 2. These values were much smaller than iron oxide application core (B-3, B-1, B- 2), in which those values were 23.2, 25.2, and 29.5 mg/L. The dissolved sulfide concentrations were quite high in the control core (A-3, A-1, A-2) with values of 73.6, 49.6, and 43.4 mg/L, respectively. Although the averaged final concentration was highest in the control case (A) in September, it was lowest in the iron hydroxide application (D) This suggests the relatively higher effectiveness of the iron hydroxide for the suppression of sulfide release. The lag time to appear significant increase in 5 mm dissolved sulfide concentration was longest in June. More than five days were necessary even in the control case. The lag time became gradually shorter in the later experiments. Especially in September, no

apparent lag time was observed.
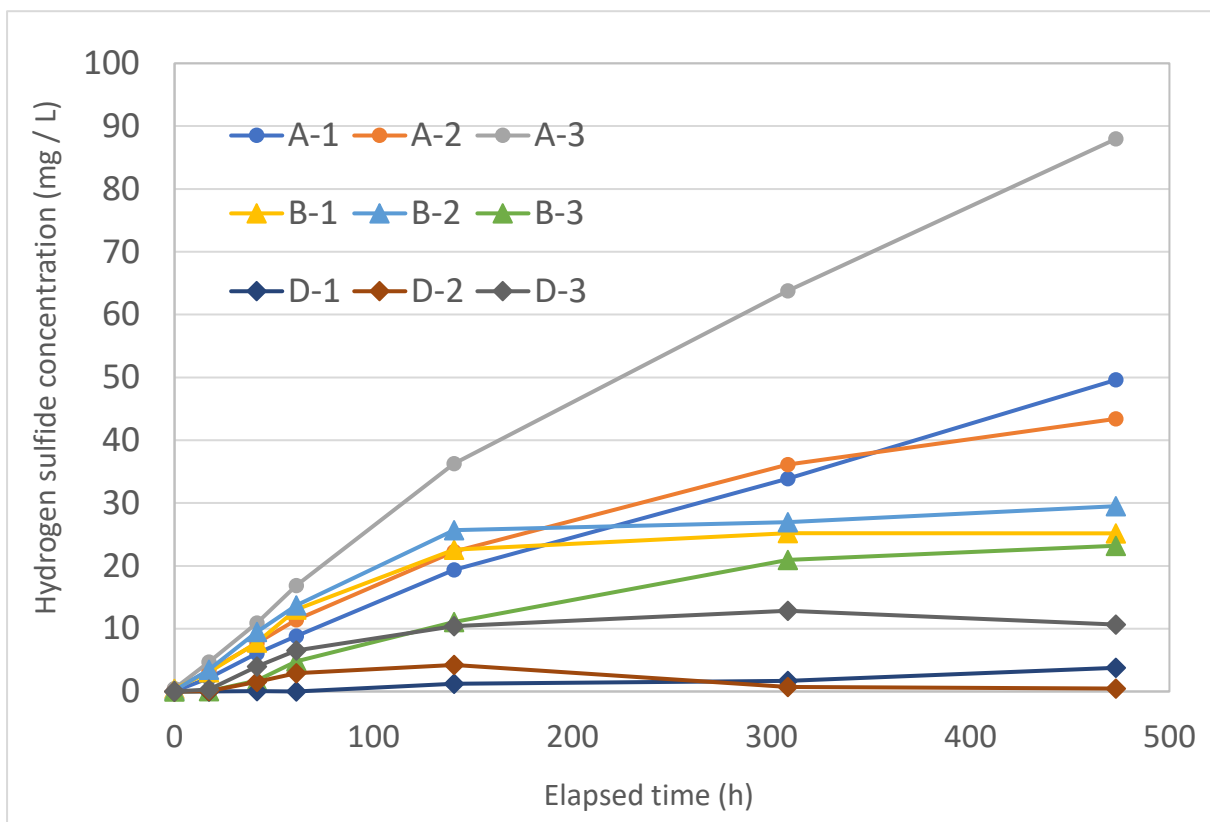
Figure 4.2.5Temporal changes in dissolved sulfide concentration in the overlying water for the September experiment

Table 4.2.4-1Analysis of variance for reading comprehension of the studied variables in the sediment.

Parameter	Periods	F Value	P Value	Result
Dissolved sulfide concentrations in the overlying water	June	3.845	0 .568	The result is not significant at p < .05.
	July	6.932	0.01	The result is significant at p < .05.
	August	6.643	0.011	The result is significant at p < .05.
	September	8.924	0 .000	The result is significant at p < .01.

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4.2.5 Sub-discussion

The performance of this experiment was monitored continuously over a period of 21 days. To view all (additive-free and irons) groups present on the overlying water, after the start-up within 2 to 4 days, as time elapses, the inlet concentration of hydrogen sulfide in the overlying water were increased gradually, this may be due to the sulfide flux, sustained by elevated pore-water concentrations, reaches the water column in the absence of dissolved oxygen in incubation. But it was confirmed that elution of hydrogen sulfide can be suppressed by adding iron material.

4.3 Comparison of hydrogen sulfide removal efficiency

This section summarizes the results of the removal efficiency of dissolved sulfide concentration in the overlying water. The average hydrogen sulfide removal efficiency on the overlying water is calculated as given in section 5.2.1, 5.2.2 and 5.2.3. The hydrogen sulfide removal efficiency can be determined by equation (1 and 2) through concentrations of hydrogen sulfide inlet rate and removal efficiency.

$$\% \ control = \frac{C_{(t)}^{-ref} - C_{(t=0)}^{-ref}}{C_{(t)}^{-ref}} \tag{1}$$

$$\% \ Iron = \frac{C_{(t)}^{-ref} - C_{(t=0)}^{-iron}}{C_{(t)}^{-ref}} \tag{2}$$

The first equation, in this case, is percentage for hydrogen sulfide production, while the second equation, is percentage hydrogen sulfide removal efficiency.

Where, $C_{(t)}^{-ref}$ is the total average of hydrogen sulfide concentration.

Where, $C_{(t=0)}^{-ref}$ is the inlt hydrogen sulfide concentation strat from ($t = 0$)

Where, $C_{(t=0)}^{-iron}$ is the outlet or removal efficiency of hydrogen sulfide using iron or iron hydroxide application.

4.3.1 Hydrogen sulfide removal efficiency (July)

There are significant differences between the control group (A-3, A-1, A-2) and the iron treatments group (B-3, B-1, B- 2). The results indicated maximum removal of hydrogen sulfide at the core (B2) were 72 percent, and the next best iron treatments group was core (B3), at 52 percent efficiency of sulfide removal, while the dissolved sulfide concentration increase in the control was not statistically significant. In fact, the highest maximum concentration of sulfide was observed with core (A2 and A3) and recorded a 97 percent increase in dissolved sulfide concentration, as shown in the following figure (4.3.1).

4.3.2 Hydrogen sulfide removal efficiency (Augustus)

The perusal of data showed that iron application had a significant effect on the percentage of removal of hydrogen sulfide from overlying water, as shown in the figure (4.3-2). After completion of the experiment, a comparison between core (B1, B2, B3) in the presence of iron and core (A1, A2, A3) in the absence of iron showed an increase in hydrogen sulfide removal by core (A1), at 76 percent efficiency of sulfide removal, followed by core (B2) of 43 percent, and lowest percentage (11 percent) was recorded in core (B3). While, 98, 96 and 95 percent yield increase from initial days of production obtained with in the control group. (A1, A2 and A3, respectively).

4.3.3 Hydrogen sulfide removal efficiency (September)

In an experiment conducted in September, iron hydroxide powder was also added to treatment groups. Percent differences between groups for group 1 untreated were core (A1, A2, A3), for group 2 iron oxide treated were core (B1, B2, B3) and group 3 iron hydroxide were followed by core (D-1, D-2, D-3). The iron hydroxide collective group indicated that the hydrogen sulfide removal efficiency reached was very high above 94 percent. Hydrogen sulfide removal efficiency up to 70 percent was achievable using iron oxide group, whereas significant drop removal efficiency was observed by core (D1). Whereas, around 96 to 98 percent yield increase from initial days of production obtained with in the control group, as shown in figure (4.3.2).
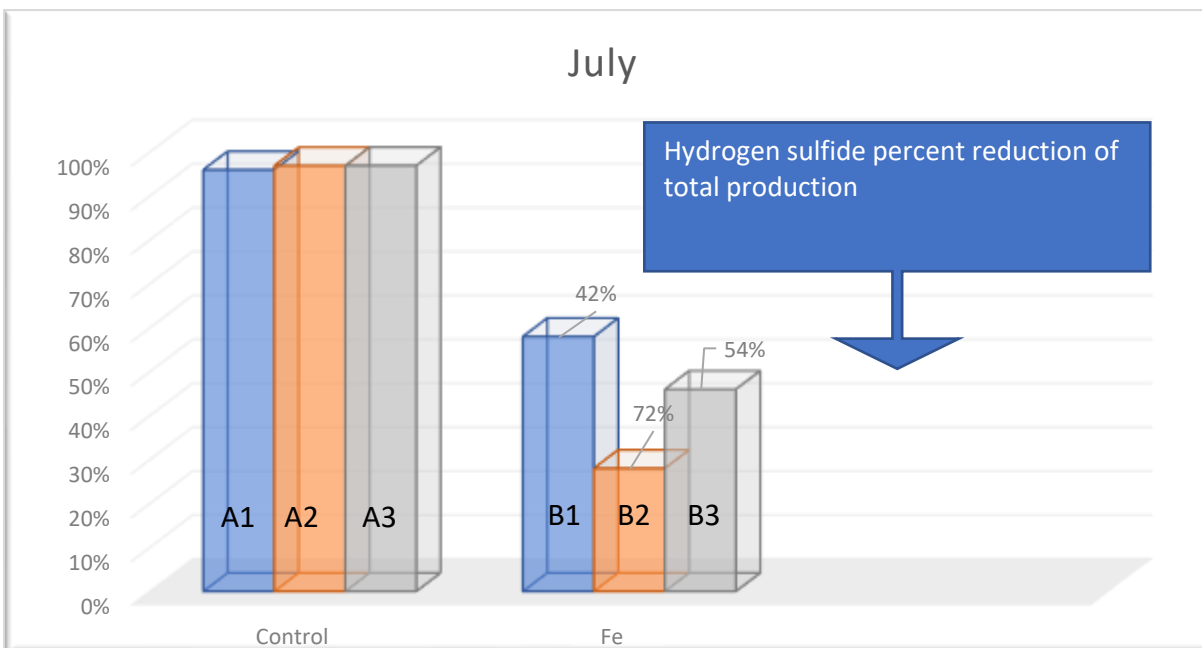
Figure 4.3.1. Percent reduction of hydrogen sulfide release rate by the addition of iron compounds
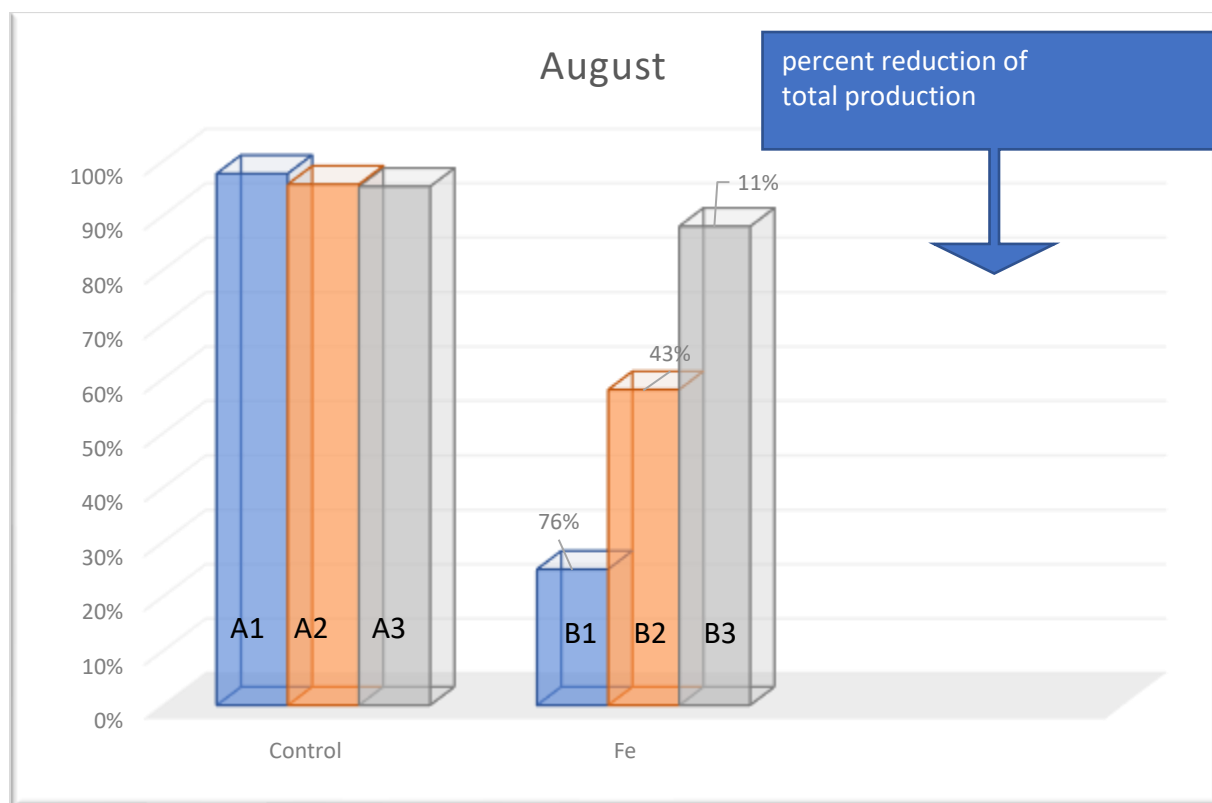

Figure 4.3.3. Percent reduction of hydrogen sulfide release rate by the addition of iron compounds
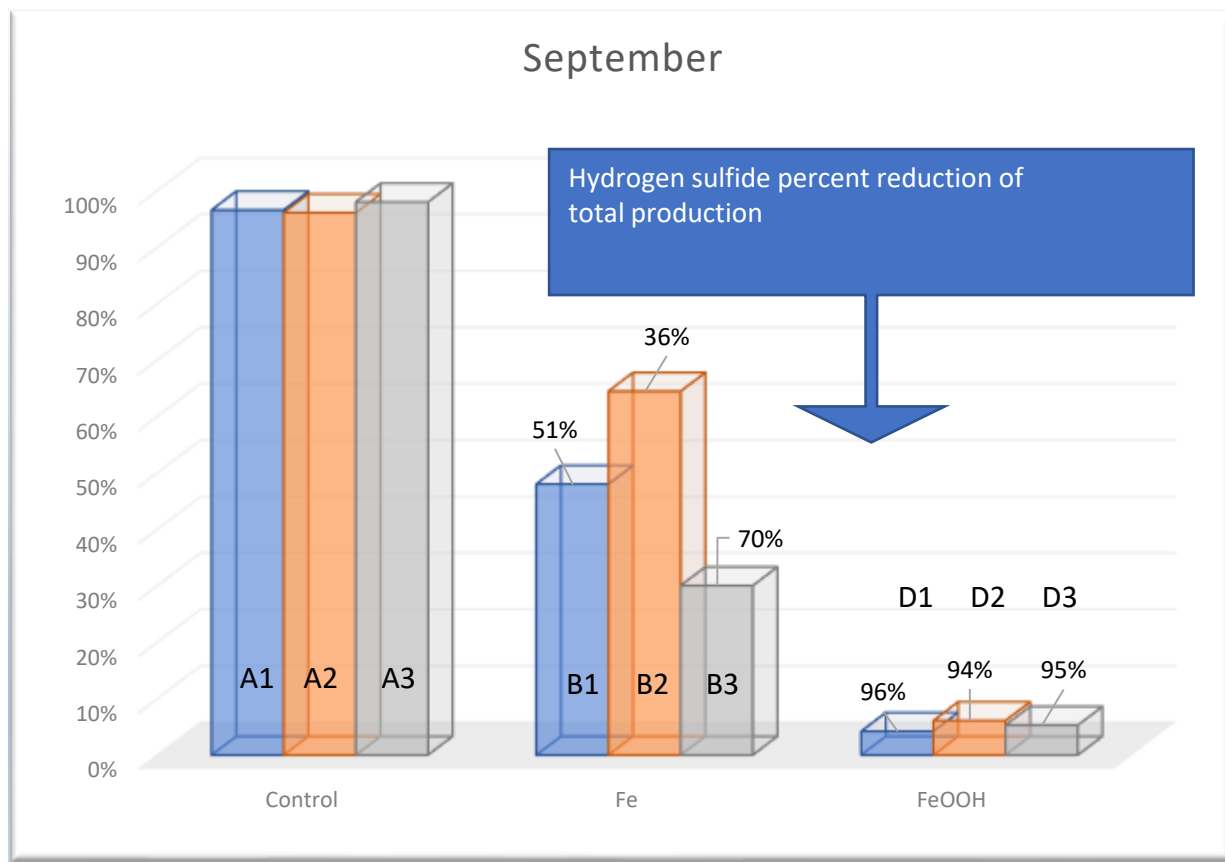
Figure 4.3.4. Percent reduction of hydrogen sulfide release rate by the addition of iron compounds .

4.3.4 Sub-discussion

A comparative study on the removal efficiency of hydrogen sulfide using (iron and iron hydroxide) groups were more efficient than the other control group and may thus be some of the hydrogen sulfides will react with iron ions in the water to produce iron sulfides. As shown in Figure 5.2.3, which present September, the maximum removal capacity for the oxidation of hydrogen sulfide in the overlying water shown with the application of iron hydroxide. Iron group achieved a removal efficiency of 70, 51 and 36 percent, while the maximum production capacity was observed in the additive-free group.

4.4 Dissolved Sulfide Release Rate

The motivation for the present study of dissolved sulfides in this study, in here, dissolved sulfide consisting of dissolved hydrogen sulfide H_2S, S^{2-} sulfide ion, hydrosulfide ion and HS^{2-}. The hydrogen sulfide thresholds must be converted to total dissolved sulfides based on the proportion of hydrogen sulfide found at a particular pH. Because of S^{2-} sulfide ion is not stable in normal sea water pH, sulfide ion concentration $[S^{2-}]$ is ignored. Therefore, the concentration of dissolved sulfide H_2S is the amount of dissolved hydrogen sulfide concentration hydrogen sulfide and the concentration of hydrosulfide ion $[HS^-]$. As, bacteria and fungi that decompose decaying organic material, in turn, consume DO for respiration, H_2S will produce and the pH tends to decrease. Therefore, the existing ratio of free hydrogen sulfide H_2S, which is considered to be highly toxic, in the dissolved sulfide increases, and the proportion of free hydrogen sulfide H2S which is considered to be the most toxic among the dissolved sulfides is 50% or more when the pH is 7 or less. So, understanding the upwelling phenomenon of anoxic water and dissolved sulfides, one of the practically important parameters is the release rate of dissolved sulfide from the sediment under anoxic conditions. Averaged release rates calculated for each time interval of the experiments are shown in Figures (4.4.1), (4.4.2), (4.3.4) and (4.3.4) for June, July, August, and September experiments.

4.4.1 Dissolved sulfide concentration change (June)

In the experiment conducted in June, the concentration of dissolved sulfide monotonically increases related to sediment remediation in all the cores. While the release rate of dissolved sulfide ranged between 2 to 1,013 mg/m2/day throughout the experimental periods (from June to September), the first month of the experiment (June) showed generally lower release of the dissolved sulfide into the overlying water: 1 – 477 mg/m2/day in core A (control) and 2 – 397 mg/m2/day for core B (iron oxide), as shown in Figure (4.4.1).
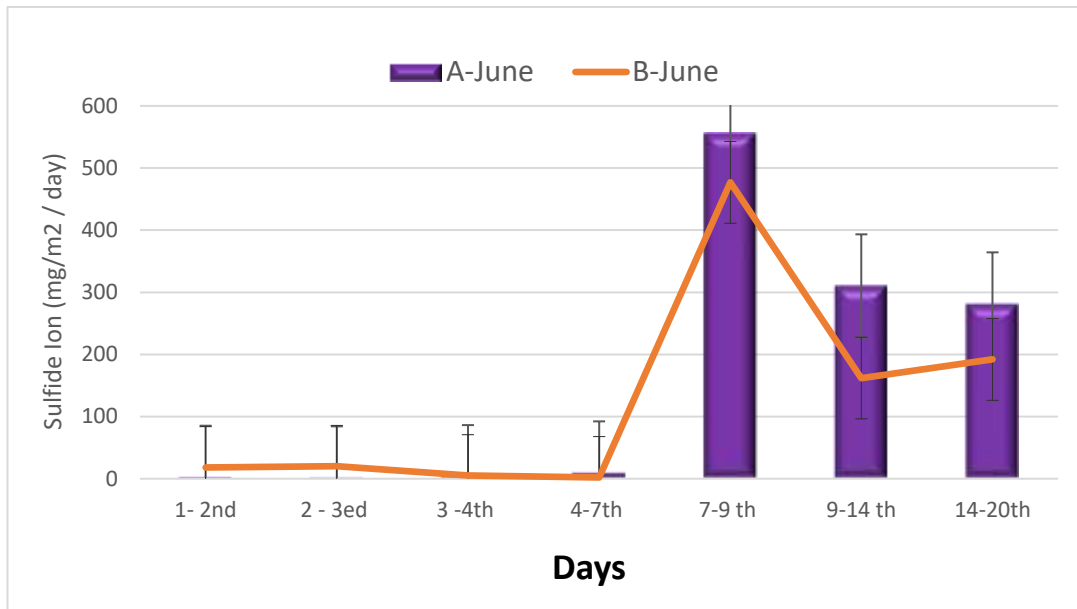
Figure 4.4.1 The release rate of dissolved sulfide for June experiment.

4.4.2 Dissolved sulfide concentration change (July)

In July experiments, the release rate of dissolved sulfide in the control cores (A-1, A-2, A-3) in turn ranged from 2 to 556 mg/m2/day and 8 to 637 "mg m2 d -1". However, in the experiment with iron material added, it ranged from 8 to 422 mg/m2/day. The result of sulfide ions is summarized in Figure (4.4.2-1).
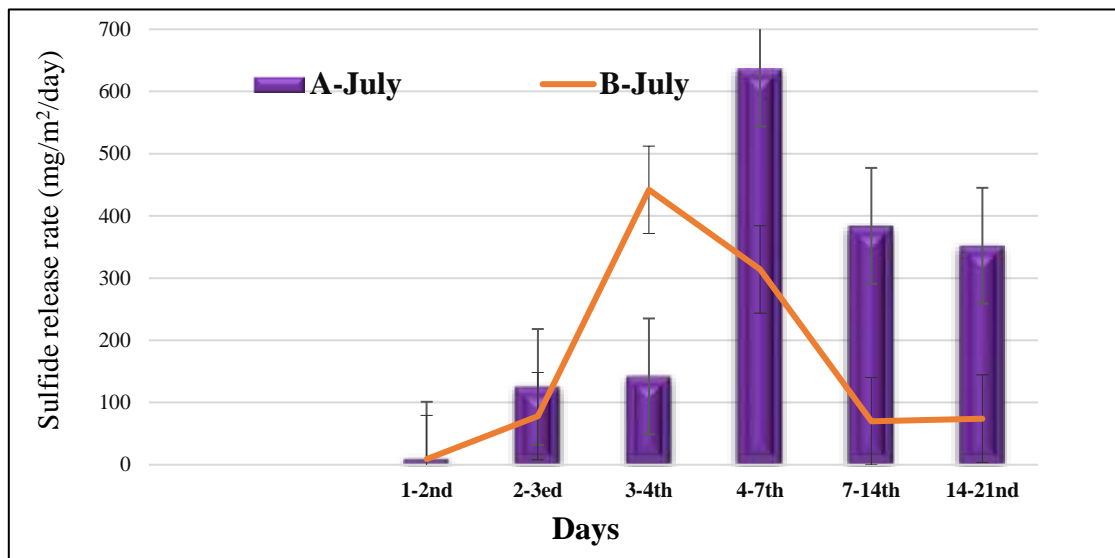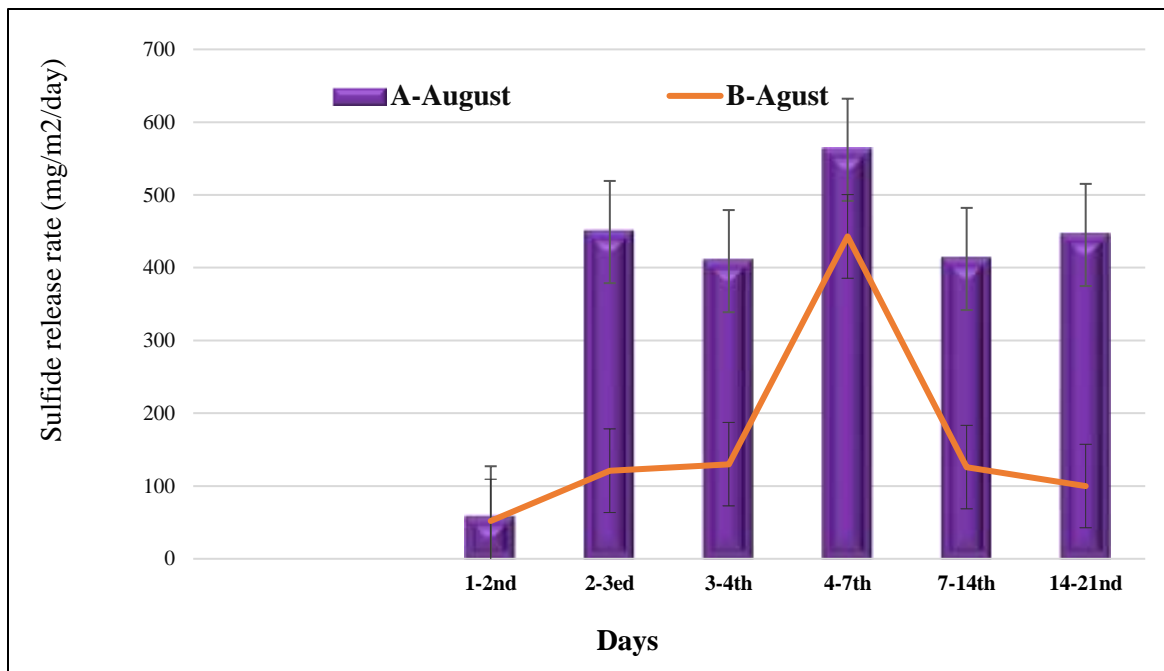

Figure 4.4.2. The release rate of dissolved sulfide for July experiment.

4.4.3   Dissolved sulfide concentration change (August)

In the experiment conducted on August, the results of the measurements of dissolved sulfide concentration shown in Figure (4.4.3-1). The dissolved sulfide concentration was high (62 mg/m^2/day – 562 mg/m^2/day) in the control group. In contrast, it was markedly low ranging from below the detection limit (52 mg/m^2/day) to 443 mg/m^2/day in the iron oxide group, by reaction between the dissolved sulfides and the iron eluted from the overlying water.

Figure 4.4.3. The release rate of dissolved sulfide for August experiment.

4.4.4   Dissolved sulfide concentration change (September)

In September experiments, dissolved sulfide concentrations in the overlying water were suppressed drastically compared to those in the control plot, and the effect has lasted for about 14 to 21 days. These results are demonstrated in Figure (4.4.3). Results of September experiment demonstrated that the release rate as well as dissolved sulfide concentrations in the overlying water were significantly low with iron hydroxide core (D-2, D-, D-3) ranging from 1 to 269 mg/m^2/day. The second lowest value of the release rate of dissolved sulfide were obtained from core (B- 3, B-1, B-2) were 116 to 845 mg/m2/day, respectively. The release rate was quite high in the control core (A-3, A-1, A-2) with values ranged from 409 to 1,014 mg/m2/day. It was supposed that

dissolved sulfide may have reacted with Fe ions eluted into overlying water and insolubilized.
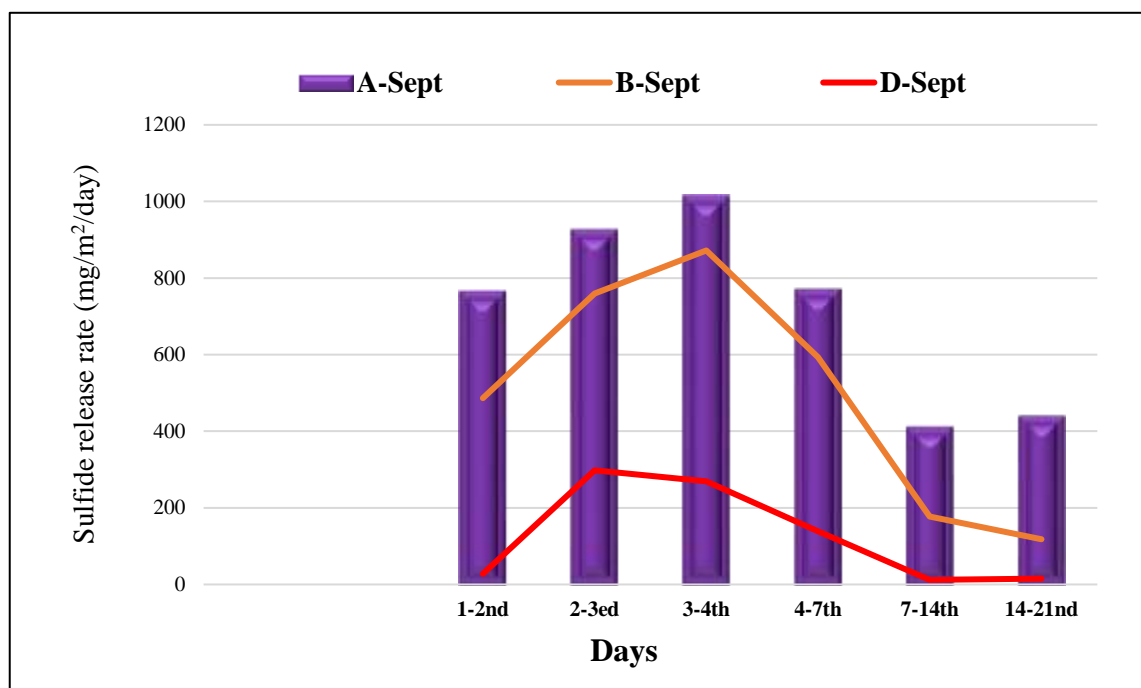

Figure 4.4.4. The release rate of dissolved sulfide for September experiment.

4.5 Temporal change in divalent iron concentration in the overlying water

Hydrogen sulfide particles in sediments can be broken up through the application of the iron, such as decreasing ionic strength, changing in electrolyte compositions from divalent to monovalent cations, when this occurs, small particles among the aggregates may be mobilized to make iron sulfide. This experiment shows that in the first step divalent iron is released through the reduction of trivalent iron, and in the next step should be divalent iron reacts with hydrogen sulfide to form iron sulfide. The obtained results are shown in figures (4.5.1).

4.5.1 Experimental results (July)

The results obtained in the present study showed that, the divalent iron concentrations were parallel with the iron group and control group during the first weeks after installation of the experiment. One week later, the divalent iron concentration in the control group was significantly reduced, and the value was lower than that in the iron group. Divalent iron concentrations range

from 0.1 to < 0.1mg/L, while the highest concentration of divalent iron was obtained in core B (iron group) ranged between (0.3 to 0.7 mg/L), as shown in (Figure 4.5.1).
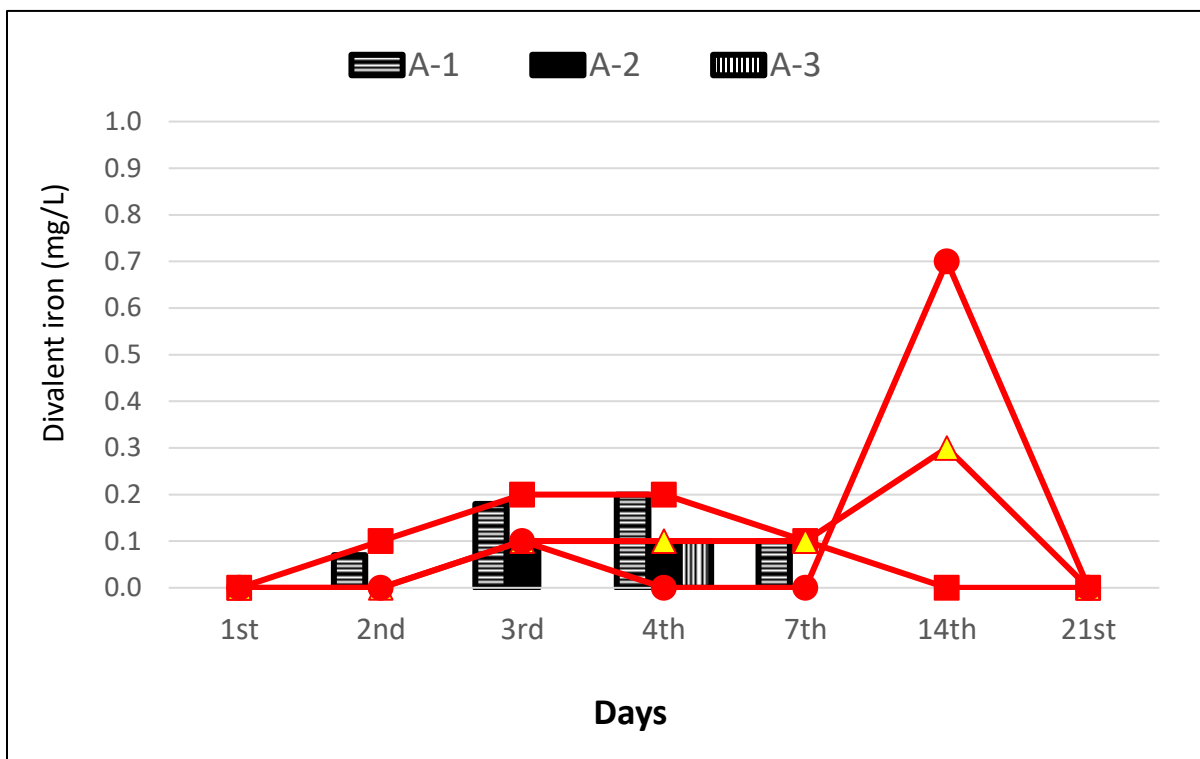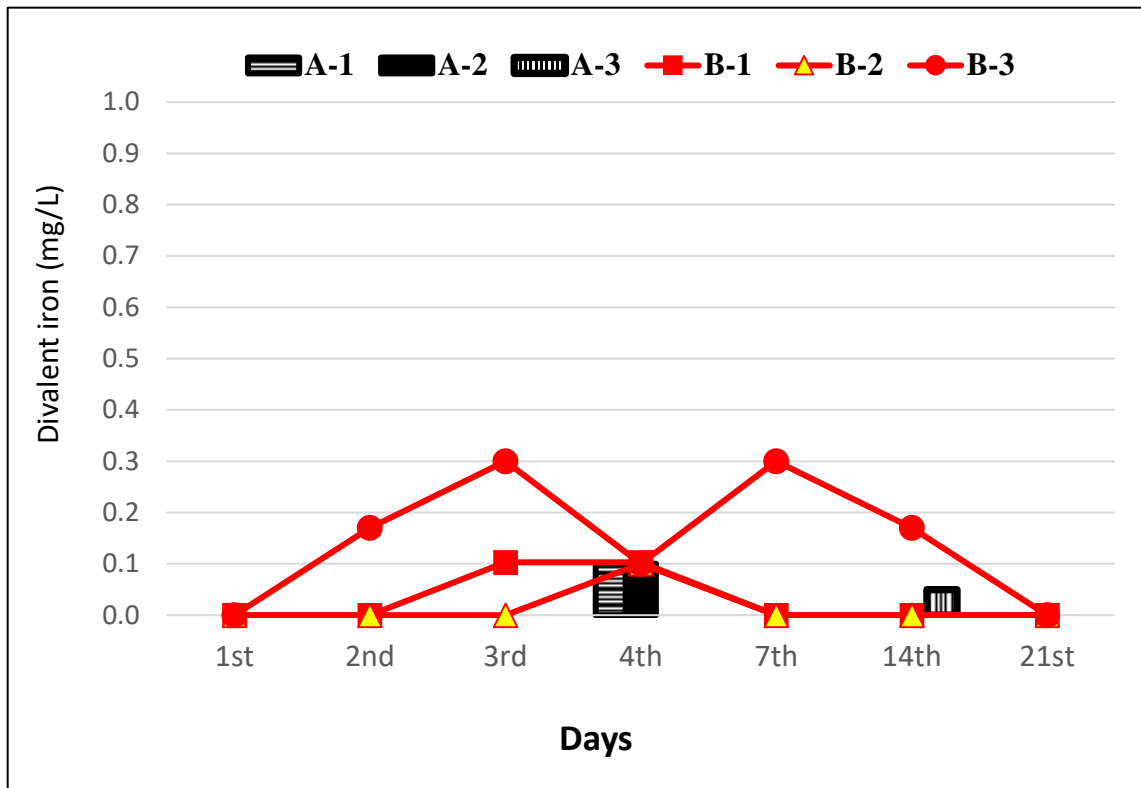

Figure 4.5.1. Time series change in divalent iron concentration in the overlying water for July experiment.

4.5.2 Experimental results (August)

In an experiment conducted in August, the concentration of divalent iron in the overlying water during the experimental period with control group (A-1, A-2, A-3) was <0.1 mg/L. The second group (B-3, B-1, B- 2), which contained 5.0gr of iron oxide. The results show that, concentrations values ranged from 0.17 to 0.3 mg/L. as shown in figure (4.5.2)

Figure 4.5.2 Time series change in divalent iron concentration in the overlying water for August experiment

4.5.3 Experimental results (September)

In this experiment, iron hydroxide was also added to treatment groups, an equal amount (5.6 g) of iron hydroxide powder were followed by (D-1, D-2, D-3). The result of the experiments demonstrated the concentration of divalent iron in the overlying water during the experimental period with control group (A-1, A-2, A-3) was < 0.1 mg/L. The divalent iron concentrations in the overlying water were significantly highest with iron hydroxide core (D-3, D-2, D-1 respectively) ranging from 0.4 to 0.9 mg / L, and the second-high value of the release rate of divalent iron was obtained from core (B- 3, B-1, B-2) were 0.4 mg / L to 0.9 mg /L, as it can be seen in Figure (4.5.3).
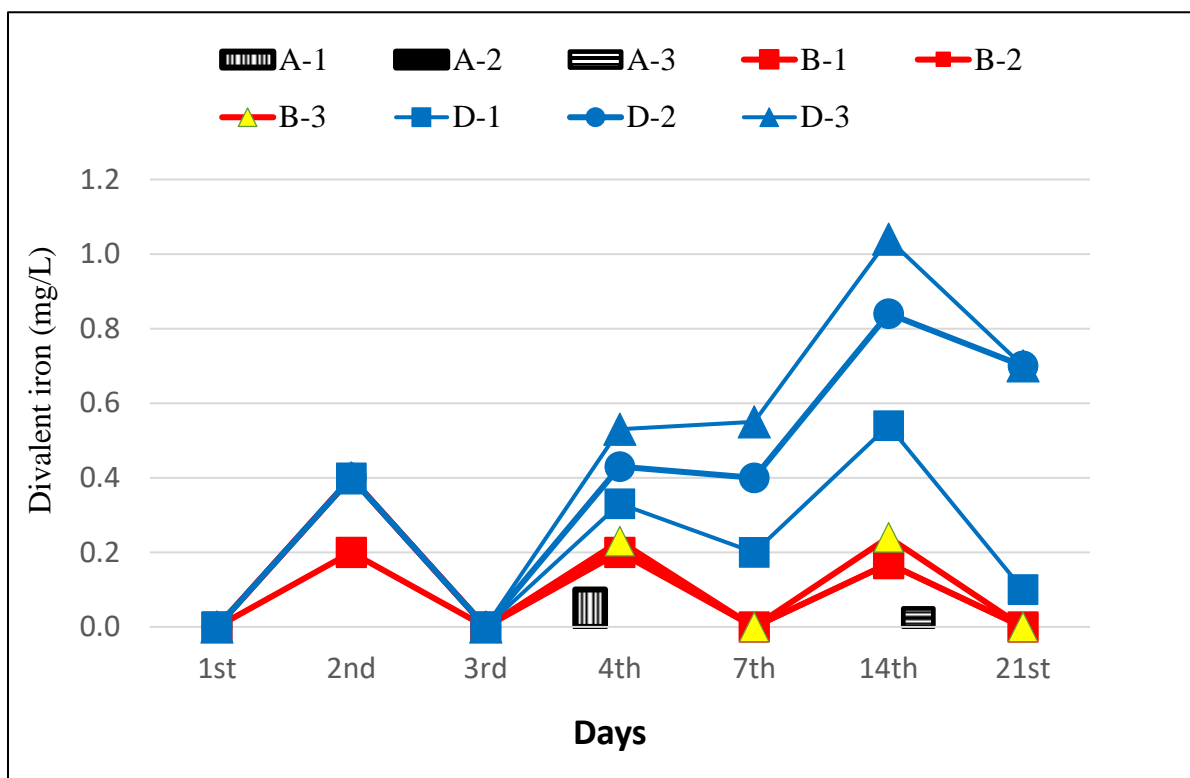
Figure 4.5.3 Time series change in divalent iron concentration in the overlying water for September experiment

4.6   Discussion of sulfide release rate and iron concentration

Determination of the reaction orders with respect to the iron group and flow rate allows a rate expression for the removal of dissolved sulfide. The reaction between dissolved sulfide and iron group is well documented. Due to its common occurrence and high reactivity under reducing conditions, the divalent iron sequestration is mainly related to the direct substitution reaction of iron sulfide rather than an adsorption reaction. Iron sulfide is thought to be potentially a major sink for iron oxide and iron hydroxide during early digenesis in anoxic conditions with the solubility of the iron sulfides controlling the reactions in the process. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS. As reported by (SHEET, n.d.) sulfate-reducing bacteria (SRB) converts sulfate in mine discharge water to sulfide essentially reversing the process of natural weathering. When sulfide is present, dissolved irons, especially divalent irons, will bind and precipitate as dense iron sulfide sludge, removing the dissolved irons from the

water. In the reducing procedure, a reduced mechanism is systematically constructed different steps, the reduction of the first bound proton in hydrogen sulfide H_2S with electrons from Fe, according to $2e^- + 2H_2S \rightarrow H2 + 2HS^{--}$. The protons in $2HS^-$ are then reduced with further electrons from iron Fe according to $2e^- + 2HS^- \rightarrow H2 + 2S^{2-}$, while $2Fe^{2+}$ and $2S^{2-}$ yield 2FeS.

In this study, figures (5.5.1, 5.5.2 and 5.5.3) presents the comparison between sulfide release rates and divalent iron concentrations for July, August, and September experiments. The divalent iron can react with dissolved sulfide to form particulate iron sulfide, which will precipitate into the sediment. Such a reaction may underestimate the release rates of dissolved sulfide. However, the concentration range of divalent iron is relatively low in these experiments. In general, it was apparent that the addition of iron resulted in an increase in divalent iron and decreased hydrogen sulfide production in the overlying water. With the control group, the inlet concentration of hydrogen sulfide was increased gradually, increasing hydrogen sulfide inlet concentration was based the time period, while the iron groups had a significant increase of divalent iron.
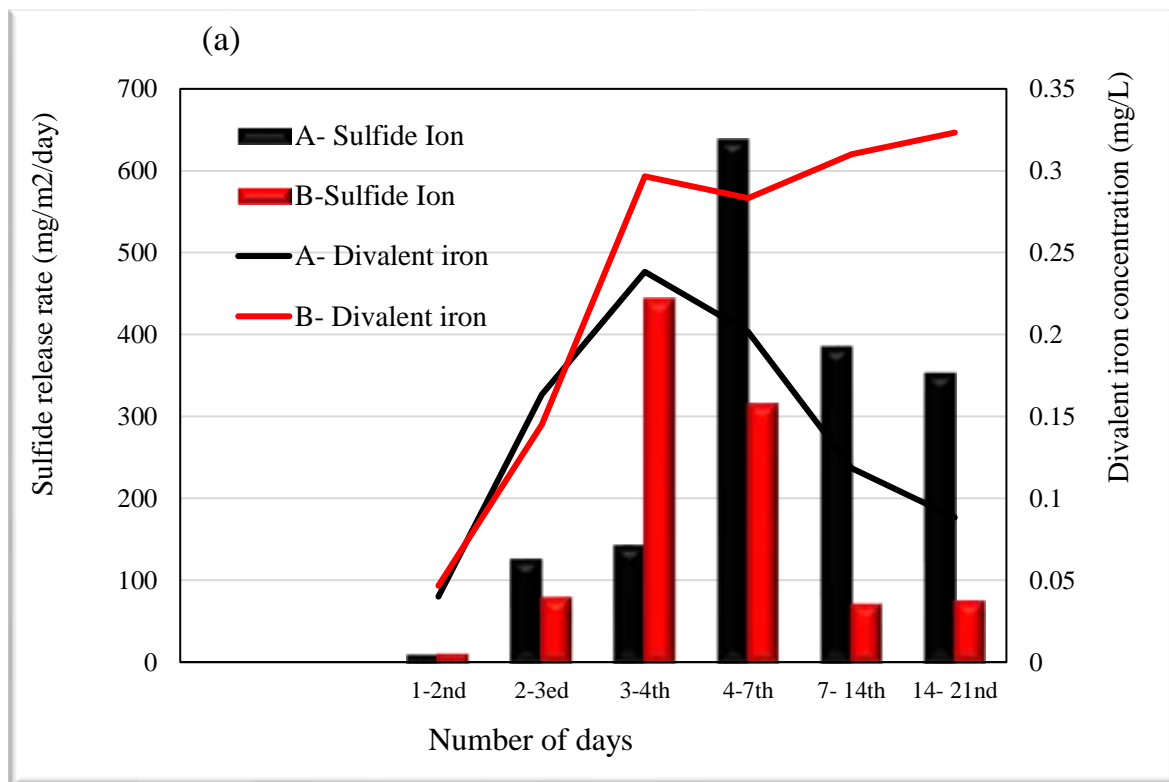

Figure 4.6-1 Comparison of sulfide release rates and divalent iron concentrations for July
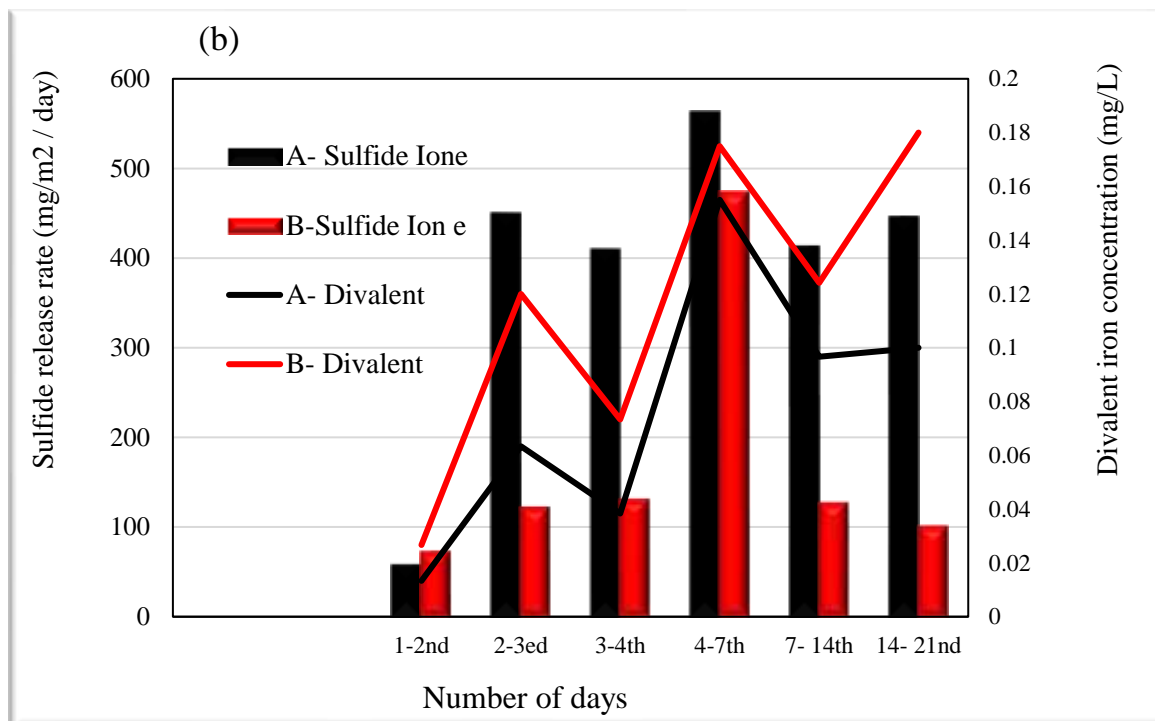
Figure 4.6.2 Comparison of sulfide release rates and divalent iron concentrations for August.
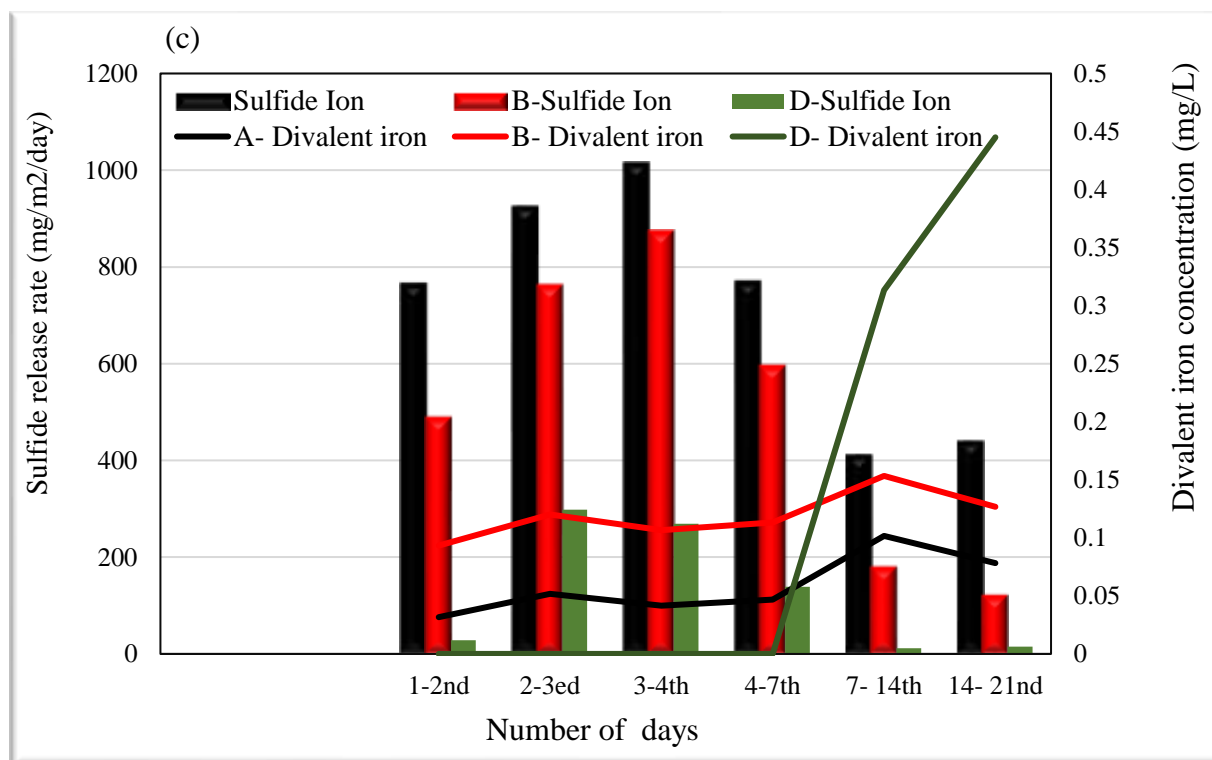

Figure 4.6.3 Comparison of sulfide release rates and divalent iron concentrations for September

4.7 Vertical profiles of sediments

Porewater profiles provide a way to evaluate the flux rates of hydrogen sulfide in the sediment and its reactions. At the end of each experiment, the sediment core was sliced vertically from top to bottom every (0~1.5 cm, 1.5~3 cm, 3 - 4.5 cm, 4.5~6 cm, 6~7.5 cm until 9 cm). In this experiment, sediment porewater was obtained by squeezing over a 0.45 µm filter, Figure (4.7.2) show the pore water profiles for June, July, August and, September. There were no clear differences in the vertical profiles of sulfide ion change between the iron construction and the attractive-free groups, a large change occurred at approximately 0~1.5, In some cases actual 1.5~3 cm. So, the active layer is the top layer of sediment that is 0~1.5 cm during the experimental period.
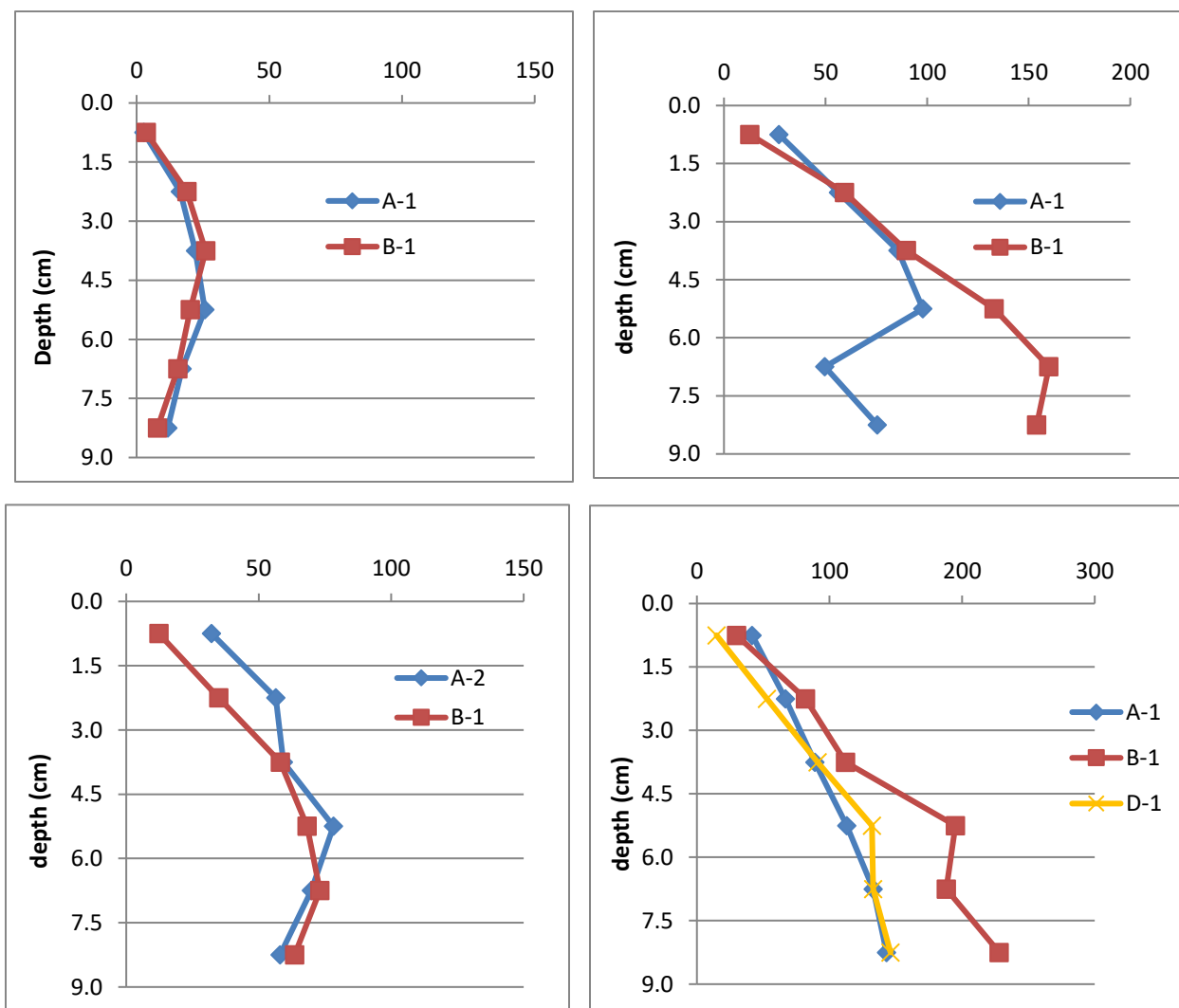

Figure 4.7.1. Vertical profiles of the hydrogen sulfide concentration for (a) June, (b) July, (c) August, and (d) September.

The average hydrogen sulfide removal efficiency on the overlying water is calculated as given below use the formula:

$$\% \text{ H2S} = \frac{C^{-\text{ref}}_{(0\sim 9\text{cm})} - C^{-\text{iron}}_{(0\sim 9\text{cm})}}{C^{-\text{ref}}_{(0\sim 9\text{cm})}}$$

Where, $C^{-\text{ref}}_{(0\sim 9)}$ is the total average of hydrogen sulfide concentration in (reference groups).

Where, $C^{-\text{ref}}_{(0\sim 9)}$ is the total average of hydrogen sulfide concentration in (Iron groups).

In general, with iron application performance, free sulfide was suppressed only below at depth of $1.5 \sim 3$ cm, as shown in the figures (5.6 1, 5.6 2, and 5.6 3). Because the iron compound was only placed on sediment surface, the iron particle did not directly reach down to react with sulfide, so that it may not affect removing sulfide., Therefore, the sample collected from $1.5 \sim 3$ cm depth was used for this analysis.
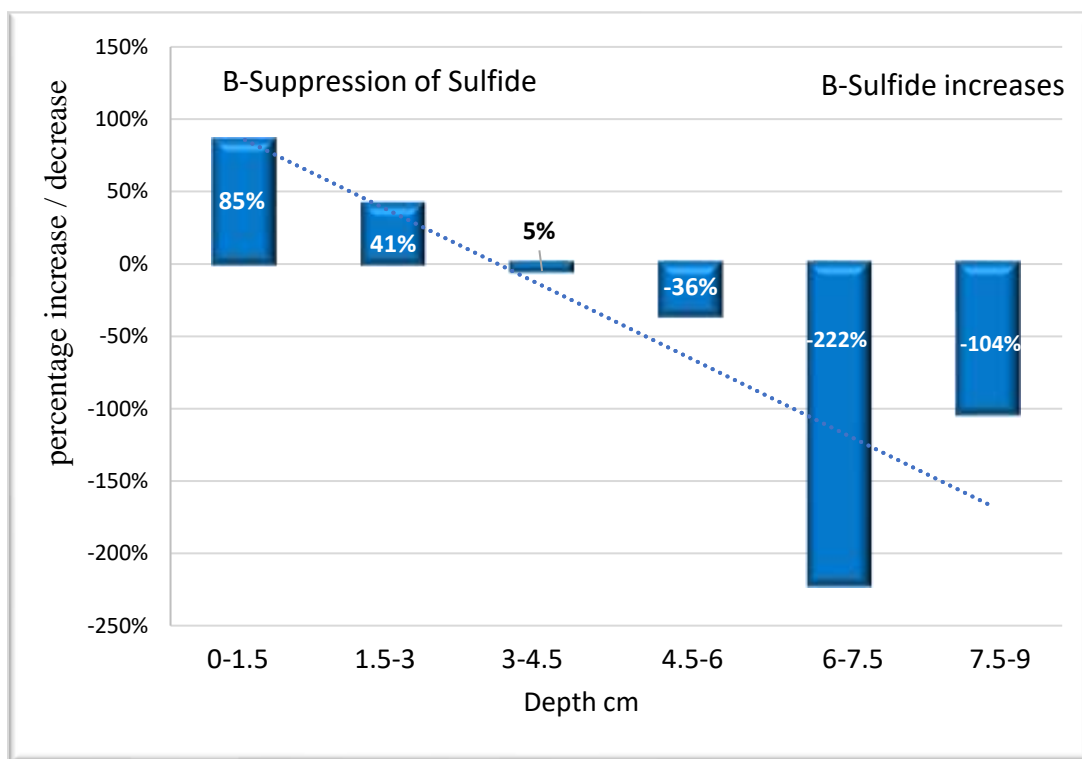

Figure 4.7-1 The vertical distribution of sulfide (July)
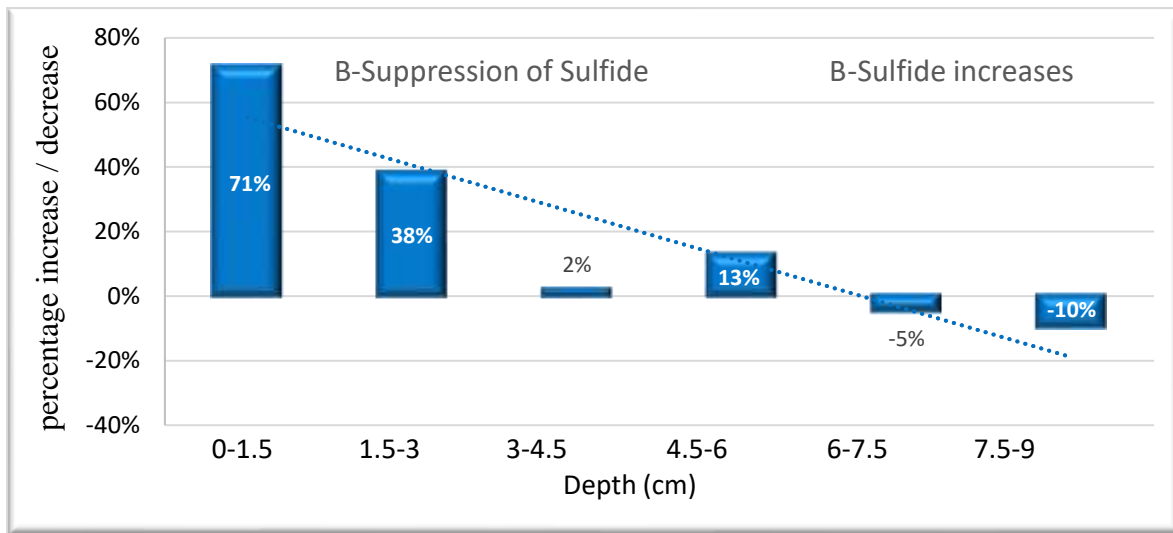
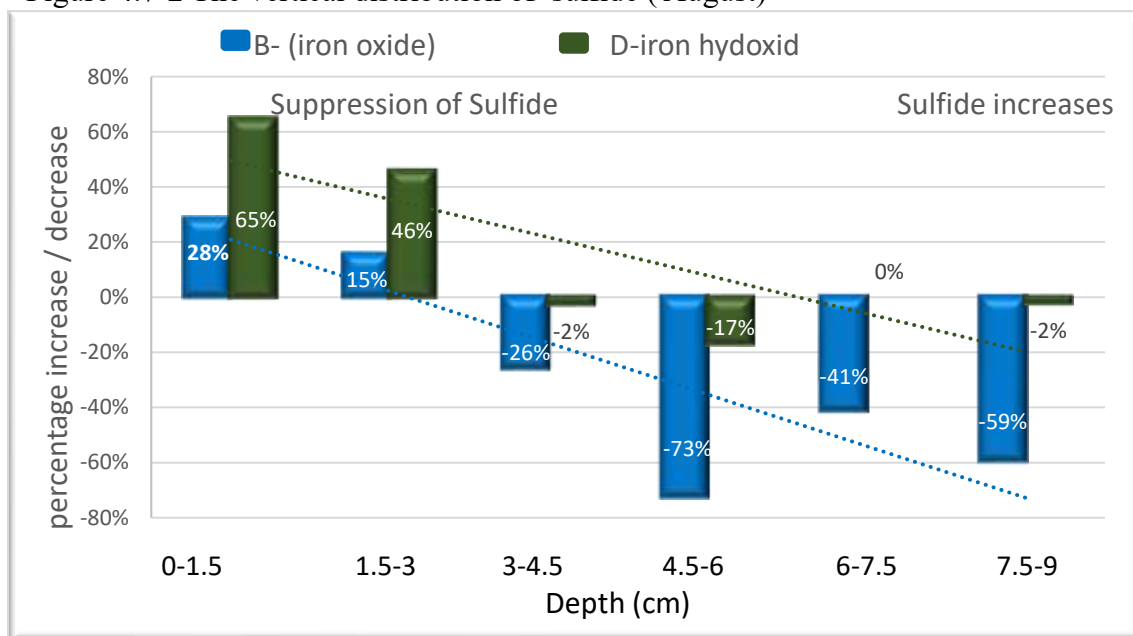Figure 4.7-2 The vertical distribution of sulfide (August)

Figure 4.7.3 The vertical distribution of sulfide (September)

4.7.1 Comparison of sulfide release rates

The untreated control group (A1, A2, and A3) was used in the experiment as a point of comparison to measure the effect of iron oxide treatment group (B1, B2, and B3) on hydrogen sulfide removal under anaerobic conditions, as shown in the figure (4.7.4). The second treatment group used iron hydroxides, with Fe (III) as the major components, can also be the electron acceptor. At the end of each incubation period (July, August, and September), pore water sulfide concentrations were measured. In an experiment conducted in July, the results indicated that the

two groups did not differ on any of the measures. Whereas, the results of the second and third experiments shown in the figure below, indicate that the average dissolved sulfides concentration in the pore water of treatment groups was significantly decrease, the final concentration of free hydrogen sulfide in pore water for iron hydroxide core (D) indicate 4.7 mg/L, these values were much smaller than iron oxide application core (B) in which that value was 20.7 mg/L. Although the averaged final concentration was highest in the control case (A) in September. This may be considered that this free sulfide formed iron sulfide by reaction with divalent iron ions in the sediment.
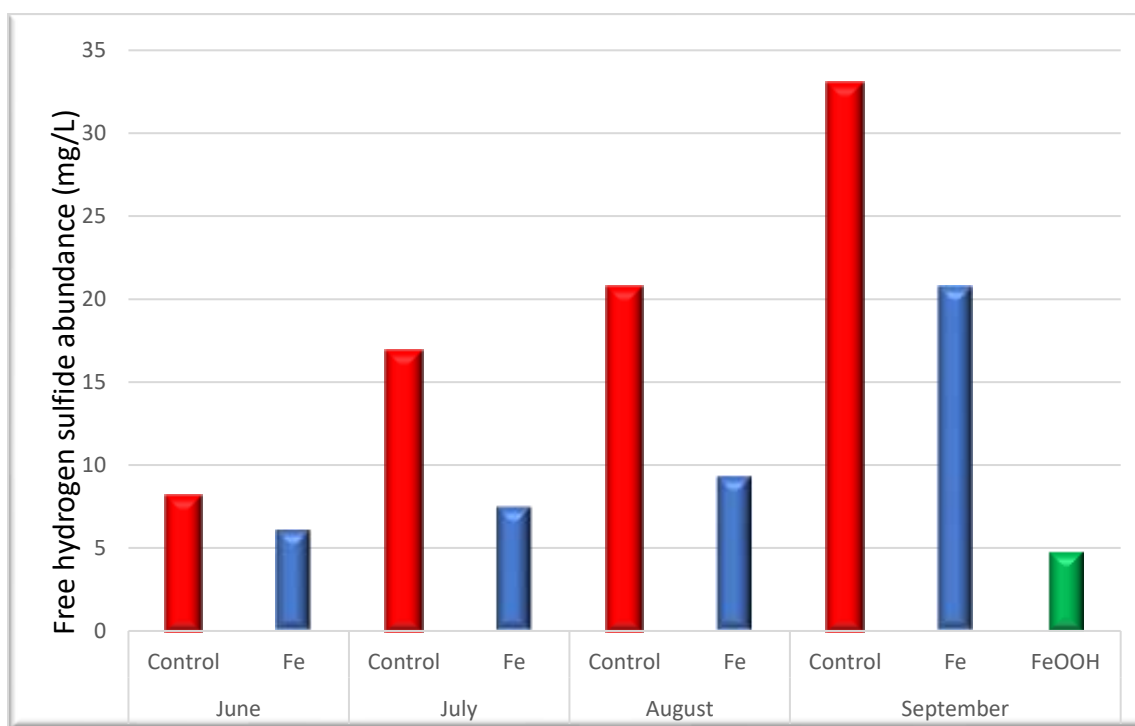

Figure 4.7.5 Sulfide ion concentration in pore water (mg / L)

4.7.2 Temporal change in divalent iron concentration in the pore water

Divalent iron was quantified according to the phenanthroline method, a method for the determination of iron using hydroxylamine hydrochloride. The result of the experiments demonstrated the concentration of divalent iron in the pore water during the experimental period with the iron hydroxide group (D) was 0.05 mg/L. The divalent iron concentrations in the pore water were significantly highest with iron oxide core (B) ranging about 0.1 mg/L, and the second-high value of the release rate of divalent iron was obtained from control (A) was about 0.07 mg/L. In an experiment conducted in July, an extremely high concentrations of divalent iron was obtained

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from iron oxide group (B) , it ranged about 0.19 mg/L, as can be seen in figure (4.7.2-1).
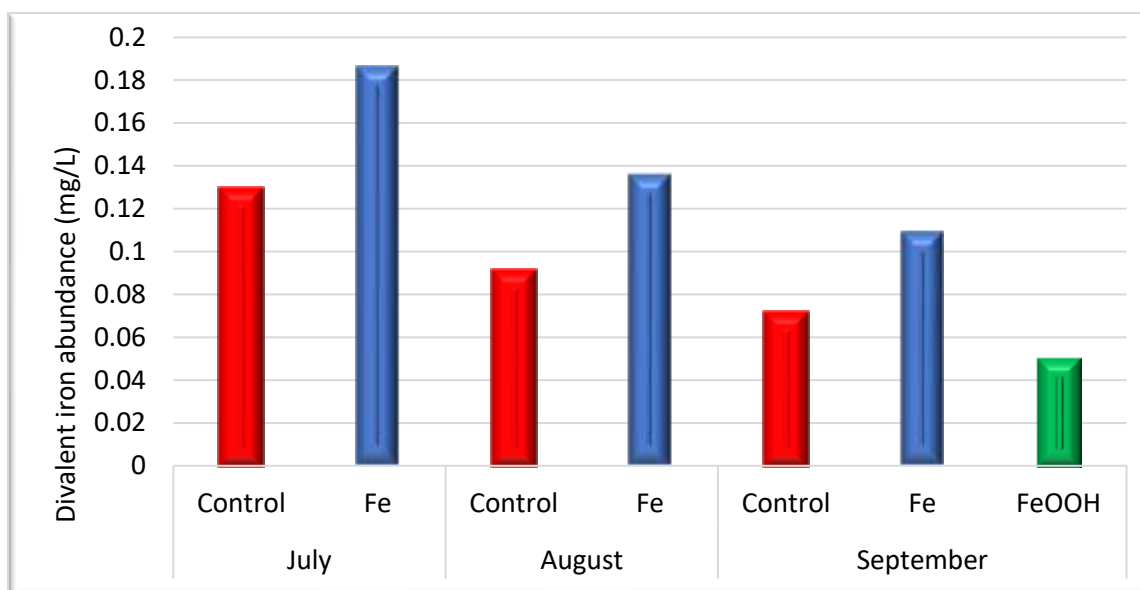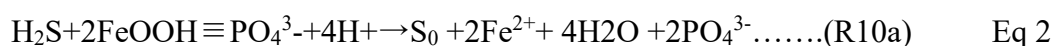

Figure 4.7.2-1 Divalent iron concentration in pore water (mg / L)

4.8 Discussion of comparison of sulfide release rates and divalent iron concentrations

The comparison of the results obtained between sulfide release rates and divalent iron concentrations, as shown in the figure (4.8.1). As you can see, the relationship between sulfide release rates and divalent iron concentrations changes between the treatment groups, this result revealed the reduction in the production of hydrogen sulfide and the conversion of the iron (II) hydroxide into divalent iron. But there was no significant change in the control group. This observation might imply that iron oxides are reduced under anaerobic conditions and the produced divalent iron will form iron sulfides through sediment. We observed a significant reduction in sulfide concentrations in iron hydroxide group (D), despite the lower content of divalent iron was observed in this group. Because the biochemical reactions considered in the sediment model are shown in figure (4.7.2-2) under anaerobic conditions double replacement reaction exchanges will occur, as per the following formula:
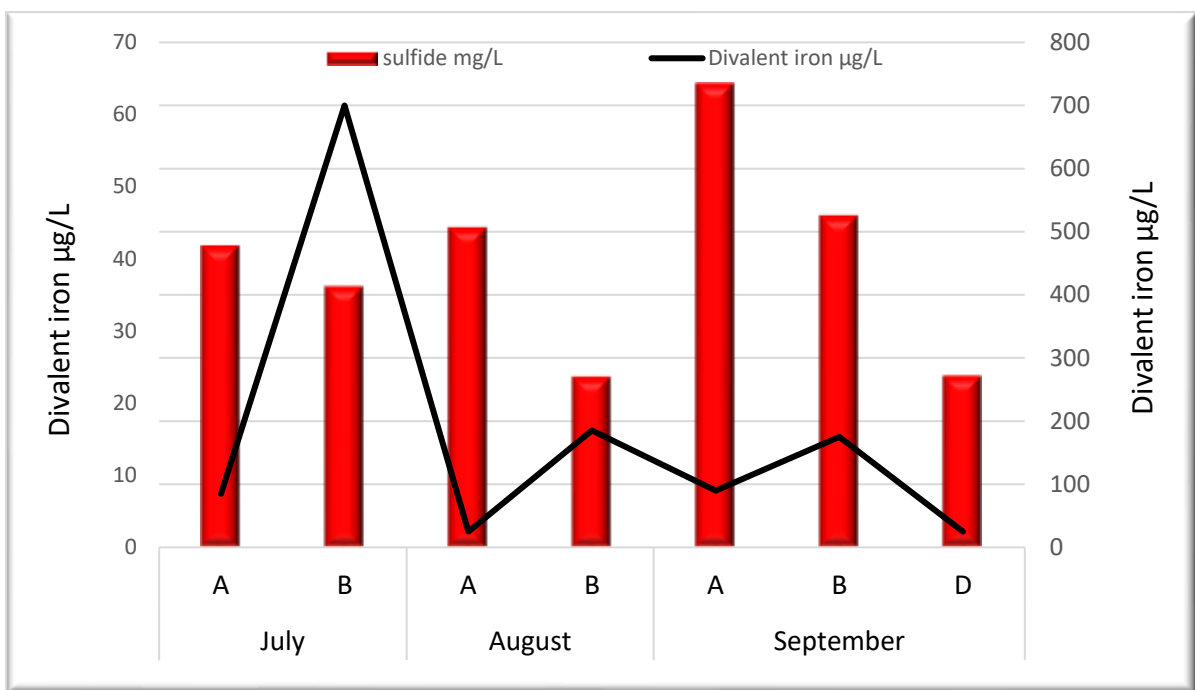
$FeOOH+PO_4^{3-} \rightarrow FeOOH \equiv PO_4^{3-}$ ……………………………………..(R7)   Eq 1

$H_2S+2FeOOH \equiv PO_4^{3-}+4H+ \rightarrow S_0 +2Fe^{2+}+ 4H_2O +2PO_4^{3-}$…….(R10a)   Eq 2

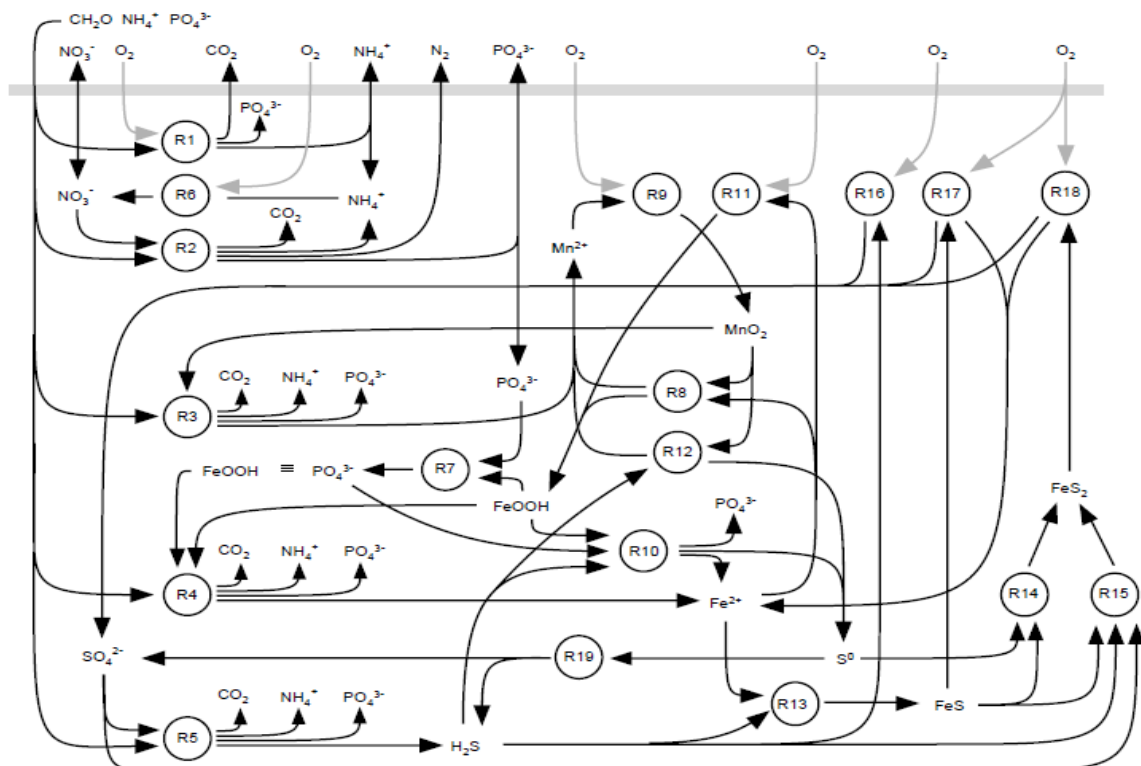Figure 4.8.2 Comparison of sulfide release rates and divalent iron concentrations.

Figure 4.7.2-2Material circulation processes modeled in this study from flossing et al, A model set-up for an oxygen and nutrient flux model for Aarhus Bay, 2004.

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4.9 Redox potential and pH profiles

At the end of the experimental periods, oxidation-reduction potential (ORP) and pH value were measured, and sediment samples were taken at several depth intervals for solid-phase analyses. The pH in the control remained steady with vertical profile and temporal variation (figures 4.9.1, 4.9.2, 4.9.3, and 4.9.4) in comparison to B and C. The sediment sample B did not show any particular trend in August. However, in other three occasions it showed a slight decrease in pH value at 1.5 cm depth and gradual increase with depth except for September when it decreased at 9 cm depth. Sediment sample C showed a sharp decrease at 1.5 cm depth in June and slight drop in all other three occasions. Thereafter, the value was fluctuating. The sample D which was measured in September showed a reasonable drop in pH at 1.5 cm depth and gradual increase till 7.5 cm depth. At 9 cm depth however, it decreased again. The increase of depth and the decreasing pH trend estimated for all the samples was 0.11 as an average. Therefore, there is no significant linear relationship between sulfide concentration and pH value (figure 4.9.9). The results of redox potential test showed a major temporal change. In June, all the samples showed positive values, whereas in other three months the values were negative except for sample C in July where it showed a larger change with a sharp drop at 1.5 cm and a gradual decrease thereafter. In June and August, the control showed lower values for ORP compared to the test samples. Other than the above, other samples did not show any trend in particular. Further, the correlation between sulfide and ORP showed a slightly negative correlation (figure 4.9.10).
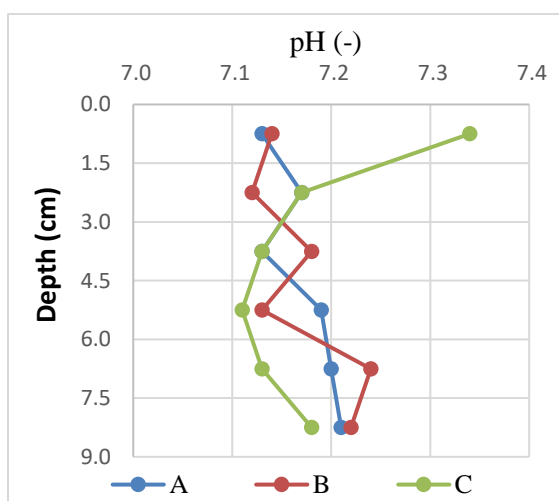

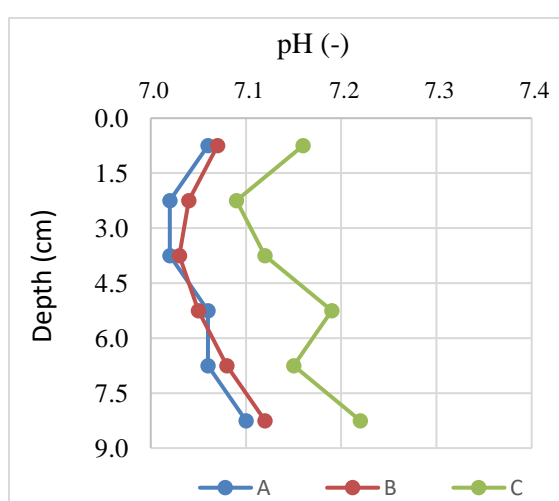Figure 4.9.2Vertical distributions of pH in pore water (June)

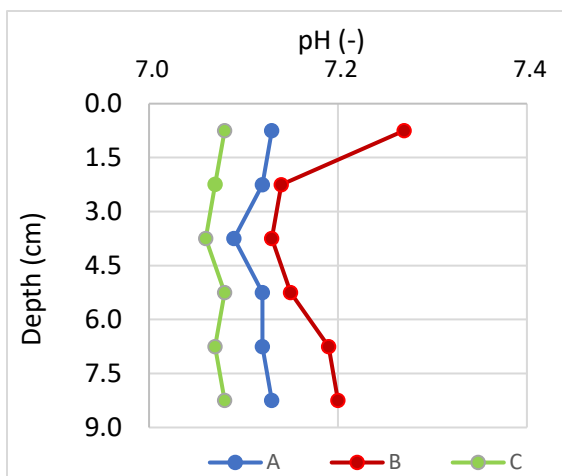Figure 4.9-2Vertical distributions of pH in pore water (July)

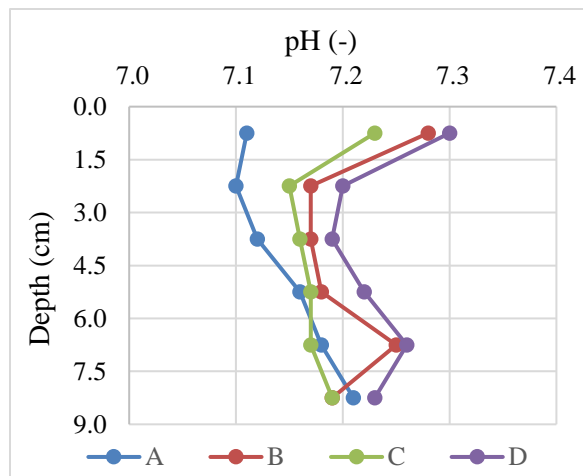Figure 4.9-3Vertical distributions of pH in pore water (August)

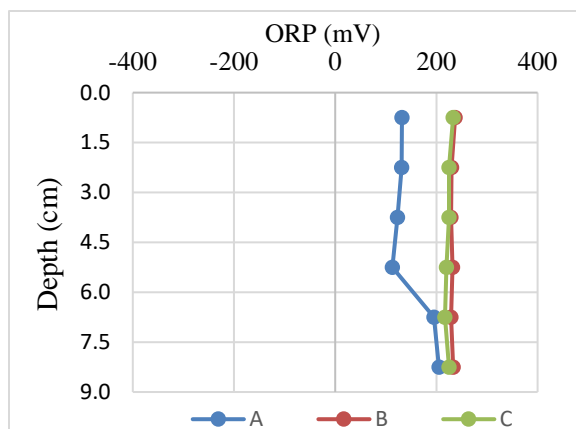Figure 4.9-4Vertical distributions of pH in pore water (September)

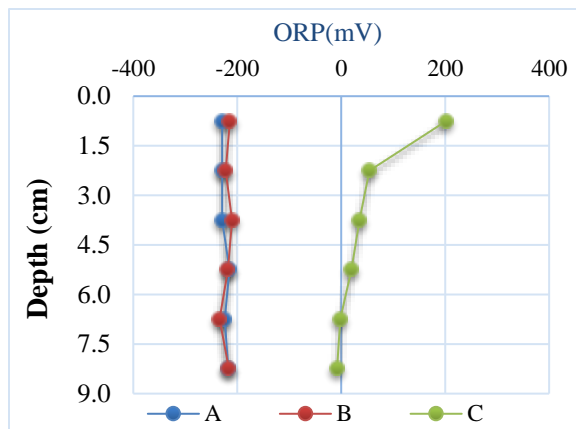Figure 4.9-5 Vertical distributions of ORP in pore water (June)

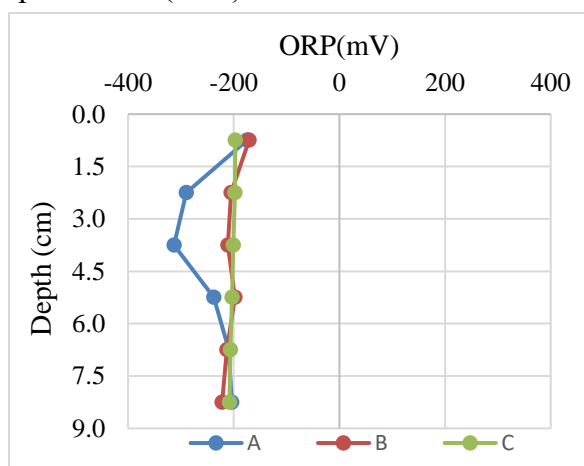Figure 4.9-6 Vertical distributions of ORP in pore water (July)

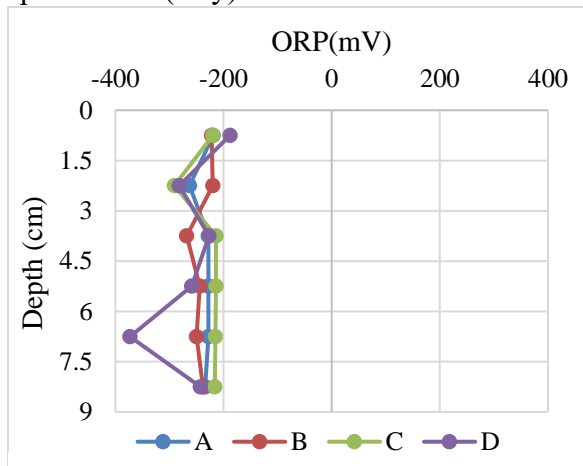Figure 4.9-7 Vertical distributions of ORP in pore water (August)

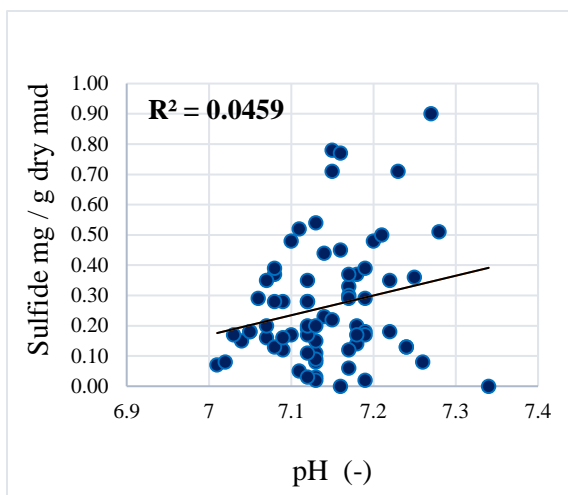Figure 4.9-8Vertical distributions of ORP in pore water (September)

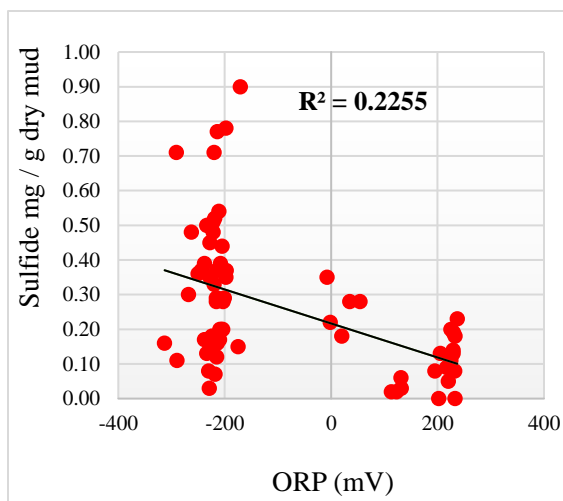Figure 4.9.9 Relationship between pH and hydrogen sulfide release rate

Figure 4.9.10 Relationship between ORP and hydrogen sulfide release rate

4.10 The rate of sulfide formation experiment

Undisturbed sediment samples were collected from Mikawa Bay. The rate of sulfide formation was performed on the sediment sample. For all the core samples, irons were not used as eluent, and the sliced sediment core samples were kept in 30 mL syringes and placed in the incubator box. During the experimental period, hydrogen sulfide rates were measured, and sediment samples were taken at several depth intervals for solid-phase analyses. it shows that it is not possible to consider the effect of an uneven amount of hydrogen sulfide in the syringe because the sediment cannot be stirred in the syringe. Therefore, the vertical distribution of the production rate was varied from month to month. The measurement interval was 1st, 2nd, 21st for July, and August, while in September we extended the date of the measurement interval, it held on the 1st, 2nd, 3rd, 4th, 7th, 14th and 21st day, after the preparation of the experiment.

4.10.1 Experimental results (July and August)

Figure (4.10.1) summarizes the average rate of hydrogen sulfide production rate in (July and August), based on the results, the concentration of hydrogen sulfide of three cores (a, b, c) decreased while on the second day of each layer and then increased. In general, the inlet concentration of hydrogen sulfide was increased gradually, increasing hydrogen sulfide inlet

concentration was based the time period, while the highest concentration of sulfide ion was obtained in cores (C 2-3cm, C 0-1cm, C 3-5cm and C 4-5cm, respectively), it was lowest in the core (C 1-2cm).
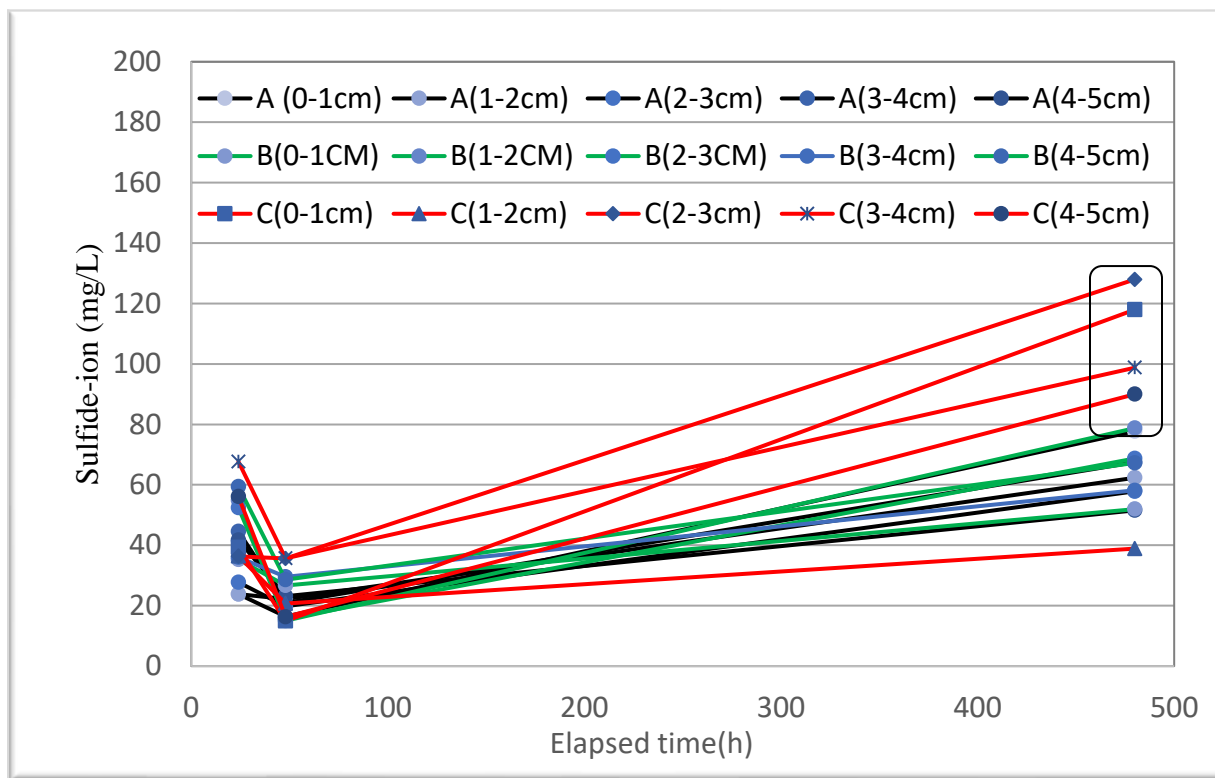
Figure 4.10.2.Hydrogen sulfide production rates for Core A, B and C (July and August)

4.10.2 Experimental results (September)

The results of sulfide ions are summarized in Figure 4.10.3. (A, B, C). After 72-hour of the experimental period, the inlet concentration of hydrogen sulfide was increased gradually, increasing hydrogen sulfide inlet concentration was based the time period. the highest concentration of sulfide ion was obtained in cores (A 0-1cm), it was lowest in the core (C 2-3cm and C 1-2cm respectively). The level of hydrogen sulfide production average for each core layer are shown in Figure 4.10.2.2. Among all sedimentary layers at different depth intervals in these cores, hydrogen sulfide production rate increased within 0-1 cm depth with a range 13.56 mg / L / day, while, there were much smaller production rates of hydrogen sulfide in the 4-5 cm layer.
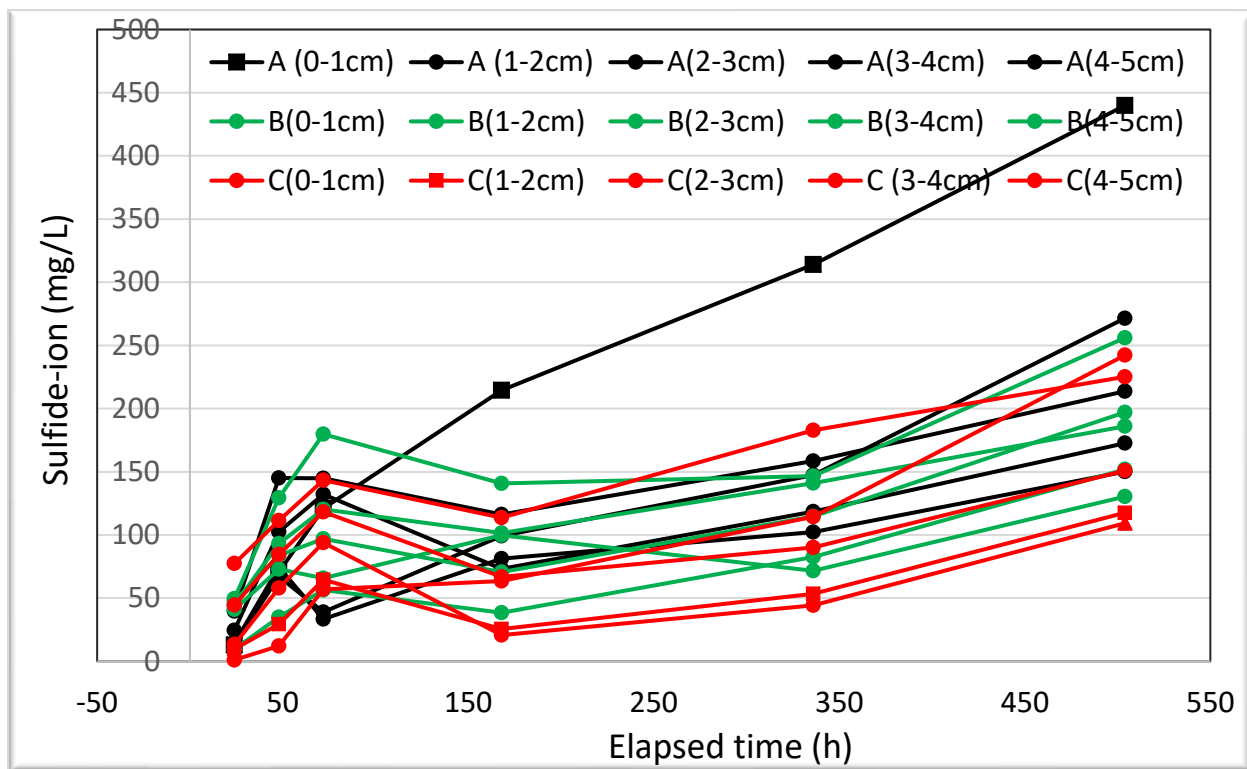
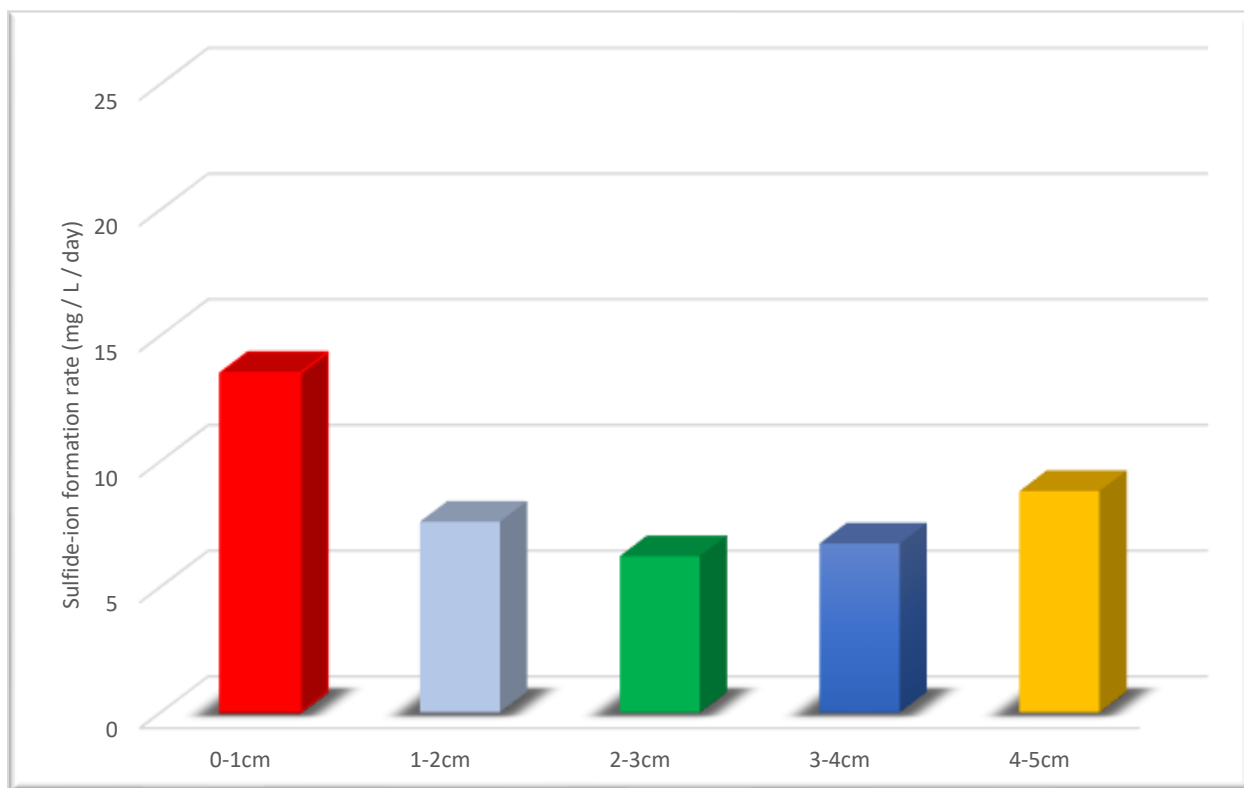Figure 4.10.2.1. Hydrogen sulfide production rates for Core A, B and C (September).

Figure 4.10.2.2. The average production rate of hydrogen sulfide at different layers (September).

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5 Experiments using steelmaking slag.

5.1 Brief introduction about steelmaking slag and pH adjustment

As mentioned briefly in the first chapter, hydrogen sulfide (H_2S) and HS^- are produced in organically enriched sediments through the reduction of sulfate ions (SO_4^{2-}) by sulfate-reducing bacteria under an anoxic condition and the dissolved sulfides formed in the sediments diffuse to the overlying water. Hydrogen sulfide is highly toxic and fatal to living organisms and consumes oxygen when oxidized. Hydrogen sulfide can be effectively removed from water by using several treatment processes. The use of irons is the most efficient and cost-effective treatment option for hydrogen sulfide removal, on the other hand, slag capping would be the second-best for remediation of sediment quality itself besides, steelmaking slag is a byproduct of iron and steel manufacturing and steelmaking slag produced from the purification process of pig iron into steel. Among the many by-products of the steel manufacturing process, Japan produces 40 million tons of iron and steelmaking slag annually. Hydrogen sulfide concentrations increase with decreasing pH, oxidation of hydrogen sulfide is also a function of ph. In addition to the formation of iron sulfide FeS and S_0, the pH values (8.0–8.5) observed in steelmaking slag applications may have a reason that changed HS^- to sulfate ion (SO_4^{2-}) (Hayashi et al., 2013; K. Kim et al., 2012; and Canadajournal, n.d. updated Sept.1992).

5.1.1 Motivation

More economical materials are advantageous for practical use &Steel making slag is a kind of byproduct in the steel making process and is produced at large amount, so that it is a promising material.

5.2 Material and methods

5.2.1 Sediment Sampling

Same method as in experiment no 1.

5.2.2 Laboratory conditions

The experiment was performed with the same boundary conditions as in experiment no 1.

5.2.3 Experimental procedure

In this study, the hydrogen sulfide release experiment with the combination of hydrogen sulfide production experiment was conducted by using steelmaking slag as iron-containing material to make clear the effectiveness of the slag and its mechanism of suppression. The bottom sediment for the present experiments was collected from Mikawa Bay, Japan. Experiments were carried out from October 24 to November 14, 2018. The slag was placed on top of the sediment. The steelmaking slag used in this study was 2 mm to 5 mm in diameter and was provided. The total of 9 pieces 3 pieces each of the three types of A: no add reference core, B: steel slag particles with a diameter of 2 mm or less and D: steel slag with a particle diameter of 2 mm to 5 mm were arranged. Slag was added has an iron content of 20%. Amount added was 25 g then that it was converted to 5 g of iron, as calculated below:

50/78.5×25=15.92g of slag was added in the test tube.

(test tube = 50 ml; Pipe area = 78.5 cm²; 1 cm deep)

Steelmaking slag is mainly composed of SiO_2 , Al_2O_3, CaO, MgO, TiO_2 , P_2O_5, MnO, T-Fe, S_0, at compositions of 29.70, 3.97, 32.60, 4.07, 1.20, 3.50, 4.65, 18.70, and 111%, respectively as per table ( )

Table 5.2.3-1Chemical composition of the steelmaking slag used in the present study.

Chemical compound name	Formula	Concentration ratio percentage
Silicon dioxide	SiO_2	29.70%
Aluminum oxide	Al_2O_3	3.97%
Calcium oxide	CaO	32.60%
Magnesium oxide	MgO	4.07%
Titanium dioxide	TiO_2	1.20%
Phosphorus oxide	P_2O_5	3.50%
Manganese oxide	MnO	4.65%
Total iron	T-Fe	18.70%
Sulfur monoxide	S0	111%

Samples were treated with sodium hydroxide (NaOH) and hydrogen chloride (HCl) to adjust the pH to 8.0 and 8.3. The experiment was conducted with five treatments (Additive-free core A, core B with 2 mm or less slag on sediment surface added, also 2 to 5 mm slag on sediment surface

added for core D, core E the pH adjusted to 8.0 and core F the pH adjusted to 8.3, and the measurement intervals were at the 0th, 3rd, and 7th days, as shown in the following table (5.2.3-2).

Table 5.2.3-3 Type and treatments detail for hydrogen sulfide control.

Core 1 (9)	Test tube A	Examination group B	Test tube D	Test tube E	Test tube F
Day 0	Initial condition				
3 Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition		pH＝8.3
7 Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition	pH＝8.0	pH＝8.3
Core 2 (10)	A	B	D	E	F
0 Day	Initial condition				
3 Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition	pH＝8.0	pH＝8.3
7 Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition	pH＝8.0	pH＝8.3
Core 3 (8)	A	B	D	E	F
0 Day	Initial conditions				
3 Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition		
7Day	Additive-free	2 mm or less Slag addition	2 to 5 mm Slag addition	pH＝8.0	pH＝9.0

5.3 Sample analysis methods

5.3.1 Sulfide release experiment

Each of the samples was examined, and the chemical and physical characteristic analyses were performed on water samples and sediment samples. The water in the core was sampled on the first, second, third, third, fourth, and twenty-first days, respectively, on the 0th day of measurement, and the contents of hydrogen sulfide and divalent iron were measured. The dissolved hydrogen sulfide concentration in the water directly above was determined by the methylene blue

method and then the absorbance was measured at a wavelength of 660 nm with a spectrophotometer. Concentrations of dissolved Fe (II) were measured by the method phenanthroline.

5.3.2 Sulfide generation rate experiment

Sample in the test tubes were stored in the water tank with a constant temperature until each measurement days, the measurement intervals were the 0th, 3rd, and 7th days. a predetermined volume of sediment was taken by a syringe from the test tube for the measurement of hydrogen sulfide. Remaining sediment in a test tube was used for pH and measure redox potential (ORP) measurement.

5.4 Results and discussion

5.4.1 Temporal changes of dissolved sulfide in the overlying water

Temporal changes of dissolved sulfide in the overlying water in each treatment are shown in figure (6.4.1.1) for the experiments conducted with steelmaking slag. The results revealed that both uses (2mm or less and 2 to 5mm) of the steelmaking slag significantly suppressed dissolved sulfide in the overlying water. In steelmaking slag of (B1 and B3) ≥ 2 mm, the dissolved sulfide concentrations in the overlying water showed a ranged from 0.02 to 0.08 mg/L, similar results were obtained with in steelmaking slag of (D1 and D3) 2 to 5 mm. Whereas the final concentration of dissolved sulfide in the overlying water for steelmaking slag of (B2 and D2) ≥ 2 mm and 2-5mm respectively, indicates 6.3, and 23.7 mg/L, respectively. In this experiment, it was demonstrated that the dissolved sulfide concentrations were significantly high in the undoped cores (A-1, A-2, A-3) were about (65.9 mg/L, 27.3 mg/L and 70.9 mg/L respectively). Moreover, statistical analysis SPSS IBM 23 software was used for statistical analysis, and there were statistically highly significant ($p < 0.01$) differences between the two groups Table (5.4.1-1).
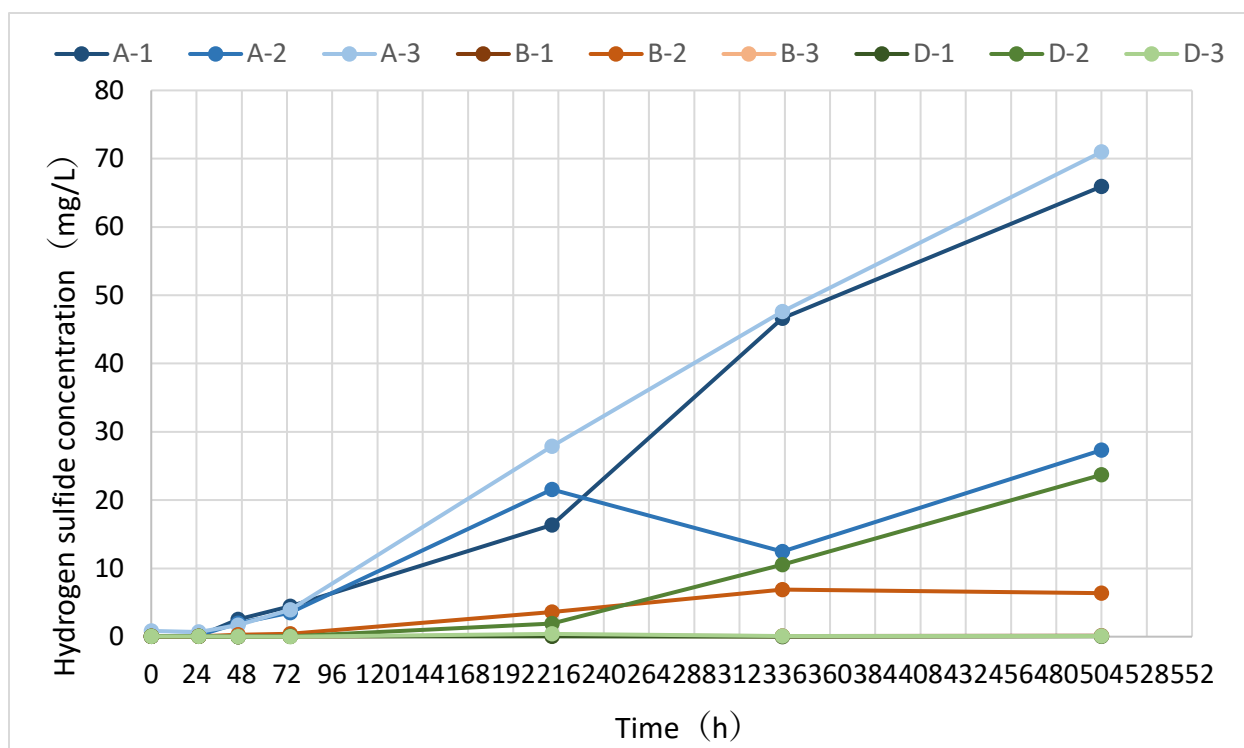
Figure 5.4.1Temporal changes in dissolved sulfide concentration in the overlying water

Table 5.4.1-2One-way ANOVA of three independent treatments

Source	Sum of squares SS	Degrees of freedom	Mean square MS	F statistic	P-value
Treatment	3,441.7550	2	1,720.8775	9.4418	0.0003
Error	10,935.7223	60	182.2620		
Total	14,377.4772	62			
Treatments pair		Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inference	
Additive-free vs 2 mm or less Slag		5.4663	0.001	** p<0.01	
Additive-free vs 2 to 5 mm Slag		5.1653	0.002	** p<0.01	
2 mm or less Slag vs 2 to 5 mm Slag		0.301	0.900	insignificant	

Dissolved Sulfide Release Rate

In the present study, the amount of dissolved sulfide concentration was reduced by the addition of steelmaking slag, as shown in the figure (5.4.2). From the average value from this experiment show that the release rate, as well as dissolved sulfide concentrations in the overlying water, were significantly low with steelmaking slag ≥2 mm (B) and steelmaking slag of (D) 2 to 5 mm were about (0.5 - 3.5 mg/L and 0.3 - 12.8 mg/L respectively). The release rate was quite high in the control core (A) with values ranged from 0.3 to 80.2 mg/L. It was supposed that dissolved sulfide may have reacted with Fe ions eluted into overlying water and insolubilized.
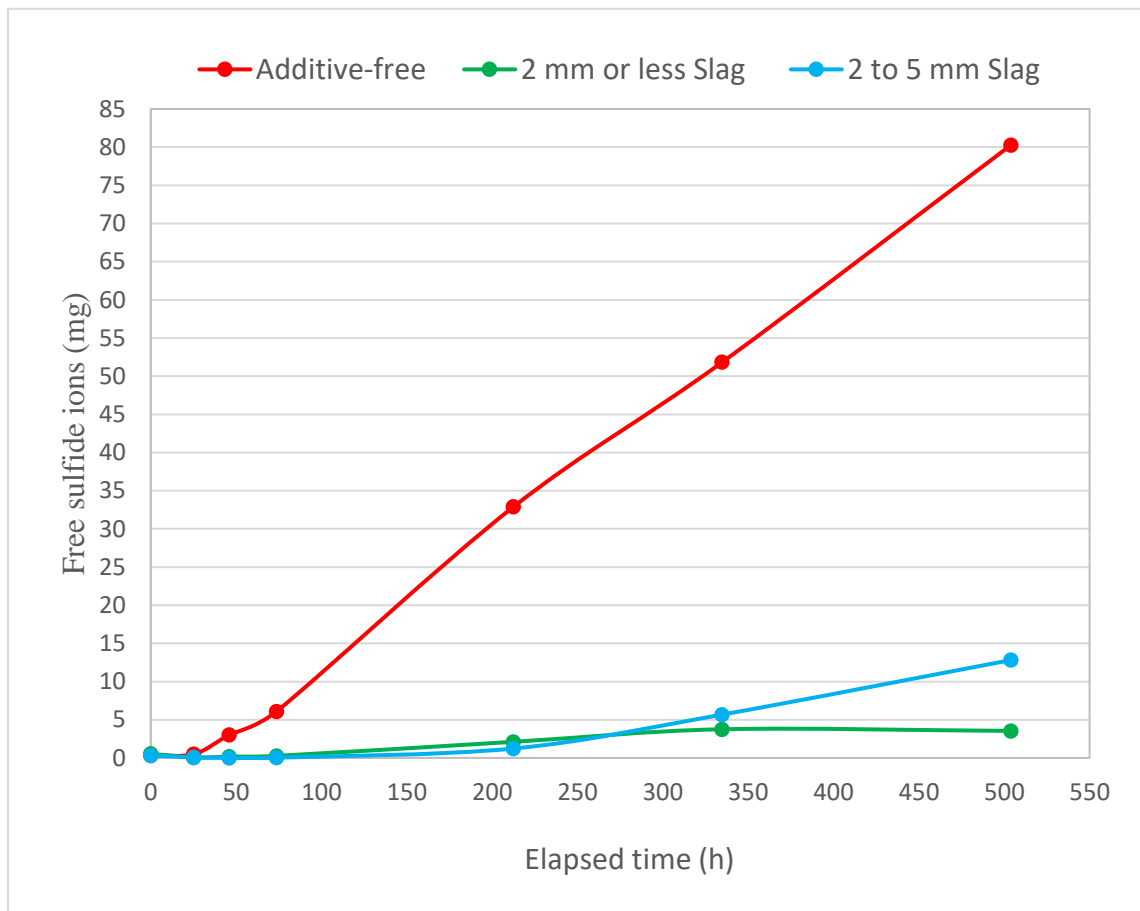

Figure 5.4.3 The release rate of dissolved sulfide experiment.

5.4.3 Temporal change of Fe concentrations

The results obtained in the present study showed that, the divalent iron concentrations were almost parallel with steelmaking slag group and control group throughout the period of the experiment. But at the end of the experimental period, from the average of three replicates, as shown in the figure ( ) low concentrations of divalent iron (0.26 mg/L) was obtained from Additive-free (A). While, the results confirm that high concentrations of divalent iron (0.49 mg/L) was obtained from steelmaking slag of (D) 2 to 5 mm, and the next high concentration (0.40 mg/L) recorded with steelmaking slag ≥2 mm (B).
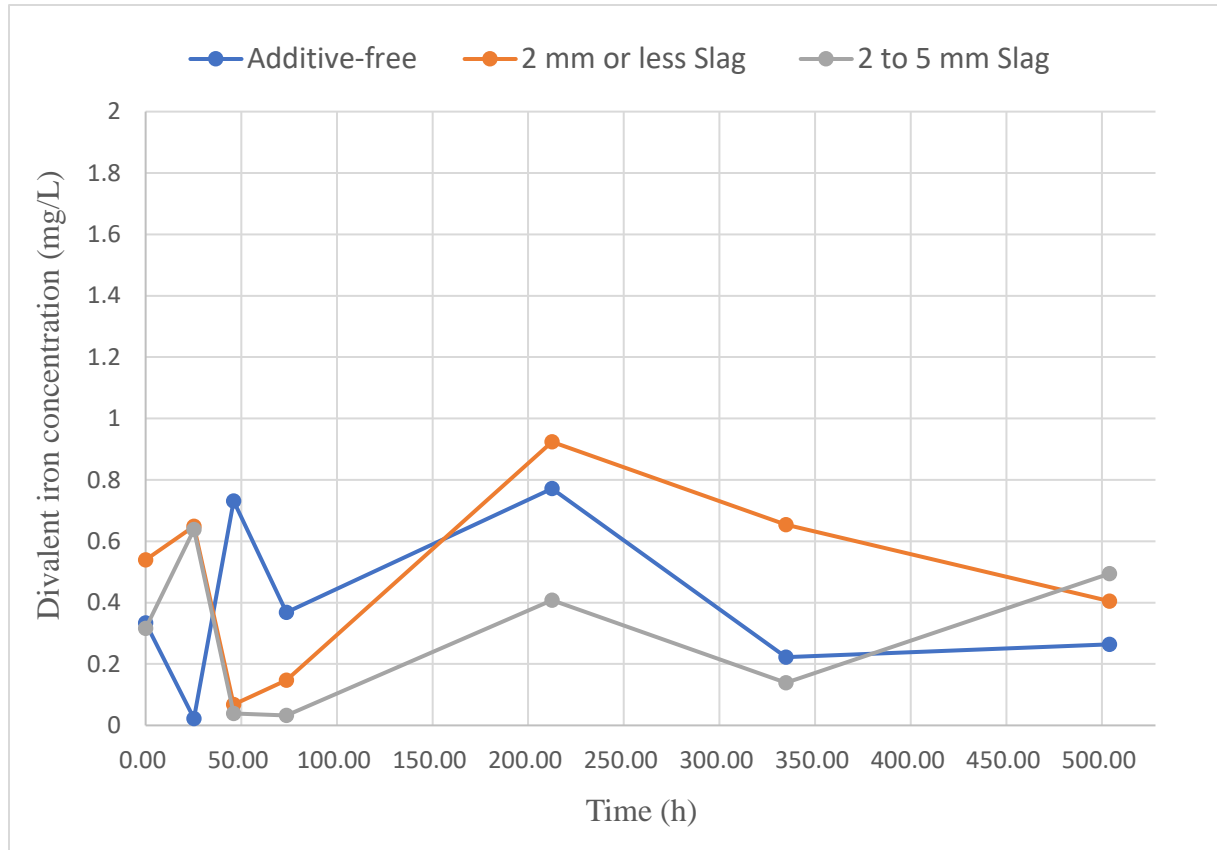

Figure 5.4.4 Time series change in divalent iron concentration in the overlying water

5.4.4 Sub-discussion

The performance of this experiment was monitored continuously over a period of 21 days. The results of figure (5.4.5) reduction of dissolved hydrogen sulfide by steelmaking slag was confirmed in both slag treatments; capping the sediments with steelmaking slag ≥2 mm, and capping the sediments with steelmaking slag 2 to 5mm. The results revealed that both uses (2mm or less and 2 to 5mm) of the steelmaking slag applications suppressed the diffusion of hydrogen sulfide in the overlying water. By the steelmaking slag of (D1 and D3) 2 to 5 mm, and steelmaking slag of (B1 and B3) ≥2 mm method, the dissolved sulfide concentration in the overlying water was significantly low compared to steelmaking slag of (B2 and D2) ≥2 mm and 2-5mm respectively, that the hydrogen sulfide removal efficiency reached was very high above 99%. Whereas, around 96 to 99 percent yield increase from initial days of production obtained with in the control group. It can be said that both uses of the steelmaking slag are much more effective at lowering the amount of hydrogen sulfide generated in the organically enriched anoxic sediments. This percentage formula was used:

$$\% \, control = \frac{C_{(t)}^{-ref} - C_{(t=0)}^{-ref}}{C_{(t)}^{-ref}} \tag{1}$$

$$\% \, \text{Iron} = \frac{C_{(t)}^{-ref} - C_{(t=0)}^{-iron}}{C_{(t)}^{-ref}} \tag{2}$$

The first equation, in this case, is percentage for hydrogen sulfide production, while the second equation, is percentage hydrogen sulfide removal efficiency.

Where, $C_{(t)}^{-ref}$ is the total average of hydrogen sulfide concentration.

Where, $C_{(t=0)}^{-ref}$ is the inlt hydrogen sulfide concentation strat from (t = 0)

Where, $C_{(t=0)}^{-iron}$ is the outlet or removal efficiency of hydrogen sulfide using iron or iron hydroxide application.
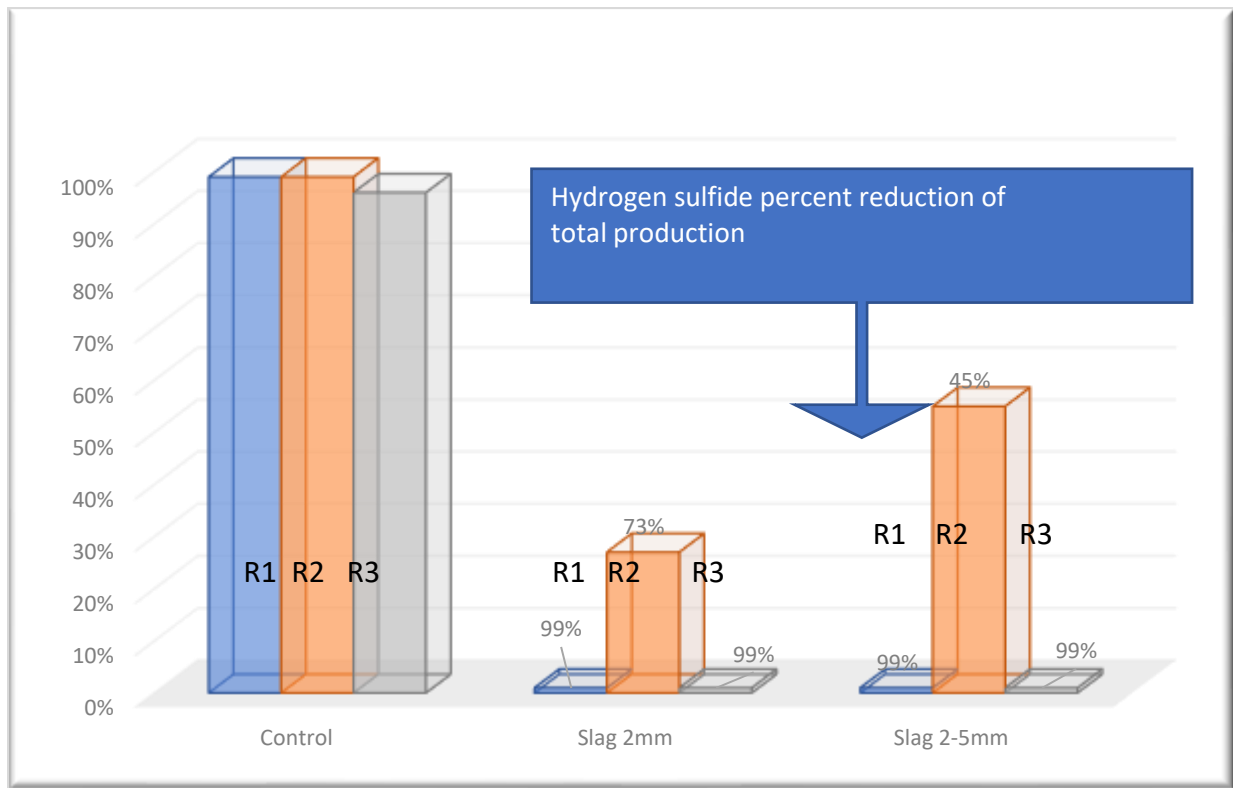
Figure 0.1 Percentage increase and decrease of changes dissolved sulfide.

5.5 Vertical profiles of sediments

At the end of experiment, the sediment core was sliced vertically from top to bottom every (0–1.5 cm, 1.5- 3 cm, 3 - 4.5 cm, 4.5-6 cm, 6- 7.5 cm until 9 cm), and pH, oxidation-reduction potential (ORP), moisture content, and free sulfide were measured, and the vertical distributions were investigated. The measurement intervals were at the 0th, 3rd, and 7th days.

5.5.1 Distributions of hydrogen sulfide in the sediment

The untreated control group (A) was used in the experiment as a point of comparison to measure the effect of steelmaking slag (2mm or less and 2 to 5mm) treatment group (B and D) on hydrogen sulfide removal under anaerobic conditions. Comparison of pH-adjusted was also added as a new group, for core (E) the pH adjusted to 8.0 and core (F) the pH adjusted to 8.3. At the end of the incubation period (Core 1, Core 2, and Core 3) dissolved sulfide concentrations measured in pore waters. The difference in sulfide generation rate experiment in figure (5.5.1, 5.5.1.2 and 5.5.1.3) shows that both uses of the steelmaking slags contain iron and the increase in pH

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suppressed hydrogen sulfide by reducing the dissolved sulfide in the sediment pore waters. Based on data obtained from steelmaking slag (B) ≥2 mm, the final concentration of hydrogen sulfide in the (core 1, core 2 and core 3) were 0.50, 5.74 and 7.33 mg/L respectively. Subsequently, by the results obtained from steelmaking slag (2 to 5mm) the concentration of hydrogen sulfide in the (core 1, core 2 and core 3) were 19.52, 10.69 and 16.28 mg/L respectively. Also results obtained in the present study showed that there were significant differences between these two groups ($P<0.01$, $P<0.05$), the p-value greater than 0.01 was obtained from steelmaking slag (B) ≥2 mm, and a p-value of less than 0.01 or equal to 0.05 obtained from steelmaking slag (2 to 5mm) treatment group (D). In addition, results obtained from pH adjustments (pH 8.0 and pH 8.3) shows with (core 1, core 2 and core 3) in low concentration of hydrogen sulfide, ranged from 19.16 to 47.98 mg/L and 72.51 to 155.63 mg /L respectively. But there were significant differences between the pH-adjusted group and untreated group, as shown in table (5.5.1-1). Whereas, significant increases in hydrogen sulfide concentrations were found in the untreated control group (Core 1, Core 2, and Core 3) indicated 81.59,160.56and 86.51 mg/L, respectively.

Table 5.5.1-2 ANOVA of four independent treatments

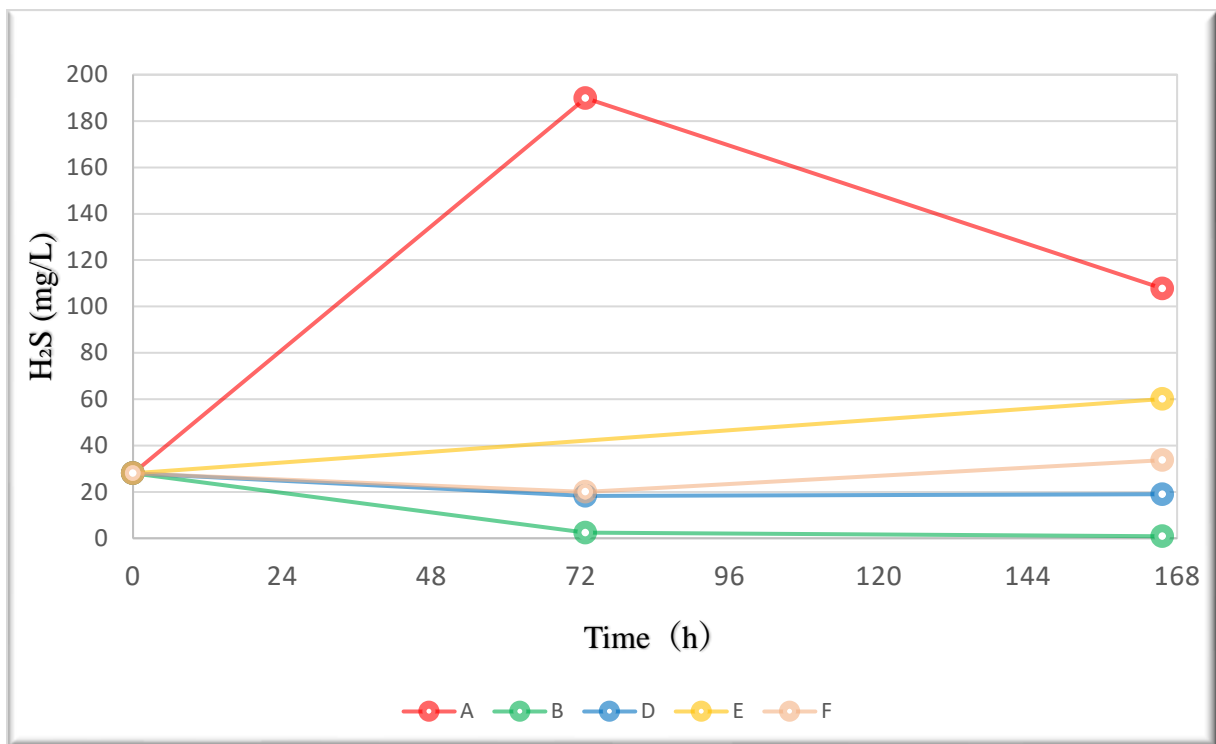| Source	Sum of squares SS	Degrees of freedom	Mean square MS	F statistic	P-value
treatment	22,105.18	4	5,526.30	4.3991	0.0048
Treatments pair	Tukey HSD Q statistic	Tukey HSD P-value	Tukey HSD inference		
A vs B	5.2864	0.0049779	** $p<0.01$		
A vs D	4.5421	0.020739	* $p<0.05$		
A vs E	2.9633	0.2419912	insignificant		
A vs F	2.0009	0.6075457	insignificant		

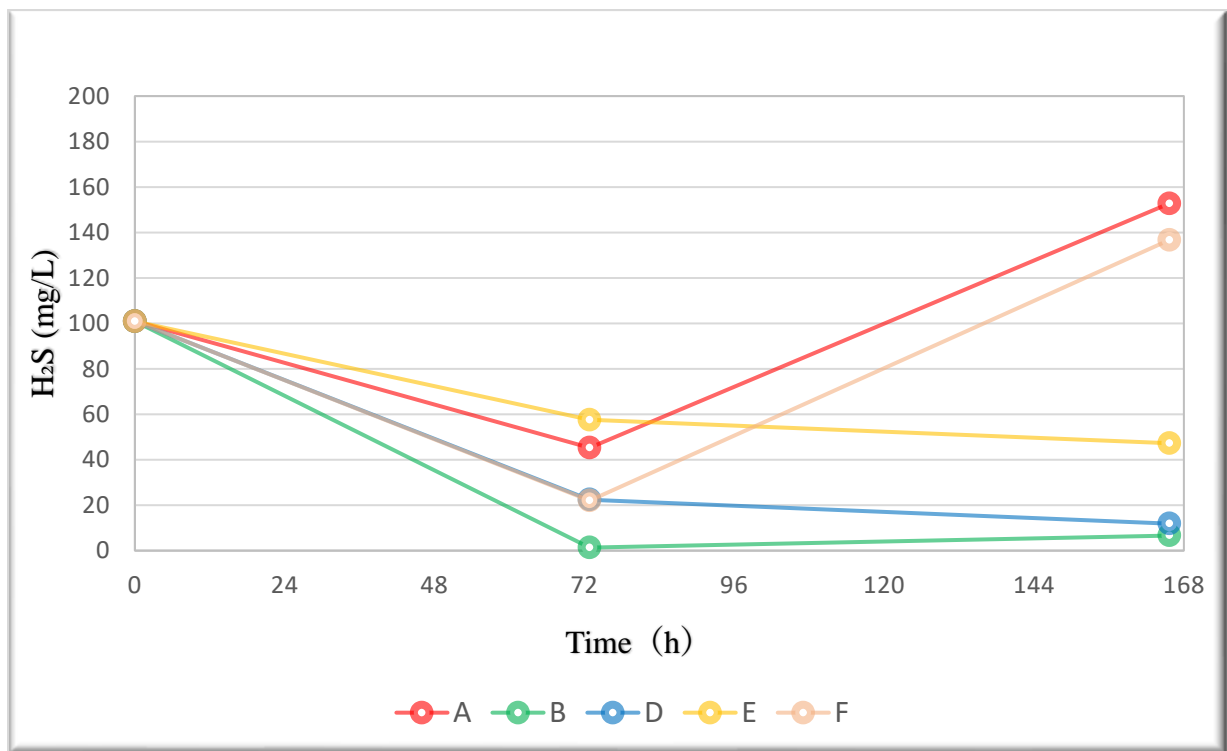Figure 5.5.2The vertical distributions of hydrogen sulfide in pore water (Core 1).

Figure 5.5.3 The vertical distributions of hydrogen sulfide in pore water (Core 2)
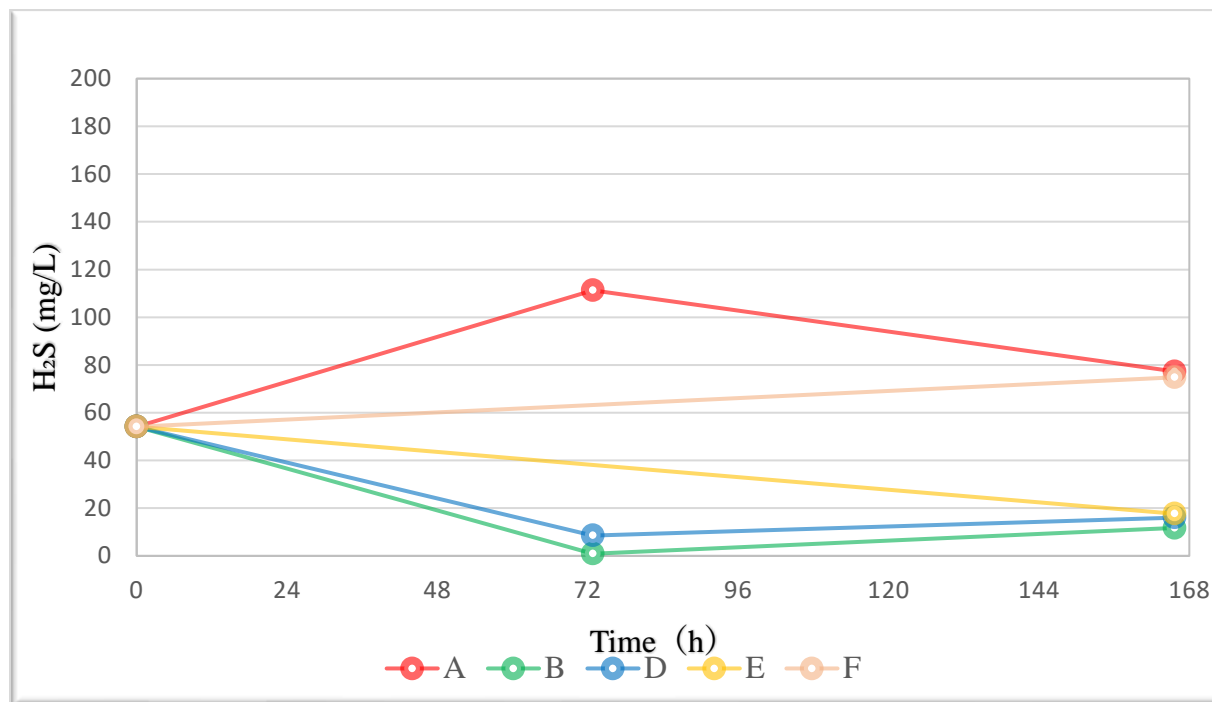
Figure 5.5.4 The vertical distributions of hydrogen sulfide in pore water (Core 3)

5.5.2 Profiles of pH and redox potential

The vertical profiles of pH are shown in figure (5.5.5, 5.5.2.2, and5.5.2.3). At the end of the experimental period, pH value and oxidation-reduction potential (ORP) values were measured and sediment samples were taken at multiple depth intervals for solid-phase analyses. As mentioned above, for core (E) the pH was adjusted to 8.0 and core (F) the pH was adjusted to 8.3, but for this experiment, the pH value of pH-adjusted E and F was lowered and could not be maintained. In general, the highest pH was recorded in core samples of steelmaking slag (B) ≥2 mm (B) and steelmaking slag (2 to 5mm), average values were (7.6 to 8.4 and 7.6 to 8.0, respectively). This is because of the presence of free lime (CaO) and free magnesia (MgO) in the steel slag. The lowest pH value (7.6 to 7.7) was recorded with untreated control group (A). The vertical profiles of oxidation-reduction potential (ORP) are   presented in figure (6.5.2.4, 6.5.2.5 and 6.5.2.6). The oxidation-reduction potential (ORP) values varied from (-460 to -580 mV) in core samples of steelmaking slag (B) ≥2 mm (B) and (-490 to   -610 mV) in core samples of steelmaking slag (2 to 5mm). The control showed lower values for ORP compared to the investigated samples. The oxidation-reduction potential (ORP) values showed only small differences between the two groups and samples did not show any trend in particular.
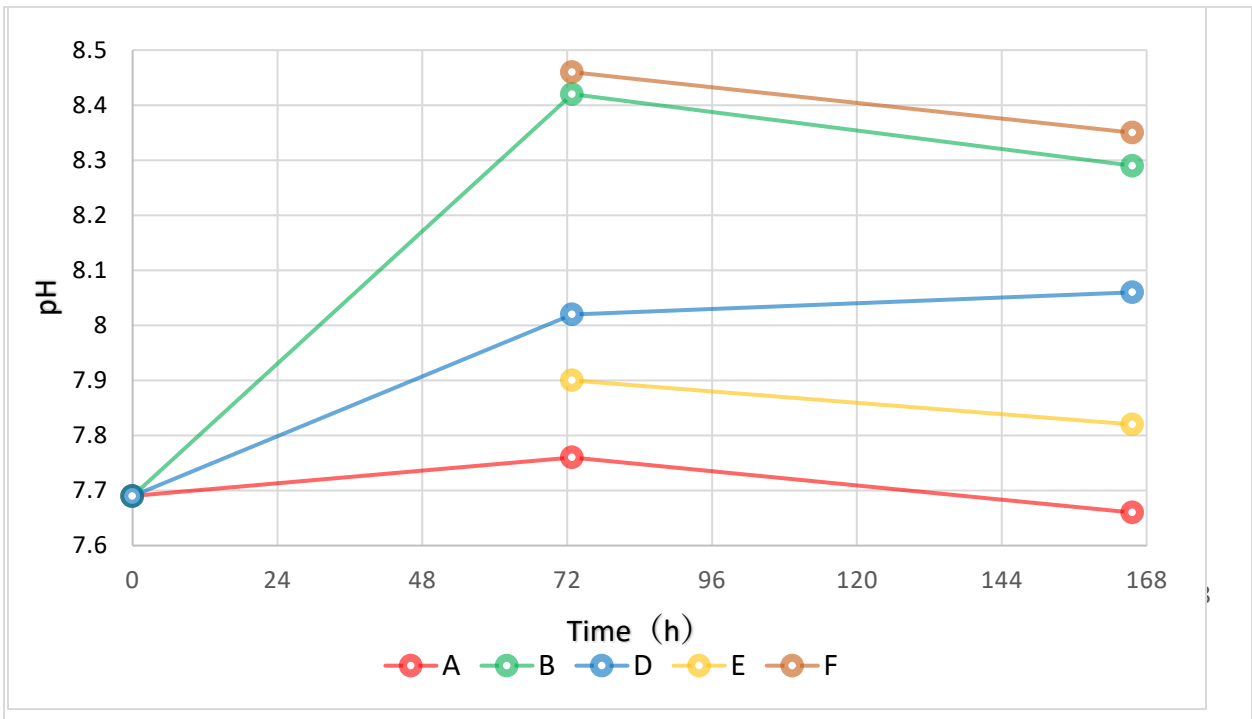
127

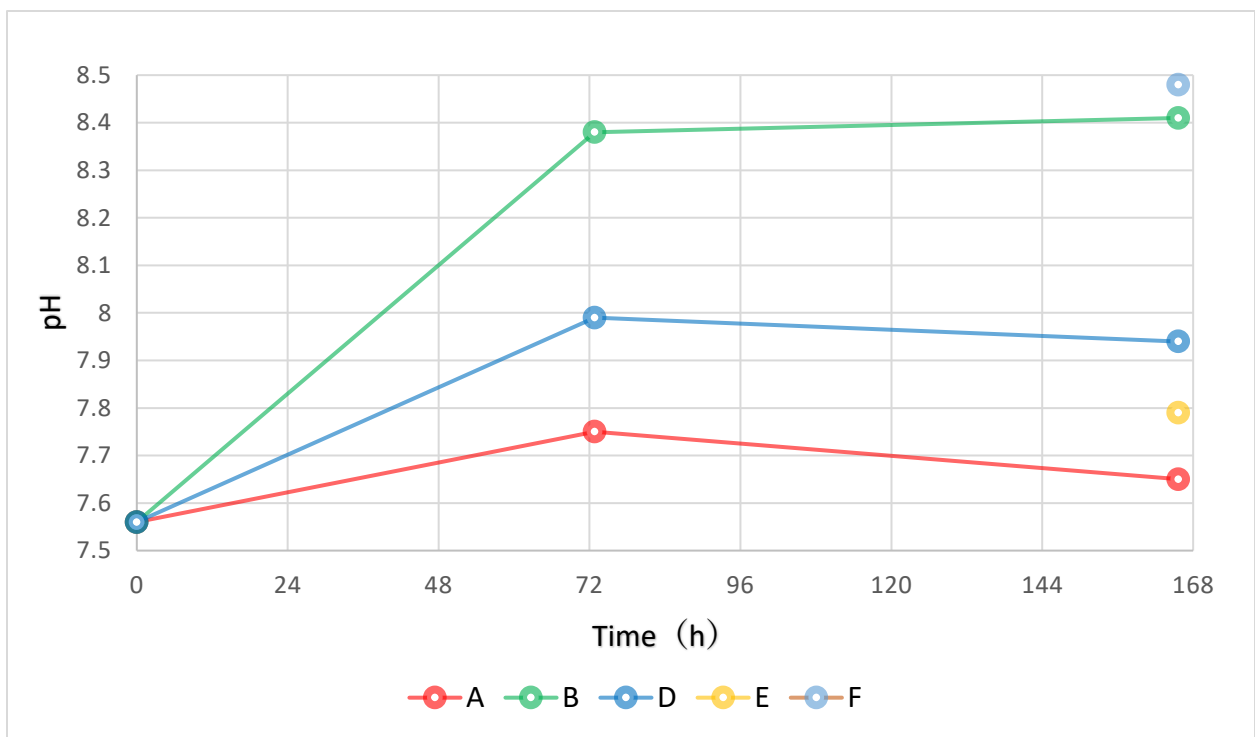Figure 5.5.8 Vertical distributions of pH in pore water (core 2)

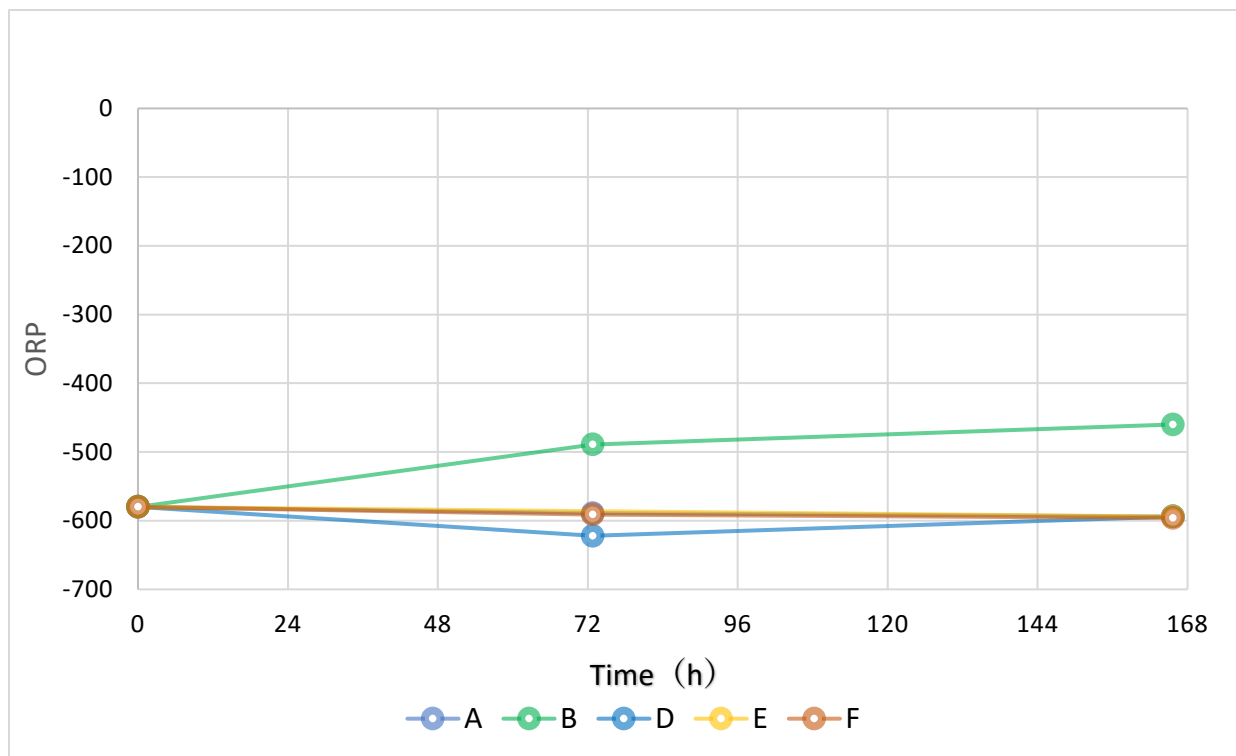Figure 5.5.7 Vertical distributions of pH in pore water (core 3)

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Figure 5.5.10 Vertical distributions of ORP in pore water (core 1)
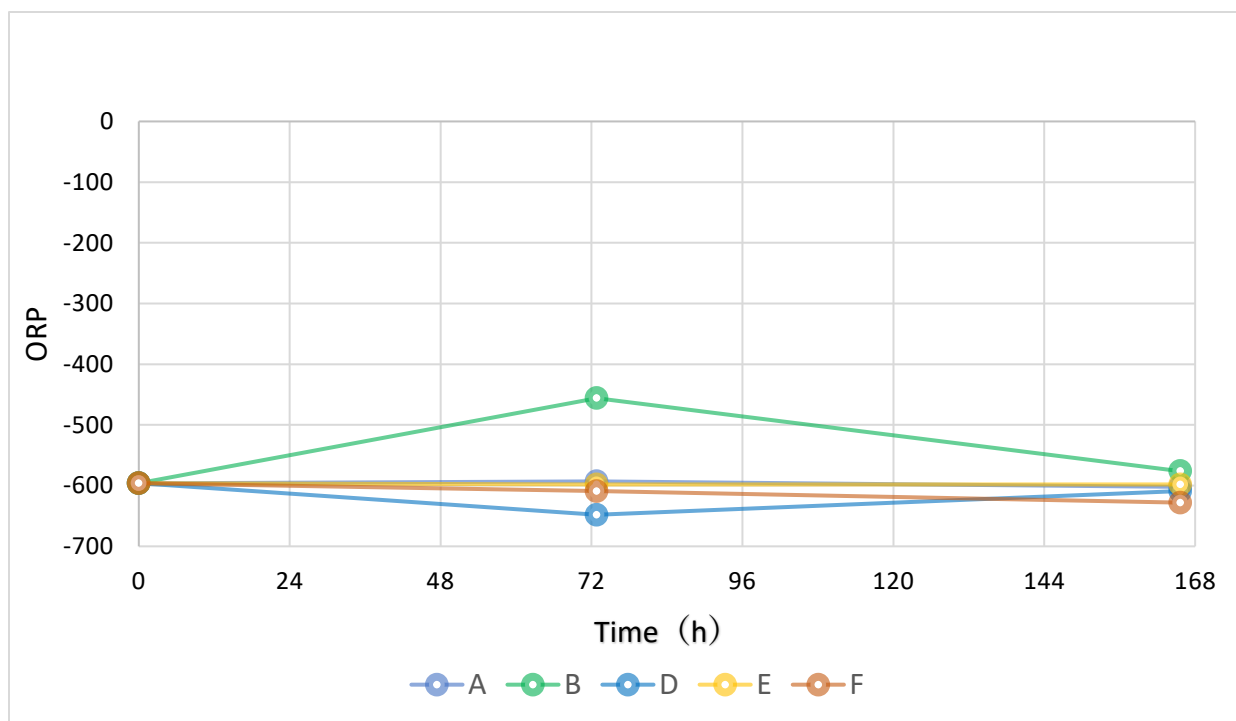
Figure 5.5.9Vertical distributions of ORP in pore water (core 2)
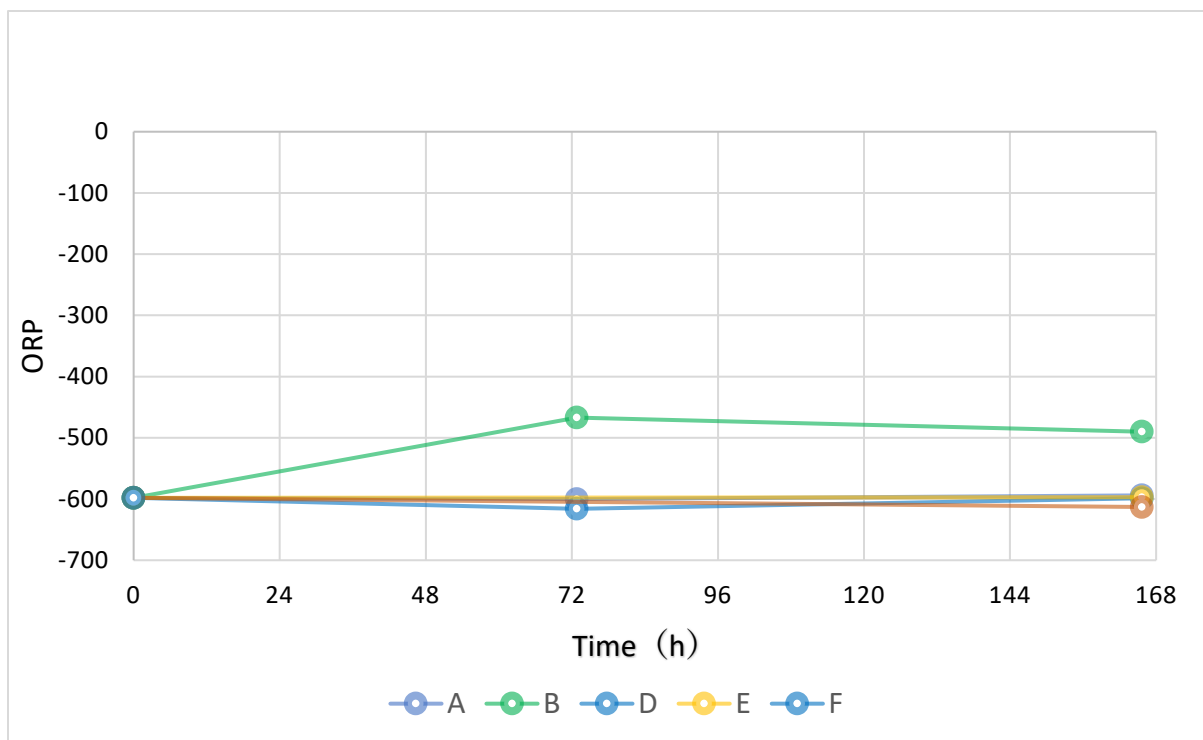
Figure 5.5.11 Vertical distributions of ORP in pore water (core 3)

5.5.3 Sub-discussion

In this experiment, the pH values showed only small differences between the two groups and samples did not show any trend in particular. There was no significant difference in pH value between groups, the general difference of the pH ranged from 7.6 to 8.4, but the figure ( ) shows, there is a negative relationship between hydrogen sulfide and pH. Kustermans, et al., (2014) reported that the acidification due to the anaerobic fermentation process can significantly increase the emission of hydrogen sulfide (g). However, the speciation of sulfide at a pH of 7 will be 50 percent hydrogen sulfide H_2S and 50 percent HS^-, but at a pH = 6 the distribution already quickly shifts to 90 percent dissolved hydrogen sulfide H_2S and 10 percent HS^-. In this respect, it is confirmed that the pH adjustment has no effect on the hydrogen sulfide reduction efficiency, but from the result of the analysis, can be confirmed that steelmaking slag can effectively remove hydrogen sulfide through oxidation as well as through its mineralization to FeS. There was also no significant difference between hydrogen sulfide and oxidation-reduction potential (ORP). On the other hand, figure ( ) shows, there is no relationship between hydrogen sulfide and oxidation-reduction potential (ORP).
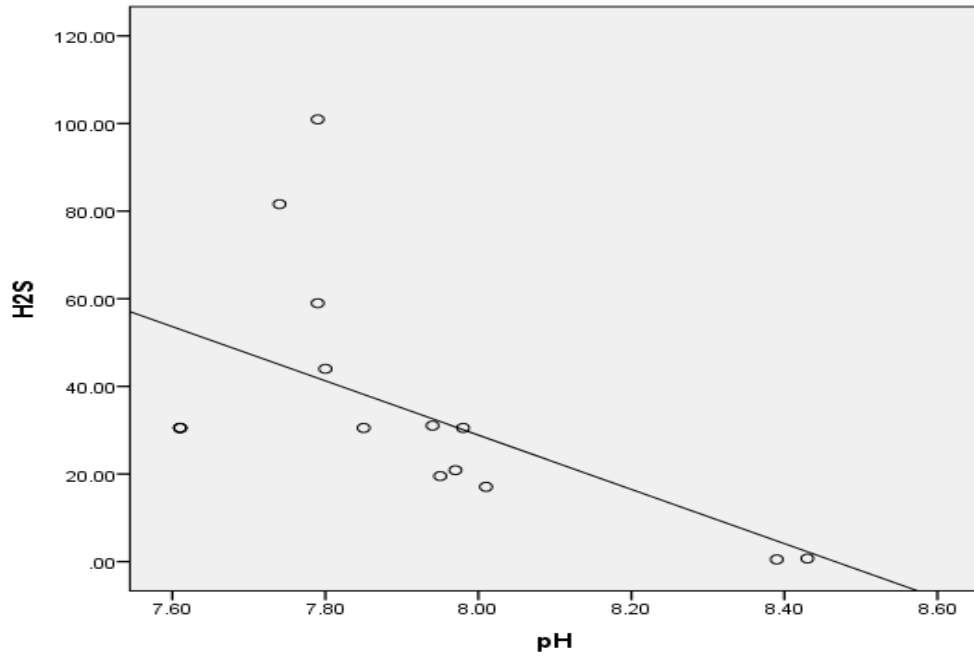
Figure 5.5.3.1 Relationships between pH value and hydrogen sulfide level in pore water
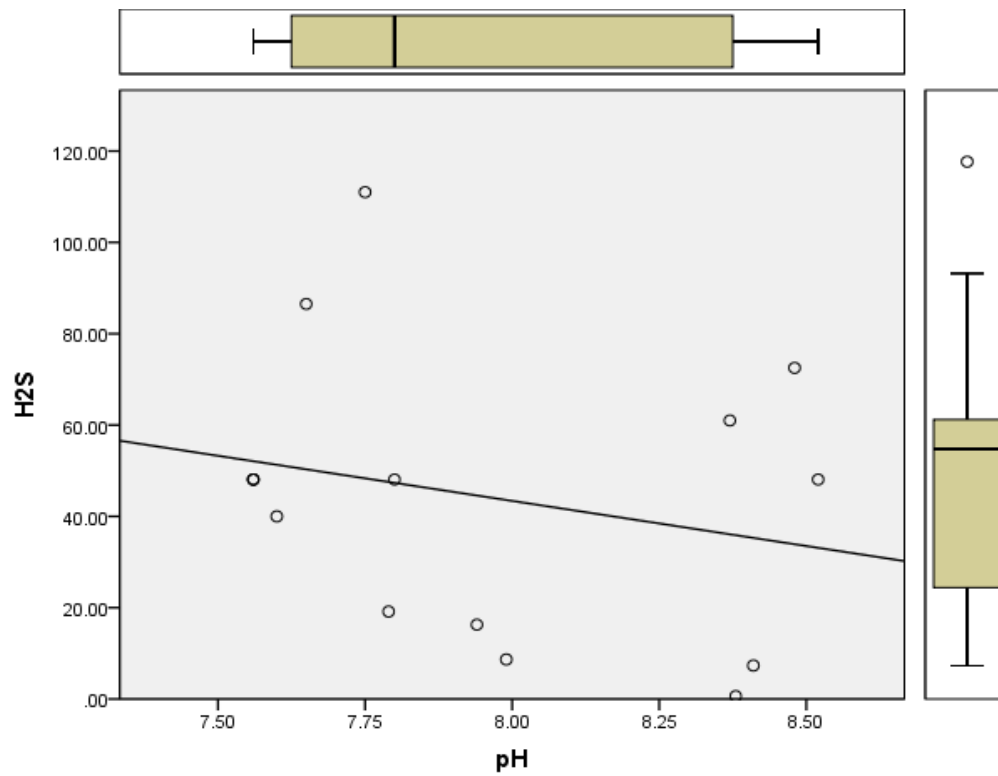
Figure 5.5.12 Relationships between hydrogen sulfide and ORP level in pore water

6 Process analysis of circulation

As is shown in Figure 7.1, in the marine sediments, under some conditions, such as biochemical and physical disturbance, the accumulation of large amounts of organic matter on the surface layer of the sediments stimulate the microbial activity in sediments and induce the available dissolved oxygen at the interface of sediments and overlying water is rapidly exhausted. Under such anoxic conditions, dissimilatory sulfate reduction occurs, and hydrogen sulfide is produced as an end-product. Much of the hydrogen sulfide produced in the sediments will react with Fe and other metals to form sulfide minerals, which, these irons and hydrogen sulfide then both are immobilized in the sediment. but due to insufficient iron minerals, some hydrogen sulfide can also escape to the water column by diffusion from the sediments. Thus, in order to determine the amount of hydrogen sulfide produced or released rate, we conducted field survey data analysis of Isa bay. Accordingly, we have decided to conduct a laboratory experiment based on the field survey results. This section focuses on developing on the results of our research work that will help make vision and mission a reality.
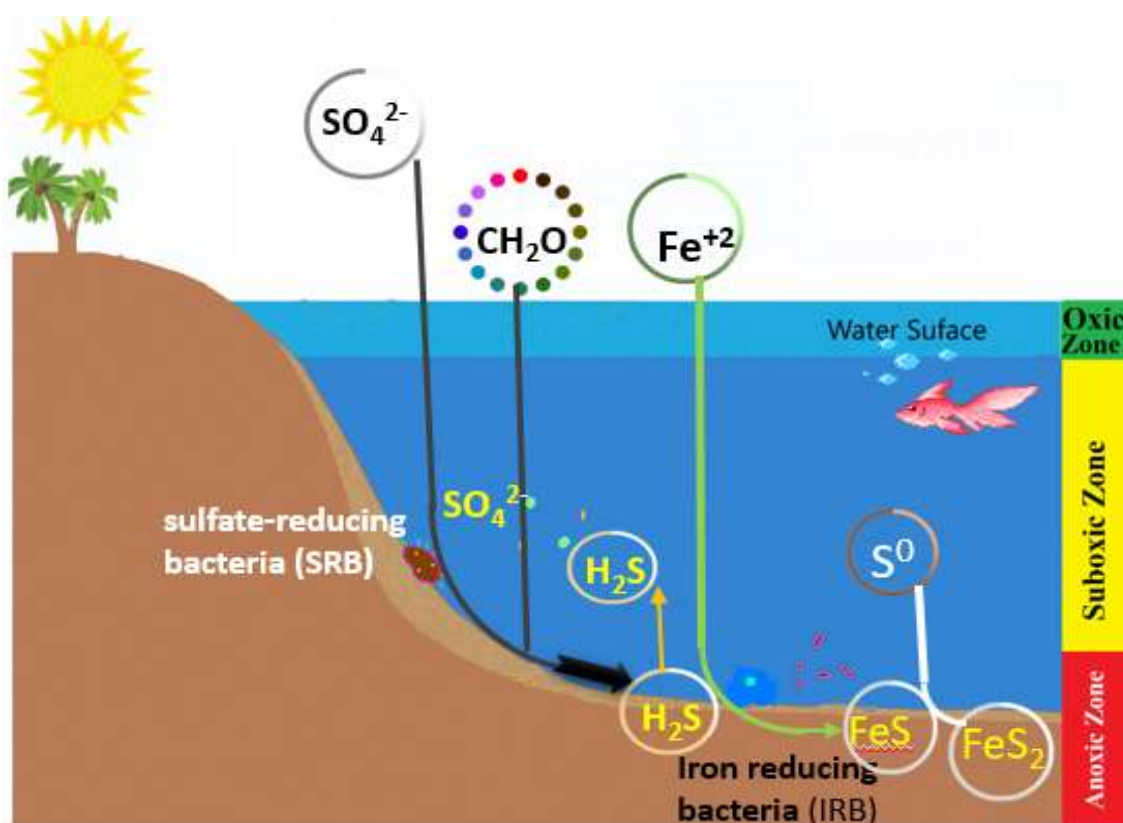
Figure 5.5.1. Drive iron and sulfur cycling in the sediment.

6.1 Comparative analysis of hydrogen sulfide release rate

To see how our lab experiment fits together with the field survey result the comparison of methods experiment is critical for assessing the systematic errors that could occur. Accordingly, our available data will answer the research question, and these approaches will provide information for practical acceptance.

6.1.1 The fundamental solution of the diffusion

6.1.1.1 *Method*

There are multiple methods that can be used to solve, but we will follow the methodology of Fossing *et al*., (2004), estimated as per equation (1), we demonstrated here one of its solutions for the one-dimensional case.

$$F_D = -\varphi D_s \frac{\partial C}{\partial x} \qquad (1)$$

Where F_D is the average flux of particles of the substance and (φ) is the porosity, (Ds) is the diffusion coefficient, and ($\partial C/\partial x$) the concentration gradient. As this is a one-dimensional ($\partial C / \partial x$ t = 0),

For diffusion in pore water between the layers, which considers the inhibition by soil particles in the mud, used as a diffusion coefficient D due to the physical properties of any substance in the water. The formula is shown below, the release rate, D-Fe and D-sulfide, is a diffusion flux at the sediment-water interface so that it can be estimated from the vertical concentration gradient as,

$$D_s = \frac{D}{1+3(1-\varphi)} \qquad (2)$$

so, D is the diffusivity of the material in pure seawater. Transport of solutes and transport of solids by bioturbation are diffusive processes, suggested that bioturbation affects solutes more strongly than solids, and temperature-dependent and value D, Kasih, et al., (2008)
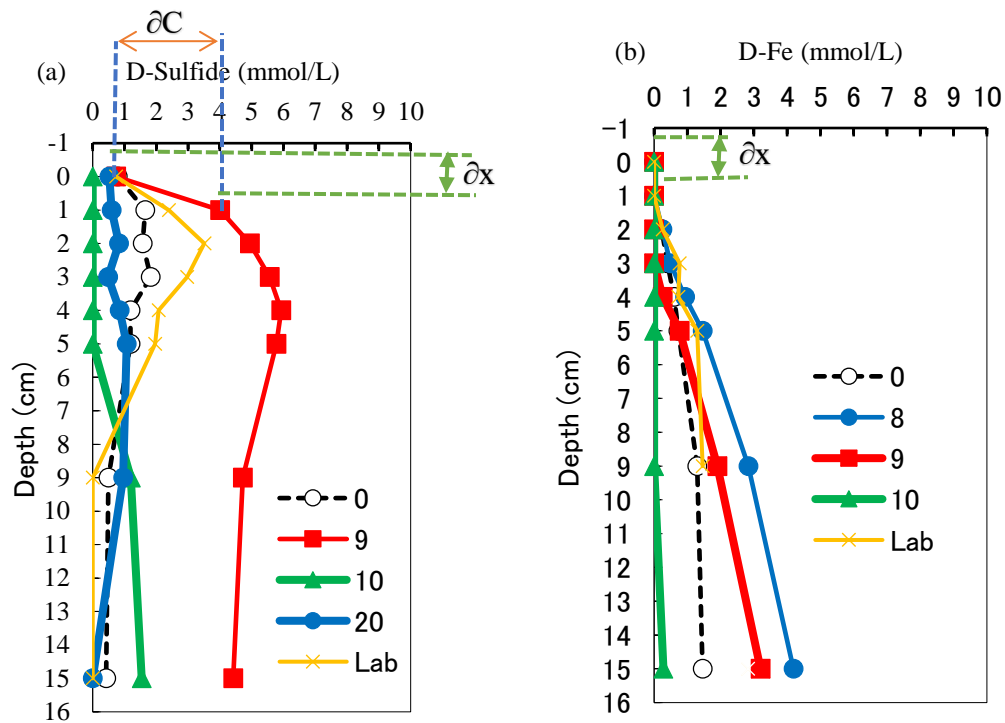
Figure 6.1.1. Vertical distribution analysis of H₂S and Fe release rate from lab experiment and field data of Mikawa Bay.

A seasonal variation in the concentrations of certain solutes indicates a proportion of the charge moves quickly to the surface of the overlying water, and that seasonal variations in metabolic activity are not controlled by temperature. Accurate evaluation of the potential of sediment D-sulfide and D-Fe release rate and its impact on overlying water is an important basis for the development of water quality, especially considering the specific seasonal variation.

In order to make clearer the difference between lab experiment and field survey based on seasonal variations, we followed the same methodology as described above. A comparison between field survey and laboratory experiments result shown Figures (6.1.1.2 and6.1.1.3). It is clear seasonal variations were found in diffusive fluxes of hydrogen sulfide and Fe across the sediment. Analysis of field data of the sediment in the dead zone of Mikawa Bay revealed an important role of Fe in suppression of hydrogen sulfide release from sediment to the overlying water. In summer season, dissolved Fe is depleted in the surface sediment so that hydrogen sulfide can release to the overlying water, while in other seasons Fe is abundant enough to suppress the hydrogen sulfide

release. Thus, the diffusive transport of dissolved Fe from sediment into the water below seemed to be the main driver in the elution of the hydrogen sulfide concentration from the benthic environment. Experimental results also showed quantitatively similar seasonal variations.

Figure 6.1.1.2. Seasonal variation of D-sulfide release rate.

Figure 6.1.1.3. Seasonal variation of D-Fe release rate.

6.2 Stoichiometry in the benthic boundary layer

Stoichiometry is the chemical part that involves using the relationship between reactants or products in the desired chemical reactions to determine the quantitative data.
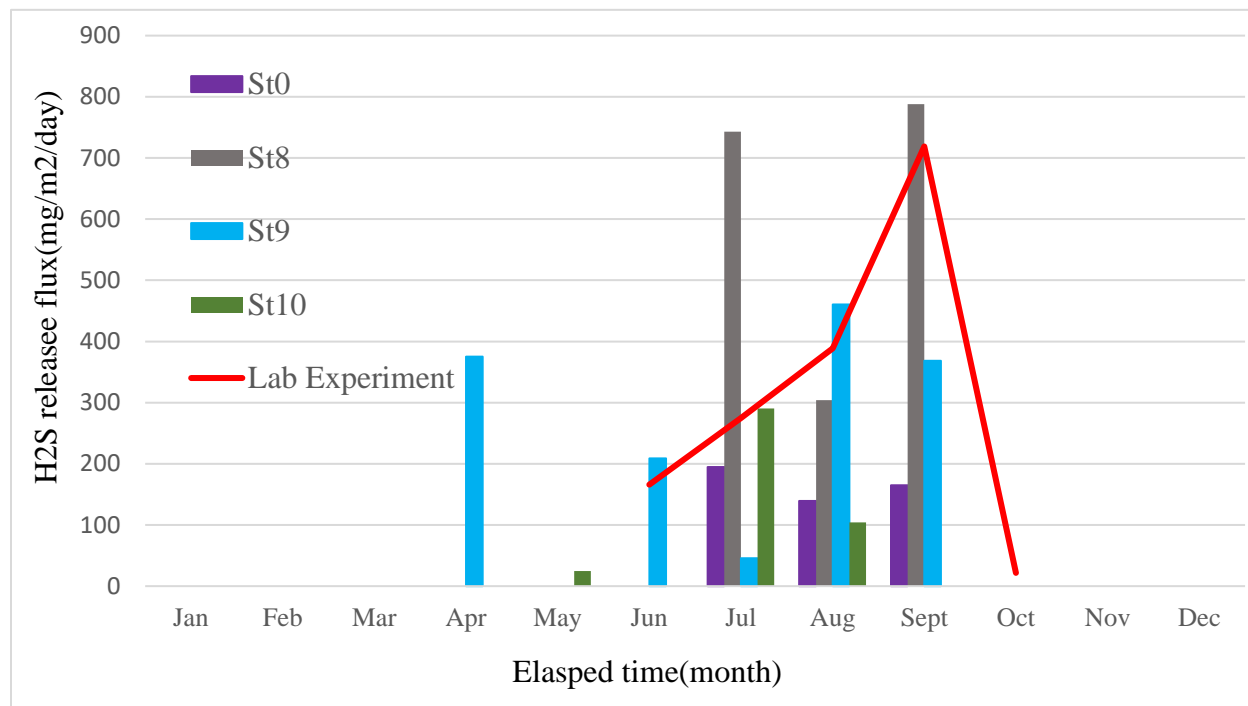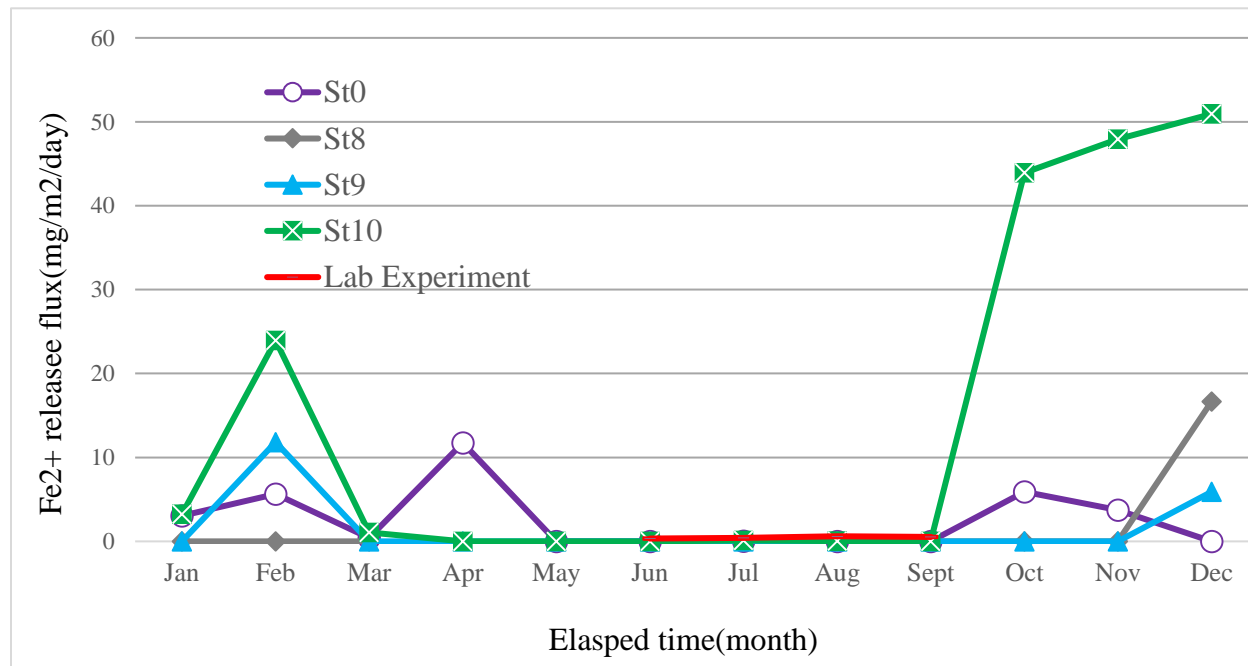
The molarity is a useful concept for stoichiometric calculations involving reactions in solution, such as precipitation and neutralization reactions. Stoichiometry indicates the changes which will occur, and their extent rate describes how the changes will occur. process stoichiometry can control technical scale processes, sulfate reduction can be represented by a pair of stoichiometric equations that describe the oxidation of an organic carbon source and the synthesis of bacterial cells. the approximate overall stoichiometric equation for sulfate reduction is two moles of carbon C is equivalent to one mole of hydrogen sulfide H_2S, accordingly, the formula is as follows:

$$2CH_2O + H_2SO_4 \rightarrow 2CO_2 + H_2S + 2H_2O$$
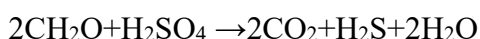
Stoichiometry of sulfate reduction was determined from the experimental data obtained from the control group elucidated the total amount of production and release rate of hydrogen sulfide in the sediment and overlying water, as shown in Figure (6.2.1).

Based on the results, hydrogen sulfide was generated at 227 mg/m^2/d, when H_2SO_4 concentration was approximately 652.9mg/m^2/d by reaction approximately stoichiometric 399mg/m2/d of CH_2O. However, the rate of sulfide diffusion to the overlying water was higher than that of sulfide production rate in the sediment. However, the rate of sulfide diffusion to the overlying water was higher than that of sulfide production in the sediment, which was approximately 719 mg/m2/d. The reason for the higher released rate of hydrogen sulfide to the overlying water may be due to the presence of disulfide residues in sediments, from past seasons, and the temperature will increase the diffusion of sulfide pool of the sediment.

Based on the amount of sulfide produced stoichiometric allows estimation of the rate and extent of product formation by measuring the change in the concentration of sulfide with time, which will follow by treatment with the iron groups.
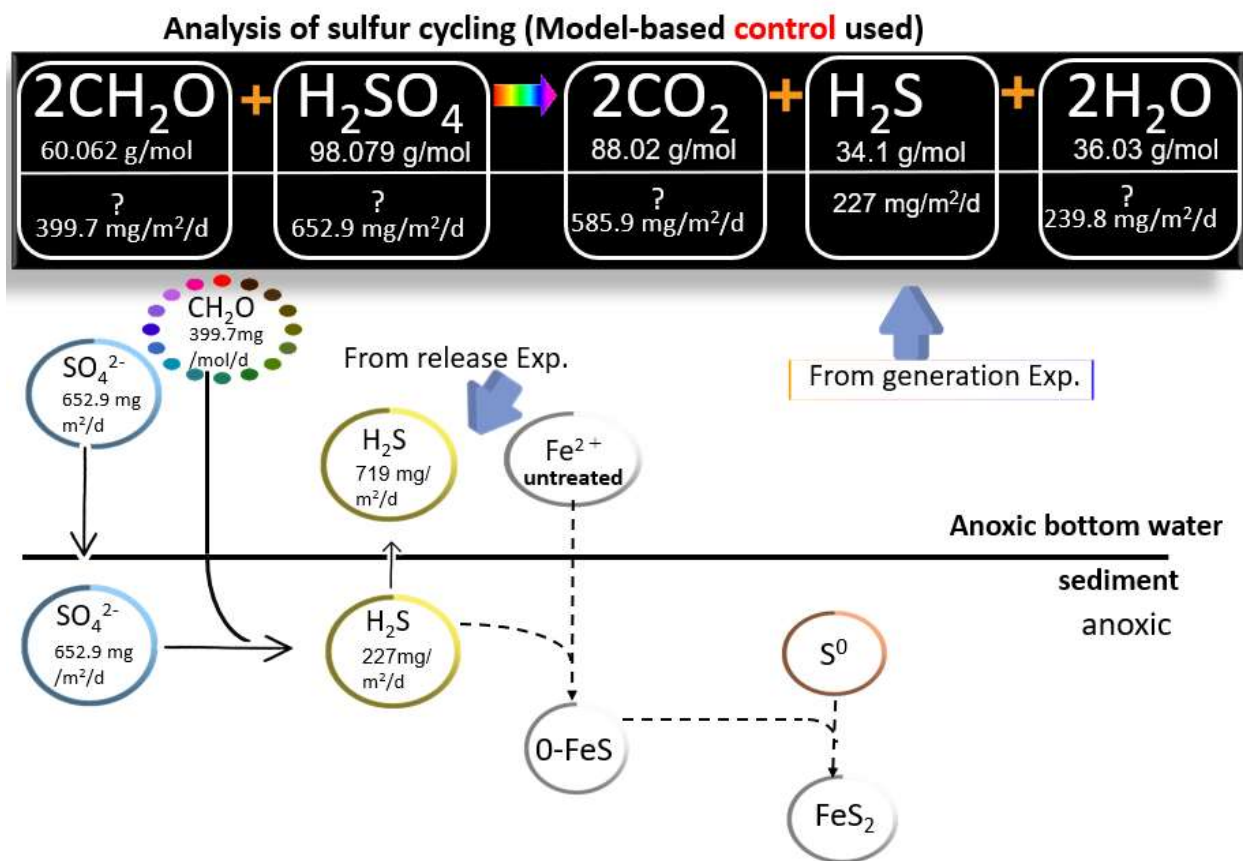
Figure 6.2.2. Schematic representing cumulative fluxes of hydrogen sulfide into the overlying water and sulfide production in the sediment..

As described in the first section, since the iron ions can eventually remove the sulfide ion (H_2S /HS^-) Considering the precipitation reaction that occurs between Fe and H_2S. When these two solutions are combined, the iron sulfides precipitate out of solution, and the approximate overall stoichiometric equation for iron sulfide precipitation is one mole of Fe is equivalent to one mole of hydrogen sulfide H_2S, accordingly, the formula is as follows:

$$H_2S + Fe^{2+} \rightarrow FeS \downarrow + 2H^+ \ldots\ldots\ldots\ldots.(1)$$

OR

$$Fe^{2+} + HS^- \rightarrow FeS \downarrow H^+ \ldots\ldots\ldots\ldots\ldots.(2)$$
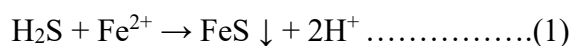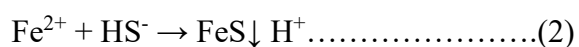
Using this stoichiometry and assuming the hydrogen sulfide pool represents that iron reacts with any hydrogen sulfide produced by sulfate reduction, thereby removing this sulfide from sediment

pore waters and precipitate black iron sulfide.

Based on the results of the experiment conducted in 2017, as shown in Figures (6.2.2) both iron treatment groups showed strong improvements on the elution of hydrogen sulfide from sediment. Compared with the control group, the rates of release of hydrogen sulfide into overlying water were significantly decreased in the iron hydroxide and iron oxide groups, data revealed that the concentration of dissolved sulfide ranged between (126 mg/m^2/d and 401 mg/m^2/d respectively). By using the above equation, estimation of the maximum (potential) iron sulfide production rate by iron hydroxide and iron oxide groups are possible at rages of (1558 mg and 830 mg respectively).

Figure 6.2.2. Schematic diagram representing the reduction in cumulative fluxes of hydrogen sulfide into the overlying water or reduce the production of hydrogen sulfide in the sediment.

Based on the results of the experiment conducted in 2018, the results revealed that both uses (2mm or less and 2 to 5mm) of the steelmaking slag applications suppressed the diffusion of hydrogen sulfide in the overlying water. In both groups steelmaking slag (2mm or less and 2 to 5mm) the suppression rates at (21.7 mg/m^2/d and 4.2 mg/m^2/d respectively).   Similarly, both steelmaking slag (2mm or less and 2 to 5mm) treatments reduced hydrogen sulfide production in the sediment ranged between (1.7 mg/m^2/d and 5.6 mg/m^2/d respectively). Using the balanced chemical equation, estimation of the maximum (potential) iron sulfide production rate by steelmaking slag (2mm or less and 2 to 5mm) treatment groups are possible at rages at (854 mg and 798 mg respectively).
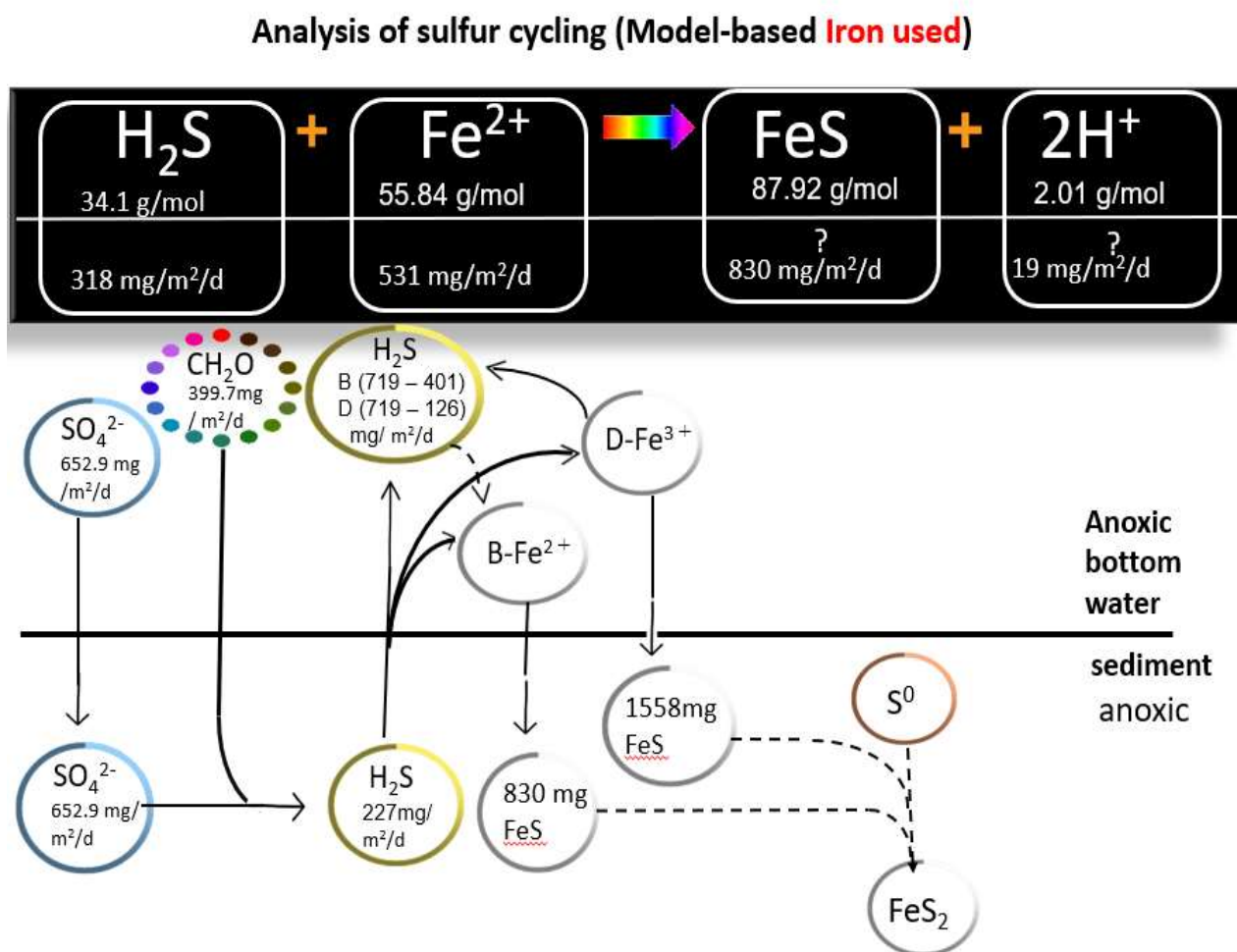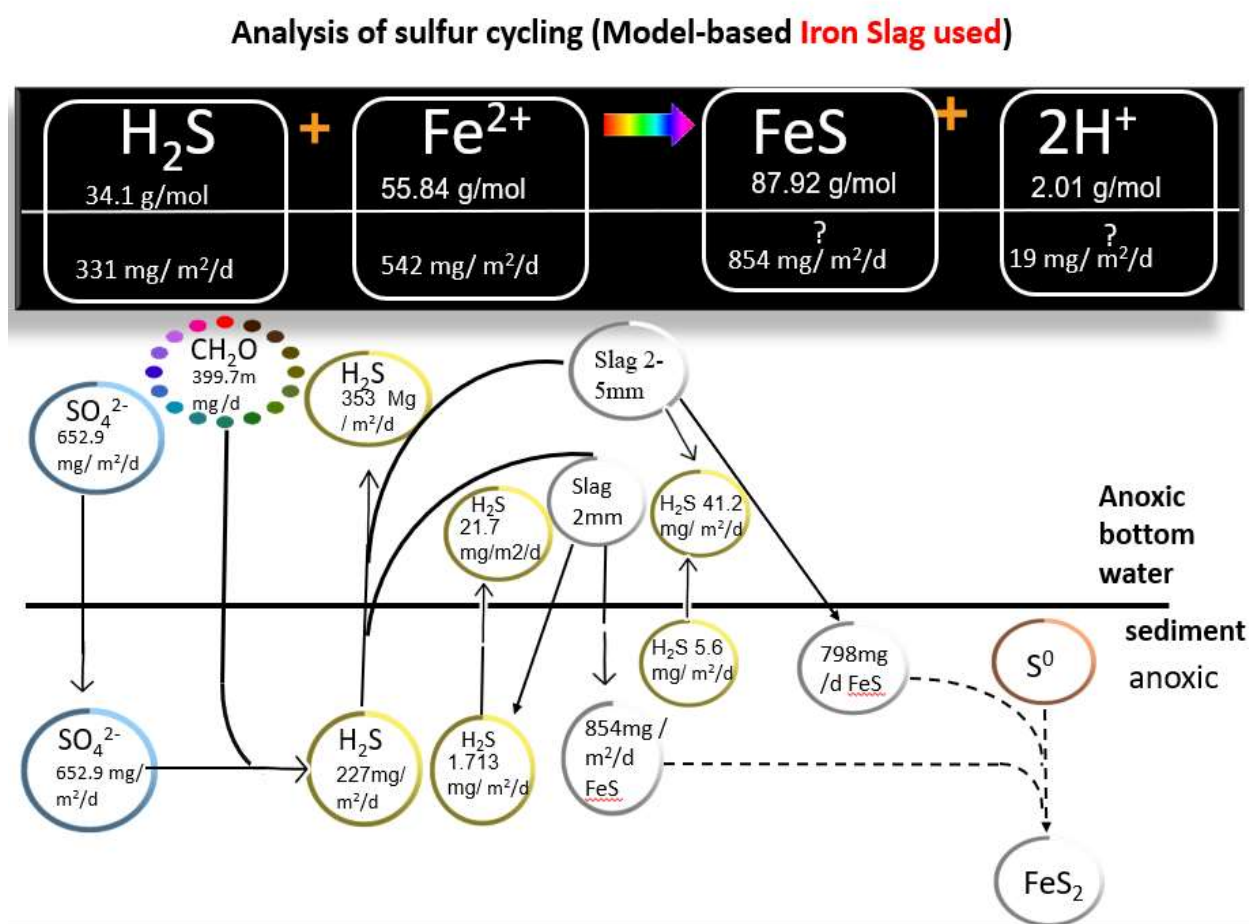

Figure 6.2.3. Schematic diagram representing the reduction in cumulative fluxes of hydrogen sulfide into the overlying water or reduce the production of hydrogen sulfide in the sediment.

6.3 General discussion

Based on the sediment survey result " provided by the Port and Airport Research Institute (PARI), which was investigated at 20 locations in Ise Bay and 8 locations in Mikawa Bay, there were apparent seasonal and spatial differences in the distribution of AVS, H_2S and D-Fe in Isa Bay and Mikawa Bay. Generally, the acid volatile sulfide (AVS) content was higher at stations (1st, 4th, 14th,18th, and 27th), and the next high concentrations with the same parameter was observed at stations (7th, 9th, and 16th). Further, water content %, total organic carbon (TOC), total nitrogen (TN), the total phosphorus (TP), and biochemical oxygen demand (BOD) content was high at (1st, 4th, 14th,18th, and 27th), as shown in Figures (3.1.4.2, 3.2.3 2 and 3.1.4.7) below. This is because, three major rivers, Kiso, Nagara, and Ebi, streams flow through the Inner part of Ise Bay, which contributes more than 80% of the total river discharge eight, during the spring and summer season, water is intensely stratified by heating and large run-off. The nearest stations to rivers are (1st, and 4th), therefore, AVS concentrations were quite high compared to other stations.

Based on the seasonal distribution trends of the of hydrogen sulfide H_2S and D-Fe. Concentrations of hydrogen sulfide H_2S were generally higher during summer season. This is because, the excess precipitation over evaporation as well as the rivers runoff freshens up the upper water layers of the Mikawa Bay. Apart from that, river discharge is expected to add nutrients to the upper layer and increase the biological productivity of Mikawa Bay, this causes oxygen depletion, creating a reducing environment in which sulfate-reducing bacteria generate hydrogen sulfide. Moreover, In the summertime, relatively weak wind cannot solve the stratification on the strong ocean through wind-driven mixing.

Finally, we concluded that the respective importance of these sources is subject to seasonal variation and seasonal variations in productivity are correlated with light and temperature, besides, the biological dominance of sulfur cycling in the Mikawa bay resulted in strong seasonal variations in dissolved sulfide flux. Runs of the model over one year displayed strong seasonal variations in particulate sulfide concentration and flux which agree with experimental data, the model can describe the seasonal variation of sulfide fluxes including the sediment-water exchanges and the vertical profiles in the pore water. Seasonal variation in sulfur and organic matter loads had significant effects on the effectiveness of the wetlands as sinks for total sulfide. The analysis of results obtained from laboratory experiments and model also showed quantitatively similar

seasonal variations.

Simulations and laboratory experiments revealed, our conducted two elution experiments using an undisturbed bottom mud core with various iron compounds added in the laboratory experiments, showed the effectiveness of iron materials for the removal of hydrogen sulfide and precipitation of iron sulfide.

Based on the 2017 experiment, iron oxide and, iron hydroxide was added to treatment groups, an equal amount (5.6 g) of iron hydroxide powder were followed by (D-1, D-2, D-3), with 5.0g of iron oxide were followed by (B1, B2, and B3). The use of iron hydroxide and iron oxide have been found to be a promising renewable solution to hydrogen sulfide control in aqueous and sediment systems. But that ferric hydroxide has a better ability to remove hydrogen sulfide. It may be because, the ferric hydroxide more attractive than iron oxide because, the presence of other ions with strong affinities for iron ferric hydroxide is known to modify the reactivity of iron-(hydro)oxide and their transformation pathways and therefore, exerts a significant influence on the properties of iron (hydro)oxides, which may modify their capacity to sequester and retain anions. The uptake of ions by ferric hydroxide proceed by two main pathways, adsorption, and coprecipitation. which, adsorption is defined as the accumulation of solutes (adsorbate) at the interface between a solid (adsorbent) and solution, and co-precipitation with ferric hydroxide occurs when an anionic species is present in the same solution as the carrier element.

In an experiment conducted in 2018, the untreated control group (A) was used in the experiment as a point of comparison to measure the effect of steelmaking slag (2mm or less and 2 to 5mm) treatment group (B and D) on hydrogen sulfide removal under anaerobic conditions. The results revealed that both uses (2mm or less and 2 to 5mm) of the steelmaking slag significantly suppressed dissolved sulfide into the overlying water and sediment systems. But that steelmaking slag (2mm) has a better ability to remove hydrogen sulfide. As the steel slag particle size decreased from 2–5 mm to less than 2 mm, the hydrogen sulfide removal efficiency increased notably. this may be because, the relative surface area per unit weight of the steelmaking slag was small because the slag used here had been cut to a fine size ($\cong 2$ mm), thereby, it is easily dispersed on the surface of the sediment and it can remove hydrogen sulfide from sediment effectively and make it easier to react with the small size of the slang. The surface sites are determined by specific surface areas

of the small particle found that the reaction rate of dissolved sulfide removal increased with increasing specific surface areas of steelmaking slag. Furthermore, the recovery in sulfide removal capacity could be attributed to the formation of amorphous or less ordered Fe on the steelmaking slag surface and the reduction in slag particle size, reported by Yin, (2016).

7 Conclusions

In the present study, we conducted two experiments aimed to evaluate the remediation efficiency of iron application to organically enrich and improve sediments environment. Experiments are conducted both in the laboratory with the same boundary conditions.

In Experiment 1 we experimentally investigated the removal of hydrogen sulfide using iron oxide and, iron hydroxide, and clarified the mechanism of hydrogen sulfide removal with the iron oxide and, iron hydroxide.

In Experiment 2 we experimentally investigated the removal of hydrogen sulfide using (2mm or less and 2 to 5mm) of the steelmaking slag and clarified the mechanism of hydrogen sulfide removal with the steelmaking slags.

Analysis of field data of the sediment in the dead zone of Mikawa Bay revealed an important role of Fe in suppression of H_2S release from sediment to the overlying water. In summer season, dissolved Fe is depleted in the surface sediment so that H2S can release to the overlying water, while in other seasons Fe is abundant enough to suppress the hydrogen sulfide H_2S release. Experimental results also showed quantitatively similar seasonal variations. These results suggest the strong possibility of sediment remediation by artificial addition of Fe containing materials to the surface sediment, especially in summer.

Our first experiment revealed that both uses of the iron and iron-hydroxide significantly reduced sulfide release flux from the sediment into the overlying water. After the 21 days incubation, the average dissolved sulfides concentration in the overlying water of treatment group was significantly decrease ($p = .0001$). No significant difference was observed between the control group after 21day incubation. Therefore, the application of iron to the sediment is a promising method to remediate contaminated sediments in eutrophic water body, although ferric hydroxide has better hydrogen sulfide removal effects. Similarly, D. E. Canfield, et al., (1992) reported that ferric hydroxide is the preferred iron mineral for sulfide removal, due to its reactivity relative to other iron (hydr)oxides, ease of preparation, and apparent stability when precipitated onto a substrate such as zeolite, and the reaction of hydrogen sulfide with iron hydroxide has the

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advantage of different color changes due to the formation of black FeS, which can be used as a warning signal for the condition of sulfides.

Our second laboratory experiment clarified the fact that steelmaking slag is effective in reducing the content of sulfides in artificial sediment. This could have been due to the reactions between iron ions eluted from the steelmaking slag and dissolved sulfide in the sediment. These results indicated that capping with (2mm or less and 2 to 5mm) of slag steelmaking is an effective technique for remediation of bottom sediments enriched organic containing hydrogen sulfide because it leads to the induction of chemical reaction between Fe and sulfides occur in sediments which did not occur in conditions naturally. Although (2mm or less) of slag steelmaking has better hydrogen sulfide removal effects.

Due to economic reasons described below, the application of steelmaking slag to the sediment is a promising method to remediate contaminated sediments in eutrophic water body.

Japan produces about 40 million tons of iron and steelmaking slag every year and has reached the level of reuse of slag near 100%. Although 60% of this is used in roadbed material and civil construction, the technology that allows the use of high added value while taking advantage of the physical properties and chemical composition of the slag has not been adequately defined (Miyata et al., 2016).

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