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DYNAMICS OF BIOGEOCHEMISRTY OF SULFUR IN LAKE MANINJAU

Cynthia Henny[*]

ABSTRACT

A natural phenomenon called as tubo belerang *had occurred repeatedly in Lake Maninjau where the sulfidic odorous water was apparent causing massive fish kill. Sulfur biogeochemistry in sulfur rich lakes can be critical when inputs of organic matter are high as in Lake Maninjau which has been exploited by floating cage fishery. The objective of the research is to study the biogeochemistry of sulfur in Lake Maninjau and to determine what factors might initiate the natural phenomenon occurence. The oxycline layer had shifted from the depth of 20-40 m in 2006 to the depth of 10-20 m in 2008. The dynamics of biogeochemistry of sulfur in Lake Maninjau could be perceived from sulfide profiles where increasing sulfide concentrations detected annualy. Higher sulfide concentrations produced indicating more sulfate was reduced in the hypolimnion layer. Sulfide concentration reached at level of 5 mg/L in the pore water of sediment. The toxic hydrogen sulfide concentrations were 10 – 120 µg/L. Sulfate concentrations ranged from 4 to 16 mg/L. Based on the pH values, the sulfur species H_2S and HS^- were present in the lake water. Most of sulfur in Lake Maninjau were deposited in the sediment as iron sulfide solids. The accumulation of organic matter in the hypolimnion in the deepest part of the lake and shifted oxycline layer in four year observation periods indicated that the effect of floating cage fishery on the lake conditions was apparently atrocious. Increased in concentration of organic matter could play an important role on the dynamic of biogeochemistry of sulfur in Lake Maninjau and could be one of the major causes that might trigger the* tubo belerang *occurence.*

Key words: Crater lake, biogeochemistry, sulfur, organic matter accumulation

ABSTRAK

DINAMIKA BIOGEOKIMIA SULFUR DI DANAU MANINJAU. *Fenomena alam yang disebut sebagai* tubo belerang *berulang kali terjadi di Danau Maninjau di mana air yg berbau sulfur menyebabkan kematian ikan secara massal. Biogeokimia sulfur di danau yang kaya sulfur menjadi sangat penting untuk dipelajari pada danau yang masukan bahan organiknya tinggi seperti di Danau Maninjau, dimana sudah terjadi eksploitasi budidaya ikan dengan keramba jaring apung. Tujuan dari penelitian ini adalah untuk mempelajari biogeokimia sulfur di Danau Maninjau dan untuk menentukan faktor-faktor yang memicu terjadinya fenomena* tubo belerang*. Lapisan oksiklin bergeser dari kedalaman 20-40 m pada tahun 2006 mencapai kedalaman 10-20 meter pada tahun 2008. Dinamika biogeokimia sulfur di Danau Maninjau dapat dilihat dari profil sulfida, dimana konsentrasi sulfida meningkat setiap tahunnya. Sulfida bahkan sudah terdeteksi di kolom air pada kedalaman 20 m. Tingginya kandungan sulfida yang dihasilkan mengindikasikan bahwa lebih banyak sulfat yang direduksi pada lapisan hipolimnion. Konsentrasi sulfida pada air pori sedimen mencapai 5 mg/L. Konsentrasi hidrogen sulfida yang toksik mencapai 10-120 µg / L. Konsentrasi sulfat di air berkisar 4 -16 mg / L. Berdasarkan pH, spesies sulfur yang dominan ditemukan di air danau yaitu H_2S dan HS^-. Sebagian besar dari sulfur di Danau Maninjau tersimpan di sedimen dalam bentuk padatan besi sulfida. Akumulasi bahan organik di hipolimnion di bagian danau yang terdalam dan bergesernya lapisan oksiklin dalam periode empat tahun pengamatan menunjukkan efek dari perikanan keramba jaring apung terhadap kondisi danau sangat buruk. Peningkatan konsentrasi bahan organik bisa memainkan peran penting dalam dinamika Biogeokimia sulfur di Danau Maninjau dan bisa menjadi salah satu penyebab utama yang dapat memicu terjadinya feonomena* tubo belerang.

Kata kunci: Danau kawah, biogeokimia, sulfur, akumulasi bahan organik

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[*] *Staf Peneliti Puslit Limnologi-LIPI*

INTRODUCTION

Lake Maninjau is a crater lake formed as a result of volcanic eruption thousand years ago. Geochemically, the lake is characterized by the geochemistry of past volcanic activity where the minerals are rich in sulfur. Rocks weathering of sulfide minerals which was originated from past volcanic activity; surface run off of sulfate from the catchment area, hydrogen sulfide from volcanic activity; soil sulfate and sulfate deposition from atmosphere may contribute to sulfur concentration in lakes. High sulfur compounds in lake may be stored in the sediment (Drever, 1997; Stumm and Morgan, 1996; Wetzel, 2001).

Lake Maninjau has been exploited by floating cage fishery for more than a decade. Previous studies reported that the exploitation of floating cage fishery with improper management and exceeding carrying capacity of the lake had deteriorated water quality of Lake Maninjau since the year 2001 (Sulastri et al, 2001; Meutia et al, 2002). A natural phenomenon called as *tubo belerang* had frequently been occurred in Lake Maninjau where the sulfidic odorous water was apprent causing massive fish kill. According to the local people, a massive *tubo belerang* occurence caused by strong wind blow was first reported fifty years ago when the lake had not yet been exploited by the floating cage fishery. The previous study predicted that the phenomenon might occur as a result of upwelling-downwelling processes due to the strong wind that caused the water turnover which then elevated the sulfide and other toxic gasses to the surface causing the water in the lake anoxic and odorous. However, there were several spatial and massive *tubo belerang* occurences had been repoted in the last ten years.

Sulfur cycle can be important in natural waters rich with sulfur coumpounds such as sulfate and organic sulfur compounds. Both inorganic and organic sulfur can be utilized by living organisms. Sulfur speciation in waters is influenced by the redox potential (pE) and pH. Predominant dissolved sulfur in water at pH 4 – 10 and pE>0 is SO_4^{2-} (oxidized form). During organic decomposition and sulfate reduction, sulfur is released as H_2S (reduced forms) at pE<0 (Wetzel, 2001; Stumm and Morgan, 1996). Elevated concentration of hydrogen sulfide of > 2 µg/L in water is very toxic to aquatic lifes (Weiner, 2000). Under oxic conditions hydrogen sulfide is oxidized rapidly. At oxic-anoxic “boundary” in deeper water column or sediment redox cycle of sulfur occurs in different oxidation stage where reduced forms of sulfur can be oxidized back to its oxidized forms. Therefore, sulfur cycle occurs very fast in the layer of redoxcline (Stumm and Morgan, 1996). Figure 1 presents sulfur cycle in lake.

Transformation of sulfur compounds by bacteria is strictly related to the carbon cycle. The process of reduction of sulfate to sulfide by sulfate reducing-bacteria (SRB) anaerobically is always coupled with the oxidation of organic compounds. This process is the major mineralization pathway in the anoxic hypolimnion of the lake. The rate of sulfate reduction depends upon the concentration of organic carbon, inorganic carbon or hydrogen as an electron donor and sulfate as an electron acceptor (Hines *et al.*, 2002; Barton dan Tomei, 1995; Widdle, 1988). Sulfide formed in the sedimen quickly diffuse into water column and is being oxidized back to elemental sulfur or sulfate. Sulfide can be oxidized by sulfur bacteria or oxygen. Sulfide oxidation by bacteria can occur aerobically and anaerobically. These bacteria are known as phototrophic sulfur bacteria. Light penentration in lake is crucial for these bacteria (Hines dkk, 2002; Barton dan Tomei, 1995; Widdle, 1988; Stumm and Morgan, 1996). Sulfide produced in water can react with iron (Fe) to form iron sulfide. Sulfide production not only causes the loss of iron in natural waters but also can release back phosphate in the water column that can lead to the lake eutrophication (Stumm and Morgan, 1996; Drever, 1997).

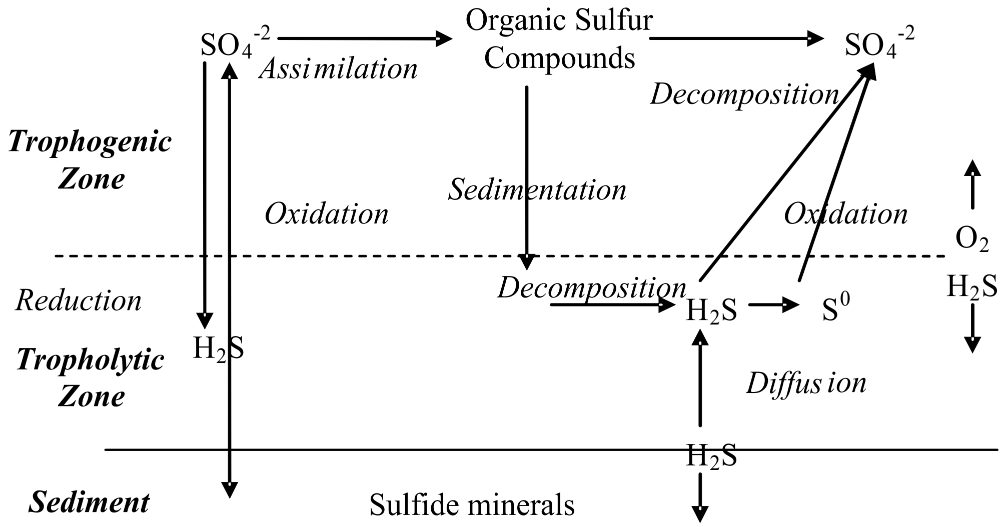


Figure 1. Sulfur Cycle in Lake (modification from Wetzel, 2001)

Sulfur biogeochemistry in sulfur rich lakes can be critical when inputs of organic matter are high. High organic matter can elevate sulfide production as a result of reduction of sulfate by sulfate reducing-bacteria in sediment water interface and hence affect water quality in lakes. The dynamics of biogeochemistry of sulfur related to high rate reduction of sulfate to sulfide in the anoxic hypolimnion as result of high organic input in Lake Maninjau could also cause the occurence of *tubo belerang* spatially in secluded area of the lakes with no flow water through especially in the rainy season when dissolved oxygen concentration in surface water was low. The diffusion of sulfide to the water surface would result in oxygen deficit in the lake water. Both sulfide and oxygen deficit cause the mass fish kill.

The objective of this research is to study biogeochemistry of sulfur and the interest process and to determine what factors might initiate the occurrence of *tubo belerang*. The knowledge of dynamic of biogeochemistry of sulfur in Lake Maninjau can help us to better understand the occurrence of *tubo belerang* in order to manage the lake properly by reducing the exploitation of the lake.

MATERIALS AND METHODS

Study Area. Lake Maninjau (surface area = 9737.5 Ha, maximum depth of 165m) is located at 461.50 m above sea level in the Western area of Sumatra (Fig. 2). The Lake Maninjau has several inlets of small streams and hotspring from the mountains. The only outlet from the lake is Antokan River where the outlet is divided into two: the narrow one directly flows from the lake and the big one which is deep water flow is controlled by the hydroelectric turbine.

Lake Maninjau is mostly surrounded by mountains. Agriculture activity in its catchment area may contribute to the phosphorous level in the lake water. The organic loadings to the lake mostly originated from the excess feeding of the floating cage fishery. There are more than 10,000 units of floating cage fishery reported in Lake Maninjau. The lake is considered as a mild eutrophic lake.

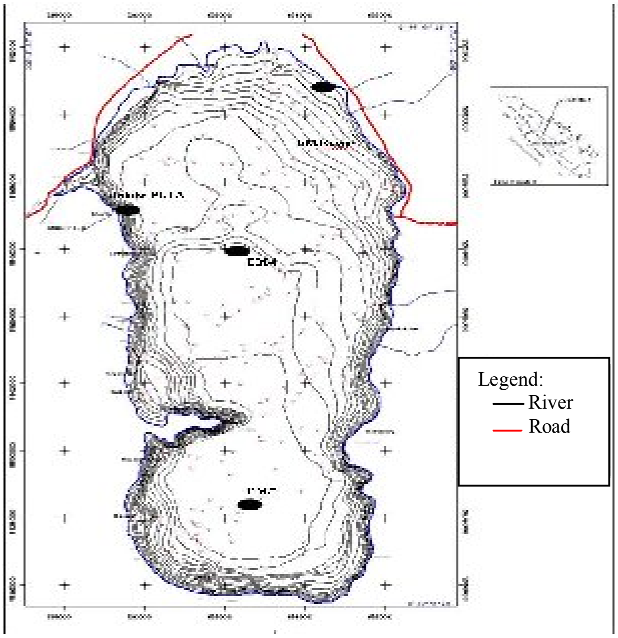


Figure 2. Map of Maninjau Lake. The Black Dots Mark the Sampling Station.

Sampling and Analytical Methods

Sampling was conducted at all selected stations (Fig. 2). Samples were collected from 2006 to 2009 in selected deep profiles especially for the deepest water area (DM7). The description of sampling stations is shown in Tabel 1. Water samples were collected using 2 L Van Dorn water sampler. Water samples were transferred to HDPE bottles. All samples were acidified except the samples for sulfide analyses. All samples were refrigerated and maintained at 4^{o}C until analyses. Water samples for sulfide analyses were drawn by a syringe via Tygon tubing to maintain the reduced condition and analized directly using HACH Method. Sediment samples were collected using Ekman Dredge.

Water temperature, conductivity, pH, DO (dissolved oxygen) and total sulfide concentrations were measured insitu. Temperature, conductivity, turbidity and pH were measured by using WQC U-10 (Horiba) and DO were measured by using YSI 6000 Data Logger. Total sulfide were measured by adding sulfide reagents to the water samples then measured by using HACH DR 2010. Sulfate and COD were measured by adding the reagents to the water samples then analized by using HACH

Tabel 1. Description and Location of Sampling Stations

Station	Location	Depth (m)	Description
DM7	S: 0^{o}22’33.0” E: 100^{o}11’35.1”	165	The deepest water
DM 4	S: 0^o 18’ 28.8” E: 100^o 11’ 35.0”	130	Central deep-water
Bayur	S: 0^{o}19’45.0” E: 100^{o}11’6.0”	30	Packed with floating cage fishery area
DM Intake	S: 0 ^{o} 17’ 30.4” E: 100 ^{o} 09’ 05.0”	15	Facing the outlet: the water uptake for hydroelectric turbine

DR 2010; TS/VS concentrations in the sediment were measured using gravimetric methods; total Fe concentrations in the sediment after digestion with acid were analyzed by using Atomic Absorption Spectrofotometer (AAS Hitachi Z-6100). All methods analysis followed the procedure of StandardMethods (APHA/WWA/WEF, 2005).

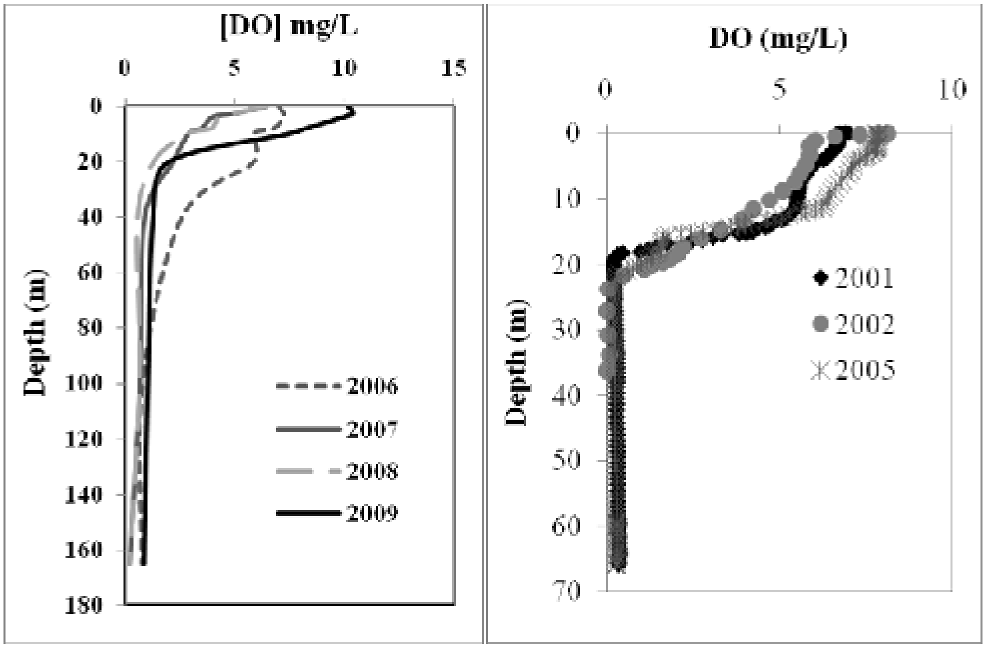
RESULTS AND DISCUSSION

The number of floating cage fishery increased every year since 2005 where the Lake was restored to improve the water qualityof the lake. There are more than 10,000 units of floating cages by the year of 2008 causing the deterioration of water quality of the lake. The long rainy season at early February 2009 had initiated the occurring of *tubo belerang* again in Lake Maninjau causing fish mass kiling. During sampling in August 2009 mass fish kill also took place again in several floating cages in secluded area which was not affected by the water current especially for the fish type which were very sensisitve to oxygen deificit in the water.

Physical and Chemical Characteristics

Dissolved Oxygen (DO), temperature and pH are the parameters that control sulfur species present in the aquatic environment. Deep profile of each parameter was observed in August or September for designated year in the deepest water station of Lake Maninjau (DM 7). DO profiles in Lake Maninjau were shown in Figures 3. The oxycline layer shifted to the upper water column from a depth of 20 - 40 m in 2006 to 10 – 20 m in 2008 and 2009.

The results indicated that the anoxic water column was increasing to up 20 m deep. The dissolved oxygen in the depth water of 20 m was less than 3 mg/L. The results of DO profile in 2008 also indicated that the conditions in Lake Maninjau worsened. The deteriorating conditions in the year 2008 had caused another *tubo belerang* occurrence in Lake Maninjau in early February 2009. The surface water DO reached at level of less than 1 mg/L at the time of the *tubo belerang* occurence. The incident had caused the fish mass kill as well. Previous studies reported similar patterns of oxyclines in Lake Maninjau in 2001 and 2002 (Figures 3) (Sulastri *et al.*,



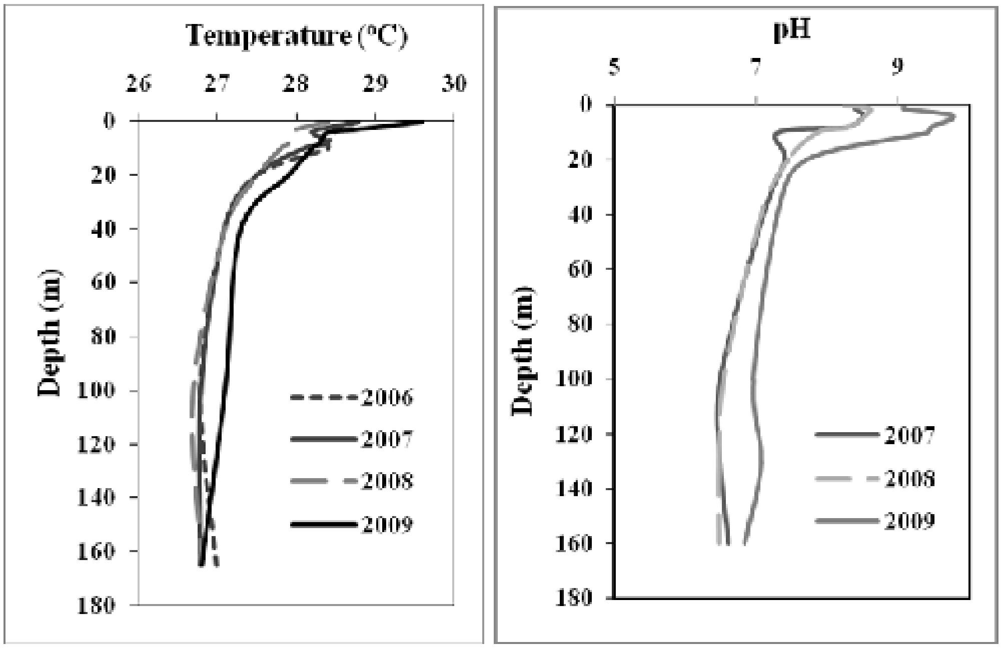
Figures 3. DO Profile of Lake Maninjau.

2001; Meutia *et al*., 2002). The deteriorating conditions in the year 2001 in Lake Maninjau had been caused by the explotation of cage fishery. The existing hydroelectric power had made the conditions worse in Lake Maninjau by closing the only water outlet gate. The water from Lake Maninjau flowed out only through the gate of the electric turbines, however, only the middle deep water was flowed out. The organic matter riched surface water was mostly trapped in the lake causing the blooming of toxic algae known as Microcystis (Sulastri *et al*., 2001). Many fish also were reported infected by the disease and the fish productions were fallen. The narrow water outlet gate to River Antokan was opened in 2003 to restore the lake water quality. The oxycline layer shifted to the deeper layer in 2005 and the water quality slightly improved (Triyanto, 2005). Based on the oxycline layer, recent conditions seemed showing the similar pattern of the conditions of the lake in 2001 and 2002. Although the narrow water outlet gate to River Antokan is opened, the water flow could not discharge most of excess organic matter causing the accumulation of organic matter in the sediment of Lake Maninjau which also affect the concentration of dissolved oxygen in the water column.

Temperature profiles of Lake Maninjau is shown in Figures 4. The thermocline layer was formed at a depth of 5 – 10 m. The thermocline shifted slightly in 2009. The temperature increased by one degree in 2009. The temperature could affect the concentration of sulfur species and the rate of microbial processes in the aquatic system (Stumm and Morgan, 1996; Hurst *et al*., 2000). The thermocline layer in 2006 – 2008 had similar patterns with thermocline layer in 2001 and 2002 reported by previous studies (Sulastri *et* a.l, 2001; Meutia *et al*., 2002). The thermocline shifted slightly to a deeper layer of 15 -20 m in 2005 (Triyanto, 2005). Lake Maninjau is a stratified tropical lake especially in the deepest part station. The temperature of the bottom water is constantly colder than the temperature of the surface water. Unlike the lakes in cold regions, most of deep lakes in equatorial regions rarely experience complete weter circulation as a result of the absence of temperature difference (Wetzel, 2001). Complete water circulation caused by the absence of temperature difference in Lake Maninjau could only happen in the shallow area of the lake or in the upper water layer starting from the layer of water at a depth of 30 m at night under extreme cold rainy season.

The pH profiles also shifted to a higher pH value above neutral in 2009 (Figures 4). The pH values in the bottom water were slightly below neutral value indicating more organic acids content in the water. The lower pH values in the bottom water were correlated with accumulated organic matter contents in the water where the fermentative bacteria will convert the complex organic compound to simple organic compound such as fatty acids or the organic acids. Besides high alkalinity content, actively photosynthetic process and microbial process of sulfide oxidation contributed to higher pH in the lake water. Increasing pH in 2009 in Lake Maninjau indicated that the lake was more eutrophic. Alkalinity concentrations in lake water ranged from18 to 55 mg as $CaCO_3$/L.

The range of surface water turbidity, conductivity, and Secchi depth of lake water column are shown in Table 2. There were no significant changes observed for turbidity, conductivity, and Secchi depth in 2006 and 2007. However, turbidity slightly increased in 2009 and the Secchi depth in Lake Maninjau decreased from 3 - 5 m depth in 2006 to a less than 2 m depth in 2008 and 2009. Light penetration or Secchi depth of Lake Maninjau in 2008 and 2009 was also reported similar to Secchi depth in 2002 which was around 2 m where the condition of Lake Maninjau was poor (Meutia, *et al*. 2002). The results indicating that the recent lake water contains more suspended solids thus light penetration is poor. Less sunlight penetration can lead to low activity of photosynthesis by algae that results in less dissolved oxygen production in lake water. During rainy season with high respiration at night, dissolved oxygen in the water could diminish rapidly in the water. The exploitation of floating cage fishery had been reported to cause increase in algal volume and the Secchi depth goes down in the Sweden Lake (Hǻkanson, 2005).



Figures 4. Temperature and pH Profiles of Lake Maninjau

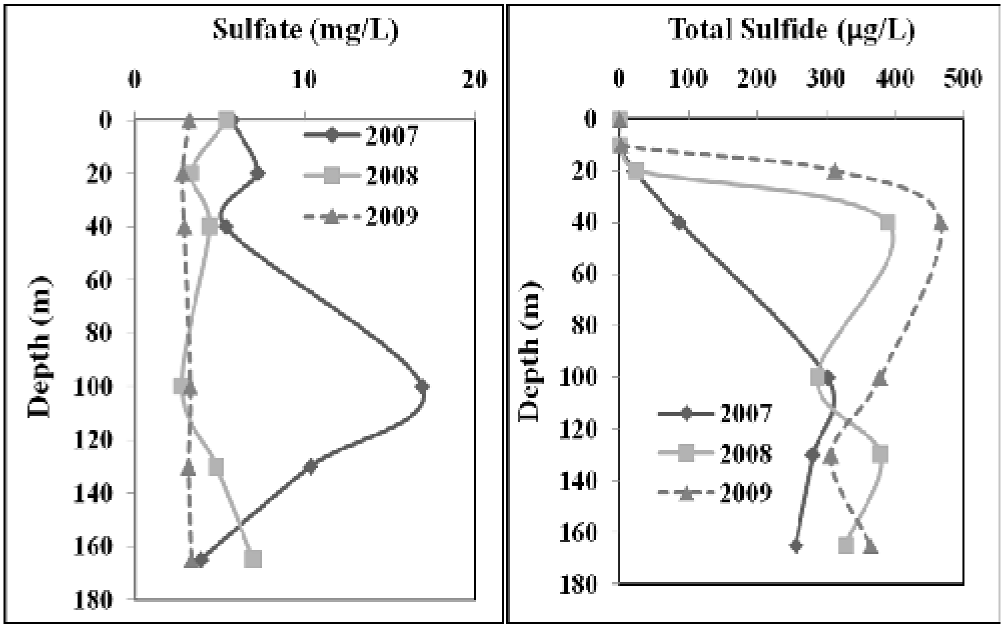
Table 2. Turbidity, Conductivity, pH and Secchi Depth of Lake Water

Parameter	2006	2007	2008	2009
Surface water Turbidity (NTU)	0-1	1-2	0-4	2-8
Conductivity (mS/cm)	0.10 – 0.15	0.10 – 0.15	0.06 – 0.47	0.1 – 0.2
Secchi depth (m)	3 – 5	3.5 – 5.5	1.9 – 2.2	1.5 – 2

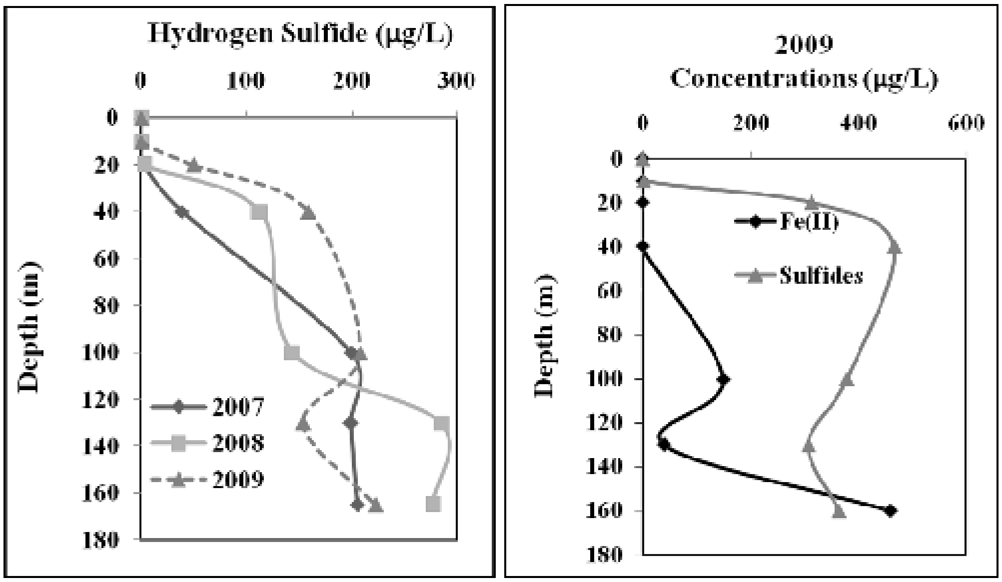
Surlfur Species.

Sulfur species measured in this study were total sulfide and sulfat concentrations. Predominant sulfide species could also be predicted based on the pH and the temperature of the lake water. Total sulfate and sulfide profiles of DM7 station could be seen in Figures 5. Sulfate concentrations were detected from the epilimnion to the hipolimnion. The sulfate was not all reduced in the hypolimnion. The cause of elevated sulfate concentrations at 100 m depth in 2007 was unclear. Oxidation of sulfide to sulfate was implausible given the very low disolved oxygen content and no light penetration to promote biotic sulfide oxidation. Sulfide profiles of Lake Maninjau shifted to a higher concentrations in 2009 (Figures 6). Overall from the year of 2007 to 2009 sulfate concentrations decreased as sulfide concentrations increased indicating more sulfate were reduced in the hipolimnion in Lake Maninjau. Sulfides are usually detected in the anoxic hipolimnion of eutrophic lakes when sulfate is present. Sulfides were produced from coupled metabolic processes of reduction of sulfate and oxidation of organic carbon or hydrogen gas by sulfate reducing-bacteria (Hines, 2000; Wetzel, 2001). Sulfide profiles were in agreement with oxycline profiles. DO concentrations in deep water columns depleted as sulfide diffused to the surface water. Sulfides were completely oxidized in the column water where DO concentrations were high. Sulfide concentrations will diminish in the oxic metalimnion due to sulfide is readily oxidized to elemental sulfur or back to sulfate either by oxygen or sulfur oxydizing bacteria (Stumm and Morgan, 1996; Hines, 2000; Wetzel, 2001). Decreasing levels of SO_4 and increasing levels of H_2S contents in lake water with depth, strongly suggests anaerobic bacterial processes are occurring through decomposition of organic matter under anoxic conditions in the sediment and in the water column. Sulfate reduction plays a pivotal role in the anaerobic environment of the lake.

Based on the water pH where the sulfides detected, both bisulfide and hydrogen sulfide existed in the wáter where hydrogen sulfide was slightly the predominat sulfide species especially in the hipolimnion in 2007 and 2008. The toxic hydrogen sulfide concentrations reached at level of 300 μg/L. Elevated hydrogen sulfide concentration above 2 μg/L in the water constitutes a chronic hazard to aquatic life. Concentration of hydrogen sulfide in non polluted waters is < 2μg/L (0.06 micromolar) with dissolved oxygen concentration of > 5 mg/L (Weiner, 2000). Sulfide concentrations in the pore water of top sediment layer from the deep-water station of DM4 and DM7 reached at level of 1-2 mg/L indicating high sulfate reduction rate in the sediment.



Figures 5. Profiles of Total Sulfides and Sulfate in Water of Lake Maninjau



Figures 6. Profiles of Hydrogen Sulfide and Profiles of Fe(II) and Total Sulfides in 2009

Besides it is oxidized back to sulfate, the loss of sulfide in water column could also due to reaction with iron to form the iron sulfide ((FeS). Profile of Fe(II) was in agreement with sulfide profile especially in the hypolimnion (Figures 5). The FeS formation could take place in the water column at the depth of 130 m. In the waters Fe and sulfides were readily forming the solid FeS which was indicated by black color sediment (Stumm and Morgan, 1996; Manahan, 2000; Weiner, 2000). The concentrations of Fe(II) were too small to control the sulfide concentrations in Lake Maninjau.

Concentrations of COD in Water ; Concentrations of Solids (TS/VS), Total Sulfur and Iron in Sediments.

Organic compounds concentrations in lake water were measured as COD (Chemical Oxygen Demand) (Figure 8). COD concentrations in the bottom lake water of deep-water stations (DM7 and DM4) increased in 2009. The waters contained more than 100 mg/L of COD were considered polluted by organic (Weiner,2000). COD concentrations in Lake Maninjau increased significantly in 2009. The highest concentrations of COD was not in area (DM Bayur station) where packed with floating cage fishery indicating that the excess organic from feeding had spread out to the deep-water area of the lake.

As the COD concentrations, the C-organic content in the lake sediments were also higher in the deepest part of the lake water stations (DM7 and DM4) (Figure 9). The results indicating that organic matter accumulated in the deep-water area was probably in simple organic compound which could be readily utlized by microbes especially sulfate reducers. The redox condition in these deepest water stations also supported active sulfate reduction process. Sulfate reduction usually occurs in the environment with the redox potential reached to -100 mV (Widdle, 1988). Sulfides were detected from the bottom water to the upper water column up to the depth of 20 m in the deep-water station, while in Bayur and Intake stations, sulfides were detected only in the bottom water in the anoxic hypolimnion area. The sulfide concentrations detected in Bayur and Intake station were much less than those of the deepest part of the lake water station. The explanation behind this, beside the organic matters were still in complex form, the redox condition in Bayur and Intake stations did not support sulfate reduction processs. The depth of DM Bayur and intake stations were 20 to 30 m, where the bottom water still contained dissolved oxygen. The active microbial process initiated in the Bayur station was probably the fermentative bacteria due to the organic matter was still in complex form. The degradation of complex substrates in the sediments of freshwater ecosystem requires several trophic groups of microorganisms. Complex substrates such as polysaccharides, protein, and lipids are hydrolyzed by hydrolytic bacteria, subsequently fermented by fermentative bacteria to a variety of intermediate products, such as short-chain VFA (acetate, propionate and butyrate), alcohols, hydrogen and carbon dioxide. Syntrophic bacteria further convert propionate and butyrate to acetate, carbon dioxide and hydrogen (Schink, 1997; Conrad,1999). VFA and hydrogen will be consumed by other hydrogen consumers such as sulfate reducing bacteria (SRB) (Widdle, 1988).

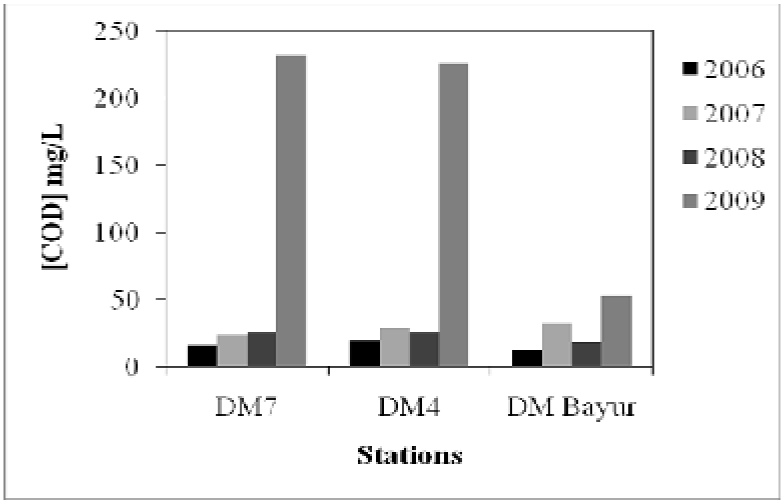


Figure 8. COD Concentrations in the Hypolimnion Water of Lake Maninjau

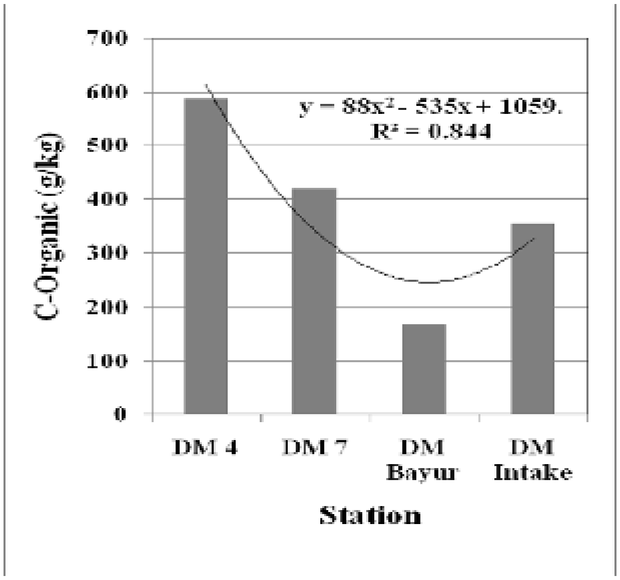
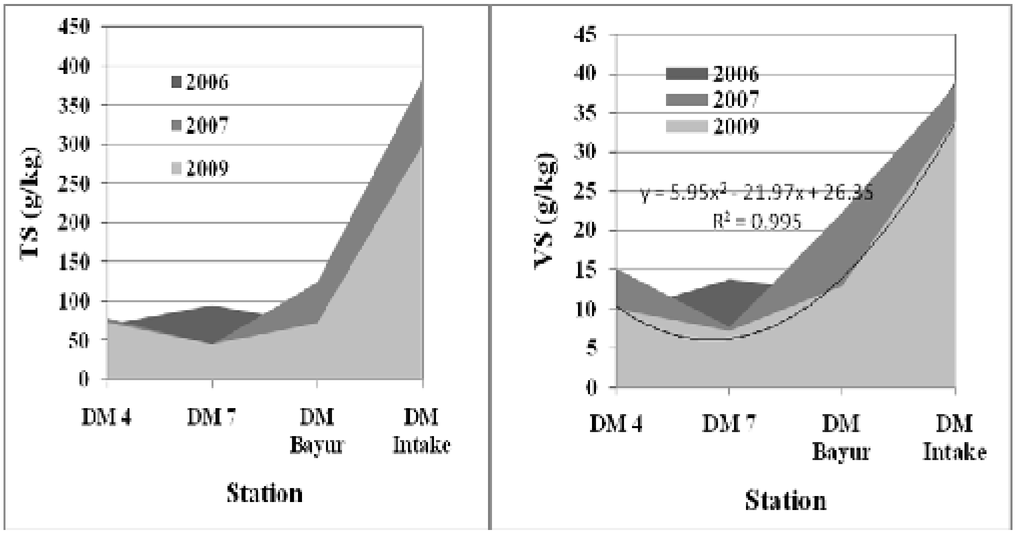


Figure 9. Distributionof C-organic in the Sediments of Lake Maninjau

Total and volatile solids were also high in the sediments (Figures 10). The solids concentrations inversely correlated with the C-organic concentrations in lake sediments indicating that portion of readily degradable organic matter in the deep water area was more than those of the shallower station which packed with floating cage fishery. Accumulation of organic matter was obvious in Lake Maninjau. Solids concentrations were clearly distributed even in the deepest part of the lake water area. Some of solids were trapped in station of DM 4 and DM 7 which are the deepest area of the lake. The water flows from satations of DM 7 pass through DM 4 and Bayur to the outlet gate, therefore the highest solids concentrations were in station of DM Intake (the outlet gate). The organic matters were transported from Bayur Station where the highest numbers of fish floating cages. Based on the current water, the area affected with the water flow is only the area with the depth of 30 to 40 m. The area of the lake with the depth more than 60 m is unlikely affected by the water flow, therefore the solids trapped in the sediments of this area would be accumulated over time. The accumulation of solids in the sediments indicating that only small portion of solids were transported from the lake to River Antokan because the gate was very small.

The accumulation of solids in the sediment could potentially trigger more sulfide productions in the anoxic hypolimnion layer. The excess organic compounds would either decompose by bacteria aerobically in epilimnion and metalimnion and anaerobically in hypolimnion or accumulate in the sediments. Increasing sulfide concentrations every year suggested that the excess organic in Lake Maninjau had elevated the reduction of sulfate to sulfide.

Low iron concentrations in water of Lake Maninjau supported the sulfide concentrations in the water column which were detected until a depth of 20 m in Lake Maninjau. Most of sulfide formed would react with iron to form iron sulfide. Total sulfur and iron concentrations accumulated in the sediments of Lake Maninjau indicating that iron reacted with sulfide in the water column and deposited to the sediments (Figure 11). Abundance iron concentrations in the sediments indicating that iron could possibly in the stable solid form such as iron sulfides and iron oxides. The slightly acid lake water in the anaerobic hypolimnia did not support the releasing of Fe(II), as a result more hydrogen sulfide was realeased to the column water.



Figures 10. Distributionof Solids (TS/VS) Concentrations in the Sediments of Lake Maninjau

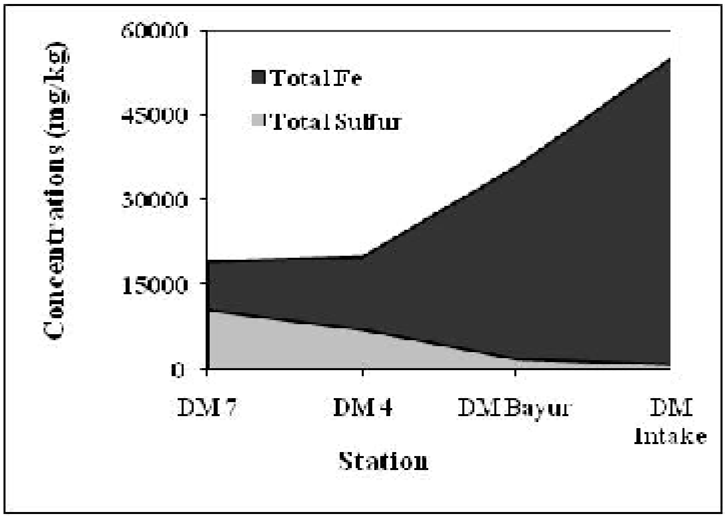


Figure 11. Total Sulfur and Iron Concentrations in the Sediments of Lake Maninjau

The predominant form of dissolved sulfur in water is sulfate. During decomposition of organic matter, sulfur is released largely as hydrogen sulfide. Reduction of sulfate to hydrogen sulfide occurs in the anoxic hypolimnion where the redox potential declines to less than 100 mV. Much of the hydrogen sulfide reacts with Fe (II) to form insoluble FeS near the sediments (Wetzel, 2001; Widdle, 1988). Under oxic condition hydrogen sulfide is oxidized rapidly abotically or biotically.

Based on the dynamics of sulfur in Lake Maninjau, the exploitation of floating cage fishery should be a big concern. High sulfate and organic compounds concentrations could promote high rate reduction of sulfate to sulfide. The conditions of the lake could be rapidly become anoxic. High hydrogen sulfide concentrations produced would diffuse into water column and by the surface mixing hydrogen sulfide could reach to the surface rapidly and caused the depletion of oxygen. The toxic hydrogen sulfide could also kill all the aquatic lifes including fish. The previous study reported that the sediment of lake amended with fish food pellets (2.8; 14.0; 28.0 mg ww g^{-1} ww^{-1} sediment; equivalent to organic matter loadings measured during fish farming), which contribute significantly to the organic matter loss from fish farms stimulated sulfate reduction up to 30 times relative to unamended sediments. Sulfate reduction was stimulated in sediments amended with food pellets where fatty acids accumulated to high levels (with acetate up to 85 mM, propionate up to 17 mM, and butyrate up to 25 mM). Sulfate reducers appeared saturated with substrates (fatty acids) even in the lowest additions (Holmer, M and E.Kristensen, 1991). Another study reported that sulfate reduction process is an important microbial process in the lake containing high sulfate when organic matter supply is sufficient. Sulfate reduction is limited by the supply of organic matter and is one of the major processes contributing to the mineralization of organic matter in this lake (Hadas *et al*., 2001). The fish kill phenomenon also reported to have occurred oftenly in a crater lake containing hydrogen sulfide in Italy as a result of the lake overturn (Caliro *et al*., 2008).

The phenomenon of *tubo belerang* reported to have occurred frequently in Lake Maninjau, which was followed by a mass fish kill. Previous study reported that due to less light intensity penetrated to the deeper water of Lake Maninjau had caused the layer of epilimnion diminishing. In this condition the wind and geothermal activity have been the major factors to cause the vertical mixing of the water mass (Apip *et al.,* 2003). The bulk of the results in this study strongly support the hypothesis that fish kill was caused by a series of events that began with the cooling of the epilimnetic waters with breaking of the thermal stratification, followed by lake overturn or a vertical mixing due to wind and the rise of toxic levels of H_2S from the reduced waters near the lake bottom. Massive *tubo belerang* reported was occurred again in February 2009 where mass fish kill took place. Several key parameters from the measurements of this study in 2008 could be developed into an early warning system in order to prevent the mass fish kill in the future.

CONCLUSIONS

Dissolved sulfur species formed as sulfate ion was distributed from the surface to the bottom, whereas sulfide compounds only detected in deeper water to the anoxic hypolimnion. Both bisulfide (HS^-) and hydrogen sulfide (H_2S) were presence with hydrogen sulfide was the predominant sulfide species. Sulfide diffused in the water column quickly oxidized in the oxic water column. Oxygen depleted sharply in a deeper column water up to a depth of 20 m where sulfide was detected. Sulfur mostly accumulated in the sediment as iron sulfide precipitation. Iron concentrations were abundant in sediment of Lake Maninjau suggesting that iron could play a major role in controlling sulfide concentrations. Concentrations of COD in the lake water were slightly high, and accumulation of C-organic and volatile solids (VS) in the sediments was observed. Organic compounds measured as C-organic and VS were abundant even in the deeper area could extend the anoxic water column to a shallower water column and enhances hydrogen sulfide production which subsequently could trigger the occurence of *tobo belerang*. The rate of organic compounds degradation needs to be determined in relation with sulfate reduction. Exploitation of floating cage fishery unquestionably could deteriorate the water quality thus could alter the lake ecosystem. Indicating of sulfide in the shallowest water column and the shallowest Secchi depth could be developed into an early warning system that the *tubo belerang* could occur imminently. Therefore, to maintain the lake water quality and to prevent the occurence of *tubo belerang*, the floating cage fishery should be limited in numbers and restricted to only in the certain area of the lake only.

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