

Interaction between Envirometal Factors and Zinc Concentration in Porewater and Roots of Rhizophora Sp. In Ampalas, Mamuju, West Sulawesi, Indonesia

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Interactions Between Environmental Factors and Zinc Concentrations in Porewater and Roots of *Rhizophora sp.* in Ampallas, Mamuju, West Sulawesi, Indonesia

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ABSTRACT

The study was to determine the concentrations of Zn in porewater and fine roots of *Rhizophora sp.*, and to examine their interactions with mangrove densities and physico-chemical. Porewater samples, fine roots, and sediments were collected in a 100 m² plot at each site with different mangrove densities. The average Zn concentrations in mangrove roots in the study area were 0 – 58.21 mg/kg, suggested the capability of mangrove roots in retaining Zn. The average dissolved Zn concentrations in porewater were 0.63 mg/L – 3.50 mg/L, illustrated the amount of Zn bioavailable form and its potential release to the adjacent environment. The Zn concentrations in porewater did not correlate significantly with the densities of mangroves. The concentrations of Zn in roots increased as the densities were higher, which is possibly caused by the absence of mangrove at Site 1. The study discovered the important roles of organic content and silt/clay in Zn sorption thus affect Zn levels in porewater. The concentrations of Zn in mangrove roots increased as the pH of sediment and porewater decreased.

Keywords : Zinc, porewater, mangrove roots, environmental variables.

INTRODUCTION

The mangrove ecosystem has numerous ecological and economic important functions (Alongi, 2002; Aksornkoae, 2004; Walters et al. 2008; Hogarth, 2015), including their capability in retaining pollutants, such as metals, to adjacent marine environment (MacFarlane, Pulkownik, & Burchett, 2003; Silva, Da Silva, & De Oliveira, 2006; Chaudhuri, Nath, Birch, 2014). Zinc is an essential element for plant growth (Broadley, White, Hammond, Zelko, & Lux, 2007), including mangroves (Marchand, Fernandez, & Moreton, 2016), which becomes one of the important topics studied in mangrove ecosystems. Zinc is involved in various enzymes in higher plants, however, in excessive concentration (i.e. at leaf Zn concentration > 100 mg/kg), it can cause toxicity to plants (Bradl, Kim, Kramar, & Stüben, 2005; Broadley et al. 2007).

The main natural source of Zn to sediments is from the chemical and physical weathering of parent rocks. The average Zn concentration of rocks in the earth's crust is approximately 78 mg/kg (Alloway, 2008). Besides that, sources from the atmosphere (e.g. forest fires, and surface dusts) and biotic

processes, such as: decomposition, leaching/wash-off from leaf surfaces can raise Zn concentrations in sediments (Friedland, 1990; Broadley et al., 2007). Anthropogenic inputs from mining, manure (Broadley et al. 2007; Chaney, 2008), fuel combustion, and sewage sludge can also increase Zn concentrations in sediments (Broadley et al. 2007). Zn rise can also come from agriculture, such as: fertilizer (Bradl et al., 2005; Chaney, 2008), a wood preservative, and an insecticide (Bradl et al., 2005). Besides natural and anthropogenic aspects, several factors, such as: pH (Du Laing, Rinklebe, Vandecasteele, Meers, & Tack, 2009), soil texture and organic matter can influence Zn concentrations in sediments (Broadley et al., 2007; Du Laing et al., 2009).

The concentrations of Zn in Indonesian mangrove areas varied. The Zn concentrations in mangrove sediments of Dumai, Sumatra were between 41.55 – 75.26 mg/kg (Amin, Ismail, Arshad, Yap, Kamarudin, 2009), while Zn sediment levels from Segara Anakan Nature Reserved were 39–154 mg/kg (Syakti et al., 2015). The concentration of Zn in sediments in mangrove of the Rawa Aopa Watumohai National Park, Southeast Sulawesi were between

8.33 – 16.16 mg/kg, while the Zn concentrations in seawater at the area were 0.13 – 0.14 mg/L (Analuddin et al., 2017). There are few published data on the Zn concentrations in porewater over the world. The Zn concentrations in porewater of mangrove ecosystem in Sarawak, Malaysia were 0.00042–0.0013 mg/L (Billah, Abu Hena, Idris, Ismail, Bhuiyan, 2014).

The mangrove ecosystem in Ampallas, District of Mamuju, Province of West Sulawesi, Indonesia, is located near fish ponds and agricultural areas, which can affect the natural levels of Zn in the area. Furthermore, fishermen's boat activities and urban effluent can also increase the concentrations of Zn in the area. Free inundation from seawater as well as river located at the left side of the study area can control the geochemical processes occurred thus affect the levels of Zn in the mangrove ecosystem. Changes of the solid phase in the environment can affect the composition of the interstitial water, thus influence the solubility and bioavailability of heavy metals (Otero and Macías, 2002). The later form could also reflect the potential amount of Zn released into adjacent environments.

This study was to examine the Zn concentrations in porewater and roots of *Rhizophora sp.* in order to evaluate the capability

of the mangrove ecosystem in retaining Zn as well as its potential to release the bioavailable Zn to adjacent environment. Furthermore, this study was to evaluate their interactions with mangrove densities and physico-chemical variables.

EXPERIMENTAL SECTION

Study sites

The study was conducted from May to August 2016 at a mangrove ecosystem in Ampallas, District of Mamuju, Province of West Sulawesi, Indonesia (**Figure 1**). The study was conducted at four sites that have different mangrove density levels based on criterion stated by Environment Ministry, Republic of Indonesia (KepMenLH, 2004) (**Table 1**).

Each site was located at a 10 x 10 m² plot. The amount of mangrove density was determined by converting the number of mangrove trees in a plot to a hectare (ha) unit. Site 1 that had no mangrove was served as the control site. Site 2 had lesser mangrove density (583 mangroves/ha) and was dominated by *R. apiculata* approximately 300 mangroves/ha. Site 3 was occupied by medium level of mangrove density (1100 mangroves/ha) and dominated by *R. mucronata* as much as 967 mangroves/ha.

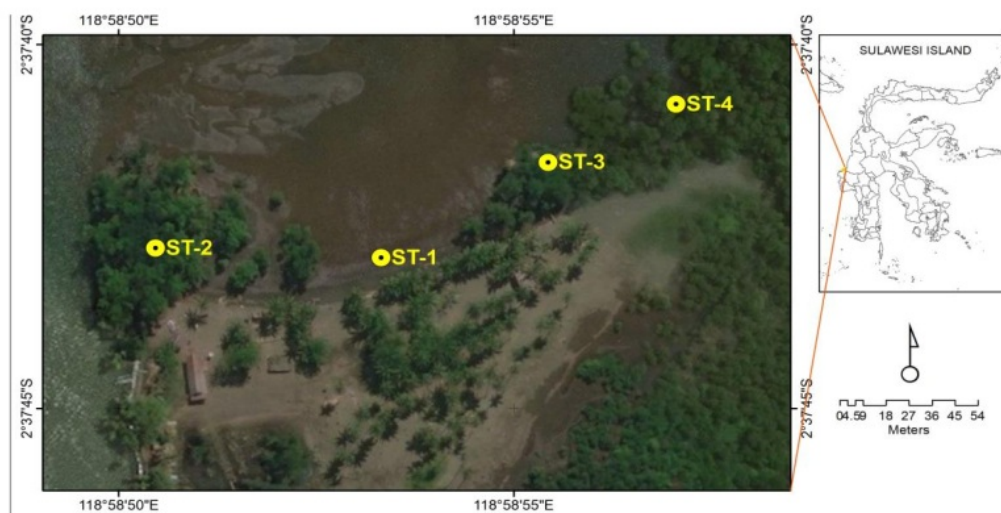


Figure 1. Location of field study in Ampallas, District of Mamuju, Province of West Sulawesi, Indonesia

Table 1. The density of mangroves at each research sites and the criterion level based on Environment Ministry, Republic of Indonesia (KepMenLH, 2004).

Site	Density (trees/ha)	KepMenLH (2004)	
		Criteria	Density (trees/ha)
1	0	-	-
2	583	Less dense	<1000
3	1100	Medium density	>1000 - <1500
4	1750	Densest	>1500

**Figure 2.** Peeping bottle designed to collect porewater sulfide. The upper side of the bottle had holes around it, covered with a soft net, and was connected to a PVC pipe

Site 4 had densest mangroves (1750 mangroves/ha) and was dominated by *R. mucronata* as much as 1417 mangroves/ha (Table 1). At each site, six mature trees of *Rhizophora* sp. were chosen as study objects and served as replications. The trees had similar heights, diameters, and visual health.

Sample collections and measurements

Fine roots that were considered as nutritive roots, up to 5 cm surface sediments (MacFarlane et al. 2003), as well as porewater samples, were collected at least one meter from each of mangrove trees. Porewater samples were collected using peeping bottles built from a 250 ml bottle connected to a PVC pipe at the bottom. This pipe served to hold the bottle firmly upright inside the soil. The upper side of the bottle had holes around it and was covered with a soft net to minimize the amount of the soil getting inside (Figure 2). The bottles were put inside the holes in the soil and buried at low tide, and kept there

overnight to ensure the bottles were filled with porewater. After removal, the porewater was transferred into sample bottles.

The pH of porewater and sediment samples were measured using pH probe meter, while the redox potential (Eh) of sediment samples were measured using Eh probe meter. The concentration of organic content was determined using the Loss on Ignition (LOI) method (Heiri, Lotter, & Lemcke, 2001). The analysis of grain size of the soil was determined using wet sieve analysis by employing a stainless steel 63 μm sieving net (Percival and Lindsay, 1997).

All samples were kept in a cool box before transported to the laboratory. Porewater samples were filtered using membrane filter 0.45 μm and preserved with 1.5 ml HNO_3 every 1 L water sample for dissolved metal analysis.

Mangrove roots were oven dried at 60 $^\circ\text{C}$ for 24 hours (MacFarlane and Burchett, 2001; MacFarlane et al., 2003; Defew, Mair, &

Guzman, 2005). As much as 0.5 g root tissues were digested with concentrated HNO₃ and H₂O₂ (Khrisnamurty, Shprirt, & Reddy, 1976). 100 ml porewater samples were digested with HNO₃ and H₂SO₄ (APHA, 1999). The concentrations of total Zn accumulated on root tissues samples as well as dissolved Zn on porewater samples were determined using ICP-OES.

Statistical analysis

This study applied several statistical analyses, using Excel and SPSS 21 to assess the variability of geochemical interactions and their correlations. A normality test was performed, and data transformation was employed for non-normal variables. The transformation types depended on the type of skewness. Spearman correlation was employed to identify the correlation between the Zn concentrations in porewater, roots and physico-chemical variables as well as mangrove densities.

RESULTS AND DISCUSSION

Physico-chemical measurements

The conditions of redox potential in study location were varied from reductive to oxidative, with average values from -73.2 to 113.6 mV (Table 2). The range of average sediment pHs was from 6.83 at Site 2 to 7.14 at Site 1. The organic contents were relatively low (1.41%) at Site 1 that had no mangrove and high (12.9%) at Site 4 that had the densest mangroves. The study sites were dominated by sand (above 95%) and a small portion of silt and clay (0.64 - 2.78%) (Table 2).

The average concentrations of dissolved oxygen in porewater were between 4.3 – 7.1

mg/L, where the highest concentration was at Site 4 that had the densest mangroves. The average pHs of porewater were between 6.59 – 7.10, where the highest average pH was located at the Site 1 that had no mangrove. The average salinities of porewater in the study area were between 25 – 29‰ (Table 3).

The concentration of metals in porewater and mangrove roots

The average concentrations of Zn in porewater in the study area were between 0.63 – 3.50 mg/L (Table 4). The lowest average Zn concentration in porewater was at the Site 1 that had no mangrove, whilst the highest concentration was at the Site 2 that had less dense mangroves. The average concentrations of Zn in mangrove roots in the study area were similar (53.73 – 58.21 mg/kg). The average concentrations of Fe in roots in the study area were between 2282.60 – 6693.52 mg/kg. The average concentrations of Mn in mangrove roots in the study area were in the range of 43.91 – 129.22 mg/kg (Table 4).

Correlations of Zn concentrations in porewater and mangrove roots to measured physico-chemical variables

Table 5 shows the concentration of dissolved Zn in porewater increased as the percentage of organic content and silt clay increased ($p < 0.01$). The concentration of Zn in mangrove roots increased as the pH of sediment and porewater decreased ($p < 0.01$). The range of dissolved porewater Zn concentrations found in study sites was 0.63 mg/L – 3.50 mg/L.

Table 2. The physico-chemical condition of sediments in the study area (n=24). Data are presented as mean +/- standard deviation

Site	Eh	pH	Organic (%)	Sand (%)	Silt Clay (%)
1.00	-23 ± 66.3	7.14 ± 0.32	1.41 ± 0.78	98.24 ± 1.62	0.64 ± 0.94
2.00	15.8 ± 107.3	6.83 ± 0.26	3.23 ± 2.56	95.79 ± 3.39	2.78 ± 2.04
3.00	-13.4 ± 74.9	6.89 ± 0.21	3.06 ± 1.51	97.38 ± 1.82	2.06 ± 1.51
4.00	-73.2 ± 113.6	6.71 ± 0.10	12.97 ± 6.61	96.51 ± 1.33	2.12 ± 1.61

Table 3. The physico-chemical condition of porewater in the study area (n=24). Data are presented as mean +/- standard deviation

Site	Dissolved Oxygen (mg/L)	pH	Salinity (‰)
1	5.8 ± 1.0	7.10 ± 0.05	25 ± 2
2	4.3 ± 1.5	6.59 ± 0.09	23 ± 3
3	6.6 ± 0.1	6.79 ± 0.05	29 ± 2
4	7.1 ± 0.2	6.8 ± 0.11	25 ± 3

As mention before, there are limited published data on the Zn concentrations in porewater of mangrove ecosystems over the world. The concentrations found in the study sites were higher than that found in New Caledonia where the average concentration was lower than 10 $\mu\text{mol}\cdot\text{l}^{-1}$ (0.6538 mg/L) (Marchand, Fernandez, & Moreton, 2016), or in Sarawak, Malaysia 0.00042–0.0013 mg/L (Billah et al., 2014). In comparison, the concentration of Zn in porewater of Jeneberang estuary, Makassar, Indonesia in West monsoon and East monsoon were 0.051–0.278 mg/L and 0.220–3.526 mg/L, respectively (Najamuddin, 2017). The values found in the study area illustrated the amounts of Zn bioavailable form that were readily taken up by mangroves, as well as indicated the amounts of dissolved Zn form that are potentially released to the adjacent marine environment.

However, the study showed that the concentrations of dissolved Zn in porewater did not correspond significantly to Zn concentrations in mangrove roots. In fact, the porewater Zn associated with organic content and silt/clay percentage, where the concentrations of dissolved Zn in porewater increased as the percentages of organic content and silt clay increased. Soil organic matter, soil type, and clay mineral content can influence Zn sorption in soil (Bradl et al. 2005; Zhou, Zhao, Peng, & Chen, 2010; Kabata-Pendias, 2011), and become some of the primary Zn fractions found in the environment (Broadley et al. 2007). In study location, organic matters were higher in

sediments that contain higher silt/clay percentages because silt/clay textures were more capable in trapping organic matter as well as binding with metals compared to sand, which due to their high specific surface area (Marchand et al., 2006). Therefore, higher concentrations of metals, including Zn were found in fine-grained soils than in sandy soils (Aham, 2007), including in mangrove areas (Tam and Wong, 2000; Zhou et al., 2010).

Similarly, high organic matter will increase sorption of metals, including Zn onto humus material (Bradl et al. 2005; Marchand et al., 2006). Zn bound to organic matter was found in New Caledonia in the anoxic conditions, while it is mainly related with the refractory phase in the suboxic conditions existed in *Avicennia* and *Salicornia* stands (Marchand et al. 2016). Remobilisation of metals from sediments to porewater can occur through chemical, biological or physical processes (Sullivan and Taylor, 2003). Rapin, Nembrini, Förstner, & Garci (1983) explained that besides adsorption on surfaces, precipitation and/or co-precipitation, desorption and dissolution were several factors that can influence metal concentrations in porewater. Decomposition of organic matters can also cause mobility of metals (Kabata-Pendias, 2011), thus increase dissolved metal concentrations released to surrounding area, including porewater. Besides that, physical action from wave released metals from silt/clay.

Table 5. Spearman correlation analysis of measured variables

	EhSed	pHSed	Organic	SiltClay	DOPw	pHPw	Salinity Pw	Density	PwZn	RootZn
EhSed	1	-0.226	0.363	-0.033	-0.201	-0.086	-0.111	-0.186	-0.206	-0.154
pHSed		1	0.227	-0.097	-0.384	.435*	0.013	-.603**	0.087	-.521**
Organic			1	.559**	.442*	-0.094	-0.142	.727**	.616**	0.249
SiltClay				1	-0.166	-0.361	-0.29	0.211	.649**	0.348
DOPw					1	0.266	0.31	.656**	0.038	0.072
pHPw						1	0.119	-0.299	-0.19	-.612**
SalinityPw							1	0.248	-0.236	0.334
Density								1	0.22	.535**
PwZn									1	0.175
RootZn										1

Note: Sed: sediment, Pw : porewater

The average concentrations of Zn in mangrove roots in the study area were categorized as normal in plants (0 – 58.21 mg/kg). Levels of 10–150 mg/kg are normal in plants, while 400 mg/kg is toxic (Mulligan, Yong & Gibbs, 2001). The concentrations of Zn in mangrove roots increased as the pH of sediment decreased. Similar conditions were found elsewhere, where metal accumulations in mangrove roots were higher under lower sediment pHs due to the mobilization of metals as exchangeable species (Harbison, 1986; Clark, McConchie, Saenger, & Pillsworth, 1997; MacFarlane et al. 2003). Lower pH in sediments resulted in lower pH in porewater thus affected the concentrations of Zn in mangrove roots due to the mobilization of Zn as indicated by strong association between pH of sediments and pH of porewater, as well as strong correlations between these two variables and Zn concentrations in roots (Table 4).

CONCLUSIONS

The average Zn concentrations in mangrove roots in the study area were 0 – 58.21 mg/kg. The range of average dissolved Zn concentrations in porewater was 0.63 mg/L – 3.50 mg/L. The Zn concentrations in porewater did not correlate significantly with the densities of mangroves. The concentrations of Zn in roots increased as the densities were higher, which is

possibly caused by the absence of root sample at Site 1 that had no mangrove. The concentrations of dissolved Zn in porewater increased as the percentages of organic content and silt clay increased, indicated the important roles of organic content and silt/clay in Zn sorption thus affect Zn levels in porewater. The concentrations of Zn in mangrove roots increased as the pH of sediment and porewater decreased.

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