

## Analysis of Horizontal and Vertical Distribution of Metal Contaminants in Water and Soil in Sumobito Area, Jombang District, East Java Province

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**Abstract.** Jombang Regency is known as one of the districts that has become a center for smelting electronic waste to extract aluminum metal since 1970. However, many industry owners are ignorant and dispose of waste carelessly into house foundations, village roads and rice field boundaries. The purpose of this study is to determine how the distribution of metal contaminant concentrations in water and soil horizontally and vertically, and what factors affect the distribution pattern of these contaminants. The methods used in this study were water and soil sampling to determine the total concentration and TCLP of As, Cd, Cu, Hg, Pb, Zn, Al, and Ni ions, and XRD analysis to determine soil mineralogy. The data was processed to analyze the type of metal fractionation. Laboratory results show that the metal content in water is below the quality standard and moves following the direction of groundwater flow. Then the distribution of metal concentrations in the soil horizontally is that the farther away from the waste slag the concentration are lower, but vertically the highest metal concentration is found at a depth of 30-60 cm. Based on the analysis conducted, it is known that the distribution of metal ions in water and soil is influenced by climatology, advection-retardation, metal fractionation, preferential flow, and reduction by plant.

**Keywords:** *hazardous waste; contaminant transport; metal fractionation; retardation; metal reduction; preferential flow.*

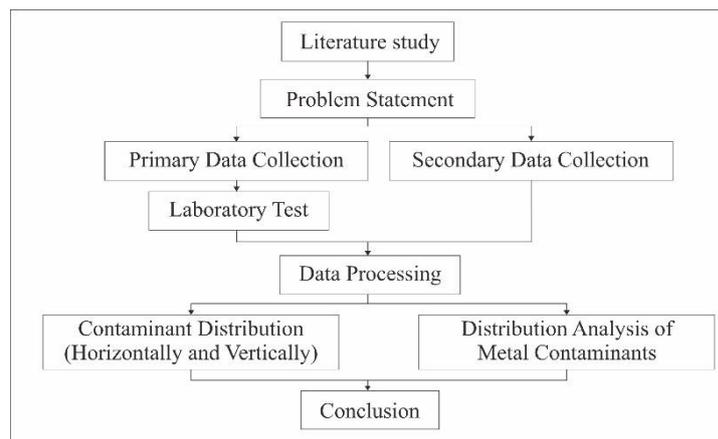
### 1 Introduction

Toxic and hazardous waste is a polluting substance which can harm the surrounding environment in air, water, and soil (Riyanto, 2012). Jombang Regency is known as one of the districts that is a center for smelting electronic waste to extract aluminium metal. There are at least 136 aluminum recycling industries spread across 14 villages in Sumobito District, Jombang Regency that have been operating since 1970 (ASPALINDO Jombang, 2016). The process of smelting electronic goods produces waste that is categorized as hazardous due to

its total concentration and TCLP values (KLHK, 2017). These smelter owners generally do not pay attention to the requirements and methods of hazardous waste treatment in accordance with the existing regulations, so that the waste is disposed carelessly into the foundations of houses, village roads, and rice field boundaries. This is very concerning, because it can endanger the surrounding living things. Thus, it is important to know how the quality of groundwater and soil in the study area, and the factors that affect distribution pattern of contaminants in groundwater and soil both horizontally and vertically. In this study, hydrogeology condition, soil mineralogy and shallow soil structure were analyzed to determine their relationship with contaminant distribution patterns.

## 2 Research Methods

The research was carried out in several stages, which are literature study, data collection and processing, and making conclusions [1]. Contaminant concentration data in groundwater and soil are processed to see how the distribution pattern both horizontally and vertically. Analysis of factors affecting contaminant distribution patterns is carried out by processing contaminant content in water and soil, hydrogeological data, and soil mineralogy.



**Figure 1.** Research chart

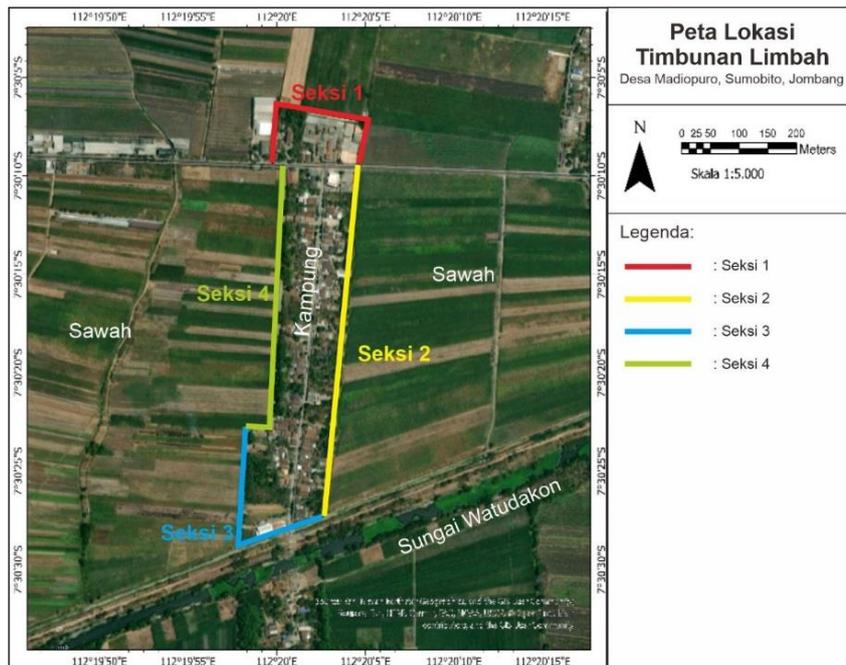
### 2.1 Research Location

Administratively, the research location is in Madiopuro Village, Sumobito District, Jombang Regency, East Java Province. With a geographical location of 7° 29' 53" S; 112° 19' 43" E to 7° 30' 36" S; 112° 20' 16" E. Lithologically, the location is composed of alluvial deposits (Santosa, *et al.*, 1992, and Noya, *et al.*, 1992), with the composition of clay - sandy clay (Hapsari, S. B., 2013). The site

is within the Brantas subwatershed, 4 km south of the Brantas River. It is part of the Mojokerto sub-Groundwater Basin, which is part of the Brantas Groundwater Basin (ESDM, 2022). Based on the aquifer productivity map, this location is in the zone of a productive aquifer system with flow through intergranular spaces, with an average pumping discharge of 5-10 liters/second.

## 2.2 Data Collection

There are primary and secondary data collected in this study. Primary data included 6 groundwater sample points, 10 waste and soil sample points, and 4 plant sample points, to determine metal ion concentrations and soil mineralogy. Soil samples were taken compositely at depths of 0-30cm, 30-60cm, 60-90cm, and 90-120cm, at a distance of 0 and 1.5m from the waste, as well as soil samples in areas considered not polluted at all. In addition, there is data on groundwater level, and soil hydraulic conductivity. Secondary data included rainfall data, and soil type. Maps of the waste dump locations and data collection can be seen in [2] and [3].



**Figure 2.** Waste stockpile location map

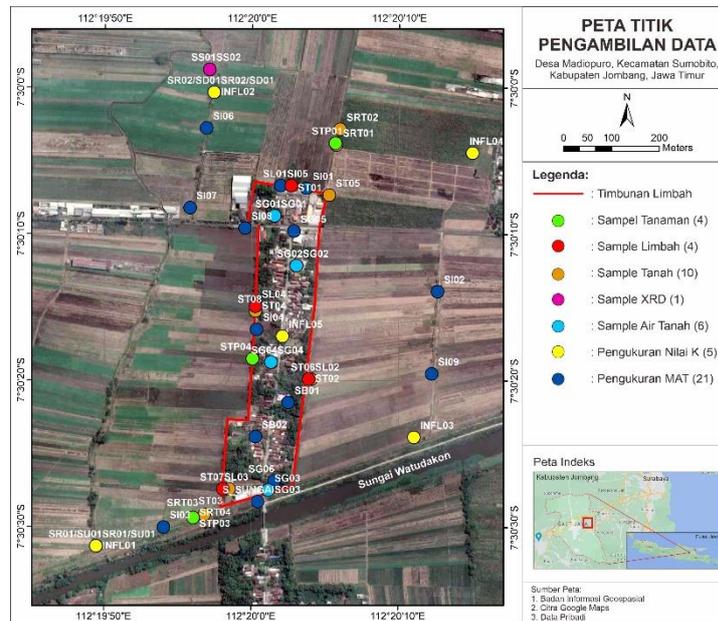


Figure 3. Data collection location

### 2.3 Data analysis

Groundwater, waste, composite soil and plant samples were tested using ICP-MS. To dissolve metal ions in soil and waste, extraction was carried out using 5ml  $\text{HNO}_3$  and 5ml  $\text{HCL}$  (Total Concentration Analysis). In addition, extraction was also carried out using water, and 5.7 ml  $\text{HOAc}$  and 64.3 ml  $\text{NaOH}$  1N (pH 5) to analysis Toxicity Characteristic Leaching Procedure (TCLP). The sample test results will provide data of total concentration (TC) of metals As, Cd, Cu, Hg, Pb, Zn, Al, and Ni, as well as Toxicity Characteristic Leaching Procedure (TCLP) values to determine the potential of waste leaching.

Soil mineralogy data was obtained from soil samples that were considered unaffected by the waste. Soil samples were taken at 1 point with 2 samples considered to represent the depth of 0-60cm and 60-120cm. The soil samples were then tested using an X-Ray Diffractometer (XRD). Total Concentration, TCLP, and soil mineralogy data will be processed to obtain information about soil fractionation towards trace metals.

Groundwater level data was obtained by measuring 20 dug wells and irrigation wells. The data are then interpolated to obtain a groundwater flow gradient map. This information can provide information on how groundwater flow patterns as a carrier medium for metal ions horizontally (advection).

Hydraulic conductivity data was obtained by taking measurements in the field with a mini-disk infiltrometer tool at 5 points. The data are then calculated to obtain the hydraulic conductivity value. K data can provide information about the speed of groundwater flow as a metal ion transport medium.

### 3 Results dan Discussion

#### 3.1 Distribution of Metal Ion Concentration in Groundwater

Data from laboratory tests on groundwater metal ion concentrations can be seen in table [1].

**Table 1.** Groundwater metal ion concentration data

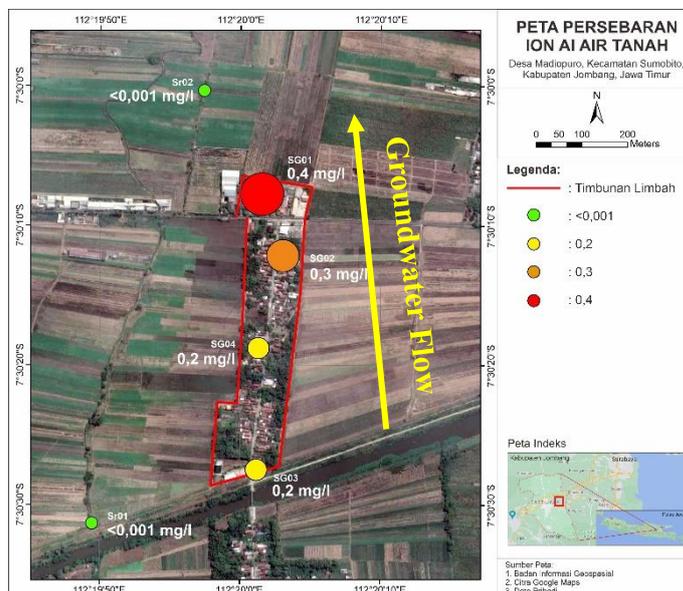
No Sample	As (mg/l)	Cd (mg/l)	Cu (mg/l)	Hg (mg/l)	Pb (mg/l)	Zn (mg/l)	Al (mg/l)	Ni (mg/l)
SG01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.41	<0.001
SG02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.29	<0.001
SG03	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.2	<0.001
SG04	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.19	<0.001
SR01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
SR02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

From the data table [1], it can be seen that in general, the concentrations of all elements are below the quality standard and very small (<0.001), except for Al ions in SG01, SG02 and SG03. This is interpreted due to several reasons. First, it can be caused by delusion by rainwater, considering that the water samples were taken at an open dug well and when collecting the samples the conditions were raining, see the rainfall graph in March 2022 in [4].



**Figure 4.** Rainfall data (BMKG and Climatecharts)

In addition to delusion by high rainfall, very small concentration values can be caused by the phenomenon of metal deposition at the bottom of the well. It's interpreted that not all contaminants from the waste are dissolved in water, but are carried in the form of a suspension phase. This was evidenced during the observation at SG05, where the water at the top looked very clear, while at the bottom of the well it looked very black. Then, the other factor is some of the metal ions are bound by the soil, causing the dissolved metal ions in water to be small. Regarding the Al values that appear, it is estimated that the source of the waste and the original soil have very high Al concentrations. When viewed in more detail, the Al value in SG01 is higher than the Al value in other wells, this is interpreted because SG01 is located in the northern part, where when viewed from the groundwater flow map [5], groundwater flow relatively flows towards the north, so that from the advection factor, metal ions originating from waste horizontally will be higher/accumulated on the north side.



**Figure 5.** Aluminium distribution and groundwater flow direction

### 3.2 Distribution of Metal Ion Concentration in Soil

Data from laboratory tests on the concentration of 8 metal ions in waste samples, contaminated soil at a distance of 0m section 1 to 4, contaminated soil at a distance of 1.5m section 1 to 4, and reference soil (uncontaminated) can be seen in tables [2], [3], and [4]. In the total concentration tables [2], [3], and [4] the darker color indicates that the concentration value of metal ions in that layer is higher than in the layer above or below it.





		60-90	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
		90-120	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Referensi	TRD01	0-30	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	4419.72	<0.002
		30-60	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	813.49	<0.002
		60-90	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	47.42	<0.002
		90-120	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	2819.13	<0.002
Referensi	TRD02	0-30	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	595.66	<0.002
		30-60	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	1156.76	<0.002
		60-90	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	461.97	<0.002
		90-120	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	406.82	<0.002

From the data tables [2], [3], and [4], it can be seen that the horizontal distribution of contaminants occurs normally where the point closer to the waste (distance 0m) is higher than at a distance of 1.5m and reference soil. But vertically, from the data table [2], it can be seen that the position of the waste is at the surface of the soil, but the contaminated soil layer below it relatively does not show the concentration of metal ions decreasing due to increasing depth. The layers with higher concentrations are in the center, even in some layers the concentration of metal ions is higher than in the waste itself. This phenomenon is interpreted to be related to the ability of the soil to bind metal ions, resulting in accumulation in certain layers. To determine this, data on the percentage of metal ion mobility [tables 5 and 6], and soil mineral content from XRD tests [figures 6 and 7] were analyzed. These data can elucidate the soil fractionation phase that is considered to be responsible for this phenomenon.

**Table 5.** % Mobility (total concentration / TCLP) distance 0m from waste

% Mobility (Total Concentration / TCLP) Distance 0m from Waste										
Seksi	Nama	Kedalaman	As	Cd	Cu	Hg	Pb	Zn	Al	Ni
1	UDS113	slag limbah	0.97	0.20	0.28		0.04	0.26		0.09
1 jarak 0	UDS13	0-30 (cm)	0.95	0.95	0.95	1.75	0.95	0.95	0.97	0.10
		30-60	0.95	0.95	0.95	< 1	0.95	0.95	0.95	0.08
		60-90	0.70	0.94	0.94	0.95	0.88	0.95	0.95	0.95
		90-120	0.92	0.93	0.95	0.86	0.90	0.95	0.95	0.95

2	UDS213	slag limbah	0.96	0.96	0.44	0.97	0.97	0.12		
2 jarak 0	UDS23	0-30	0.95	0.95	0.95	< 1	0.95	0.95	0.24	
		30-60	0.95	0.95	0.95	< 1	0.95	0.95	0.26	
		60-90	< 1	< 1	100	< 1	100	100	0.95	27.99
		90-120	< 1	< 1	< 1	< 1	< 1	< 1	< 1	
3	UDS313	slag limbah	0.96	0.97	0.24	0.08	0.97	0.25		
3 jarak 0	UDS33	0-30	0.95	0.95	0.95	< 1	0.95	0.95	0.95	
		30-60	0.94	0.95	0.95	< 1	0.95	0.95	0.95	< 1
		60-90	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
		90-120	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
4	UDS413	slag limbah	0.97	0.96	0.03	0.04	0.96	0.12		
4 jarak 0	UDS413	0-30	0.94	0.94	0.94	< 1	0.94	0.03	0.95	0.94
		30-60	0.94	0.94	0.94	< 1	0.94	0.13	0.95	
		60-90	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
		90-120	100							

**Table 6.** % Mobility (total concentration / TCLP) 1.5m distance from waste

% Mobility (Total Concentration / TCLP) 1.5m Distance from Waste										
Seksi	Nama	Kedalaman	As	Cd	Cu	Hg	Pb	Zn	Al	Ni
1 jarak 1.5m	UDS19	0-30	0.95				< 1		< 1	
		30-60	0.95				< 1		< 1	
		60-90	100				< 1	< 1	< 1	
		90-120	100				< 1		< 1	
2 jarak 1.5m	UDS28	0-30	< 1		< 1		0.96	100	< 1	
		30-60	< 1		< 1		< 1	< 1	< 1	
		60-90	< 1					< 1	< 1	
		90-120	< 1		< 1		< 1	< 1	< 1	
3 jarak 1.5m	UDS38	0-30	< 1		< 1		< 1	< 1	< 1	< 1
		30-60	< 1						< 1	< 1
		60-90	< 1						< 1	
		90-120	73.33				< 1	92.14	90.61	< 1

4 jarak 1.5m	UDS48	0-30	< 1	67.72	0.66	< 1	
		30-60	0.66		< 1		< 1
		60-90	74.29	< 1	< 1	< 1	< 1
		90-120	84.00	< 1	< 1	37.08	19.71

Qualitative analysis results					
Phase name	Formula	Figure of merit	Phase reg. detail	DB card number	
Labradorite - from	Ca0.68 Na0.30	1.163	ICDD (PDF2.DAT)	01-083-1372	
Halloysite-7A	Al2 Si2 O5 ( O H )4	0.873	ICDD (PDF2.DAT)	00-029-1487	
Quartz, low	Si O2	2.637	ICDD (PDF2.DAT)	00-005-0490	
Andradite	( Ca2.97 Mg.02	0.578	ICDD (PDF2.DAT)	01-074-1559	
Muscovite 2M1 - from	K Al2 ( Al Si3 O10 )	1.594	ICDD (PDF2.DAT)	01-082-0576	

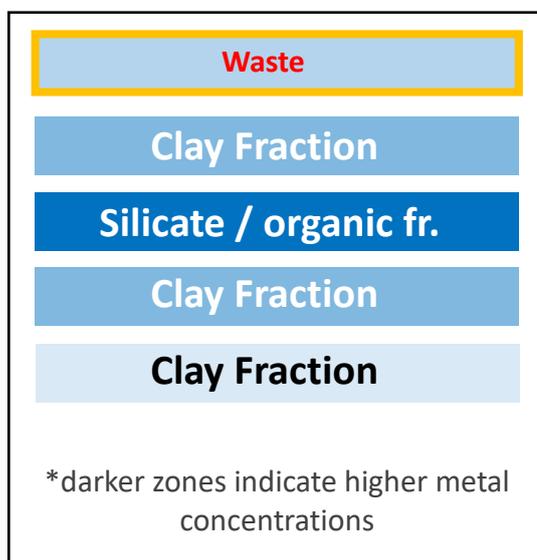
Figure 6. Soil mineralogy at 0-60cm depth from XRD test

Qualitative analysis results					
Phase name	Formula	Figure of merit	Phase reg. detail	DB card number	
Labradorite - from	Ca0.68 Na0.30	0.911	ICDD (PDF2.DAT)	01-083-1372	
Halloysite-7A	Al2 Si2 O5 ( O H )4	1.312	ICDD (PDF2.DAT)	00-029-1487	
Muscovite 2M1 - from	K Al2 ( Al Si3 O10 )	1.831	ICDD (PDF2.DAT)	01-082-0576	
Quartz, low	Si O2	1.234	ICDD (PDF2.DAT)	00-005-0490	
Andradite	( Ca2.97 Mg.02	2.957	ICDD (PDF2.DAT)	01-074-1559	

Figure 7. Soil mineralogy at 60-120cm depth from XRD test

From tables [5] and [6], it can be seen that the soil layers with high metal ion mobility are in the upper layer (0-30 cm) and lower layer (60-120cm), while in the middle layer (30-60cm) the mobility is small, less than 1%. The phenomenon of metal ion mobilization in soil is closely related to the soil fractionation factor. Tessier, A. (1979) explains that soils with certain mineralogical composition and environmental conditions can affect the ability of soil to bind metal ions. From the XRD results, it can be seen that the minerals contained in the soil are silicate mineral groups such as labradorite, muscovite, quartz and andradite, as well as clay minerals, namely halloysite. Tessier, A. (1979) states that sequential fractionation can be in the form of bonds to exchangeable (clays) (fraction 1), bonds to carbonates (fraction 2), bonds to iron and manganese (fraction 3), bonds to organic material (fraction 4), and bonds to silicate minerals (fraction 5/residual). Each fraction has specific requirements for the bonding and release of metal ions in the soil, and there is a specific extraction SOP in the laboratory for testing each fractionation phases.

TCLP testing in this study was carried out with water and HOAc-NaOH, and from these extractions there are metal ions that are dissolved or released from bonding with soil. When referring to the sequential fractionation testing procedure of Tessier, A. (1979), metal ions in fraction 1 (clay minerals) can be released with water, and metal ions in fraction 2 (carbonates) can be released by HOAc-NaOH. From these tests, the initial assumption is there is a layer of soil that tends to be weakly binding is soil with clay mineral content, and which tends to be strongly binding is soil with carbonate mineral content. However, the XRD results at both 0-60cm depth [Fig. 6] and 60-120cm depth [Fig. 7] did not show any soil layers containing carbonate minerals, but rather silicate minerals. Thus, the next assumption is that soil layers that tend to accumulate metal ions are soils with silicate mineral content. In addition to the residual silicate fraction, another possibility is the presence of an organic fraction, where organic material in the soil, although not visible by XRD, is very likely to be contained in the soil considering that the research area is rice fields. The conceptual model of this statement could be seen in Fig. [8]



**Figure 8.** Conceptual model of metal accumulation and metal fraction in each soil layer

So it can be concluded from the metal fractionation factor, soils that have a high total concentration with low mobility (middle soil layer) contain silicate minerals and organic materials as strong metal ion binders, because they can only be released by extreme environmental conditions (strong acids or strong bases). While the upper and deeper soil layers contain clay minerals as metal ion binders, where metal ion bonds in the clay mineral sheet structure are susceptible to

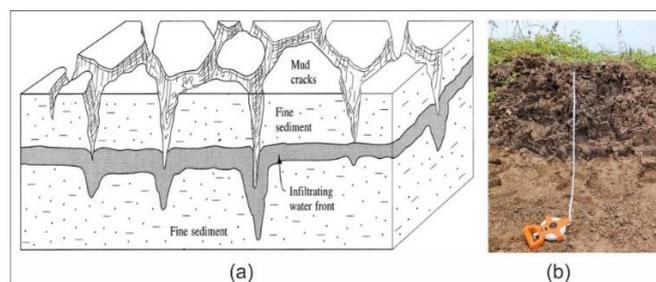
release by water under natural conditions. The process of accumulation or binding of metal ions by soil minerals can also be helped by the long contact period of the solution with the soil, because when viewed from the soil hydraulic conductivity value [Table 7], the value tends to be small so that groundwater moves slowly.

**Table 7.** Hydraulic conductivity data

No Sample	K (cm/s)
INFL01	1.02E-05
INFL02	1.84E-04
INFL03	7.42E-04
INFL04	2.71E-06
INFL05	7.26E-04

Especially for the Al mineral which is quite random in its occurrence, this is interpreted to occur because Al, apart from coming from waste, is already high in natural soil. This can be seen from the soil mineral compounds that almost all contain Al. The waste layer has a lower total concentration which is interpreted to be due to the leaching process considering that rainfall in this area is high and stockpiling has been done for a long time.

Another analysis that can affect the concentration of metals at the top is due to the preferential flow phenomenon. Preferential flow is a phenomenon of vertical flow in the soil with non-uniform velocity due to the presence of fractures that channel (bypass) surface water to deeper soil layers (Fetter, 2018). The preferential flow phenomenon can be seen in [9a] and [9b]. The preferential flow phenomenon is common in irrigated areas composed of clay, where plant roots and clay shrinkage trigger the appearance of fractures. Under these conditions, surface water carrying metal ions can flow directly to deeper layers so that under special conditions it does not have time to accumulate in shallow soil layers (Garrido, F., 2012).



**Figure 9.** Preferential flow phenomenon

The next factor that can affect the reduction of metal ions in the upper soil layer is reduction by plants. Plants, as living things that absorb water and nutrients in the soil, will absorb metals if the water and soil contain them. The term phytoextraction or phytoremediation is quite widely researched as a natural remediation method that is quite efficient (Sibero N. H. B. T., 2019). Although rice plants in the study area are not included in hyperaccumulator plants, they can still absorb a certain amount of metal content in shallow soil. This is evidenced by the discovery of metal content in plant samples [table 8].

**Table 8.** metal ion concentration in plants.

No	Seksi	Nama	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Al (mg/kg)	Ni (mg/kg)
1	1	STP01	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	15.57	<0.002
2	2	STP02	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	25.26	<0.002
3	3	STP03	0.01	<0.002	<0.002	0.01	<0.002	<0.002	59.09	<0.002
4	4	STP04	0.02	<0.002	<0.002	<0.002	<0.002	<0.002	26.18	<0.002

#### 4 Conclusion

Based on the research that has been done, it can be concluded that the horizontal distribution of contaminants in groundwater is high at the northern point, this is interpreted due to groundwater flow factors. The low concentration is interpreted due to the delusion factor by rainwater and the deposition of metal minerals at the bottom of the well. The distribution of metal contaminants in the soil, horizontally, is that the farther away from the waste source, the concentrations tends to smaller, but vertically, the higher layer of metal concentrations is relatively in the middle soil layer (30-60cm). Factors that influence the distribution of metal concentrations are the soil fractionation phase of metals, preferential flow, and reduction by plants and microorganisms. However, the most significant factor is the soil fractionation, which is influenced by the mineralogical content of the soil, and the preferential flow phenomenon that can be clearly seen in the field. Further research related to the saturation index of the water and the abundance of microorganisms in the soil can be conducted to more accurately explain the factors affecting metal distribution patterns.

#### Acknowledgement

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