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To cite this article: N T Ngoc *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **266** 012006

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Heavy metal speciation in landfill leachate and its association with organic matter

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Abstract. This study investigated the speciation of heavy metals in the landfill leachate, which was collected from Nam Son sanitary landfill site in Hanoi, Vietnam. Physical fractionation was implemented using 1 μm glass fiber to separate the particulate fraction of heavy metals from the dissolved one. Then, supeliteTM DAX-8 resin was employed to separate humic substances as the dissolved organic fraction and the dissolved inorganic fraction. Excitation-Emission Matrices (EEMs) fluorescence spectroscopy was applied to estimate the footprint of organic matter's components. The results suggested that heavy metals in Nam Son landfill leachate were mainly present in the dissolved inorganic fraction, followed by complexes with humic substances, including humic and fulvic acids. A majority of Fe, Cu, Ni, and As formed chelates with humic substances while around 62% of Al existed in the particulate fraction. The existence in the particulate, dissolved organic and dissolved inorganic fractions varied significantly among investigated heavy metals. From heavy metal and organic matter binding, it was discovered that the dissolved organic matter (DOM) played a crucial role in heavy metal speciation in landfill leachate. This finding may be useful for predicting the mobility of heavy metals in the environment as well as the effects of humic substances on the coagulation process used in the landfill leachate treatment.

1. Introduction

Rapid industrialization, population growth and changes in consumption patterns have led to the formation of a large amount of solid waste. Solid waste that is not properly treated will have negative impacts on the environment [1]. There are many solid waste disposal methods, of which the landfill has been considered as the most environmentally-friendly and economical method [2].

Nevertheless, a major concern of landfills is the generation of leachate, which is defined as dark-colored liquid primarily produced when rainwater percolates through open landfills or through the cap of completed ones [3]. Landfill leachate and gas are two potential contamination sources affecting the surrounding environment, their long – term environmental impacts may last for some decades [4]. Landfill leachate may affect natural resources such as surface water, groundwater, soil and may bring harmful effects to the environment and public health [5]. The reason is in the landfill there may be many toxic compounds such as aromatics, halogenated compounds, phenols, pesticides, heavy metals and ammonium [6]. Contaminants in landfill leachate can be classified as: organic components (volatile fatty acids, humic acids and fulvic acids), inorganic components (chloride, sulphate, phosphate, ammonium, and sodium), heavy metals (nickel, manganese, iron, zinc, lead...), metalloid (arsenic...) [7], suspended solids [6]. The municipal landfill leachate was a mixture of high strength



organic and inorganic contaminants. During the stabilization process in landfill sites, the biodegradable fraction of organic compounds in leachates disappears and refractory humic substances (HS), which are mainly humic acids (HA) and fulvic acids (FA), take their place [8]. Humic substances, which have several functional chemical groups (carbonyl, hydroxyl, carboxylic acid, phenolic ring, and quinone), may combine with ions (Fe^{2+} , Fe^{3+} , Mg^{2+} and Ca^{2+}) and form chelate complexes [9, 10]. Municipal solid waste (MSW) derived DOM had a high affinity for Cu, Pb, Cd, Zn, and Ni (especially for Cu and Pb); thus, increasing the mobility of heavy metals in water contaminated by leachate [11, 12, 13]. Therefore, the treatment of landfill leachate plays a crucial role in preventing water sources from pollution and to ensure the safety of the environment [7]. The complexation of organic ligands and colloidal matters in leachate has an important influence on mobilization and attenuation in soil [6]. Understanding the quantity and composition of landfill leachate is necessary for determining the risks of environmental pollution and the design of efficient wastewater treatment systems [14].

Fluorescence Excitation-Emission Matrix spectroscopy (EEMs) has been widely used as a highly sensitive, fast, inexpensive and nondestructive analysis technique that requires little sample preparation to characterize fluorescent dissolved organic matter [15, 16]. The EEMs analysis is commonly carried out by observing the fluorescence peaks with a comparison of the intensity of individual peaks [17]. This research utilized on EEMs as a technique to fingerprint organic components in leachate samples which heavy metal may interact with. However, to date in Vietnam, there have been no reliable data on the characteristics and hazardous levels of landfill leachate, there is still a lack of systematic research on the composition of landfill leachate. In particular, heavy metal speciation and its relationship with the organic matter have not been investigated in Vietnam yet. Therefore, a deeper understanding of DOM-metals binding in landfill leachate is of great significance.

This research, implemented with landfill leachate from Nam Son landfill, has the following objectives: (i) to determine preliminary speciation of heavy metals based on different size fractions (ii) to identify categories of dissolved organic matter, in which heavy metal exists in and (iii) to investigate components of the dissolved organic matter in the landfill leachate.

2. Material and methods

2.1. Landfill site and sample collection

2.1.1. Landfill site description The leachate samples were collected at various sampling points. The outlet of the leachate treatment system at Nam Son landfill site was not accessible. Therefore, this study only investigated the inlet of the system by collecting leachate samples at the leachate collection pond. Nam Son landfill, which belongs to Nam Son waste treatment complex, is the biggest landfill in Hanoi. It is 19 years old and in the stabilized methanogenic phase. It is located in Soc Son district and about 50km from the Hanoi city center. Most of Nam Son landfill area is located in Nam Son, Bac Son, and Hong Ky communes, at an altitude of 20-200m above sea level. The topography is lower in the direction from north to south, from west to east. The Nam Son landfill area has the tropical monsoon climate, which is characterized by the rainy season and dry season. The rainy season lasts from May to October and the dry season lasts from November to April. The annual average temperature of about 25°C, the annual average rainfall of around 1600-1700mm, the average humidity of 79% make favorable conditions for solid waste decomposition [18].

2.1.2. Leachate samples collection. To characterize the heavy metal existing forms of landfill leachate, the raw leachate samples were taken from 21st September 2017 to 4th March 2018 during the rainy and dry seasons. In all, 4 leachate samples before going through the wastewater treatment system of Phu Dien Company, were collected from the leachate collecting pond of Nam Son landfill and contained into the 5-L bottles. The leachate containing bottles were subsequently capped, labeled and preserved at 4°C in the refrigerator for further processing. All landfill leachate analyses were

conducted at Vietnam Japan University in Vietnam, Kyoto University and Ritsumeikan University in Japan. The leachate samples were taken on 21st September, 3rd November, 15th December 2017 and 4th March 2018 were named as NI-1, NI-2, NI-3, and NI-4, respectively.

2.2. Sample preparation

2.2.1. Filtration. Leachate samples were filtered through 4 different pore size filters such as membrane filters (pore size 5 μm , 0.45 μm , and 0.1 μm ; Merk Millipore, Darmstadt, Germany) and a glass fiber filter (pore size 1 μm ; GS-25 Advantec, Tokyo, Japan). The 47 mm diameter filters were put on a filter holder (Merk Millipore, Darmstadt, Germany). The leachate samples were filtered by sucking using hand or vacuum pumps.

2.2.2. Separation of DOM. Superlite™ DAX 8 resin of 40-60 mesh, specific surface 140m²/g, 225 Å pore size, and 0.79 mL/g pore volume (Sigma-Aldrich, Bellefonte, USA) was used to separate DOM (adsorb and remove humic substance) from the dissolved inorganic matter. 18 mL of the resin was packed in 25 mL of syringe column and washed by 0.1 N NaOH and 0.1 N HCl to remove organic impurities. A leachate sample after 1 μm filtration was acidified to pH = 2.0 by addition of hydrochloric acid and directly flown through the resin column for NI-1 and NI-2. In case of NI-3 and NI-4, the acidified filtered sample was firstly filtered through 0.45 μm filter and then was run through the resin column. The first 20 mL of eluate from the resin was discarded and then the eluate was collected. The eluate was named as “after DOM separation”.

2.3. Measurements

2.3.1. Physiochemical parameters of the leachate samples. Measurements of pH, conductivity, dissolved oxygen (DO) and oxidation-reduction potential (ORP) were carried out at each sampling occasion in the laboratory within 24 hours using Multifunction portable meter HQ40D (HACH, Loveland, USA). Biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total phosphorus (T-P) data were kindly provided by Prof. Soda, Ritsumeikan University and Dr. Hang, Vietnam Japan University. Total nitrogen (T-N) and ammonia nitrogen (NH₄-N) were measured for NI-1 and NI-2 at Kyoto University. T-N was measured by persulfate digestion followed by UV measurement and NH₄-N was measured using AutoAnalyzer II (Technicon - SEAL, UK).

2.3.2. Metal analysis. The leachate samples (2mL) were mixed with 5mL acids HNO₃ (60%) and 1mL HCl (35%) then digested for 2 hours by High-Performance Microwave Digestion System (ETHOS One; Milestone, Sorisole, Italy). The digested sample was filtrated using 1 μm pore size filter before injection in the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Yttrium was used as an internal standard for ICPMS measurement. ICP-MS (X-series 2; Thermo Fisher Scientific, Massachusetts, USA) was used to measure Mn, Ni, Cu and As with the m/z ratio of 55, 60, 65, 75 respectively. ICP-AES (IRIS Intrepid II; Thermo Electron, Massachusetts, USA) was used to measure Al, Fe, Ca, and Mg.

2.3.3. Fluorescence spectroscopy analyses by three-dimensional excitation-emission matrix. The excitation-emission matrix (EEM) was measured using Fluorescence Spectrophotometer F-7000 (Hitachi, Tokyo, Japan). All samples were diluted at the ratio of 1/20. Both excitation and detection of emission fluorescence were scanned from the wavelength 200 to 800 nm with speed of 60000nm/min at slit width 5nm for both excitation and emission. The spectrometer used a xenon excitation source and 1-cm cuvette, S/N condition was 800RMS.

3. Results and discussion

3.1. Physico-chemical parameters of in influent leachate samples

Table 1 shows the quality of influent landfill leachate of 4 samples. The pH ranged from 8.4 - 8.7, showing weak basic. The results are consistent with findings published by other authors [19], [20], [21]. Alkaline environment indicates that the leachate of Nam Son landfill has completed the acidification phase and is in the methanogenic phase. This is reasonable because Nam Son landfill is old and has the age of 19 years. Old leachate from the methanogenic phase is dominated by refractory compounds and the lower concentration of volatile fatty acids (VFAs). This is due to their conversion into CH₄ and CO₂ as the final products of the second fermentation. Stabilized leachate color becomes dark brown with the malodorous smell, because of the appearance of the high content of humic substances including humic acid and fulvic acid compounds. All the landfill leachate samples had low DO (< 0.5mg/L). The DO result indicates an anaerobic condition. This is also verified by the negative ORP of the samples (<- 340 mV).

Table 1. Physico-chemical parameters of influent landfill leachate

Parameter	NI-1	NI-2	NI-3	NI-4
pH	8.6	8.7	8.4	8.6
Conductivity (mS/cm)	11	12	-	17
DO (mg/L)	<0.5	<0.5	<0.5	<0.5
ORP (mg/L)	-368	-394	-	-342
BOD (mg/L)*	330	469	960	-
COD (mg/L)*	-	1400	2000	-
BOD/COD*	-	0.40	0.46	-
T-N (mg/L)	460	560	-	-
T-P (mg/L)	-	15.3	15.1	-
NH ₄ -N (mg/L)	59	59	80	-

*Those data were provided from Prof. Soda and Dr. Hang.

COD ranges from 1400 - 2000 mg/L. BOD ranges from 330 to 960 mg / L. BOD / COD ratio fluctuates from 0.40 -0.46, which is lower than that of the young landfill (0.5 -0.8), but relatively high compared to older burial sites (0.1 - 0.2). Therefore, Nam Son leachate can be effectively treated by biological treatment. T-N concentration ranges from 460 - 560. NH₄- N concentration ranges from 59 - 80 mg/L. T-P concentration is around 15mg/L. The sample leachate was not discharged directly but treated to improve water quality. Therefore, the effluent quality standard is not applied to these values. However, they were compared to the standard limit for the B1 of QCVN25: 2009/BTNMT. The standard limit of COD, BOD, T-N and NH₄ - N are 400mg / L, 100mg / L, 60mg / L and 25mg/ L, respectively. The water quality parameters of the leachate samples were significantly higher than the standards. Moreover, the standard limit of T-P for the C of QCVN24: 2009/BTNMT is 6 mg/ L. The T-P in the sample was also higher than it.

3.2. Metal analysis and size distribution

3.2.1. Metal concentration in raw leachate samples. Table 2 shows the concentration of 8 elements including Al, Fe, Ca, Mg, Mn, Ni, Cu and As in the leachate samples for 4 different sampling times. In general, the concentration of the 8 elements was different and most elements varied according to the

time of sampling. It is clear that Mg, Ca showed the highest concentrations (50 - 260 mg/L), which is and followed by concentration of Fe and Al with 5 – 12 mg/L for Fe and 0.6 -3 mg/L for Al. Mn, Ni, As showed lower concentrations (0.01 – 0.2 mg/L) and Cu showed the lowest concentrations around 0.01mg/L for 4 measuring times.

Table 2. Metal concentrations of influent leachate samples. mg/L

Sample	Al	Fe	Ca	Mg	Mn	Ni	Cu	As
NI-1	2.4	6.8	109	212	0.05	0.15	0.01	0.16
NI-2	3.5	12.0	52	230	0.12	0.16	0.01	0.15
NI-3	0.6	5.4	265	188	0.01	0.02	0.01	0.02
NI-4	1.2	6.2	123	218	0.01	0.02	0.01	0.03

3.2.2. The percentages of different fractions among metals. From empirical observation, 4 different pore size filter papers including 5, 1, 0.45, and 0.1 μm were used to separate different fractions at first. However, sometimes the cake layer was formed during filtration, and thus affecting the concentration of heavy metal. Then 1 μm glass fiber filter (GS-25) was decided to be used for the separation of the particulate fraction. This separation is similar to the separation of suspended solids from dissolved matter widely used in environmental engineering procedure (Standard method, JIS, 2016)

The heavy metal in leachate samples were divided into 3 fractions by filtration and separation of DOM such as 1) Particulate (larger than 1 μm), 2) Dissolved organic (smaller than 1 μm and adsorbed on DAX 8 resin) and 3) Dissolved inorganic (smaller than 1 μm and going through DAX 8 resin = after DOM separation). The amounts of 3 fractions of heavy metals in leachate samples were estimated as follows:

- 1) Particulate: (Original sample) - (passing through 1 μm filter)
- 2) Dissolved inorganic: (after DOM separation)
- 3) Dissolved organic: (passing through 1 μm filter) - (after DOM separation)

Table 3 shows the percentages of 3 fractions for different metals in 4 samples. The particle fraction, which is retained on the surface of the filter medium, is calculated by the difference between the original sample and filtrate sample after passing through 1 μm filter. It matches the research in [22] pointing out the size to distinguish dissolved and particulate matter is not rigidly determined, ranging from 0.001 to 1 μm because it depends on some conditions such as filter load, leachate properties, the pressure difference across the filter, area of filter surface, particle shape, size, compressibility of solid. During filtration, the suspended solid materials build up a filter bed on the filter medium and may disturb filtration; this is referred to as the filter cake layer affecting the filtration process [23]. It is clear that the distribution of the heavy metals between the different size-fractions includes particle, dissolved organic and dissolved inorganic showed significantly large variations. Especially the percentage of particle fraction of each metal is significantly different among different sampling times.

Table 3. The percentages of different fractions among metals

Sample	Fraction (%)	Al	Fe	Ca	Mg	Mn	Ni	Cu	As
NI-1	Particle	100	25	77	6	74	3	6	6
	Dissolved organic	0	35	0	0	5	2	0	8
	Dissolved inorganic	0	40	23	94	21	95	94	86
	Sum	100	100	100	100	100	100	100	100
NI-2	Particle	100	38	12	1	19	0	0	0
	Dissolved organic	0	24	5	0	8	66	52	1
	Dissolved inorganic	0	38	83	99	74	34	48	99
	Sum	100	100	100	100	100	100	100	100
NI-3	Particle	0	0	0	0	0	6	75	0
	Dissolved organic	26	5	3	0	2	39	1	31
	Dissolved inorganic	74	95	97	100	98	55	24	69
	Sum	100	100	100	100	100	100	100	100
NI-4	Particle	46	8	0	0	65	7	61	1
	Dissolved organic	14	26	16	0	7	46	26	16
	Dissolved inorganic	40	66	84	100	28	47	13	83
	Sum	100	100	100	100	100	100	100	100
Average	Particle	62	18	22	2	39	4	35	2
	Dissolved organic	10	22	6	0	5	38	20	14
	Dissolved inorganic	28	60	72	98	55	58	45	84
	Sum	100	100	100	100	100	100	100	100
Standard deviation	Particle	48.2	17.0	37.1	2.7	35.8	3.0	37.8	3.2
	Dissolved organic	12.7	12.6	6.9	0.2	2.8	27.0	24.6	12.9
	Dissolved inorganic	35.5	26.8	33.4	2.7	37.2	26.4	35.6	12.3
	Sum	100	100	100	100	100	100	100	100
Variation (SD/Average)	Particle	0.78	0.95	1.66	1.64	0.91	0.76	1.06	1.79
	Dissolved organic	1.26	0.56	1.17	0.48	0.51	0.70	1.24	0.93
	Dissolved inorganic	1.25	0.45	0.47	0.03	0.68	0.46	0.80	0.15
	Sum	100	100	100	100	100	100	100	100

It is noticeable that the percentage of different fractions of Al was variable among different sampling times. For the first time and second time, the percentage of the particle fraction of Al accounted for 100% whereas, for the third time, Al did not exist in the particle fraction. For the fourth time, Al was fractionated into three fractions: 46% particle, 14% dissolved organic and 40% dissolved inorganic fraction. This indicates that the existence of Al among different fractions in landfill leachate

was influenced by environmental conditions, the content of aluminum in the soil, seasonal precipitation change. The dissolution of Al into the aqueous environment primarily depends on the pH and temperatures of solutions. While Al can dissolve well in acid and alkaline conditions, it is insoluble in a neutral environment. Time may influence the detachment of particles and colloids or dissolved matter and thereby affecting the heavy metal content of the leachate sample.

Figure 1 illustrates the average percentage of the metals in the different fractions. The results of analyses performed on the leachates suggest that most of the metals were concentrated in dissolved inorganic matter corresponding to the green bar on average. The percentage of the dissolved inorganic fraction of most of the elements was high accounting for 30 to 98 % total concentration, in which Mg in dissolved inorganic fraction was most dominant compared to other metals. For complexation between metals with dissolved organic matter, it varied but still presented in significant parts of total concentrations for Fe, Cu, Ni, As. The highest percentage of dissolved organic fraction was for Ni (38%) and followed by Fe (22%), Cu (20%) and As (14%). The Cu result showed similar to previous studies such as Jencen and Christensen (1999) and Claret *et al.* (2011) reporting 20-60% and more than 90%, respectively.

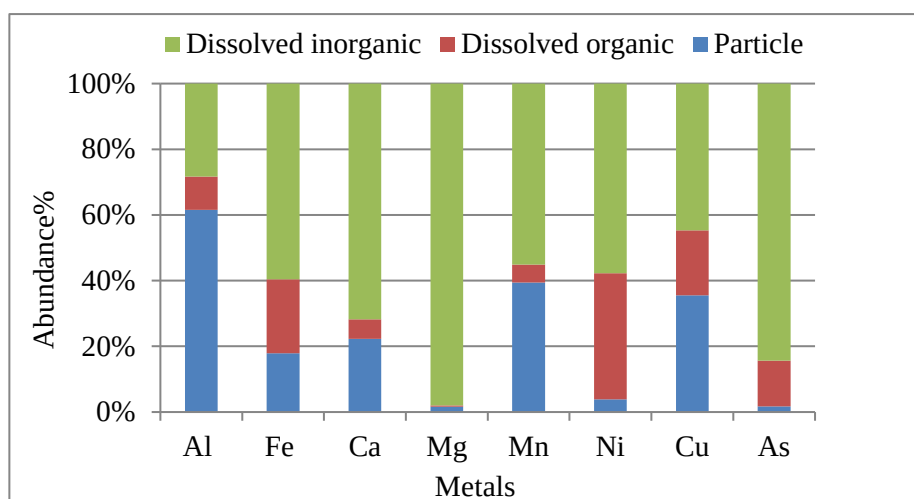


Figure 1. Average percentages of the metals in the different fractions

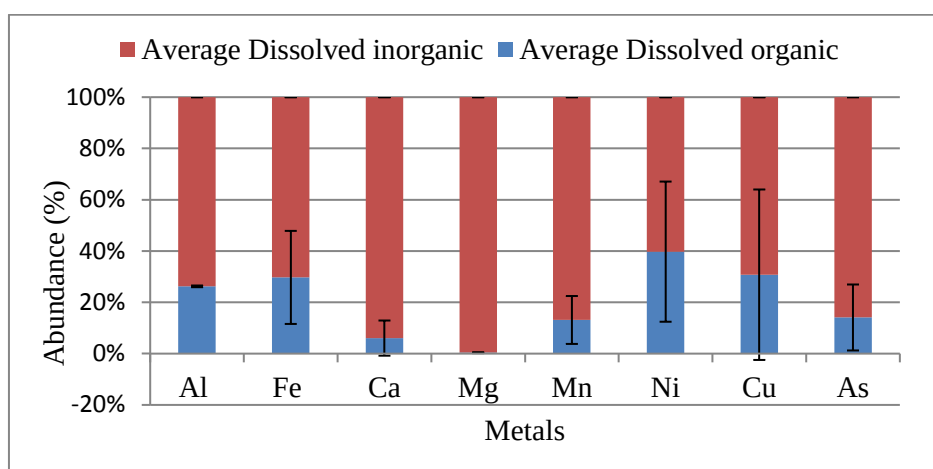
Most of Al fraction presented in particle fraction 62% on average, this result is suitable with that of Wu *et al.* (2011) showing that 99-100% of Al was found in the particulate/colloidal matter > 0.45 μm . The percentages of particulate fractions for Fe, Ca, Mn, Cu were 18-39%. With the lowest percentage, particle fractions accounted for less than 5% total concentration for Mg, Ni, As.

3.2.3. The percentages of fractions in the dissolved matter. Table 4 shows the percentages of metals in organic and inorganic forms in the dissolved fraction. It is obvious that the deviations among samples are quite small. The concentration of metals in particulate fraction changed significantly by the time from in August to March, whereas the dissolved fraction was more stable. In near future, more samples will be collected to compare the difference of heavy metals' profile in the wet and dry seasons because the precipitation will considerably affect heavy metal behaviors in the environment.

Table 4. Percentage of the dissolved organic and dissolved inorganic fraction

Sample	Fractions %	Al	Fe	Ca	Mg	Mn	Ni	Cu	As
NI-1	Dissolved organic		47	0	0	20	2	0	8
	Dissolved inorganic		53	100	100	80	98	100	92
	Sum		100	100	100	100	100	100	100
NI-2	Dissolved organic		39	6	0	9	66	52	1
	Dissolved inorganic		61	94	100	91	34	48	99
	Sum		100	100	100	100	100	100	100
NI-3	Dissolved organic	26	5	3	0	2	41	5	31
	Dissolved inorganic	74	95	97	100	98	59	95	69
	Sum	100	100	100	100	100	100	100	100
NI-4	Dissolved organic	26	28	16	0	21	50	66	16
	Dissolved inorganic	74	72	84	100	79	50	34	84
	Sum	100	100	100	100	100	100	100	100
Average	Dissolved organic	26	30	6	0	13	40	31	14
	Dissolved inorganic	74	70	94	100	87	60	69	86
	Sum	100	100	100	100	100	100	100	100
SD	Dissolved organic	0.3	18.1	6.9	0.2	9.3	27.3	33.2	12.9
	Dissolved inorganic	0.3	18.1	6.9	0.2	9.3	27.3	33.2	12.9
Variation	(SD / Average)	0.004	0.258	0.073	0.002	0.108	0.454	0.48	0.15

The average percentages of dissolved organic and dissolved inorganic fractions are shown in **Figure 2**. Dissolved inorganic fraction constitutes more than 60% of the dissolved fraction of all the metals. Fe, Ni, Cu are found in the association with organic matter in 30 – 40% of the dissolved fractions. It is followed by Al, As and Mn. The percentages of dissolved organic fraction are low for Ca and Mg. Nevertheless, at high raw concentration, Mg and Ca have the possibility to compete with divalent cations for complexation with organic matter.

**Figure 2.** Average percentages of dissolved inorganic and organic fractions

3.3. DOM characterization

Three-dimensional Excitation-Emission Matrix was used as a crucial tool in fingerprinting the main components of landfill leachate, especially dissolved organic matter. These following figures are fluorescent spectra of 4 samples divided into two groups. The first group is the sample NI-1-5 and NI-2-5 before using DAX 8 resin to adsorb organic matter and the second one is the sample NI-1-6 and NI-2-6 after using DAX 8 resin. Each group consists of the sample taken in August and the rest one taken in November. In general, the signal of November sample looked more condensed compared to that of August sample. It can be explained by the fact that the organic matter content in the leachate sample collected in November was higher than August sample. Total nitrogen and BOD in November were also higher than those of sample taken in August.

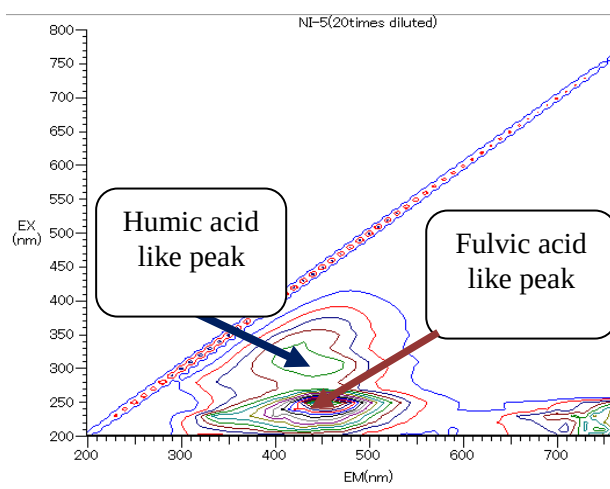


Figure 3. EEMs Fluorescence spectra of sample NI-1 after 0.1 μ m filtration

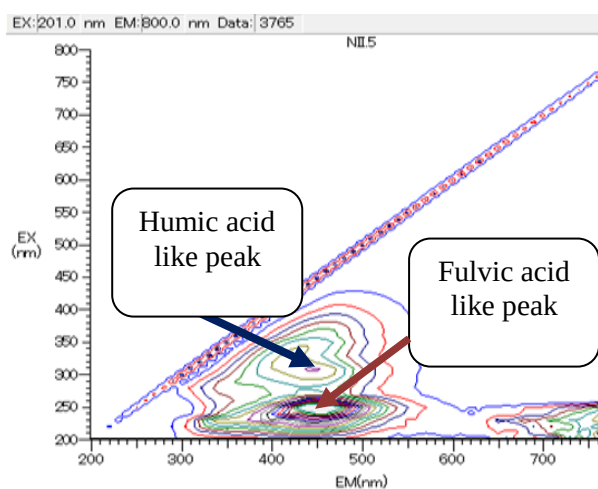


Figure 4. EEMs Fluorescence spectra of sample NI-2 after 0.1 μ m filtration

In **Figure 3** and **Figure 4**, it is obvious that the leachate showed the existence of humic substances with the presence of humic acid and fulvic acid. Specifically, one is the fluorescent peak showing λ_{Ex} around 250nm and λ_{Em} from 400 -500 nm which was considered as fulvic acid. Another peak presented at λ_{Ex} around 300nm and λ_{Em} from 400 -500nm, which was attributed to humic acid. These results are consistent with those of previous studies about prominent organic matter in the landfill leachate, It was reported that the peaks at λ_{Ex} = 220-270nm and λ_{Em} = 380-550 represented for fulvic acid-like fraction [24, 25, 17] while was humic acid-like fractions could be found at the peaks λ_{Ex} = 300-370nm and λ_{Em} = 400-500 nm [26, 27]. The existence of fulvic-like and humic-like components in DOM at Ex/Em of 200-250 nm/ 380-550 nm and 250 - 400 nm/ 380-550 nm respectively were also reported in [16, 28]. This study also agrees with another research indicating that the fulvic-like component in composting leachates can be detected at the peaks λ_{Ex} = 240-270 nm and λ_{Em} = 410-440 nm [29].

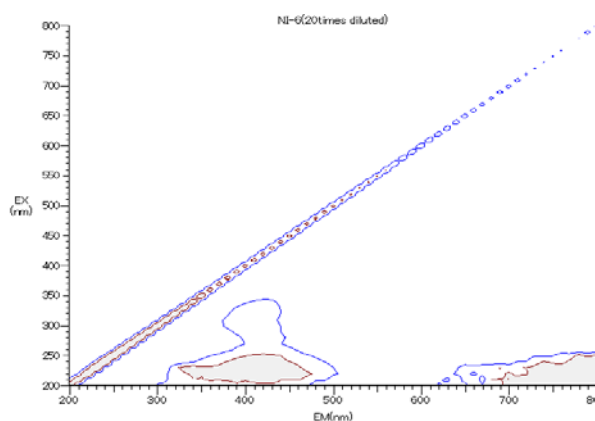


Figure 5. EEMs Fluorescence spectra of sample NI-1-6

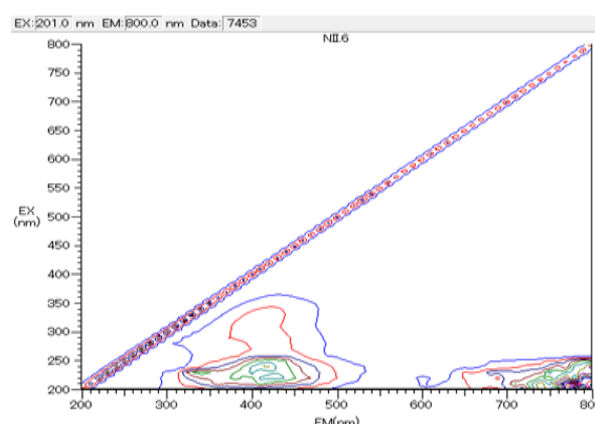


Figure 6. EEMs Fluorescence spectra of sample NI-2-6

In **Figure 5** and **Figure 6**, the humic substances were absent in the inorganic fraction. They were contained in the dissolved organic fraction. That was why there was no fluorescence peak of humic substances or fulvic substances on the spectra. Therefore, in the organic separation process, humic and fulvic substances were removed by acidification, filtration and DAX adsorption processes. This indicated that most components of organic matter are humic substances, which were non-biodegradable substances in the leachate samples and were seen on the spectra by using EEMs. It is considered that fluorescence can be used as a rapid and sensitive tool to estimate the organic matter composition of landfill leachate. From the result of different fractions of heavy metals and other elements as well as the footprint of organic matter compound, it can be concluded that humic substances in the leachate have a strong interaction with metals in the discharged water environment.

3.4. Effect of DOM on heavy metal speciation in leachate

The composition of landfill leachate at Nam Son landfill was complicated and it varied by sampling time. Humic substance (HS) in the leachate including humic acids (HA) and fulvic acids (FA) may interact with ions such as Mg^{2+} , Ca^{2+} , Fe^{2+} , and Fe^{3+} and form chelate complexes [9]. In this research, the complexes, which were formed by the combination of dissolved organic matter and Fe, Ni, Cu, were found to be significant. Other metals like Ca, Mg at high concentrations also compete with these heavy metals to combine with organic matter in the leachate. HS with its heterogeneity and mobility plays a crucial role in conveying metals from the leachate to the environment. Therefore, DOM-metals ions interaction may lead to difficulty in the treatment of metal-rich wastewater. Therefore, understanding the speciation and behaviors of heavy metals and its combination with organic matter will enhance the treatment efficiency, and thus mitigating adverse impacts of heavy metals on the environment. For example, the dissolved organic matter may interact with coagulants that contain Fe, Ca, Al ions. So, it will affect the coagulant dose for removing turbidity. Since Nam Son is old landfill, which is characterized by the proliferation of non-biodegradable organic matter, physical and chemical methods are highly recommended to enhance treatment performance [30]. However, further investigation is needed for further research.

4. Conclusions

The present research has determined the speciation of heavy metals in landfill leachate by using physical fractionation (particulate and dissolved fraction); separated the dissolved inorganic fraction from dissolved organic fraction, and investigated the association with organic matter of heavy metal species. The main findings can be summarized as follows:

In order to fractionate heavy metals, it is important to choose screen filters with well-defined, appropriate size to minimize sorption to the filters and desorption from the filters and cake layer

filtration. Using 1 μm glass fiber filter was enough to separate metals into particulate and dissolved fractions.

The main parts of the heavy metals in landfill leachate were present in dissolved inorganic fraction and complexes with humic substances, including humic acid and fulvic acid. The humic substances formed chelate with most metals, especially Fe, Cu, Ni. The presence of humic substance may affect coagulation process used in leachate treatment.

The distribution of the particulate fractions was significantly varied among different heavy metals. In contrast, the distribution of dissolved inorganic matter, dissolved organic matter was more comparable among different heavy metals.

Acknowledgments

This work was supported by the Master's Program in Environmental Engineering, Vietnam Japan University - VNU, Kyoto University, and Ritsumeikan University. The authors also wish to thank Prof. Soda Satoshi from Ritsumeikan University for providing help with BOD and EEMs measurements.

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