

Study on behavior of heavy metals in semi-aerobic landfill sites of municipal solid waste incinerator residues

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2020

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**都市ごみ焼却残渣の準好気性埋立地における
重金属類の挙動に関する研究**

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2020

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ABSTRACT

Incineration is becoming popular for municipal solid wastes treatment in many countries, therefor the disposal of incinerator residues will attract more and more attention. Currently, the major method is landfilling, while researches related to the utilization of incineration residues are becoming popular. To estimate the environmental risk and potential resources in landfills, we have to investigate closed and under operation landfill sites of incinerator residues. Heavy metal has been confirmed to be abundant in the incinerator residues, which should be paid serious attention to. To better understand the general behavior of heavy metals in semi-aerobic landfills of incinerator residues, we conducted a field sampling investigation of two Japanese landfill sites. We also collect data from the local landfills' administrators for further analysis in this research. The field samples were tested by several methods to identify the composition and speciation distribution. Together, with the data collected from the local landfills' administrators, the full-set of data were used for a general total mass balance analysis of several heavy metals. The content of heavy metals in vertical landfill layers varies and the difference between incinerator residues and the other waste is significant. The extracted incinerator residues still could pass the Japanese leaching test. However, the speciation analysis result suggests a potential risk under acid condition, which needs to be paid more attention to by operators of the landfills. The result of mass balance suggested that heavy metals in incinerator residues released through the leachate slightly in semi-aerobic landfill after long-term landfilling (around 40 years). Cu, Pb, Cd, and Zn present a higher potential risk than Cr and Ni.

Keywords: *Incinerator residues, semi-aerobic landfill, heavy metals, potential environmental risk, mass balance.*

Introduction

The global municipal solid waste (MSW) generation has reached 2.01 billion tons in 2016, and 36.7% of the waste is landfilled. A landfill has been considered as the MSW treatment for a long history. The early landfill was simply considered an improvement of open dump because the odor, flies, rats and other bad effects from the waste caused the serious environmental problem. After human being's life was heavily affected by open dumping waste, they tried to bury the waste by using natural soil or other material to isolate waste to the environment. But the rainfall could reach the waste and react with the waste in

anaerobic condition, the waste generates methane, H_2S and leachate contain a high concentration of toxic matters. The gas could escape through the gaps between solid particles, and leachate could reach the groundwater and be transported for a long distance. Therefore, more strict technology was introduced to control the by-products from landfill sites, to prevent them from releasing from the landfill area. Lining system and gas, leachate collection system was applied at the end of 20 centuries, at that time the technology we called sanitary landfill has been widely accepted and adopted worldwide. In several developed countries, the small nation's land space makes people realize that it's hard to build new landfill spaces. On one hand, to reduce the final landfill waste became very important. On the other hand, the decreasing of unrenewable natural material became a hot topic, "Sustainable" started to be a popular concept and spread fast. Intermediate treatment such as incineration and composting was adopted to reduce the landfill waste amount and recover energy from the waste. What landfill has to take care of is the residues after those treatments.

The landfill technology usually buries waste in sealed space, which is an anaerobic condition. However, a semi-aerobic type landfill is popular in Japan. In this type of landfill, the air is supplied spontaneously through the leachate collection pipe that has a bigger diameter than regular ones. Thus, the leachate collection pipe has two functions, collecting the leachate and intake of the air. This method is adopted through Japan right after the first semi-aerobic landfill was constructed in Japan in 1975. This method also introduces the evolution of the concept of "landfill". A landfill starts to become a purification zone, not only the storage of waste. The faster the waste reaches the final storage quality, the less economic burden and potential risk to our environment.

Incineration has been considered as the primary treatment for MSW since the 1960s in Japan. By-products from incineration, bottom ash (BA) and fly ash (FA), started to be landfilled since then. As the development of the society, the waste sending to landfill site has become only incinerator residues and incombustible waste, and the incinerator residues account for 90% by 2016. Therefore, the landfills in Japan could be considered as monofills of incinerator residues with such a high proportion of incinerator residues. And the semi-aerobic type makes it more unique in the world. Heavy metals are reported high concentrated in the MSW incinerator BA and FA, and they are a big threat to public health and the surrounding environment. However, there are limited researches associated with studying the behavior of heavy metals in semi-aerobic incinerator residues landfills. To estimate the risk of heavy metals from this type landfill, we extraceted samples from two landfills in Japan. To better understand the general behavior of heavy metals, we collected data from landfill administrators to compare with experimental data. After several tests, we would like to classify the risk level of current landfills, and propose comments on constructing sustainable landfill strategy.

Materials and Methods

Two landfill sites (A and B) in one Japanese city have been selected as the target subjects. They are both typical Japanese type landfill, which is semi-aerobic incinerator residues landfill. We extracted a total of nine core samples from these two landfill sites to profile the current waste layers in the landfill area. More detailed information could be found in chapter 3.

Sample pretreatment includes the drying process (wind, heat, and freeze), sieving, and milling. The drying method is chosen according to the later analysis. More detailed information could be found in Chapters 4, 5 and 6. We used a 2 mm sieve to isolate fine particles from coarser ones. We also picked up the glass, ceramics, metals, plastic, and bricks. The fine particles were ground gently using a ceramic pestle and mortar. Composition analysis was conducted by x-ray fluorescence (XRF-1700, Shimadzu) and a carbon-hydrogen–nitrogen (CHN) detector (MT-2, Yanaco). To calculate total heavy metals content, samples were digested using a microwave digestion system (Ethos 1, Milestone), and the digestion solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP IRIS Intrepid Duo Thermo ELECTRON, Japan) and inductively coupled plasma mass spectroscopy (ICP-MS, X series 2Xt, Thermo Fisher Scientific, USA). The leaching test was performed on the landfill waste samples using the Japanese Leaching Test-13 (JLT-13). We used ultra-pure water to extract heavy metals from samples at a ratio of 1:10 (g/mL). The sequential extraction procedure was conducted to selected samples. Detailed information could be found in chapter 5. We also checked several samples XRD result to identify the crystal components. SEM-EDS was conducted to check the heavy metal chemicals in the samples. X-ray absorption fine structure of Pb and Cu has been measured for several samples to identify the species.

We asked for the historic monitor data from local landfill administrators. We selected and organized the data for further analysis. We set up the mass balance model based on the works of literature.

Results and Discussion

The general content of heavy metals has been detected. The contents of these heavy metals followed the order of $Zn > Cu \geq Pb > Cr > Ni > Cd$. Generally, the waste layer samples had much higher contents of heavy metals than did the cover soil, soil layer, and clay layer samples. Figure 1 shows the vertical distribution of heavy metal content in one of the core samples. The differences between the no-waste layer and the waste layer are significant. It's also concluded that the heavy metal content is still high in the landfill, and needs to be paid more attention.

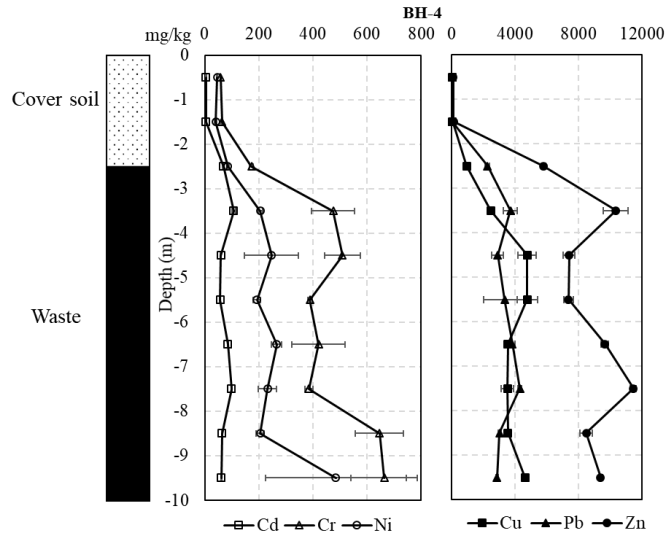


Figure 1. Vertical distribution of the heavy metals in BH4. It's also concluded that the heavy metal content is still high in the landfill, and needs to be paid more attention.

A PCA analysis based on the element's composition has been conducted to figure out differences between the samples. Figure 2 shows the PCA result. The differences between the two landfill sites are very clear. Cl and S contribute the most between fresh incinerator residues and aged residues. The long-time landfill will make Cl and S inside incinerator residues decrease significantly. We also selected the samples for sequential chemical extraction procedure based on the result.

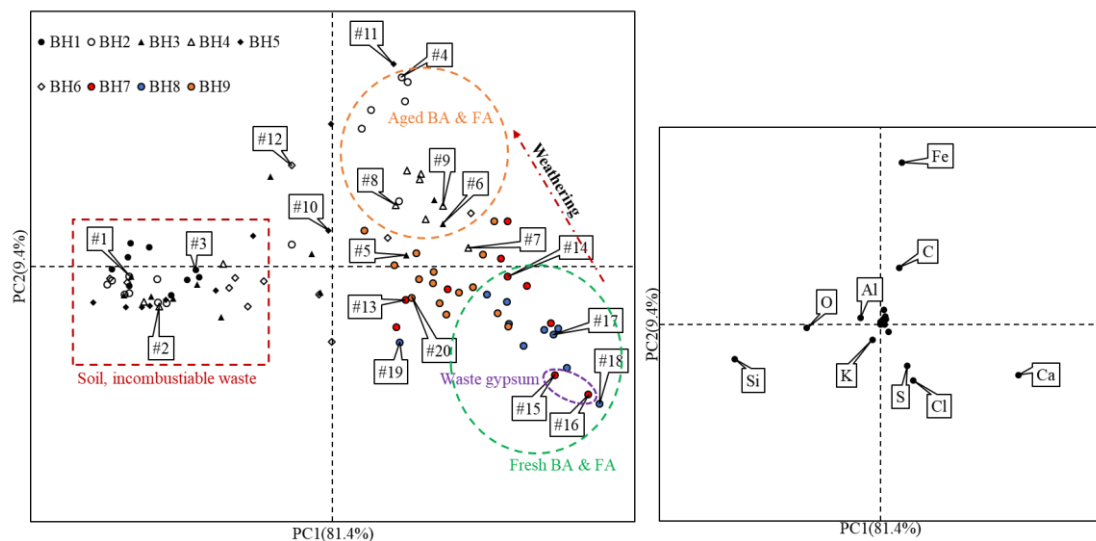


Figure 2. PCA analysis based on the elements' composition.

The sequential extraction result could be used to assess the potential environmental risk from the heavy metals, even though all the samples have passed the Japanese leaching test. The high ratio of the acid-extractable fraction of Cd, Pb, Zn, and Cu suggested the high potential risk level from the landfilled incinerator residues. There's no significant correlation between landfill waste age and speciation distribution, it's suggested that the speciation distribution according to sequential extraction procedure didn't change so much. The XAFS experiment result suggested the Cu and Pb might have changed the chemical species after landfill.

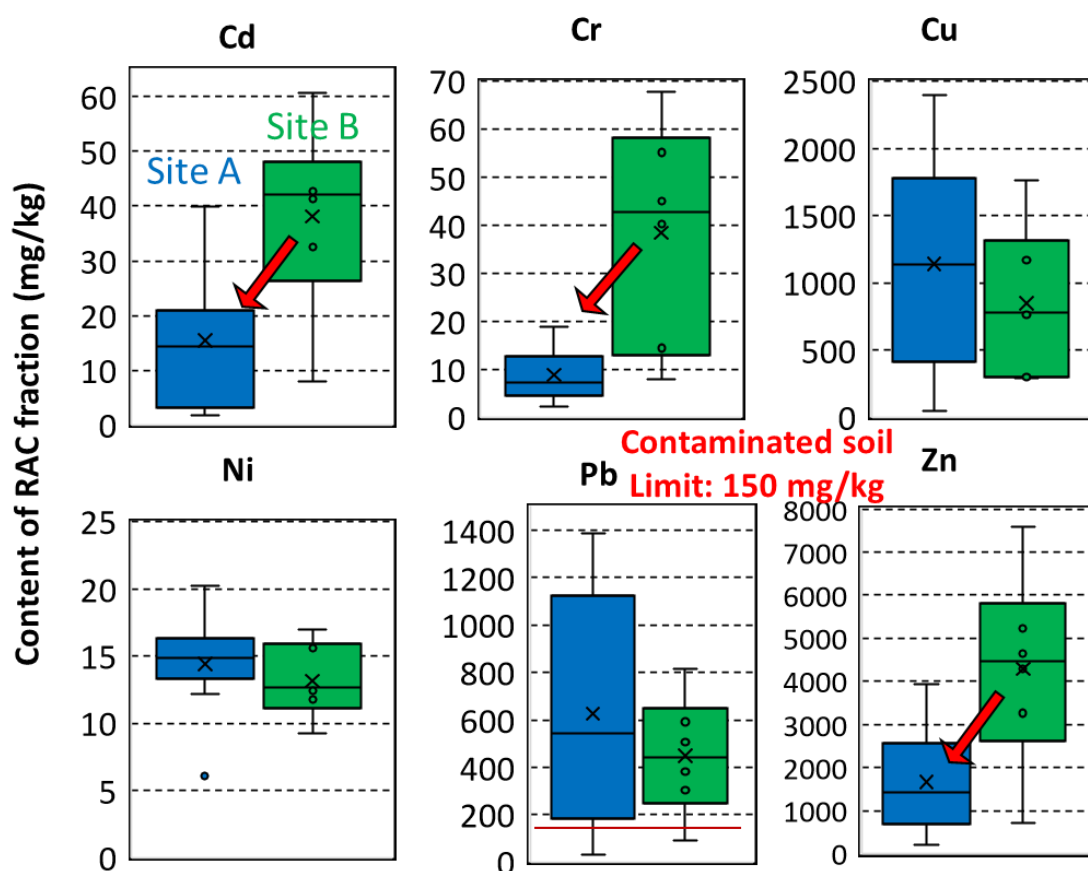


Figure 3. Potential environmental risk assessment by RAC content.

Table 1 Mass balance result of this study

Waste	Landfill (1975-2015), Japan		
	Incinerator residues with incombustible waste		
	Input (t)	Output (kg)	Leaching rate (%)
Cd	83	3.5	0.0042
Pb	5700	55	0.0010
Cu	14000	57	0.0004
Zn	16000	300	0.0019
Hg	6.6	1.5	0.022
Cr	600	40	0.0065

The mass balance result is shown in Table 1. The total input mass of heavy metal and released mass from the leachate have been calculated. The leaching rates of heavy metals over an almost 40-year period (1975–2015) were 0.0042% (Cd), 0.001% (Pb), 0.0004% (Cu), 0.0019% (Zn), 0.022% (Hg) and 0.0065% (Cr), respectively. Very limited heavy metals have escaped from the landfill, and it's believed the releasing will not change so much, while the pH is still high in the landfill area. Some results from this part suggested the application of chelate reagent is a success. More similar works should be conducted in the future.

Conclusion

In this study, we investigated the typical Japanese landfill site by sampling core samples from two landfill sites. We collected the data of landfill sites from the landfill administrators for full-scale evaluation on the behavior of heavy metals in landfilled incinerator residues. And we tried to use field sample data combined with historic monitor data to analyze the mass balance of several heavy metals. The results suggested the landfilled incinerator residues from both sites had very high heavy metal content, and that means the residues still present a huge potential environmental risk as the source of heavy metals. Even though the leaching test presented no samples exceed the limits of Japanese government regulation, the speciation analysis still implies a high potential hazard level of Pb. The mass balance result suggests a low leaching ratio of heavy metals from the closed landfill site. However, the leaching of heavy metal still happens and will continue. Due to the high potential environmental risk of Pb, the aftercare of the closed landfill should not be terminated under the current situation. Chemical species changing didn't strongly affect the Pb behavior in SEP test, which implies the potential risk will continue for a long time. It's better to consider mining old landfills than terminating the aftercare of old landfills in Japan.

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CHAPTER 1

INTRODUCTION

1.1 Background

While the fast urbanization and the increasing of population, environmental pollution problems have occurred widely all around the world. The pollutants generated from human activities are destroying our living environment. Serious pollutions damage human health and even take human lives. “Minamata disease” and “Itai-Itai disease” are two famous environmental pollution incidents that happened in Japan¹. These incidents were all caused by huge damage from heavy metals to our bodies. The scientists found the heavy metals could accumulate through the food chain in human bodies, however, most of the pollution sources come from human activities. Improperly disposal of heavy metal contained waste plays an important role.

For improving the living environment of human beings, people are trying to study the pollutants and develop the treatment technology for the pollutants. However, complex pollutants make it difficult to find a general way to be treated. The disposal of municipal solid wastes (MSWs) is becoming a great burden to our society from the megacities. The general treatment methods for MSWs are landfill, composting and incineration in most countries²⁻³. Among these methods, the landfill is widely applied because of the lower costs and low technology level, and it could be considered as the final sink for solid wastes. However, the secondary pollution from landfills is more serious because of the concentrated leachate, which contains a very high concentration of organic and inorganic pollutants⁴⁻¹⁰. In addition, landfill requires large land space which is becoming harder and harder to address because of the urban expansion. These adverse facts limit the application of landfill technology, but it’s irreplaceable in the current social system.

“Reduce, reuse and recycle” (3R), a sustainable society concept has been proposed by researchers to establish an environmentally friendly society since the end of the 20th century in Japan¹¹. Figure 1-1 shows a brief material flow cycle in Japanese society. Under the instruction of the “3R” policy, source separation of solid wastes process reduces the number of wastes that need to be disposed of, meanwhile, the recyclable wastes could be reused as products or material. The separated combustible waste will directly be sent to incineration plants in Japan. Recently, the rising awareness of “Waste to Energy (WtE)” encouraged the application of incineration to MSWs¹²⁻¹³, which will be certainly considered by more and more countries in the world. Therefore, incineration technology for MSWs treatment keeps attracting the attention of developed and developing countries currently. The high efficiency of volume reduction and energy recovery from wastes are two major reasons for the utilization of incineration. However, the by-products from incinerators, bottom ash, and fly ash, still need to be handled carefully¹⁴⁻¹⁵.

The bottom ash (BA) mainly contains fewer pollutants than fly ash, it could be recycled as a material for construction purposes. However, some heavy metals (Cu, Cr, and Ni) could be very high content in the BA. Fly ash (FA) is considered as a hazardous material

because of the high content of heavy metals and dioxins, it needs to be pretreated before disposal or recycling. Utilization of incinerator residues (BA and FA) have been widely studied and applied recently all around the world, however, there's still a large number of incinerator residues that were temporarily stored or landfilled in landfill sites. And these landfill sites need to be studied carefully for environmental potential risk assessment. In addition, we have to improve landfill technology and management toward a sustainable society. Furthermore, to estimate the potential resources in one old landfill could benefit future works like landfill mining.

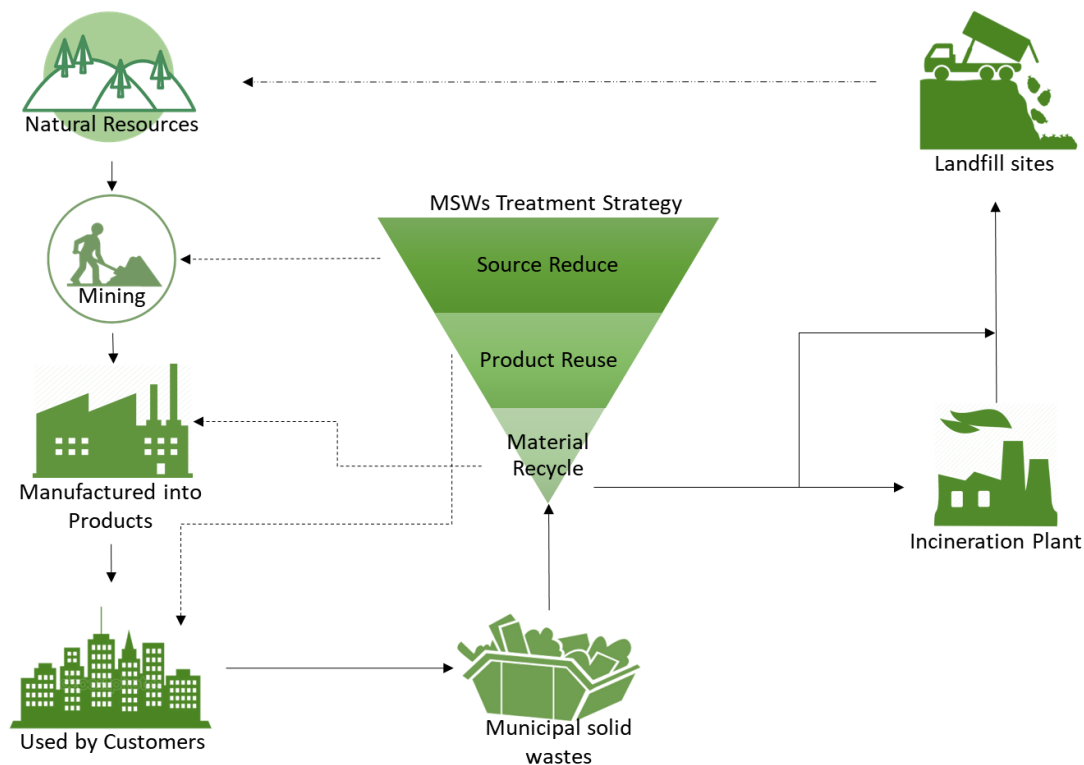


Figure 1-1 Brief social material flow in Japan. (The icons were downloaded from the internet.)

1. 2 Typical Japanese landfill sites

In Japan, the disposal of MSWs starts from open dumping without any control just like the other countries. The most famous open dumping site in the 1950s was “Yume - no - Shima” at Tokyo Bay¹⁶. Serious pollution came from the site waken the awareness of people to find an environmentally friendly way to dispose the MSWs. Because of the limit of land space, Japan needs technology to reduce the number of wastes to be landfilled as much as possible. Therefore, incineration has been widely applied for MSWs treatment since the 1970s, and it became the primary disposal method for MSWs. However, the final disposal of wastes is still the landfill.

In this system, by-products, which contains bottom ash (BA) and fly ash (FA), from incineration were sent to landfill sites mostly. With the increasing proportion of incineration, the landfill received more and more incinerator residues (BA and FA). In addition, Japan stopped to send combustible wastes to landfills. This became one very special feature of a typical Japanese landfill.

With the rising attention to landfill controls, Japan started to set up the guidelines for MSWs landfills. Figure 1-2 presents the development of the guidelines from the 1960s to 2000. The regulations became more and more strictly as the increasing public awareness of the pollution came from landfills. Japanese scholar, Prof. Hanashima started to research the “Semi-aerobic type landfill”¹⁷, and this method spread around the nation quickly because of the high decomposition efficiency of landfill wastes. “Semi-aerobic type landfill” is quite different from the “anaerobic type landfill”, which was widely used around the world, and this was another special feature of a typical Japanese landfill. The difference between “anaerobic” type and “semi-aerobic” type will be described in Chapter 2.

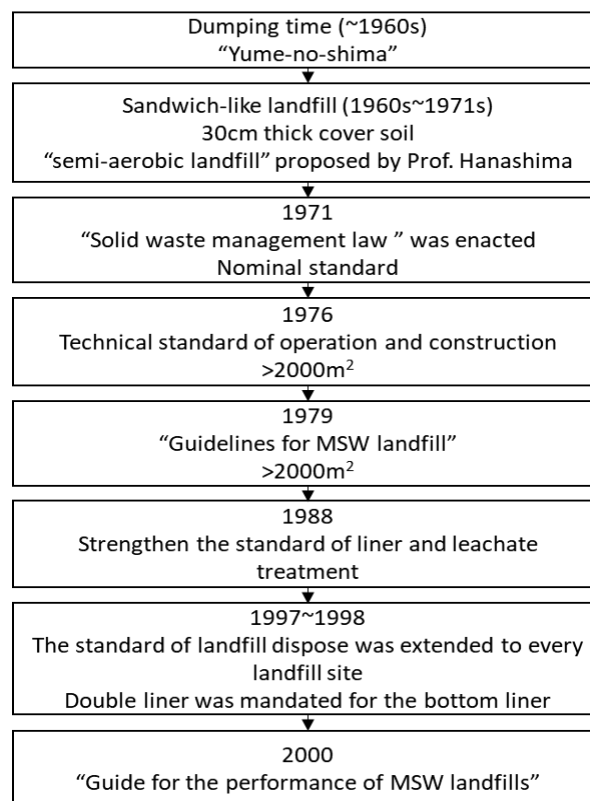


Figure 1-2 The development of the guidelines for MSWs landfill in Japan¹⁷.

These two special features of Japanese landfill sites make them different from any landfill sites in other countries. However, the increasing incineration facilities in other countries lead to a problem to dispose of MSWs incineration BA and FA. Currently, the major method is still landfill. In addition, the “semi-aerobic type landfill” is also accepted by

many developing countries. Therefore, the Japanese type landfill could be a popular type in the near future.

1. 3 Heavy metals in the typical Japanese landfill sites

We concluded two major special features of typical Japanese landfills above, one is the waste composition consists large proportion of incinerator residue¹⁸, some landfills even only have incinerator residues and incombustible waste. Another one is the landfill style is “semi-aerobic” type, it started from Japan and widely conducted in Japan¹⁷. These two special features make typical Japanese landfill different from the landfills from the other countries. Therefore, the study of typical Japanese landfill sites could be considered as studying the incinerator residues behavior under semi-aerobic landfill conditions.

When referring to the incinerator residues, the key points will be focused on the major pollutants in them, which are the high content of heavy metals and dioxins. The incineration process reduces the carbon, hydrogen, sulfur, and nitrogen content of combustible wastes. Those inorganic elements (like heavy metals) left inside bottom ash and fly ash are concentrated because of the loss of organic elements. During the incineration, dioxins likely chemicals could be generated and remain inside the residues. Heavy metals and dioxins are known to be harmful to human health. Different heavy metals cause different diseases to the human body, and dioxins are highly toxic and can cause reproductive and developmental problems, damage the immune system, interfere with hormones and also cause cancer¹⁹⁻²¹. Both of them could pass through the food chain and could accumulate in human bodies. The landfilled incinerator residues are long-term potential pollution sources to the surrounding environment, especially those old closed landfills near the residential area of citizens. The aftercare of one closed landfill is necessary to prevent this kind of risk, however, it’s still unclear to decide when to terminate the aftercare process.

Heavy metals inside incinerator residues have been studied in many countries recently, the total content and speciation distribution have been studied in many cases. Some researchers also tried to study the landfill of incinerator residues; however, the landfill type wasn’t mentioned so much in their reports^{14, 22}. In addition, the reported real cases on monofills for incinerator residues are very limited worldwide. Therefore, it’s important to study the behavior of heavy metals and dioxins in the landfill of incinerator residues. We just focused on the heavy metals in this research.

1. 4 Research purposes

Landfill as the final dispose site of MSWs will be constructed continually all around the world, because the generation of MSWs can’t be avoided. In spite of the increasing

attention to constructing a sustainable society in Japan, there is still a remarkable amount of wastes that need to be landfilled at the end of material flow (Figure 1-1). A closed landfill is a potential pollution source for the environment; therefore, it needs to be monitored and maintained for a certain period of time. The environmental risk from landfill sites needs to be estimated before the termination of aftercare. Recently, the rising attention of landfill mining encourages scholars to evaluate the potential resources of closed landfills, investigation works of this research also could be used to achieve this purpose.

Therefore, in this study, we took samples from two real landfill sites from one city in Japan. Nine boreholes (BHs) were extracted from different parts of these two landfills to investigate the heavy metals content and other characteristics for estimating the potential environmental risk. Also, the potential environmental risk of heavy metals has been estimated through various measurement methods. Furthermore, to better understand the general behavior of heavy metals under semi-aerobic landfill condition, a complete mass-balance of several heavy metals have also been estimated. Finally, the potential resources of heavy metals have been evaluated. All of the works were done for the purposes presented below:

- (1) To estimate the heavy metals' potential hazard level from the current landfill area, the general composition analysis of landfilled samples was conducted by element analysis methods;
- (2) To estimate the potential environmental risk of heavy metals in the future, we conducted various measurements to selected samples to analyze the speciation and species distribution;
- (3) To better understand the general behavior of several heavy metals and salts element in one closed landfill, a general mass balance of heavy metals was estimated;
- (4) Through the works above, we would like to enhance the knowledge in this field and give suggestions to the future design of similar landfills or constructing a sustainable landfill strategy.

1. 5 Thesis structure

This doctoral thesis includes three research contents: 1) the investigation of elements in field samples from two typical Japanese landfill sites; 2) the potential environmental risk assessment of several heavy metals through various measurement methods; 3) a full-scale mass-balance of several heavy metals in one closed landfill. The organization of this thesis could be found in Figure 1-3 below:

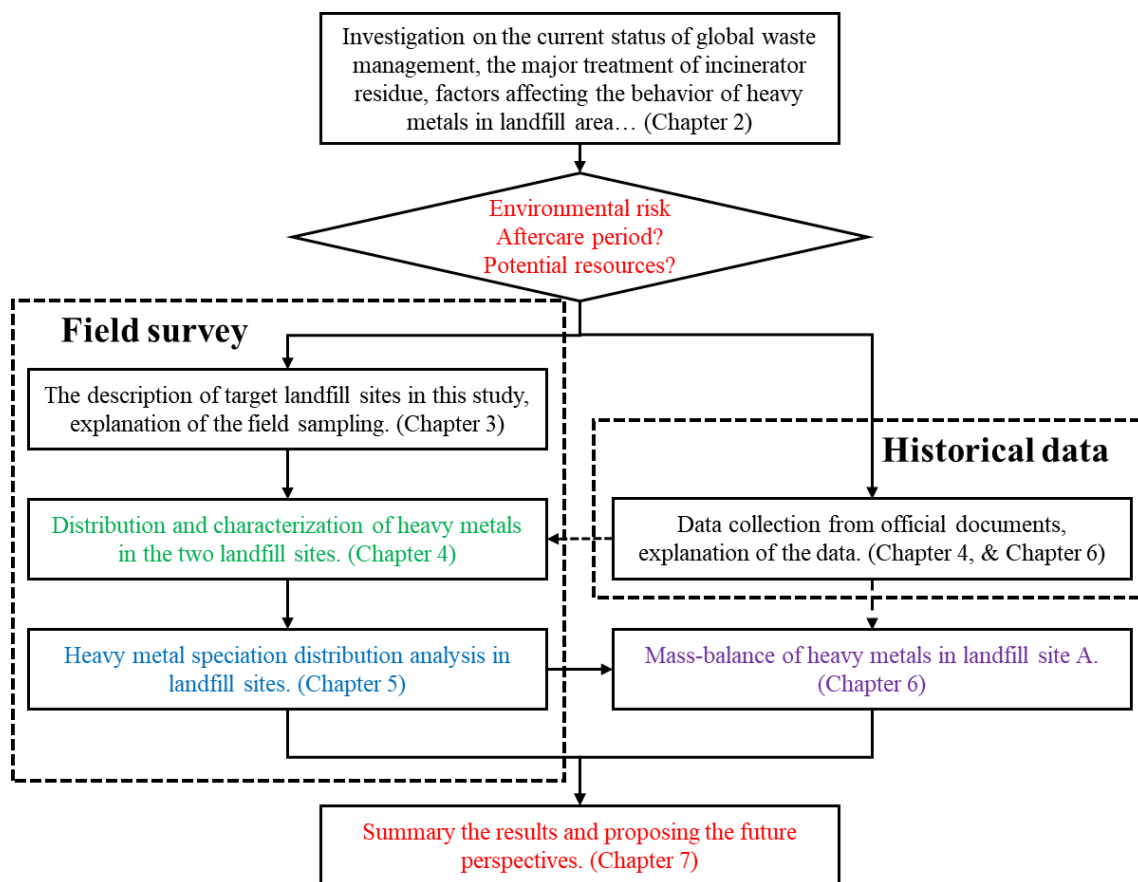


Figure 1-3 The structure of this doctoral thesis.

Chapter 1 mainly explains the definition of “typical Japanese landfill” and points out the two major special features which are different from the landfills from other countries. And this kind of combination (semi-aerobic landfill of incinerator residues) will be popular in the world. Also, Chapter 1 briefly introduced the major purposes of this research.

Chapter 2 is a review of literature related to waste management, the disposal of incinerator residues and landfill technology. Firstly, it presents the current status of global waste management; secondly, the development of landfill technology has been described; thirdly, a worldwide treatment of incinerator residue situation has been presented and discussed; fourthly, the factors could affect the behavior of heavy metals in semi-aerobic landfills and some conclusions of previous studies; at last, the researches related to mass-balance in landfills have been discussed.

Chapter 3 is a detailed description of sampling landfills. In this chapter, basic information including the capacity, geographical environment and weather condition is presented firstly. After that, the landfill waste source of these landfill sites, the incineration plants of this city are described; at last, the sampling process is described.

Chapter 4 presents the lab experiment results of collected samples from these two landfill

sites. The element composition of samples was measured by X-ray fluorescence (XRF-1700, Shimadzu) and a carbon-hydrogen–nitrogen (CHN) detector (MT-2, Yanaco). To analyze total heavy metals content, samples were digested using a microwave digestion system (Ethos 1, Milestone), and the digestion solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP IRIS Intrepid Duo Thermo ELECTRON, Japan) and inductively coupled plasma mass spectroscopy (ICP-MS, X series 2Xt, Thermo Fisher Scientific, USA). The results are analyzed through statistical analysis. Several samples were selected for further estimation based on the statistical analysis results.

Chapter 5 contains the result of the leaching test, the sequential chemical extraction, X-ray absorption fine structure (XAFS) measurement, X-ray diffraction (XRD), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). The results from these measurements are discussed together to find the changing of species of heavy metals under semi-aerobic landfill conditions and evaluate the potential environmental risk in the future.

Chapter 6 explains the process of mass-balance calculation of several heavy metals in the landfill site A. The result is presented and discussed with the field sampling result. The general mass flow of several heavy metals has been presented in this chapter.

Chapter 7 is a summarization of all results from this research. Based on the result, future perspectives are proposed.

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CHAPTER 2

LITERATURE REVIEW

2. 1 Global MSW treatment strategies

A simple “Take-Use-Dump” pathway since ancient times has been used for a long time in human history¹. However, the rapid consumption of natural resources after the industrial revolution caused a serious impact on the environment and our life. On the one hand, it causes environmental pollution accidents when people mistreat the waste generated from human activities. On the other hand, the no-renewable raw natural material is decreasing while the need is growing. Therefore, the principal for waste management has changed since the human being aware of the crisis of natural resources, and that leads to the changing of waste management strategies. Figure 2-1 presents the changing of waste management strategies from a linear passage to a circular approach. The linear strategy has been progressively abandoned in most countries, while it still exists in some developing countries. Nowadays, the circular passage is widely accepted and applied in developed countries, like Germany, the United States, and Japan. Landfill in this strategy is considered as the “Final sink” for MSWs.

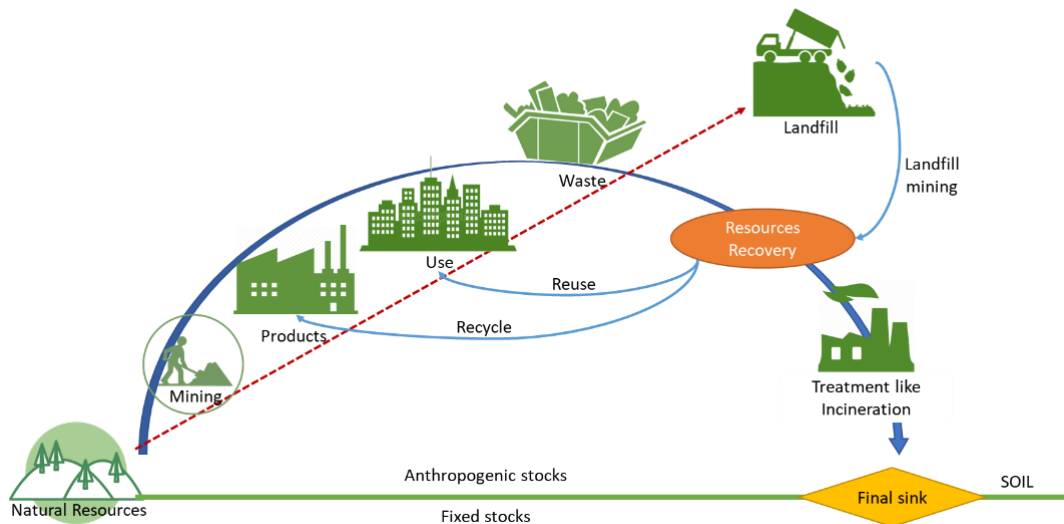


Figure 2-1 Landfill as the final sink in circular waste management strategies in the material's life cycle¹.

Paul Brunner and other experts in the field proposed the concept of “Final sink” to approach a sustainable and environmentally friendly society²⁻⁴. A final sink is designed to hold the waste in order to weaken the mobility of pollutants for more than ten thousand years, therefore, the final sinks do not have any negative impacts on the environment. In addition, residues from these landfills may be recovered in the future. In conclusion, a final sink landfill could be considered as the tomb for products. Even though the strategy has improved, the current global waste management still facing a serious situation.

2. 1. 1 MSW generation

While significant efforts have been done to improving the recycling rate of waste, the municipal solid waste generated from human daily life is still increasing globally. According to the report from the World Bank, the total MSW generation worldwide is 2.01 billion tons in 2016, and it's predicted to reach 3.40 billion tons by 2050⁵. Around 33% of the MSW wasn't managed in an environmentally safe manner. It's also reported that 16% of the world's population from high-income countries generate about 34% of the world's waste. However, when looking forward, the waste generated from low-income countries is expected to increase by more than three times by 2050. Figure 2-2 presents the world map of waste generation per capita per day in 2016. It's obvious to find north America, Europe, South Asia, Latin America, and Russia generate more waste per capita than the other regions. However, Japan generates waste of around 0.50 to 0.99 kg/capita per day, it's the excellent achievement of constructing a sound material cycle society under the “3R” policy.

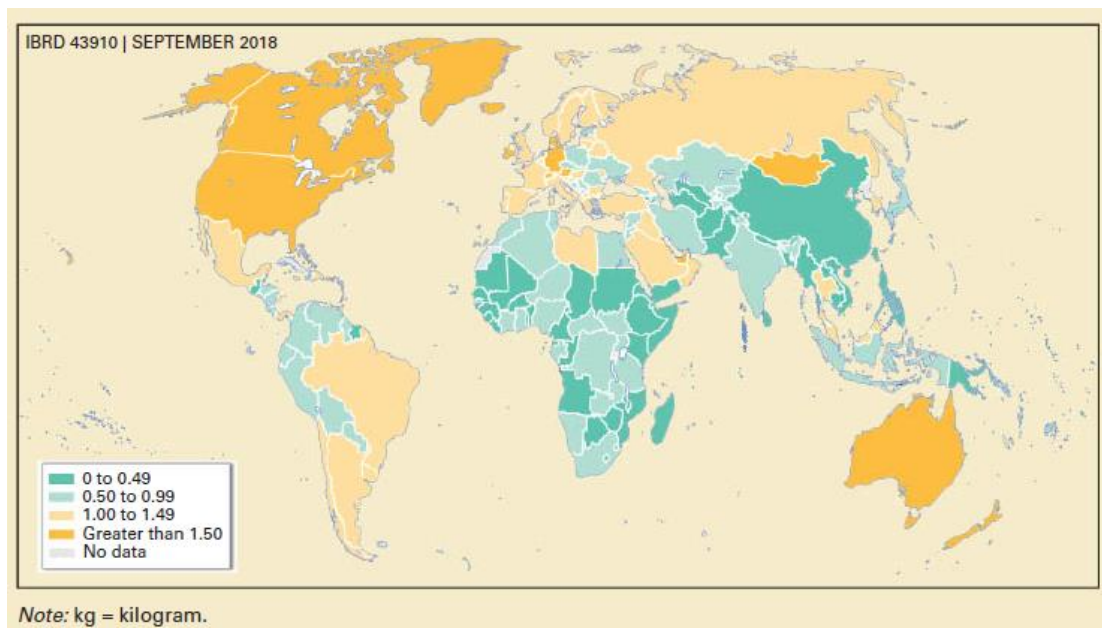


Figure 2-2 The world map of waste generation per capita per day⁵.

Figure 2-3 shows the waste generation amount and waste generation per capita per day in different regions in the world⁵. East Asia and Pacific generate the largest amount of waste (468 million tons), and the Middle East and North Africa generate the least (129 million tons) waste. However, the waste generation per capita per day in North America is much higher than the other regions. Kaza estimated the correlation between waste generation and GDP level and urbanization rate⁵. It's predictable that the waste generation will keep increase when the GDP and urbanization rate increase. The emergency situation that

comes from MSWs is still serious.

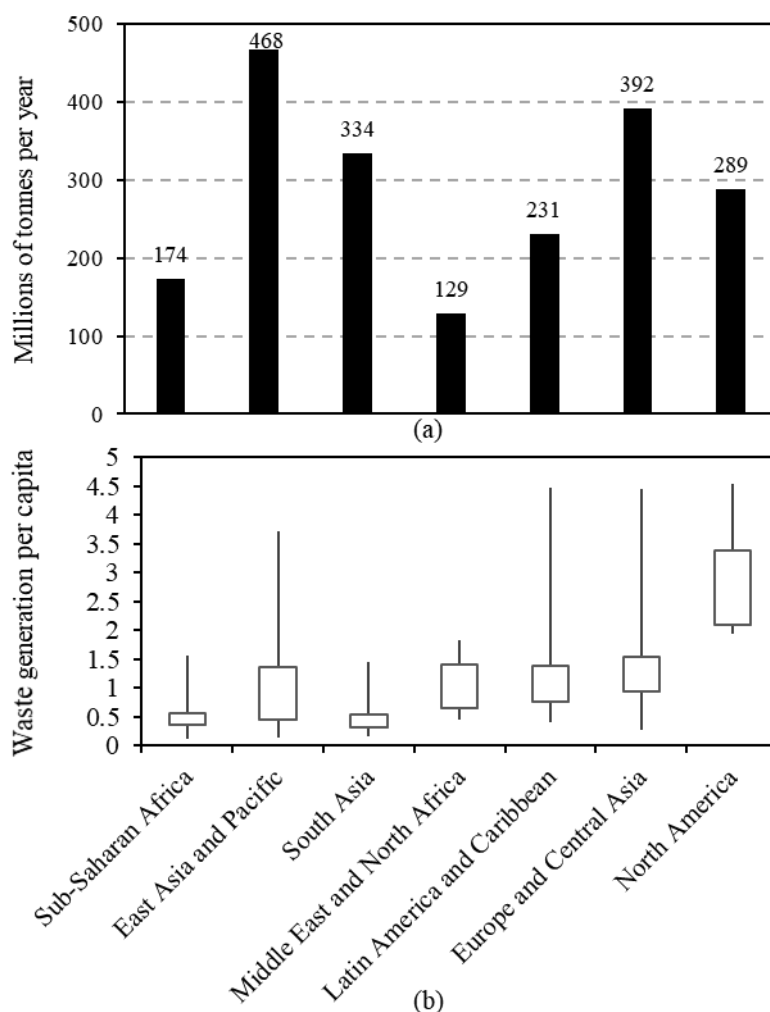


Figure 2-3 (a) Waste generation from different regions. (b) waste generation per capita in different regions⁵.

However, some developed countries like Japan have stopped the increasing trend of waste generation. One reason is the decrease in the population in these countries, another reason could be the effort from the construction of a sound material sustainable society. Reducing, reusing and recycling has been performed quite successfully in Japan and some European countries. The practice of waste management in these countries should well be studied and spread to other countries.

2. 1. 2 MSW composition and disposal

It's reported that global MSW composition consists of 44% food and green waste (figure 2-4), 38% dry recyclables (plastic, paper, cardboard, metal and glass), 2% rubber and

leather, 2% wood and 14% other waste⁵. However, the waste composition varies between different countries. The high-income countries generated more paper, plastic, glass and metal, whereas the middle and low-income countries produce more food and organic-rich MSW. Different waste should be treated precisely with a different method, but most of the waste isn't handled right. Figure 2-5 shows the world MSW disposal and treatment status in 2016. 33% of world waste is still open dumped, and the ratio is quite high (75% and 69%) in South Asia and Sub-Saharan Africa, and no open dumping waste in North America⁵. The open dumping waste should be a great potential pollution source to our environment.

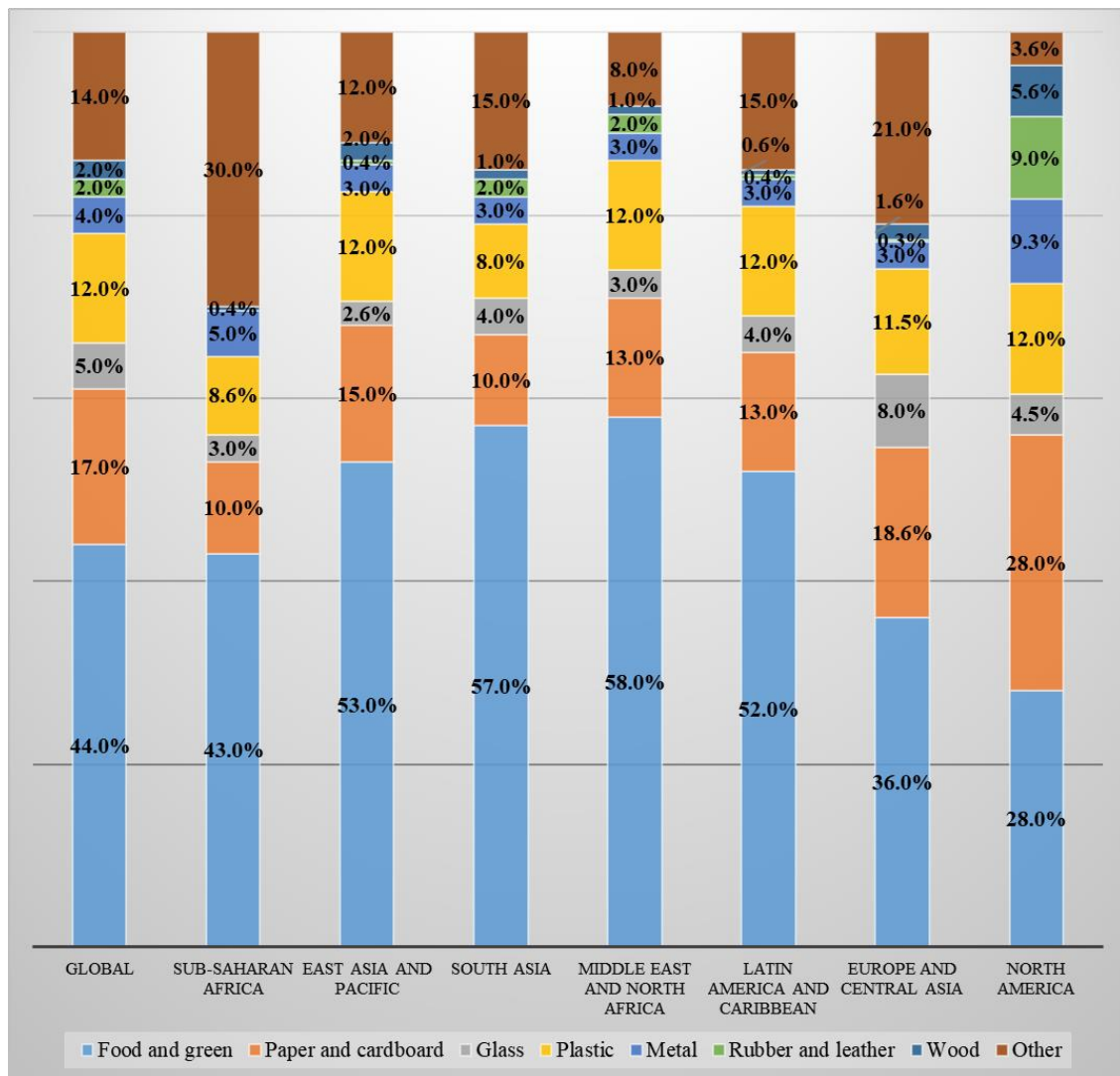


Figure 2-4 Global and regional waste composition⁵.

Currently, landfill as one of the major treatments for the disposal of MSWs is still widely applied worldwide (totally about 36.7%)⁵. Composting and incineration are also used for unrecyclable waste as treatment. Actually, directly landfill of collected MSWs are still the most used method in most developing countries. Without a source classification of MSWs,

landfill waste will consist of a large number of organic matters as shown in Figure 2-5. And most of the landfills were constructed in an anaerobic type, these landfills have been considered as huge bio-reactors recently, and could generate a huge amount of greenhouse gases. To avoid greenhouse gases changing the global climate, gas collection and utilization have been adopted. Unlike landfills, the other intermediate disposal methods would generate residues after treatment. However, the residue from those treatments still need to be handled, and this makes the landfill sites could be considered as the destination of the wastes, which means whatever enters the cycle, will end in a landfill. According to the development of the waste management strategy we discussed, it's believed the landfill waste will slowly change from the original collected MSW to the residues after intermediate treatments.

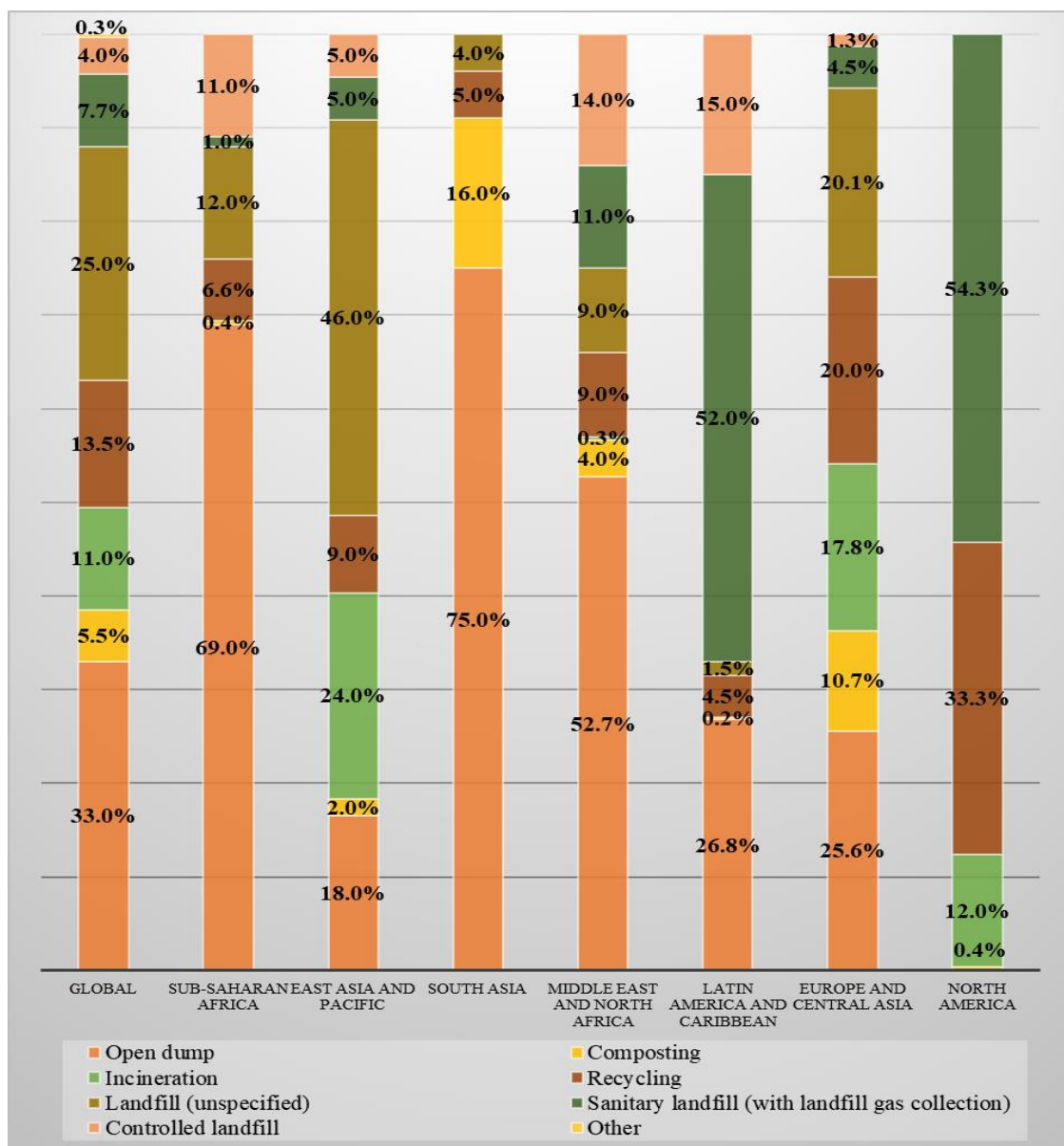


Figure 2-5 Waste disposal and treatment worldwide. (Modified from Kaza et al. (2018)).

The spreading of the concept “Waste to Energy” will enhance the application of incineration all around the world¹⁰⁻¹⁷. Fast developing countries (China mainland, Southeast Asia countries) have built more and more incineration plants for MSW. The number could be more in the future. Therefore, the landfills will receive more and more incinerator residues in the future in these countries. Standing the global perspective, we need to study incinerator residues in landfill sites.

2. 1. 3 MSW management and disposal in Japan

The history of waste management in Japan could be backtracked since the beginning of its modernization until today. The need for waste management came from the awareness of public health problems caused by improperly treated wastes. The early Cleaning Act was enacted in 1900 has defined the collection and disposal of waste as the obligation of municipalities and establish a waste administration system⁶⁻⁸. This act also stated that the waste should be incinerated if possible, and this made incineration became the first choice of waste disposal in Japan until today. Figure 2-6 presents the trend of the annual amount of landfill waste (the waste sent to landfill) in Japan from 1978 to 2014⁹. The significant decrease in the amount of final disposal waste is coming from the efforts of waste reduction from the source. Not only the total landfill waste has decreased, but also the landfill waste composition has changed (see Chapter 3).

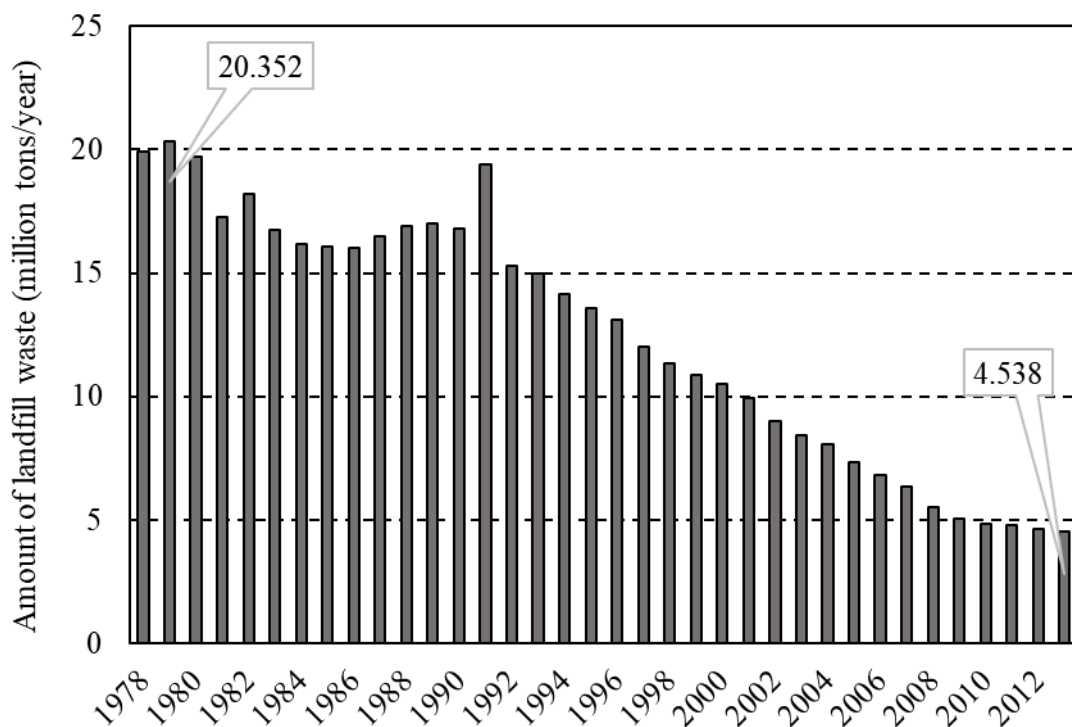
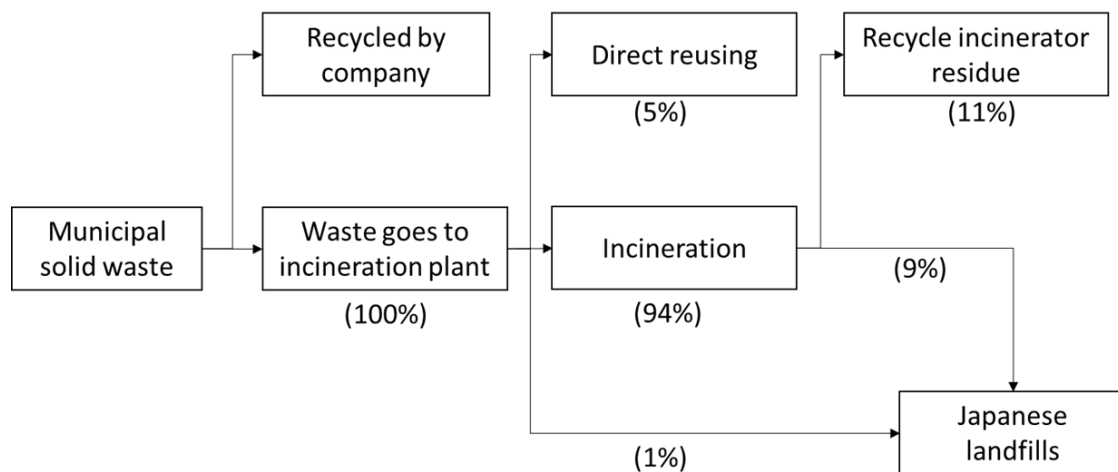


Figure 2-6 The trend of the annual amount of final landfill waste⁹.



Japanese municipal solid waste management mode(Data from 2016)

Figure 2-7 Simple MSW treatment material mass flow in Japan⁹.

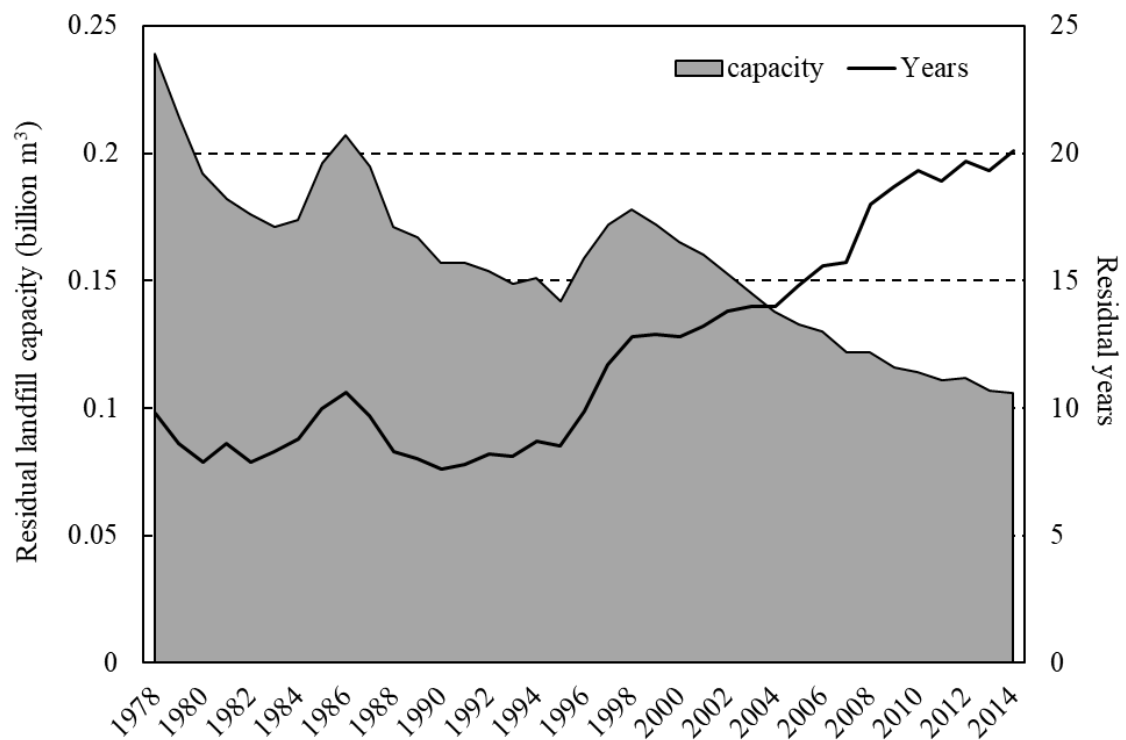


Figure 2-8 Annual residual landfill capacity and predicted years in Japan⁹.

In Japan, the total MSW generation is 43.2 million tons in 2016. Among that, only 3.98 million tons were landfilled. Figure 2-7 presents a simple material mass flow of MSW in Japan⁹. We have described the main disposal treatment of MSWs in Japan in Chapter 1, the primary method is incineration, the landfill has been considered as the secondary or final treatment method. Therefore, most of the waste is incinerated in incineration plants,

and the residues after incineration normally go to landfills. Because Japan has set up one relatively strict waste source separation rule for the citizens, most of the recyclable waste is directly reused and recycled before entering the treatment stream.

However, landfills are going to be fulfilled in the near future. It's estimated that the total capacity of landfills in Japan could still be used for around 20 years, as shown in Figure 2-8, and the total capacity was 0.106 billion m³ in 2014⁹. Comparing with the capacity in 1978 (0.239 billion m³), the total landfill space has decreased by 56% in the past 35 years. Even though the Japanese government has increased the residual years of landfill space by efficient works under the "3R" policy, the shortage of landfill capacity still needs to be seriously considered. Technology like landfill mining could be one choice to solve the problem. However, the feasibility of landfill mining should be assessed before we conduct the landfill mining to one closed landfill site.

2. 2 Landfill for incinerator residues

2. 2. 1 Development of landfill technology in Japan

The early landfill was simply considered an improvement of open dump because the odor, flies, rats and other bad effects from the waste caused the serious environmental problem. A chart of the technical evolution of landfills could be found in Figure 2-9^{1,10}. After human being's life was heavily affected by open dumping waste, they tried to bury the waste by using natural soil or other material to isolate waste to the environment. But the rainfall could reach the waste and react with the waste in anaerobic condition, the waste generates methane, H₂S and leachate contain a high concentration of toxic matters. The gas could escape through the gaps between solid particles, and leachate could reach the groundwater and be transported for a long distance. Therefore, more strict technology was introduced to control the by-products from landfill sites, to prevent them from releasing from the landfill area. Lining system and gas, leachate collection system was applied at the end of 20 centuries, at that time the technology we called sanitary landfill has been widely accepted and adopted worldwide. In several developed countries, the small nation's land space makes people realize that it's hard to build new landfill spaces. On one hand, to reduce the final landfill waste became very important. On the other hand, the decreasing of unrenewable natural material became a hot topic, "Sustainable" started to be a popular concept and spread fast. Intermediate treatment such as incineration and compost was adopted to reduce the landfill waste amount and recover energy from the waste. What landfill has to take care of is the residues after those treatments. This development just fits the circular waste management strategy we have described before. However, the old anaerobic landfill has many disadvantages, the most important is that it takes a too long time to stabilize the landfill waste.



Figure 2-9 Chronological development of concepts, technologies, and management procedures for waste landfilling¹.

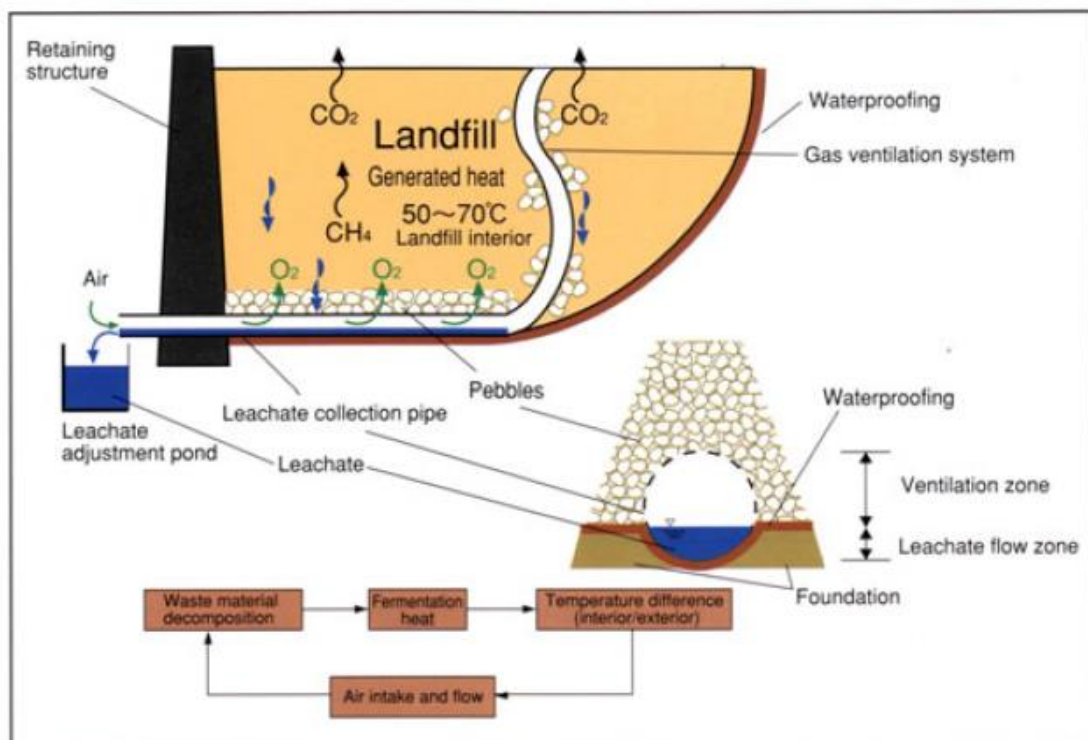


Figure 2-10 Semi-aerobic landfill configuration illustrative diagram¹⁹.

In Japan, the landfill technology research was started by Prof. Masataka Hanashima from

Fukuoka University in 1966. The early landfill technology usually bury waste in sealed space, which is an anaerobic condition. However, Prof. Hanashima tried to inject air (O_2) in landfilled waste from the bottom of the landfill in order to enhance the stabilization speed of solid waste. Even though it could stabilize the waste quickly, the huge energy consumption is a big problem to stop this method to be spread. After many experiments, a new design of landfill type has been invented, which we called semi-aerobic type landfill now, or “Fukuoka Method”. In this type of landfill, the air is supplied spontaneously through the leachate collection pipe that has a bigger diameter than regular ones. Thus, the leachate collection pipe has two functions, collecting the leachate and intake of the air¹⁹.

This method is adopted through Japan right after the first semi-aerobic landfill was constructed in Japan in 1975. Figure 2-10 presents a digraph to set up the leachate collection system in a semi-aerobic landfill, and how the air could get inside the landfill waste layer. This method also introduces the evolution of the concept of “landfill”. A landfill starts to become a purification zone, not only the storage of waste. The faster the waste reaches the final storage quality, the less economic burden and potential risk to our environment. Currently, a semi-aerobic type of landfill isn’t widely used worldwide. However, some countries start to accept this method and apply it.

Comparing to the normal anaerobic type landfill, semi-aerobic could cost higher during the operation period, and needs a higher technology level. And because of the injection of air, the generation of greenhouse gases will decrease certainly. However, landfill waste in Japan is most incinerator residues, which contain very low organic matter. The generation of greenhouse gases is lower than the common landfill waste. The anaerobic type landfill needs a longer time for the aftercare period, and the treatment of leachate needs higher technology and cost. Semi-aerobic landfill could be a better choice for constructing new landfills in other countries¹⁹⁻²².

2. 2. 2 Monofills for incinerator residues

While the development of landfill technology, the waste sent to landfills has also changed. It’s found that landfill waste consisted of 90% incinerator residues and 10% incombustible waste in Japan through Figure 2-7. The percentage of incinerator residues in the past wasn’t as high as now, but the major landfill waste in Japanese landfill sites is incinerator residues. Therefore, the landfills in Japan could be considered as incinerator residues monofills. It’s reported that some countries (including Japan, USA) dispose of BA and FA together in the same landfill cell, while some countries from the EU started to treat them separately since 2000²³⁻²⁵. Old landfills received both BA and FA could be found around the world, but monofill in semi-aerobic type could only be found in Japan. The unique combination of incinerator residues and semi-aerobic landfill should be studied for this kind of landfill may appear in other countries, too.

2. 3 The current global treatment status of incinerator residues

A landfill is a huge potential pollution source to our environment because of the waste we buried. And different waste contains different pollutants. In chapter 2. 1. 2, we have present the MSW composition worldwide. Food and green (organic-rich) waste are the major components in most countries. However, chapter 2. 1. 3 shows the major landfill waste in Japan is residues from incineration plants and incombustible wastes (9: 1 in 2016). The semi-aerobic type landfill of incinerator residues is the most popular combination in Japan.

Table 2-1: The utilization of MSW incinerator BA in different countries²⁶.

Countries/regions	Year	Mass of Incinerator BA (10 ⁶ t)	Reuse (%)	Remarks
Czech Republic	2013	0.168	90%	Landfill construction
Denmark	2013	0.631	99%	Building/road construction, Embankments
France	2013	2.7	80%	Road construction
Germany	2013	5	65%	Civil works
Ireland	2013	0.0405	N.A.	Civil works
Italy	2013	0.963	71%	Concrete civil works, the base material for landfill
Netherlands	2013	1.7	100%	Road construction, Embankments
Norway	2013	0.25	52%	Landfill construction
Portugal	2013	0.202	21%	
Spain	2013	0.349	N.A.	Road base, aggregate in concrete
Sweden	2013	0.88	9%	Civil works and landfill construction
UK	2013	N.A.	57%	Road construction; concrete aggregate
Japan	2010	3.12	44%	Cement clinker
Singapore	2014	0.2	0	Landfill
Taiwan	2008	0.714	15%	Cement clinker
USA	2013	N.A.	10%	Road construction and landfill
Canada	2006	0.18	10%	90% landfill

Incinerator residues normally include bottom ash (BA) and fly ash (FA). Bottom ash is generated in the furnace after burning the MSW, it's usually quenched by water after transported from the furnace. The fly ash usually is defined as the particles captured by the air pollution control system. Also, there's another kind of residue from the

incineration system, like the boiler ash from the heat recovery section, it depends on the incineration system. But in this thesis, we consider the FA include all of the residues except BA (because the report from the government didn't separate them in detail, and the residues are disposed of together).

BA is generally considered as a normal waste that could be landfilled in a normal landfill site or recycled as a construction material. However, FA is widely considered as hazardous waste because of the high concentration of dioxins and heavy metals. A summary of the utilization of BA is shown in Table 2-1. Even though there are many practices of utilization BA as road, cement and building material, there's still a large amount of BA is sending to the landfill site²⁶⁻³⁵.

FA as the hazardous material is not allowed to enter the ordinary landfill, it needs to be stabilized before final disposal. Melting, chemical stabilization, chemical extraction, cement solidification, and sintering are the traditional methods that have been developed to treat the FA. Recently, researchers tried to develop the procedure of recycling FA as construction material after washing or another pretreatment³⁴⁻³⁵. But most of them are still tested in the lab experiments. In Japan, the incinerator FA is usually treated by the chelate reagent before sending it to the semi-aerobic landfill together with BA. The sampling landfill sites in this research are typical Japanese landfill (semi-aerobic) receiving only incinerator BA and FA with incombustible waste. The BA and stabilized FA still contain a high content of heavy metals, which certainly could be a potential risk to our environment and need to be studied.

2. 4 Heavy metals in landfill sites

The working group "pHOENIX" from Europe, which established in 2002, investigated the environmental impact of various utilization of incinerator residues technologies and final disposal (landfill). According to the results that came from lab-scale and small field-scale experiments, the important factors affecting physical and chemical processes inside a landfill for incinerator residues were concluded. Leachate generation, gas production, and temperature development have been determined as main processes affect the environment surrounding the landfill, and certainly affect the behavior of heavy metals inside the landfill²⁵. In the former part, the target landfills have been introduced. They are typical Japanese type landfill, which is the semi-aerobic type and receives only incinerator residues and incombustible waste. And the incinerator residues account for more proportion, 90% in 2016. Therefore, the landfill could be considered as monofills for incinerator residues. In addition, there are low organic matters in incinerator residues. The gas such as methane generation from this kind of landfill will be less than regular MSW landfills. The temperature inside the landfill hasn't been monitored in this study, therefore, the gas and temperature will not be discussed in this paper. The effects of leachate could

be classified as the liquid to solid ratio (L/S), pH, redox condition and substance inside the leachate. Figure 2-9 shows a process of how the rainfall affects the heavy metals inside the landfill³⁶⁻³⁹.

Leachate is the dissolution of a soluble constituent from a solid phase into a solvent. The water mainly comes from the rainfall, penetrating through the cover soil to the waster layer. In a semi-aerobic landfill. The leachate collection allows air injection. So, some parts of the landfill are aerobic, some are anaerobic. These two different zones have completely different redox conditions. The pH varies because of the input waste; therefore, the behavior of heavy metals is totally different between different zones. In this paper, we just focused on general behavior in the solid phase⁴⁰⁻⁵².

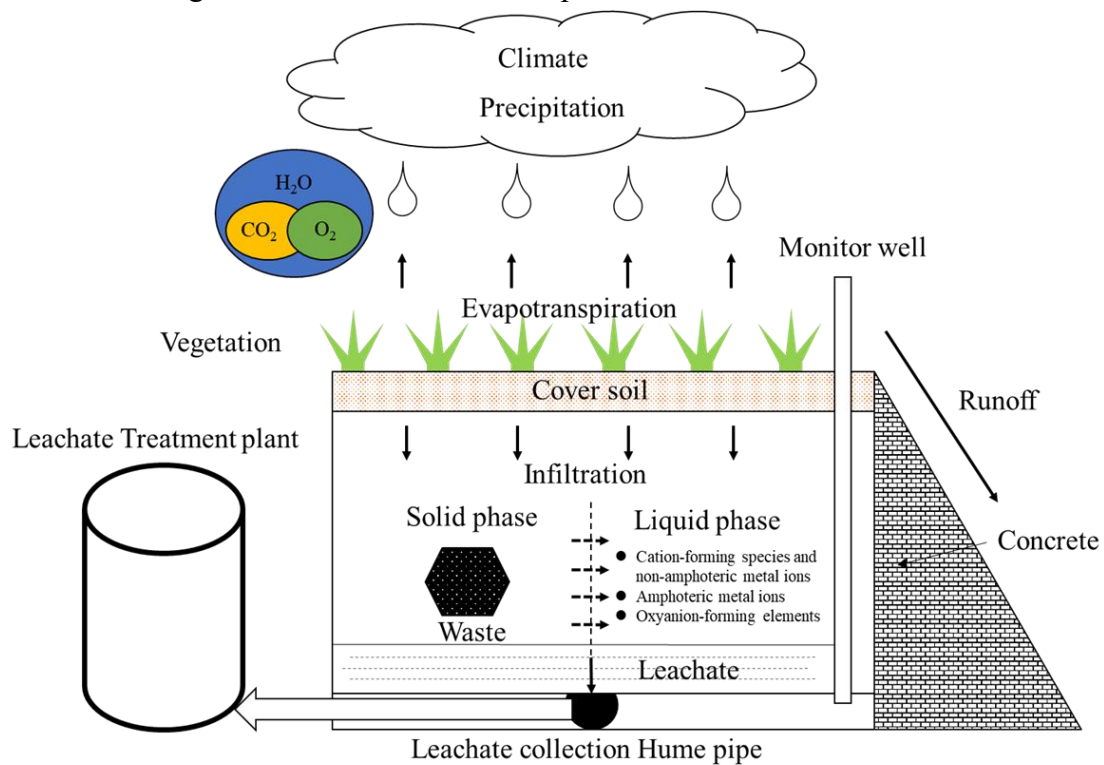


Figure 2-9 Leachate generation and reactions in the landfill site.

2. 5 Mass balance of heavy metals in a landfill site

The mass balance could be calculated by measuring the initial load associated with the waste input, the collected gas and leachate, and the total withheld by the lining system. The difference between the initial load, the collected load, and the residual stored amount represents the load released into the environment through the uncontrolled dispersion of leachate and gas. It's a good method to understand the general behavior of heavy metals in the landfill site^{1, 53-58}.

Currently, there's no report on heavy metal mass balance analysis in a full-scale landfill

⁵³⁻⁵⁸. Belevi suggested using a mathematical model for evaluation of the long-term behavior of MSW waste in landfills⁵³⁻⁵⁴. Therefore, it's possible to predict when the "final storage quality" of one closed landfill could be achieved. Incinerator bottom ash samples were collected and analyzed for the prediction of incinerator bottom ash landfills. And it's reported laboratory experiments of samples can't predict the chemical behavior of bottom ash in landfills. The condition of a real landfill environment can't be simulated in the lab simply, the field sampling and monitor of a real landfill are necessary. Determining the mass balance of elements in a landfill is a good way to understand their general behavior. Cossu discussed the role of mass balance work in a landfill site¹, several models have been proposed to estimate the different elements (carbon, nitrogen, sulfur and trace elements) inside one landfill. It is not easy to carry out systematic and accurate mass balance analyses in full-scale landfill sites. There have been few studies estimating the mass balance of elements in landfill sites⁵⁵⁻⁵⁸. We would like to explore this field and offering a meaningful experience for future studies.

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CHAPTER 3

DESCRIPTION OF THE TARGET LANDFILL SITES AND SAMPLING PROCESS

3. 1 The geographic location and weather information

3. 1. 1 The geographic location

We selected two landfill sites in Japan as the research targets. Figure 3-1 shows a brief map of these two landfill sites. The geographic condition of these landfill sites is also different. Site A was constructed on the plain near a river, it covers approximately 0.365 km² area. Site B is in a valley, and it covers approximately 0.24 km² area. The capacity of sites A and B is 2,900,000 m³ and 4,500,000 m³ respectively.

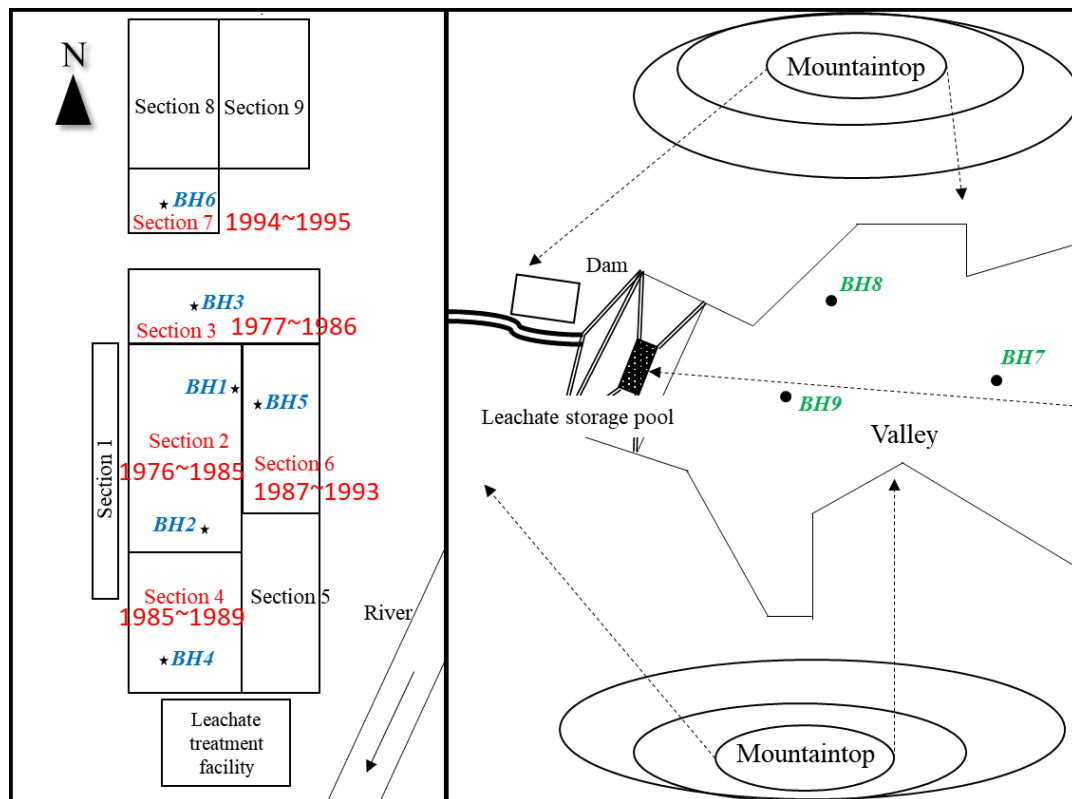


Figure 3-1 The brief map of Landfill Site A (left) and B (right) with sampling points.

According to the record from the Japanese government, the landfills in Japan are constructed mostly in four kinds of geographic conditions: valley (or hillside); shore (or offshore); wetland, and plain. Figure 3-2 shows a share of these four kinds of landfills in Japan in 2014¹. It's obvious to find that around 98% of the landfill facilities and of 73% of residual capacity is constructed in the valley and plain in Japan, therefore, the sampling sites in this study could be considered as the landfill representatives in Japan.

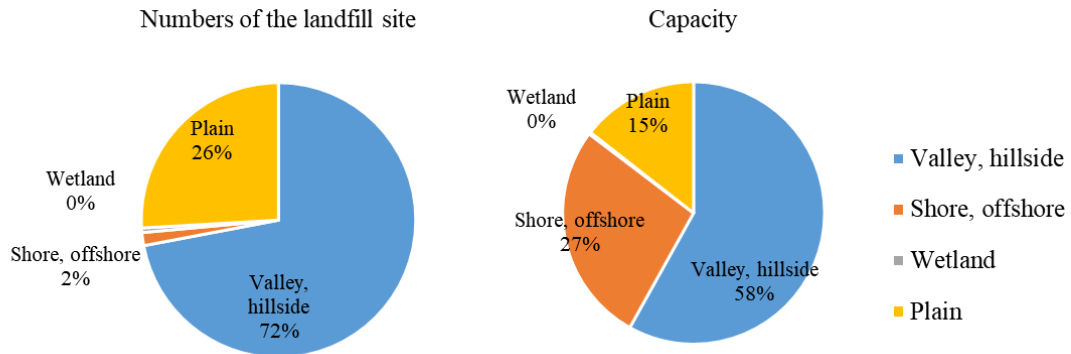


Figure 3-2 The share of different kinds of landfill sites according to geographic locations. The left pie chart is based on the number of landfill facilities, and the right one is based on the residual landfill capacity¹.

3. 1. 2 Weather condition

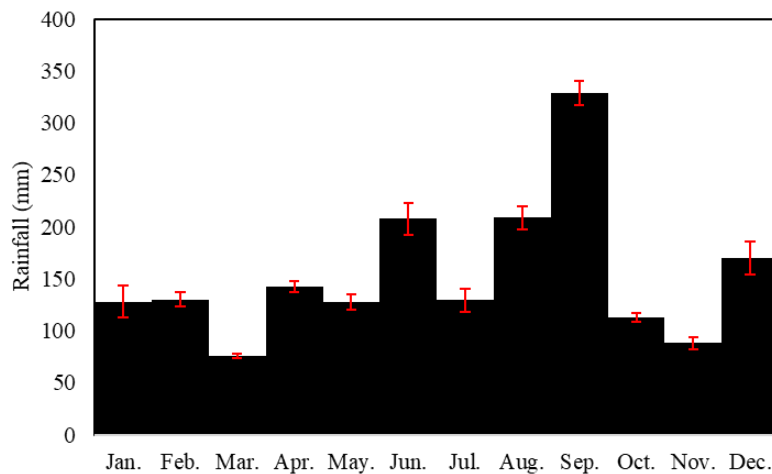


Figure 3-3 The rainfall distribution in 2016².

The landfill sites locate on the mainland of Japan, far from the coast. Both sites have a typical monsoon climate, with hot and rainy summers and relatively cold and dry winters. Figure 3-3 shows the rainfall distribution in 2016. The amount of rain in summer is larger than in winter. The leachate collection system is set up in both sites, too. The collected leachate is sent to the treatment facility near the landfill sites. The leachate collection system was set-up and worked before the area started to be used. The local government has set up landfill leachate quality investigation procedures to monitor the leachate quality in the landfill sites after the operation of site A. The correlation between rainfall and leachate generation will be discussed in Chapter 6.

3. 1. 3 Operation period of the landfill sites

Site A was used from 1975 to 2000, and site B started to be used since the closure of site A until now. Currently, about one-fourth of the capacity of site B has been fully filled, and it's predicted that it could be still used for more than 50 years. However, the annual MSWs generation is decreasing, the years of use could be longer than prediction. Site A has two major landfill sections, original design area, and extended area. These two sections could be classified into small landfill areas according to the operation period. Table 3-1 shows the detailed information of each area in site A².

Nine landfill area could be found from Table 3-1 in site A. The depth of different parts is almost the same, less than 10 meters. The landfill waste in site A is not only incinerator residue and incombustible waste, but also there's soil extracted from construction works. However, there are only incinerator residues and incombustible waste in site B. The operation period of BHs in site B could be in the order: BH9, BH7, and BH8 (old to new).

Table 3-1 The detailed information of the landfill area in landfill site².

	Area (m ²)	Operation period	Landfill depth (m)	Contents
Area 1	39,000	1975~1982	4.5~6.0	Incombustible waste and incinerator ash
Area 2	66,700	1976~1985	7.1~10.1	
Area 3	51,300	1977~1986	6.9~9.9	Incombustible waste and incinerator ash
Area 4	40,100	1985~1989	7.9~10.9	
Area 5	33,000	1987~1993	8.0~9.9	Soil form construction works
Area 6	32,500	1987~1993	8.0~9.9	Incombustible waste and incinerator ash
Area 7	12,300	1994~1995	8.8	
Area 8	41,100	1994~1997	8.8	Incombustible waste and incinerator ash
Area 9	49,000	1996~2000	8.8	

3. 2 The structure of the landfill sites

Both sides were constructed as a “semi-aerobic” type to enhance the decomposition speed of landfill waste². Figure 3-4 shows the structure of site A, it looks like a “sandwich”, and so it's called “sandwich” type. At the bottom side, there's a liner to stop leachate from a leak. The material is earthen material or man-made waterproof sheet. the leachate collection pit and pipes were also constructed at the bottom side. Despite the leachate, the groundwater near the landfill area is also collected and sent to the treatment facility in some time. The waste was filled layer by layer with intermediate cover soil between them. Concrete walls and steel plates were set up at the edge of the landfill site to stop the leak

of leachate. And there's a final cover soil on the top of landfill area when it's full filed. The structure of site B is similar to the site A. However, site B is in the valley, the depth of site B is deeper than site A. In addition, the site B was constructed after serious investigation by the government and well designed, the leachate collection system was also effective due to the natural topography or terrain.

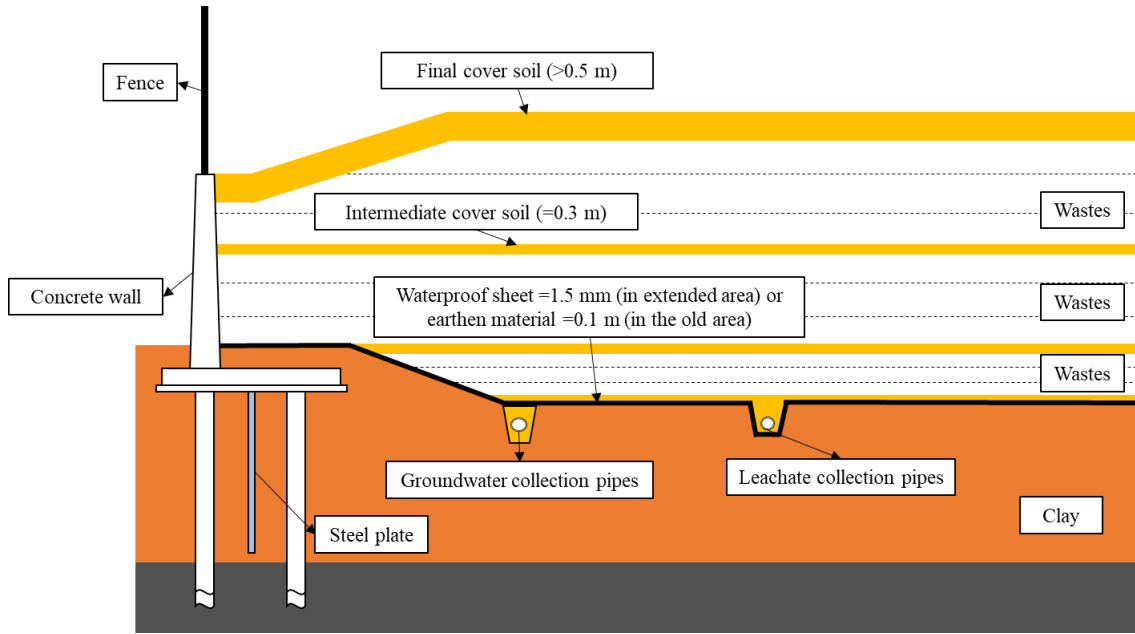


Figure 3-4 The landfill structure of site A².

3.3 The sources of incinerator residues

These two landfill sites were constructed to finally dispose of the MSWs generated from the City. As we described before, the combustible waste is sent to the incinerators directly, the incombustible waste will be pretreated before the final landfill. According to the historical records², the total amount of landfill waste (not including soil waste and cover soil) for the 25 years was about 4.07 million tons in site A. The composition of the landfill waste was 1.03 million tons of incombustible waste and 3.04 million tons of incinerator residues. Figure 3-5 shows the landfill waste composition in site A from 1975 to 2000. Although the composition fluctuated, the fluctuation was generally within 10–20%, which means that the composition of the landfill waste is similar in different areas of the landfill. For site B, the incinerator residue takes more proportion than incombustible waste, because the regulation for landfill waste becomes more and more strictly. Also, site B receives some industrial waste (like plaster) because of the lack of landfill space.

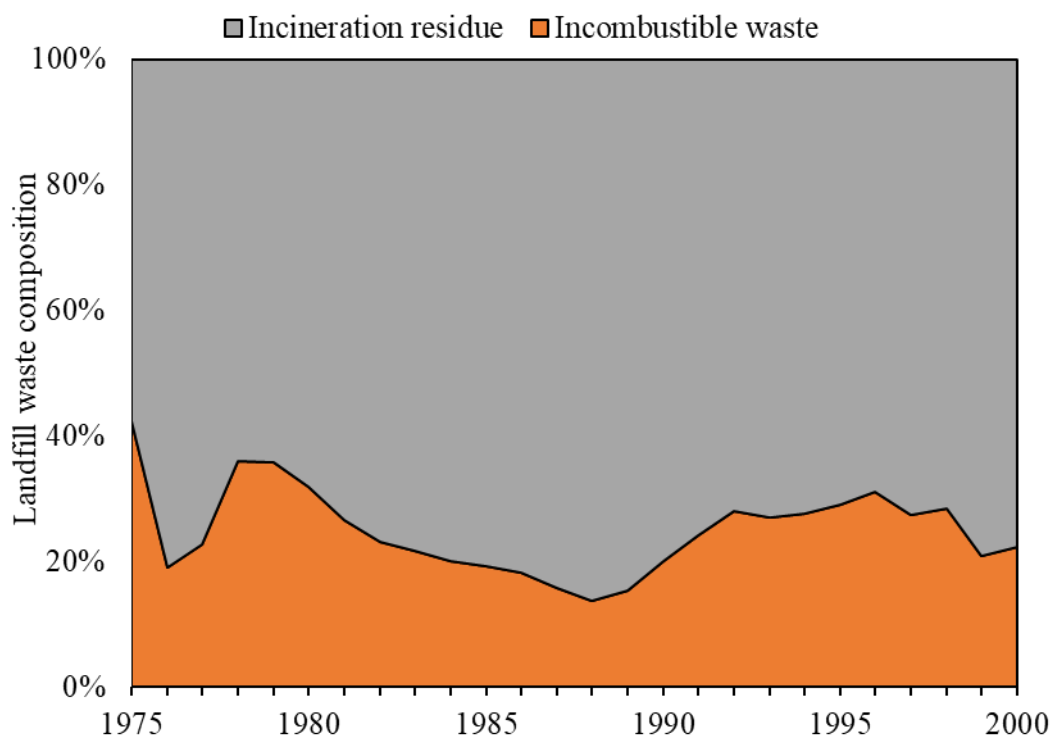


Figure 3-5 The landfill waste composition in the landfill site A²⁻³.

Table 3-2 Characteristics of the incineration plants⁴.

Incineration plant	Begging time	Capacity (Tons/d)	The Num. of furnaces	APC system
A	1975	400	2	Lime spray & EP*
B	1975	600	2	Lime spray & EP
C	1986	600	2	EP & Gas scrubber
D	1975	600	3	Lime spray & EP for furnace 1, 2 EP & Gas scrubber for furnace 3
E	1980	600	3	EP & Gas scrubber

*Electrostatic precipitator

There were five MSW incineration plants in the city, and the characteristics of these incineration plants are summarized in Table 3-2. All of the incineration plants use continuous stoker-type furnaces from different companies. However, two different air pollution control (APC) systems are in operation, namely lime spray plus an electrostatic precipitator (EP), and an EP with a gas scrubber; thus, FA neutralized by $\text{Ca}(\text{OH})_2$ and EP ash were both sent to these landfill sites, in addition to BA. Consequently, dissoluble salts

such as CaCl_2 contribute significantly to the mass loss from the landfill waste when rainfall passing through the waste layers. The government also monitored the total content of some heavy metals in the incinerator residues (mixed BA and stabilized FA). Therefore, the it's possible to calculate the initial heavy metal input into the landfill, the detailed information could be found in the later chapters.

3. 4 The sampling process

The sampling positions included six points in landfill site A and three points in site B. We marked the positions as BH1~BH6 from site A, and BH7~BH9 from site B. Figure 3-1 shows the detailed position of each one borehole. In landfill site A, we knew the exact landfill year of the waste in Table 3-1. For example, in the sampling area of BH1, waste was deposited from 1976 to 1985, so for BH2~BH6, which could be confirmed from Table 3-1. The sampling instruments and procedures were supported by the Shimadzu Corp. We extracted 10 m core samples each for BH3, BH4, BH5, BH6, BH7 and BH8, 9 m for BH1, 13 m for BH2, and 15 m for BH9. After extracting the core samples, we took photographs of them, and then stored them in wooden cases wrapped in plastic film before sending them to the laboratory. Then, we collected soil samples at 1-m intervals from each core in the lab. In total, 102 samples were collected from the nine boreholes. We stored each sample into two groups. One group was pretreated and analyzed for composition and heavy metal concentrations, and the other group was stored in vacuum bags under -30°C for speciation analysis. The whole procedure could be found in Figure 3-6. A more detailed procedure will be presented in later chapters.

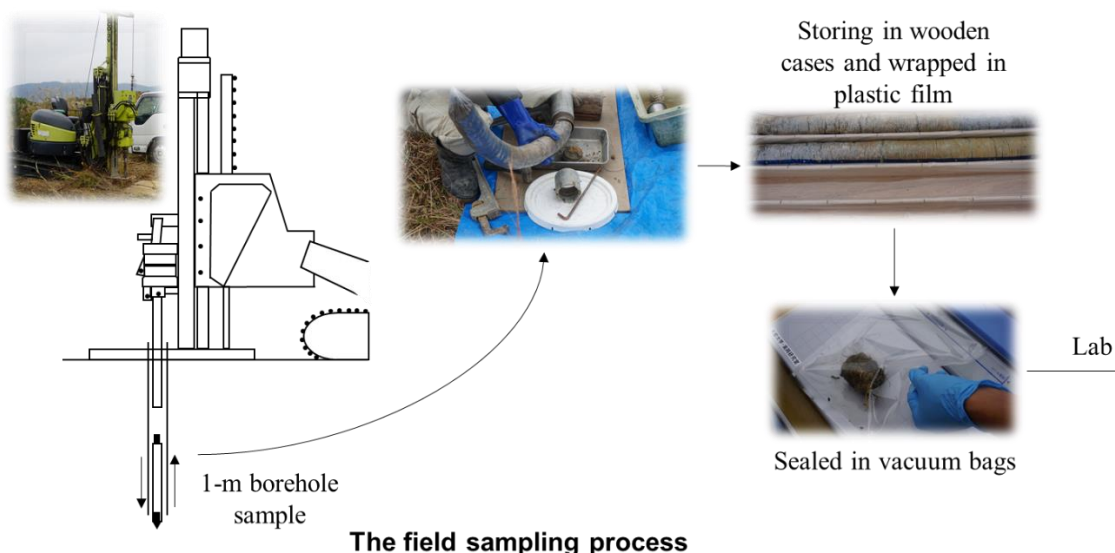


Figure 3-6 The procedure of field sampling process

Figure 3-7 shows the cross-sectional view of each BHs, the layers of no-waste and waste were classified clearly in the chart. The waste layer contains incinerator residues and incombustible wastes. It's difficult to identify them through observation, so further analysis is needed to clarify the different wastes.

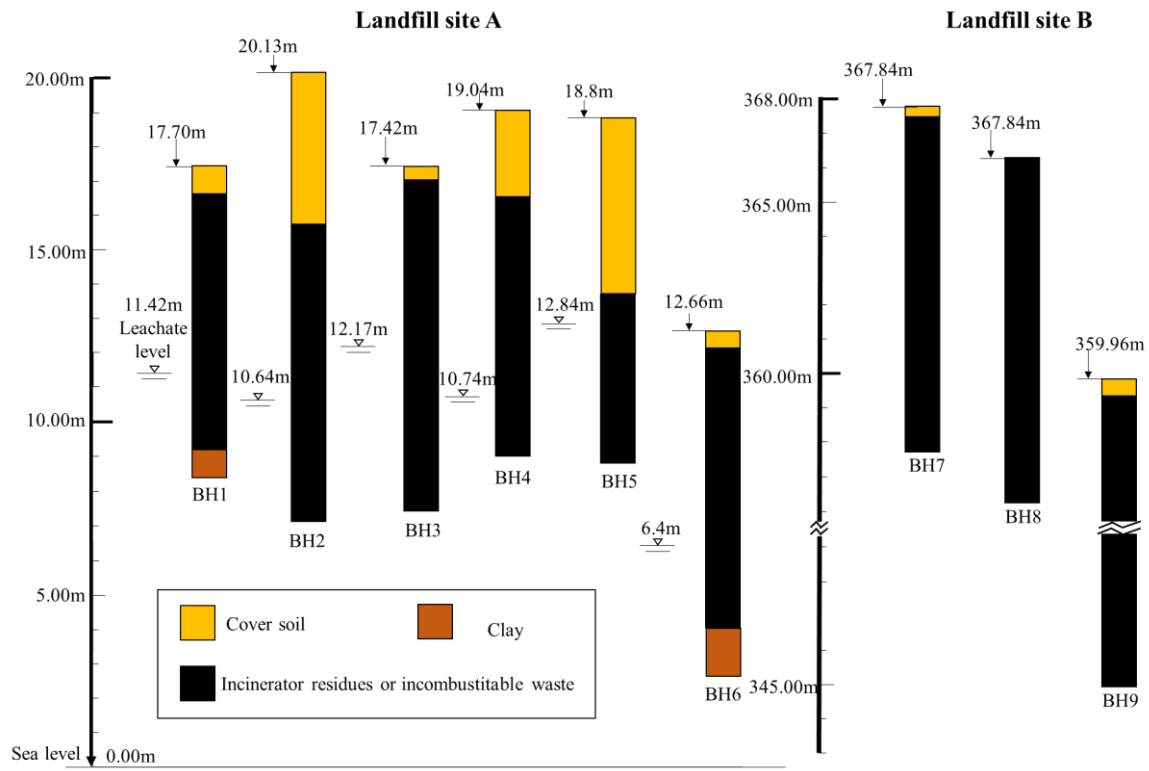


Figure 3-7 The cross-sectional view of each borehole samples.

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CHAPTER 4

DISTRIBUTION AND CHARACTERIZATION OF HEAVY METALS IN THE LANDFILL SITES

4. 1 Introduction

We have demonstrated that municipal solid waste (MSW) landfills have been constructed and filled progressively around the world. The landfills can be considered final sinks for consumed natural resources, which enter the material cycle of human society¹. As a final storage site, closed landfills need to be monitored for many years to avoid leakage of toxic materials. Tightly controlled landfill technology systems have been developed to prevent contamination from landfill sites, including waste, leachate, and landfill gases. However, the threat of landfills to their surroundings remains, especially in the case of unsanitary landfills constructed in the past.

Numerous studies have examined environmental contamination around older-type landfill sites²⁻¹⁰. Some studies have reported that pollutants from the landfill area, such as sodium, calcium, chloride, and heavy metals, can enter the surroundings easily and reach river water or groundwater. Others have concluded that heavy metal contamination around the landfill site was insignificant. Generally, the presence of contamination was closely related to the type and amount of wastes dumped, the dumping method, the condition of the natural surroundings, and the climate. Primarily, the type of waste determines the toxic compounds in a landfill.

Generally, the landfill waste in most countries consists of large amounts of organic wastes (including food residues, paper, plastic, and wood), as in China, where more than 50% of landfill wastes are organic compounds¹¹⁻¹⁵. However, landfill waste in Japan is quite different¹⁶⁻¹⁷. Incineration has been the main treatment technology for MSW in Japan since the 1970s, and the residue from incineration (including bottom ash and fly ash) contributes a large amount of the wastes for landfills, accounting for 50–80% of the total landfill waste¹⁶⁻¹⁷. Nowadays, almost all MSW landfills in Japan receive only incombustible waste and MSW incinerator residue. This particular composition of landfill waste makes Japanese-type landfills unique in the world. Recently, some developing and developed countries, such as China, Malaysia, and Vietnam, have started to enhance their incineration ability for disposal of MSW because of the increasing attention paid to converting “waste to energy” and the lack of landfill space¹⁸⁻²⁰. A portion of the incinerator residue generated will have to be sent to landfills because there is no efficient way to dispose of all incinerator residue²¹⁻²². An annual government report indicated that more than half of the incinerator residue in Japan, mainly bottom ash, is currently recycled for use as a construction material. Nevertheless, the stabilized fly ash and residual bottom ash are landfilled. These Japanese-type landfill sites for incinerator residues generate small amounts of organic matter in the leachate and contain low levels of greenhouse gas emissions²³. More attention to the concentrations of heavy metals in incinerator residues is needed, as few studies have examined these.

He et al¹⁵ conducted a full-scale investigation of heavy metals in one landfill site in China,

but the landfill waste composition was very different from the composition of Japanese-type landfills. Bulen et al²³ studied the heavy metals in the leachate generated from Japanese-type landfills using simulation cells. The waste consisted only of incinerator residue and incombustible wastes. After a 1-year experiment, they found that the leaching of heavy metals was not significant under either aerobic or anaerobic conditions. The researchers also found no meaningful correlation between the oxidation-reduction potential and heavy metal concentrations in the leachates. Kamura et al²⁴⁻²⁵ also investigated the distribution of heavy metal content in a Japanese landfill site. They concluded that there was no correlation between depth and heavy metal concentration. However, there has been no definitive study of heavy metals in this type of landfill.

In this chapter, to estimate the heavy metal characteristics of a Japanese landfill site better, two actual Japanese landfills were sampled to investigate the waste layers. During its operation, the landfill received only incombustible waste and incinerator residues, which were also rare cases in the 1970s in Japan. Borehole (BH) samples were taken and tested to obtain the current heavy metal contents in specific locations of the landfill. We also obtained data on heavy metals in landfilled incinerator residues from local government records. The raw content of heavy metals in landfilled incinerator residues during a specific year could be calculated from the data. A comparison of the raw heavy metal contents with those determined in the current study allowed estimation of the mobility of heavy metals, which has not been reported previously.

4. 2 Material and Methods

The core samples were taken from the two landfill sites as we have described in chapter 3. In the lab, we collected samples at 1-m intervals from each core, so we totally collected 102 samples from the nine BHs. Each sample has a mass of about 1 kg. Then we separated each sample into two groups, each consisting of one-half of the original sample. One group of samples was pretreated and analyzed for composition and heavy metal content, and the other was used for the leaching test or other tests. In this chapter, we focused on composition analysis. The first-group samples were pretreated by drying, sieving, and milling. The samples were dried in an oven for 24 h at 105 °C, and the moisture content of each sample was calculated. Then, the dried samples were sieved through a 2mm sieve to separate fine particles from coarser particles. Generally, the large particles were stone, glass, and pieces of iron and brick. The sieved fine particles were ground gently using a ceramic pestle and mortar.

4. 2. 1 Composition and total heavy metal content measurement

The pretreated soil samples were analyzed by x-ray fluorescence (XRF-1700, Shimadzu)

and a carbon-hydrogen–nitrogen (CHN) detector (MT-2, Yanaco). To calculate total heavy metals content, samples were digested using a microwave digestion system (Ethos 1, Milestone), and the digestion solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP IRIS Intrepid Duo Thermo ELECTRON, Japan) and inductively coupled plasma mass spectroscopy (ICP-MS, X series 2Xt, Thermo Fisher Scientific, USA). Samples (0.1 g) were digested with HNO₃, HF, and H₂O₂ mixed at a ratio of 7:2.5:0.5, respectively, and the metals Cd, Cr, Cu, Ni, Pb, and Zn were measured. The digestion method was evaluated by treated standard sample NIST SRM2711a (Montana soil) to check the recovery rate. We obtained recovery rates of 102, 111, 109, 145, 95, and 92%, respectively, for the six heavy metals. Three replicates of each sample were analyzed by microwave digestion and CHN detection, and one measurement of each sample was conducted for XRF measurement.

4. 2. 2 Historic data collection and analysis

In this part, we collected historical data on the heavy metal concentrations in incinerator residues from the local government. We obtained data on the heavy metal (Cd, Cr, Cu, Pb, and Zn) concentrations in the incinerator residues of every MSW incinerator from 1981 to 2000. The period 1981 to 2000 is just within the operating span of the landfill site A, which means that all data were obtained from incinerator residues that were sent to the landfill site A. The analysis process is illustrated in Figure 4-1. We estimated the raw heavy metal concentrations in the wastes using Eq. (4-1), and the results are shown in Table 4-1.

$$HMC_{(year)} = \sum_{i=1}^n HMC_{n(year)} \times N_n \quad \text{Eq. (4-1),}$$

where $HMC_{(year)}$ is the estimated heavy metal concentration in the landfill waste for a given year, $HMC_{n(year)}$ is the heavy metal content in the incinerator residue generated from plant n during that year, and N_n is the incinerator residue generation percentage of plant n. Table 4. 1 shows the estimated heavy metal concentrations for each year. As illustrated in Table 3. 2, we knew the operating time for each BH (e.g., for BH1 and BH2, the operating time was 1976 to 1985), and thus we could calculate the original heavy metal concentrations using Eq. (4-2):

$$HMC_{0(BHn)} = \frac{HMC_{(year)} \times M_{(year)} + \dots + HMC_{(year)_t} \times M_{(year)_t}}{M_{(year)} + \dots + M_{(year)_t}} \quad \text{Eq. (4-2)}$$

where $C_{0(BHn)}$ is the original heavy metal content in BH n (BHn), and $M_{(year)}$ is the incinerator residue generation during that year. We used the years of operation of each BHn. Because site B is still under operation, it's hard to proceed with similar work.

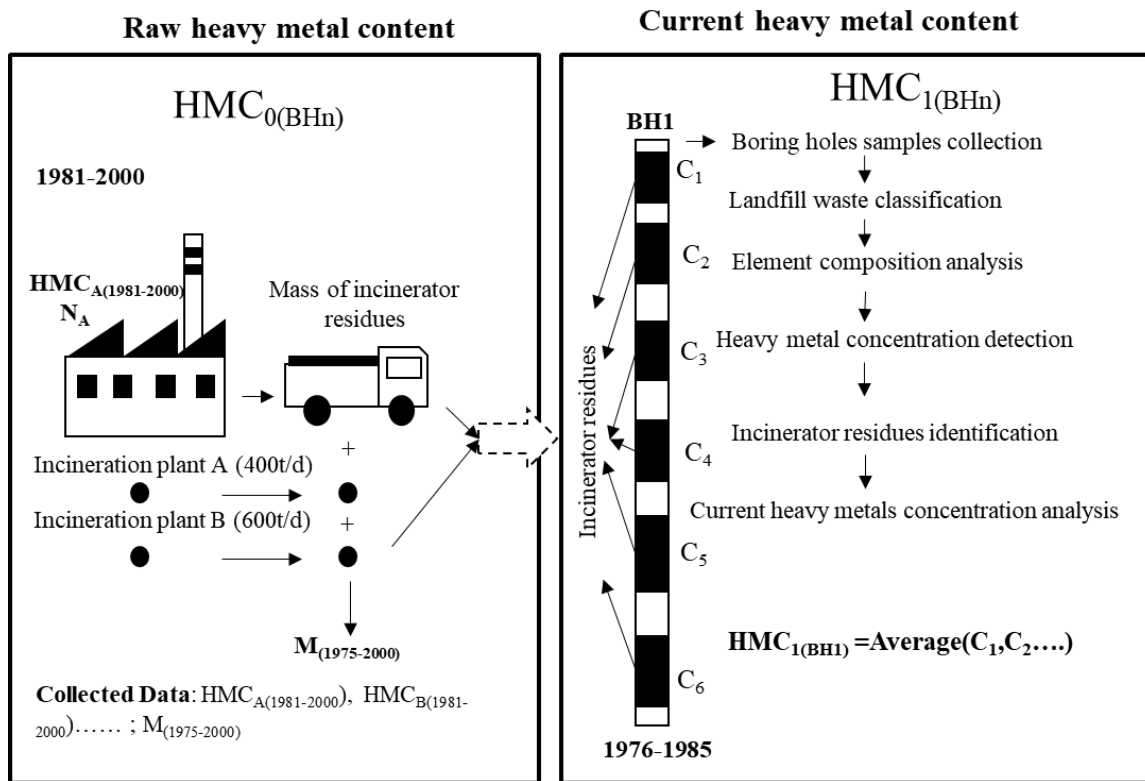


Figure 4-1 Data calculation process of historic data and measured data

Table 4-1 Estimated heavy metal contents in the incinerator residues (mg/kg).

Year	Cd	Pb	Cu	Zn	Cr	Amount of incinerator residue (tons)
1981	36.9	1510	3510	5980	194	101,816
1982	20.0	1400	3360	5190	415	105,353
1983	29.2	2480	6140	6020	432	102,423
1984	30.9	2360	3490	5200	171	108,241
1985	17.1	2500	1650	4940	336	113,317
1986	33.6	1900	2640	7620	118	114,975
1987	36.1	1850	2040	5440	221	118,177
1988	34.4	2430	8690	7130	175	123,268
1989	20.6	3590	9260	6800	164	131,189
1990	44.6	2250	8070	7630	159	127,849
1991	27.2	3290	2040	9680	211	128,313
1992	34.3	2480	9070	9770	189	125,675
1993	58.0	2520	11900	9800	151	124,960
1994	50.7	4150	5510	7720	88.9	128,809
1995	34.8	2160	5760	6690	293	129,562
1996	53.6	2500	4800	10200	140	129,449
1997	50.9	2950	2730	5900	311	124,629

1998	51.6	2120	3640	7230	271	120,963
1999	46.9	2430	5930	5300	304	127,120
2000	44.6	2590	9080	8000	515	128,024

4. 3 Results and Discussion

4. 3. 1 Composition analysis result

The XRF result of the samples provided total element composition information for each BH samples. Table A1 in the appendix shows the values of the XRF and CHN results in both sites, please check the Table in the Appendix files. To better analyze the result, we summarize the results by the type of sample: landfill waste, cover soil, soil, and clay (Appendix Table A2). Because the site B is still under operation, the cover soil might not be applied in some parts of the landfill area.

Through Table A1 and A2, it's found generally, the main elements in the samples were O, Si, and Ca, which contributed more than 70% of the total. The waste samples obviously had higher Ca contents and lower Si contents than the no-waste samples. The waste samples also appeared to have higher C, S, and Cl contents. The higher C content may have come from wastes such as pieces of wood and pieces of plastic. The higher contents of Cl and S must indicate the presence of incinerator residues. Samples from site B have higher Cl and S content, which implies the difference between fresh and aged incinerator residues. Furthermore, because the Cl and S contents in the incinerator fly ash were reported as being relatively higher than those in the bottom ash, the positions of highest Cl and S contents in each core may be positions where fly ash was dumped. Some researchers have reported that the Cl in fly ash exists mostly in soluble form, so it could be washed out by rainfall easily²⁶⁻²⁷. The concentration of Cl in the landfill waste from site A maintained a low level, about 0.09–0.33%, which is quite smaller to the Cl content in raw incinerator fly ash (usually about 10% or higher). Dissolvable salts such as CaCl₂, NaCl, and KCl, released substantially from the wastes, could be one reason for the low contents of Cl. Therefore, incinerator residues in site A did experience a long time washing by the rainfall. Cl and S content in site B is much higher than site A, but they are still lower than what reported in the fresh incinerator residues. This could imply the release of Cl from the waste body could last for years. Further discussion will be done in the next sections and chapters.

4. 3. 2 Heavy metal contents in the landfill site

The mean values of heavy metal (Cd, Cr, Cu, Ni, Pb, and Zn) contents are shown in Table 4-2. The contents of these heavy metals followed the order of $Zn > Cu \geq Pb > Cr > Ni > Cd$. Generally, the waste layer samples had much higher contents of heavy metals than did the cover soil, soil layer, and clay layer samples. BH4 had the highest heavy metal contents among all points, but BH5 had the highest content of Ni among all points. Although the contents of Cd were relatively low, the levels in several samples still reached the level of incinerator fly ash²⁶⁻²⁷, which is higher than that in ordinary soil.

Table 4-2 Heavy metal contents of collected samples. (mg/kg, dry basis).

	Depth (m)	Type	Cd	Cr	Cu	Ni	Pb	Zn	Num. of samples
BH1	0~0.8	Cover soil	4.67	81.7	89.3	60.7	48.8	231	1
	0.8-1.6	Waste	6.59	84.6	376	47.6	193	646	1
	1.6-4.25	Soil	7.92	100	501	55.4	217	853	2
	4.25-4.7	Clay	4.37	68.1	94.9	48.1	47.1	216	1
	4.7-8.2	Soil	3.35	125	80.7	94.1	22.3	111	3
	8.2-9.0	Clay	1.23	79.4	51.1	61.7	22.9	82.2	1
BH2	0	Surface soil	1.00	57.7	26.8	62.2	23.8	84.8	1
	0-4.5	Cover soil	1.10	61.8	43.3	61.3	25.2	91.1	5
	4.5-13	Waste	30.4	341	2260	177	1700	4820	9
BH3	0	Surface soil	1.19	70.5	49.8	71.9	37.6	103	1
	0-0.4	Cover soil	1.51	62.8	60.5	53.2	75.3	201	1
	0.4-10	Waste	26.5	202	967	111	1110	3770	10
BH4	0-1.7	Cover soil	4.62	61.7	39.5	43.5	23.3	100	2
	1.7-10	Waste	75.6	457	3520	240	3270	8730	8
BH5	0-1.2	Cover soil	3.40	56.4	27.4	31.9	10.9	60.8	1
	1.2-5.1	Soil	4.06	59.6	172	46.7	21.3	162	4
	5.1-10	Waste	17.6	346	2230	284	1440	3220	5
BH6	0-0.5	Cover soil	1.99	83.1	52.5	88.2	56.6	184	1
	0.5-8.6	Waste	5.23	201	1180	82.3	1310	998	9
	8.6-10	Clay	1.33	75.2	36.3	92.1	27.0	106	1
BH7	0.3-10	Waste	52.0	398	2160	244	1310	5990	10
BH8	0-10	Waste	43.0	321	1870	138	1310	5380	10
BH9	0.5-15	Waste	70.0	395	2340	232	1490	6900	15

Figures 4-2 and 4-3 show the heavy metal content distributions in sites A and B. It's found most of the metal contents were present at lower content ranges, especially Ni (0–400 mg/kg) and Pb (0–4000 mg/kg). Some metals were present at intermediate content ranges. We could find lower content samples from site A than site B. Taking Cd, Cu, and Zn for example, the content distribution peaks are 0-20, 0-1000, and 0-2000 in site A, while the peaks are 40-60, 2000-3000, and 6000-8000 in site B. These differences could come from many reasons, however, what we could conclude is that the content of Cd, Cu, and Zn is higher in site B.

We compared the heavy metal content in the samples from site A and site B, the result could be found in Figure A4-1 (Appendix). The result has been tested by the Mann-Whitney test, it's found the Cd, Cr, Ni, and Zn from site B is larger than site A at $p=0.05$ level significantly. However, The Cu and Pb aren't significantly different between sites A and B.

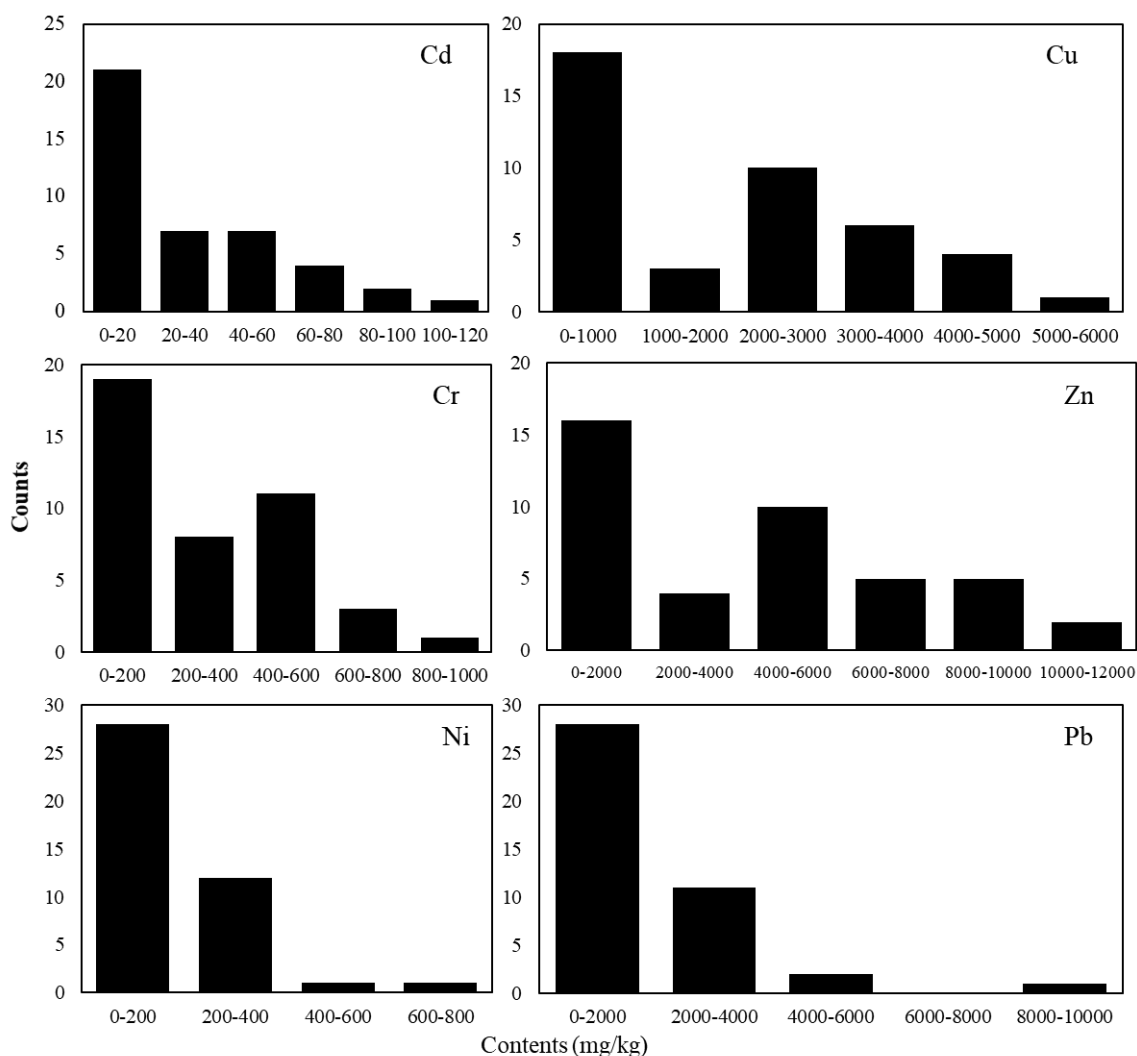


Figure 4-2 Heavy metal content distribution in landfilled incinerator residues (site A).

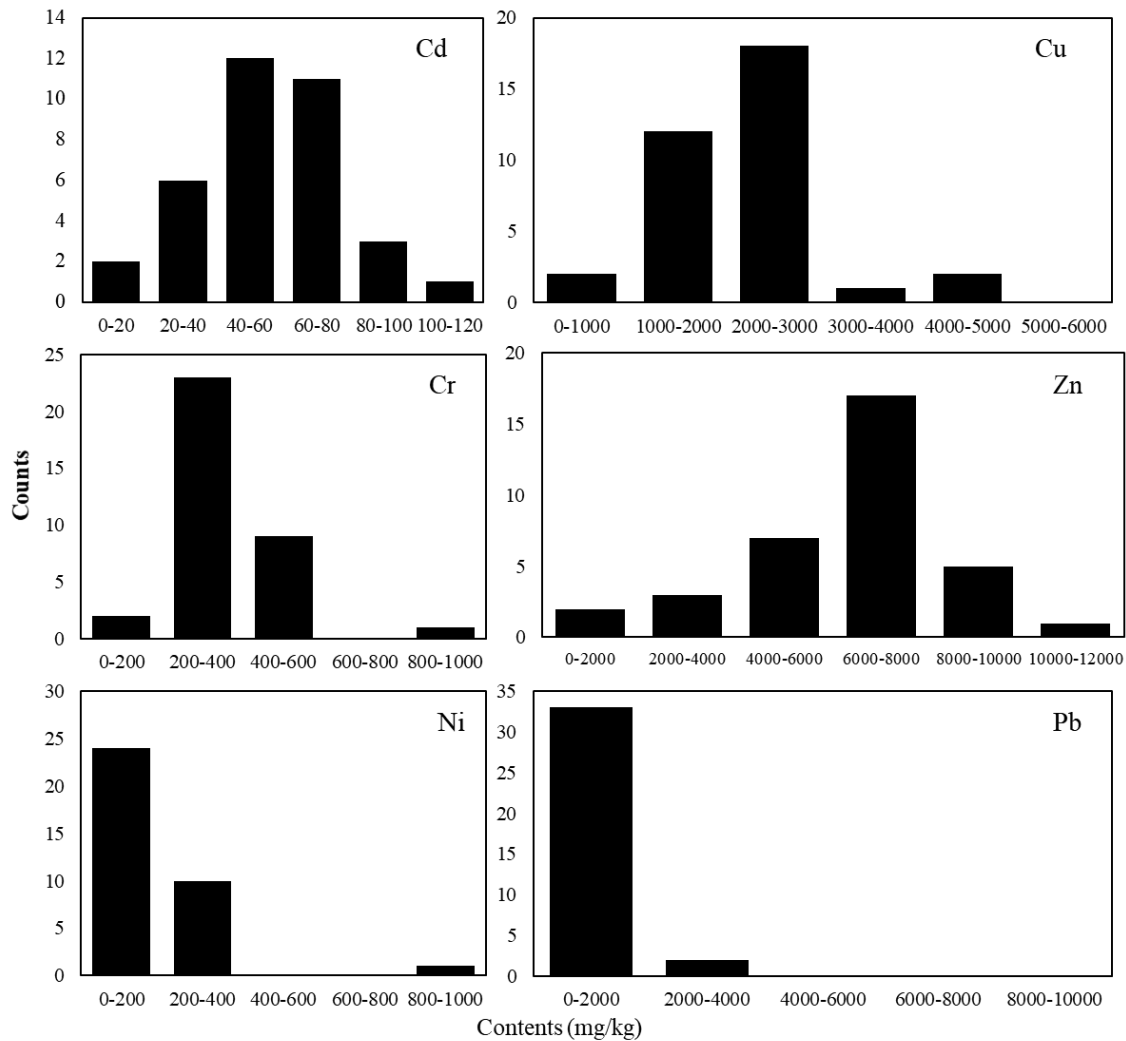


Figure 4-3 Heavy metal content distribution in landfilled incinerator residues (site B).

We also collected published data on the heavy metal contents in MSW incinerator fly ash and bottom ash from Japan²⁸⁻³⁰. A comparison of the results is shown in Figure 4-4. We found two datasets in Jung et al., pertaining to the incinerator residues generated during 1993–2000 and in 2004³⁰. The heavy metals, especially Cr, Cu, Pb, and Zn, in fly ash, had larger ranges from 1993–2000 than 2004. The average heavy metal content in the current study was generally between the average content of raw fly ash and that of bottom ash. Therefore, our samples comprised a mixture of incinerator fly ash and bottom ash. In comparison, the average content was close to the heavy metal contents of raw fly ash and bottom ash, and a similar result between sites A and B implies that a low release of heavy metals from the landfill sites.

Other Japanese scholars have also investigated the heavy metal contents in landfill waste, revealing contents of Cu, Pb, and Zn of 100–10000, 500–5000, and 1000–20000 mg/kg, respectively²⁴⁻²⁵, in agreement with our results. However, in He's result, the heavy metal

contents of Cd, Cu, Cr, Pb, Ni, and Zn were 4.7–11.3, 107–320, 323–545, 206–665, 39.6–101, and 384–913 mg/kg, respectively¹⁵. By comparing He's data with the data from this work, it can be determined that the contents of Cu, Pb, and Zn are much higher in a Japanese landfill than in a Chinese landfill. The most possible reason is the difference in landfill waste composition.

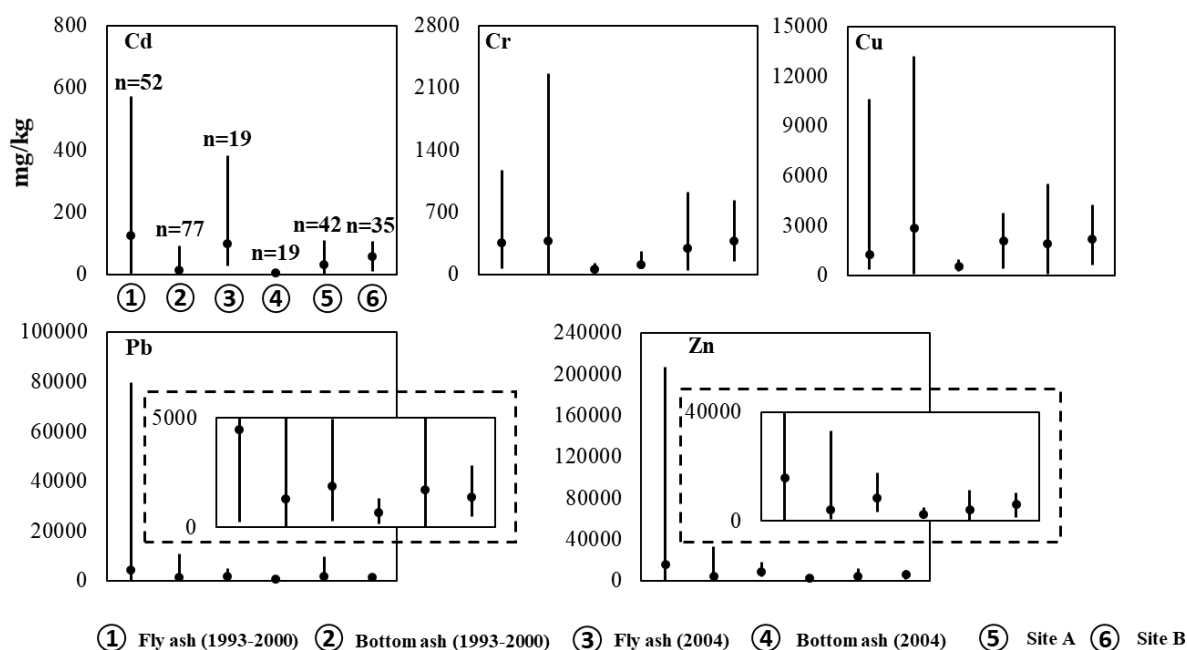


Figure 4-4 Comparison of heavy metal contents with data from the literature.

4. 3. 3 Pearson correlations analysis among elements

Pearson correlation analysis was applied to the element contents of each sample (total of 67 samples from site A, and 35 samples from site B). All statistical analyses conducted in this research were performed by PAST software²⁹. All elements were compared using the same unit (% , w/w) when conducting the analysis. A Pearson correlation coefficient (r) value $>\pm 0.8$ indicates a very strong relationship, and $r >\pm 0.6$ indicates a strong relationship. Correlations were deemed significant at $p < 0.05$. Table 4-3 presents a portion of the Pearson correlation analysis results for all samples (the full results are provided in the Appendix).

Very strong positive correlations were observed for C–N, Fe–Cr, and some other pairs in the no-waste samples from site A, and for Si–O, Si–K, Mg–P, Mg–Cd, Ti–Cd, Cr–Cu, Mg–Zn, P–Zn, and Cd–Zn in the waste samples of site A. The strong correlations among Zn, Cr, Cu, and Cd imply that these metals have similar distributions in the landfill. However, no strong correlations between heavy metals (except Zn–Cd) could be found in

site B. The strong correlation between Na-Cl could suggest the existence of NaCl.

Table 4-3 Pearson correlation analysis results for no-waste samples and waste samples.

Sample type	Correlation	Element pairs (Pearson correlation coefficient (r))
No-waste samples	Very strong correlation ($0.80 < r < 1.00$)	Ti-Fe (0.81), Fe-Cr (0.93), P-Cd (0.83), P-Cu (0.81), P-Pb (0.85), P-Zn (0.90), S-Pb (0.82), S-Zn (0.81), C-N (0.84), Cu-Zn (0.90), Pb-Zn (0.96).
Waste samples (Site A)	Very strong correlation ($0.80 < r < 1.00$)	O-Si (0.90), K-O (0.81), K-Si (0.88), Ti-Mg (0.87), Mg-P (0.87), Ti-P (0.84), Cd-Mg (0.83), Cd-Ti (0.84), Cu-Cr (0.91), Mg-Zn (0.88), Ti-Zn (0.86), P-Zn (0.84), Zn-Cd (0.94); Ca-O (-0.82), Ca-Si (-0.90), K-Ca (-0.88), H-Si (-0.8), Cr-O (-0.81), Cr-Si (-0.82), Cu-Si (-0.84), Zn-O (-0.80).
Waste samples (Site B)	Very strong correlation ($0.80 < r < 1.00$)	Ca-Si (0.93), Na-K (0.82), Na-Cl (0.90), Zn-Cd (0.81); Na-O (-0.89), Cl-O (-0.96).

Table 4-4 presents the correlations for the pairs S–heavy metal and Ca–heavy metal in site A and site B. The total heavy metal content (THM) is equal to the summed contents of Cd, Cr, Cu, Ni, Pb, and Zn. It has been reported that sulfates can be reduced to S^{2-} under the anaerobic conditions in a landfill site³⁰. Generally, S^{2-} reacts very easily with some heavy metal ions to form substances with low solubility. A strong correlation between the contents of heavy metals and S may imply the presence of metal sulfides. We obtained strong correlations between several metals and S, such as Cd–S and Cu–S, in the no-waste samples, but no strong correlations were found in the waste samples from both sides. This result does not agree with the results reported by Jung et al., but their landfill samples, unlike those of Japanese landfill waste, contained many organic compounds, and the activity of sulfate-reducing bacteria would be stronger in their landfill than in the landfill studied in this research.

However, as shown in Table 4-4, strong positive correlations were observed between Ca and heavy metals in the waste samples from site A, but weak negative or no correlations between heavy metals and Ca could be found in site B. It's reported calcium-based polymers can adsorb some heavy metals, which could be one factor preventing heavy metals from being released. The correlations between Ca and the heavy metals may imply a potential role of Ca. Site B is new and most of the incinerator residues were landfilled within 10 to 15 years. The function of Ca salts might not present through the composition analysis, because the dissolvable Ca salts are still inside the waste body. However, the long-term washing in site A has removed most of the dissolvable Ca salts, the left

insoluble Ca adsorb some heavy metals to prevent leaching. So, it could be found a strong correlation between heavy metals and Ca in site A.

Table 4-4 Pearson correlations for S-heavy metal and Ca-heavy metal relationships.

	Site A				Site B			
	S		Ca		S		Ca	
	(r)	(P)	(r)	(P)	(r)	(P)	(r)	(P)
Cd	-0.16	0.31	0.68	0.00	-0.46	0.01	-0.42	0.01
Cr	0.17	0.29	0.72	0.00	-0.49	0.00	-0.10	0.59
Cu	0.11	0.49	0.73	0.00	-0.44	0.01	-0.10	0.59
Ni	-0.08	0.59	0.56	0.00	-0.34	0.04	-0.06	0.74
Pb	-0.13	0.43	0.42	0.01	-0.49	0.00	-0.08	0.66
Zn	-0.20	0.20	0.73	0.00	-0.61	0.00	-0.18	0.30
THM	-0.12	0.46	0.75	0.00	-0.64	0.00	-0.17	0.34

4. 3. 4 Principal component analysis based on element composition

Principal component analysis (PCA) is a good mathematical method to extract useful information from samples with too many variables. Therefore, it's an effective way to analyze our data with the help of PCA. The PCA was also conducted by PAST software. The PCA of the element compositions result was presented in Figure 4-5 and Table A4-7. It's found that two principal components (PCs) explained 90.8% of the variability in the dataset. Thus, most information could be presented by these two PCs.

The loading plot indicated that Ca, S, Cl, Si, O, C, Al, and Fe were effective variables regarding waste composition (Figure A4-2). PC1 shows the different content of Ca, Si, and O mostly, whereas Si, Ca, S, Cl, Fe, and C determined PC2. These elements could be used for the classification of fresh and aged incinerator residues. Usually, the raw Ca content in raw MSW incinerator fly ash and bottom ash is greater than that of Si because of the neutralization reagent. After buried in the landfill sites, the weathering process will release soluble salts from incinerator residues. With leaching, Ca could dissolve and thus continually decreased in content in the solid phase. A lower Ca content in the samples and high concentration in the leachate implies that the waste released dissolvable calcium salts into the leachate. The similar things could also happen to Cl, because raw incinerator residues consist of higher content Cl than aged incinerator residues. In the scores plots of Figure 4-5, the samples in the left quadrants have higher Ca contents, which suggests that these samples were derived from locations where fresh incinerator residues were or leaching is difficult. The color dots (samples from BH7, BH8, and BH9) almost gather in the fourth quadrant, it shows the significant distance between samples from sites A and

B. Therefore, the samples in the figure could be classified into three groups: fresh BA and FA, aged BA and FA, and incombustible waste and soil. Samples from the same BH did not show close proximity within the plot, demonstrating the complex composition of the wastes.

This work is also a prework for the next chapter to select testing samples, we will refer to this result again.

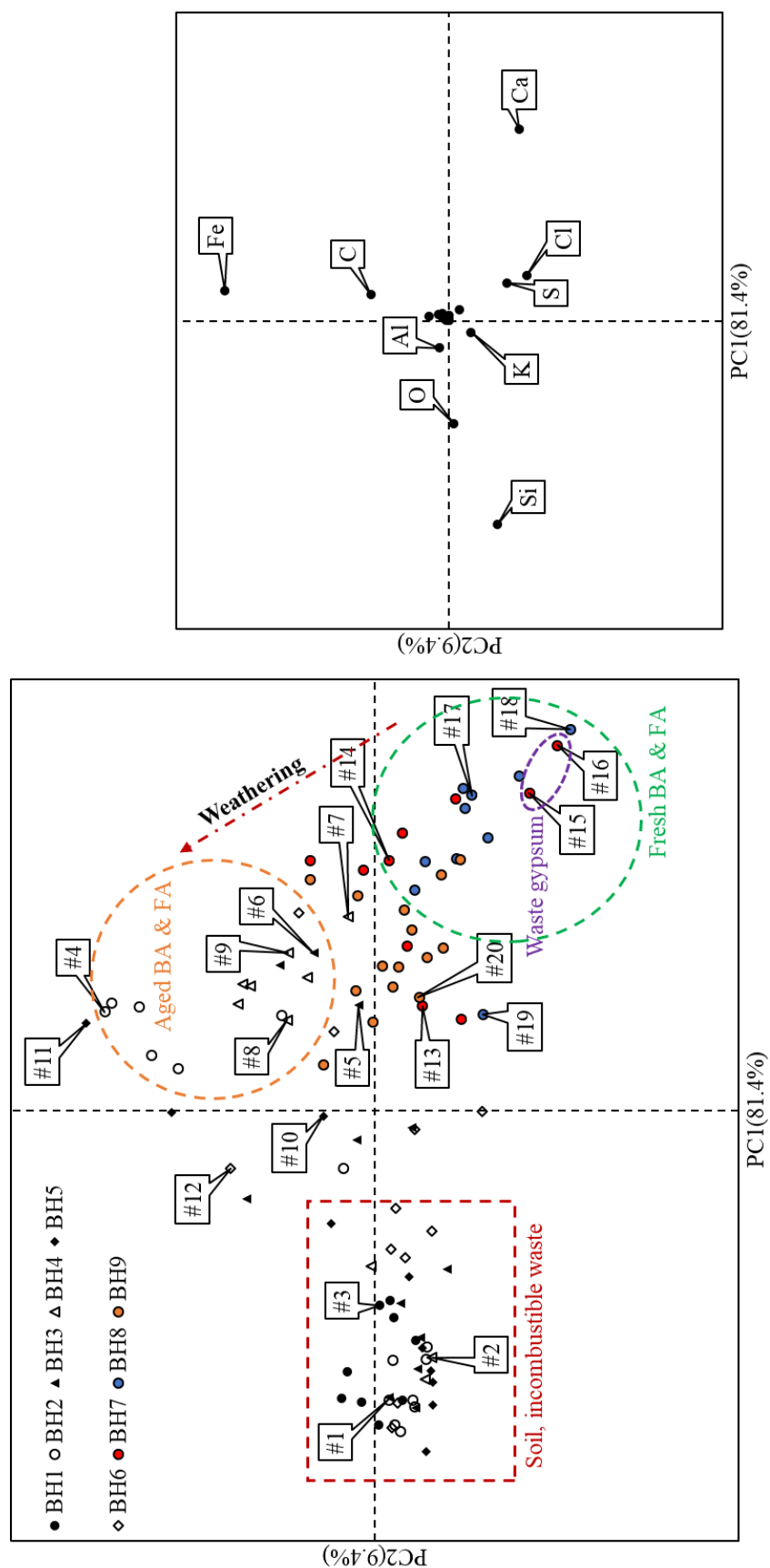


Figure 4-5 PCA result for all samples based on element composition. Scores plotting (left) and loading plotting (right).

4. 3. 5 Vertical distribution of heavy metals

Figure 4-6 (1-9) presents the distributions of heavy metal contents at each point.

In BH1, the highest heavy metal contents occurred near the depth of -2 to -3 m (surface is 0 m), and the sample points near this position also showed higher Cl and S contents than did those at other depths in BH1. As shown by the cross-section plot (Figure 3-7), the waste layer (dark-gray small pieces) was identified near this position. BH2 was also from Area 2 of site A. However, unlike BH1, BH2 had much higher heavy metal concentrations in the waste layers. The highest concentrations occurred around the depth of -5 to -6 m, near the demarcation point between the cover soil and waste layer, but a zone of lower concentration was found below that layer. The waste at this lower position contained pieces of ceramics and brick, which came from incombustible waste. Beneath that layer, the heavy metal concentrations increased again to high levels.

BH3 exhibited a similar trend. Heavy metals showed high levels near -1 to -2 m and then decreased to relatively lower levels around -2 to -5 m. Below that, the concentrations increased to high levels again and then decreased again to low levels at the bottom of BH3.

In BH4 and BH5, high heavy metal contents occurred in the waste layer. In BH4, no particular distribution could be found (the heavy metal contents remained almost the same). However, in BH5, the bottom part of the BH obviously contained higher heavy metal concentrations than the top part.

In BH6, the heavy metal concentrations fluctuated in different layers, even though the waste layer. Three sampling positions showed heavy metal concentrations relatively higher than the other positions.

BH7, BH8, and BH9 are from site B, and the landfill waste is similar to each other. So, the heavy metal contents are similar, too. In BH7, at 5~6 m and 8~10 m, the heavy metal content decreased. And in BH8, 9~10 m also has lower heavy metal content. Because these positions were filled with waste lime, plaster and concrete. The other parts of BH7 and BH8 didn't change so much. In BH9, as deepest drilling, the heavy metal content of each depth was almost the same, except the top, where the cover soil is. Because the waste had been just landfilled in site B. This heavy metal vertical distribution might not change, yet.

In site A, the waste in the landfill had been buried for more than 20 years, and some BHs included waste that had been buried for more than 40 years. Because the waste layers still contain high concentrations of heavy metals, it seems that heavy metals remain at their original positions in the waste. Cl contents in the waste layers were lower than those in the raw incinerator bottom ash and fly ash, which means that the condition of the landfill is suitable for leaching of its easily dissolvable salts, but heavy metals seem to be relatively immobile.

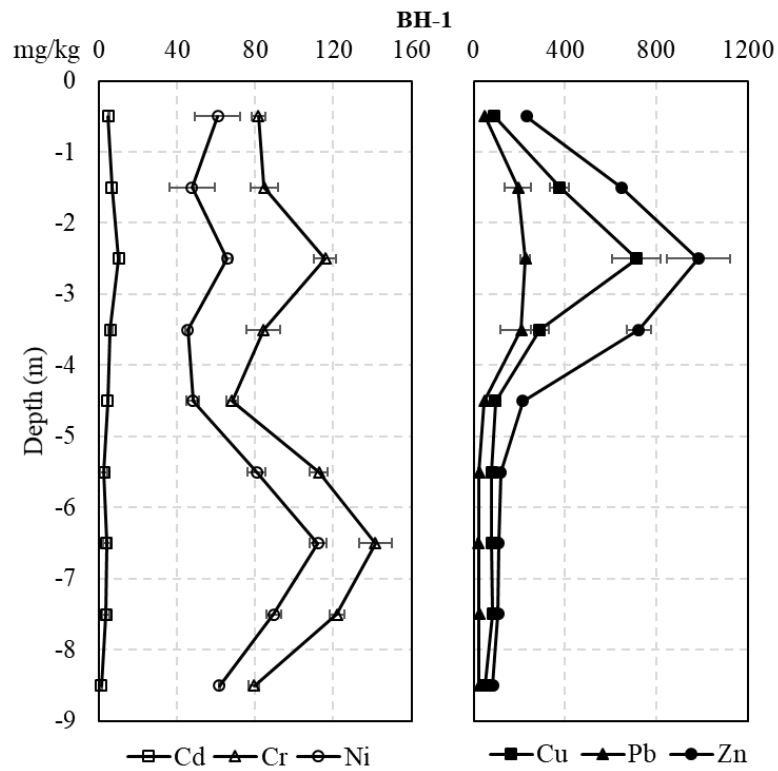


Figure 4-6 (1) Vertical distributions of heavy metals at BH1.

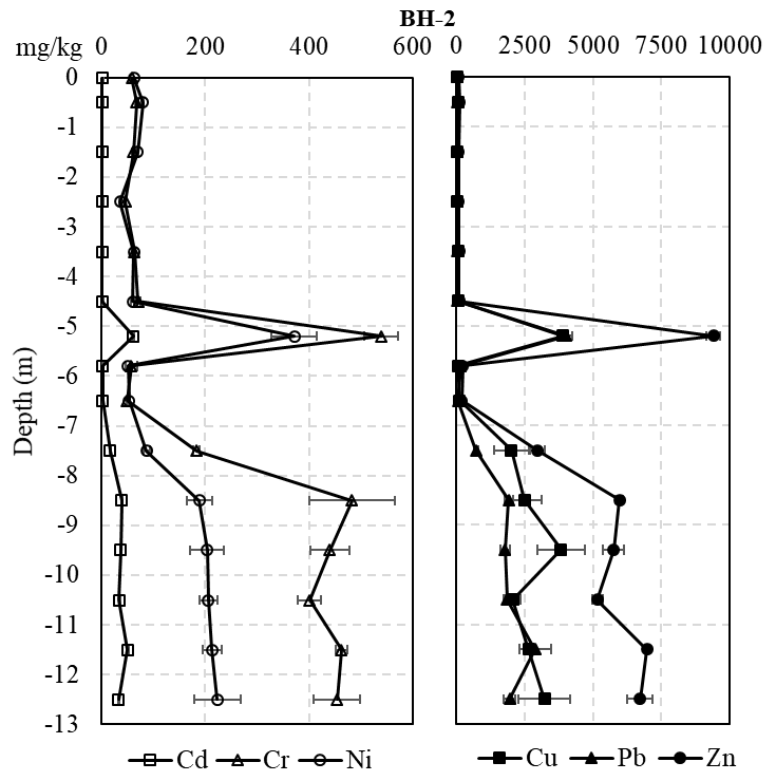


Figure 4-6 (2) Vertical distributions of heavy metals at BH2.

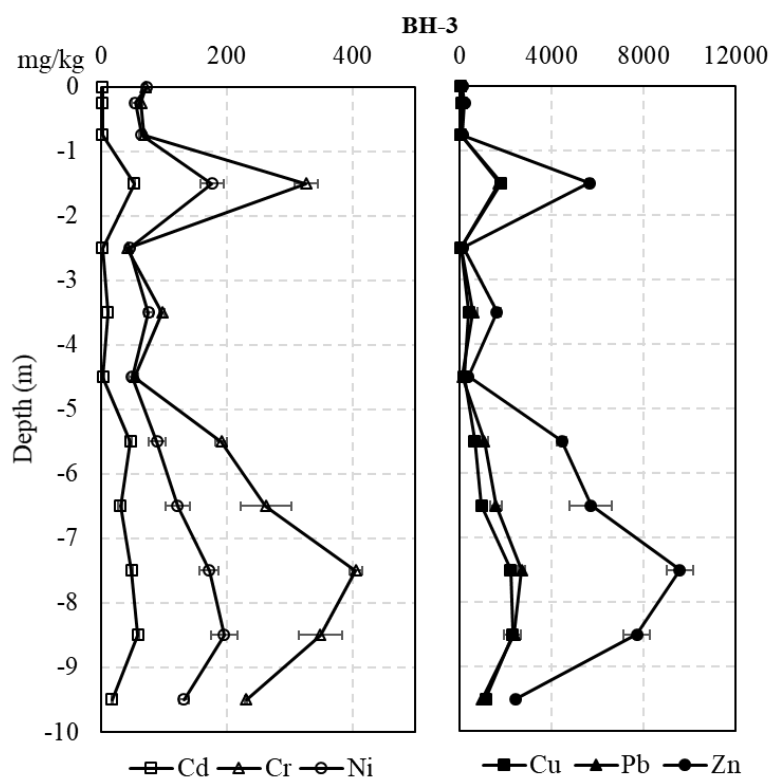


Figure 4-6 (3) Vertical distributions of heavy metals at BH3.

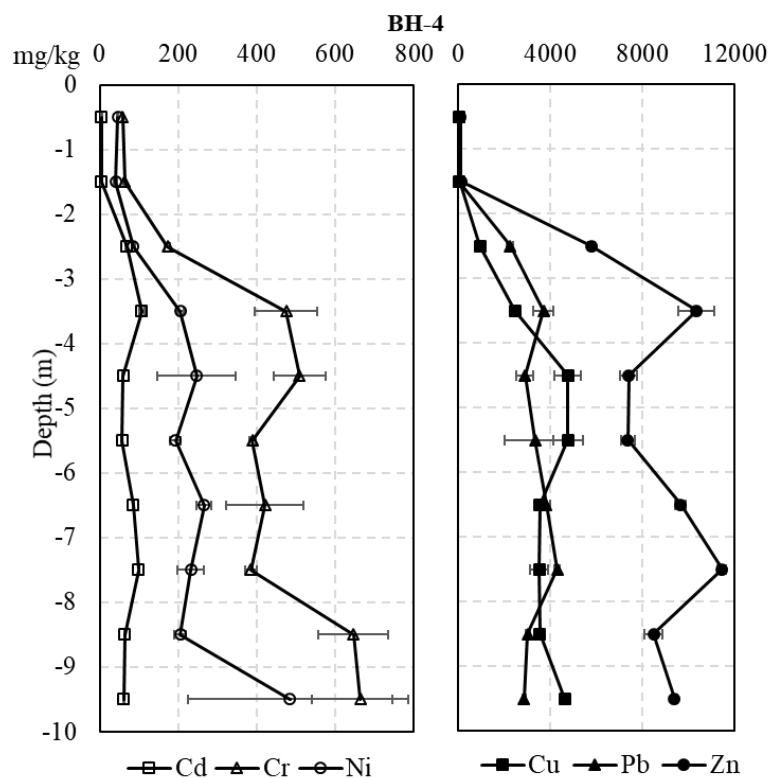


Figure 4-6 (4) Vertical distributions of heavy metals at BH4.

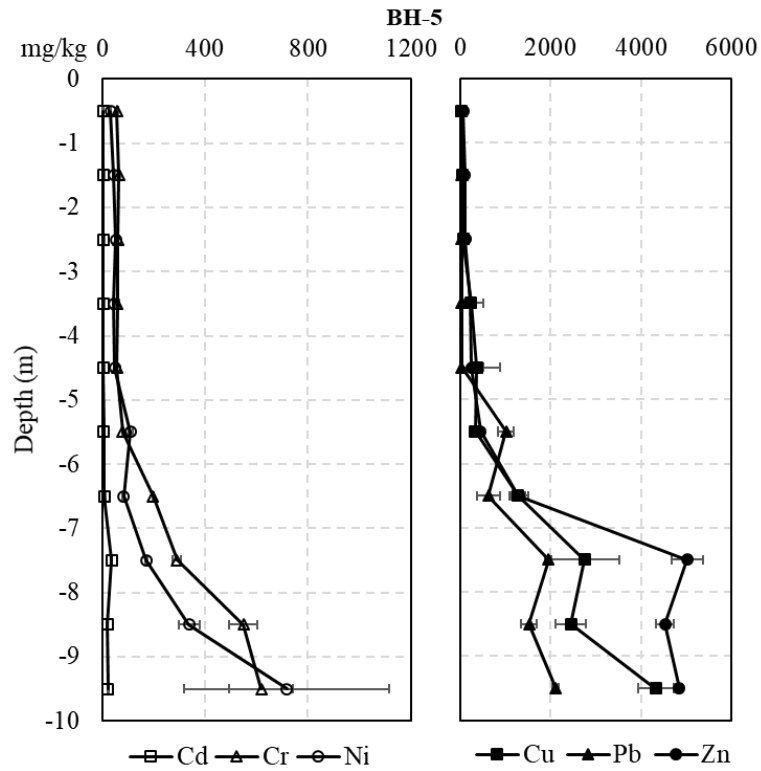


Figure 4-6 (5) Vertical distributions of heavy metals at BH5.

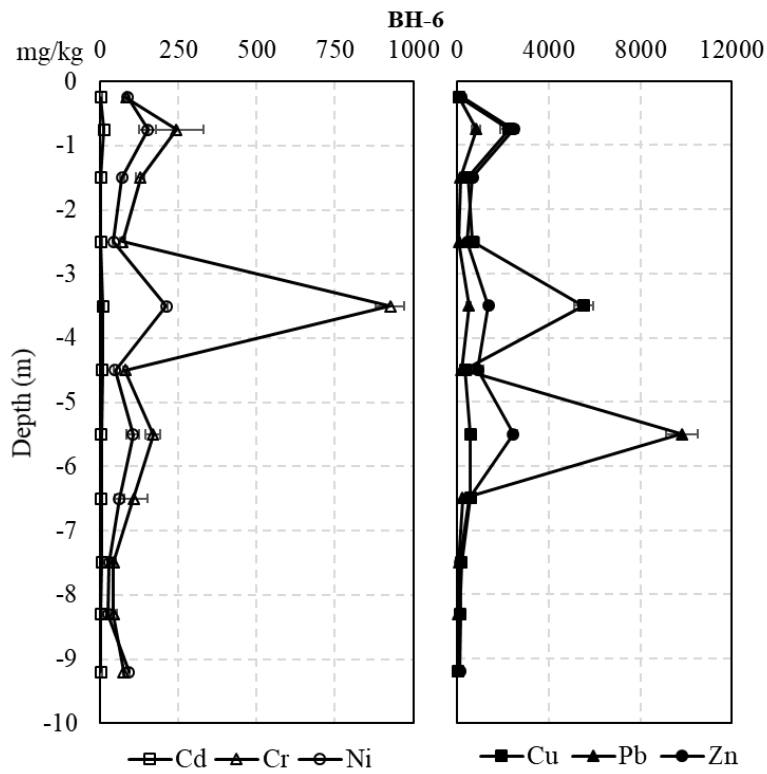


Figure 4-6 (6) Vertical distributions of heavy metals at BH6.

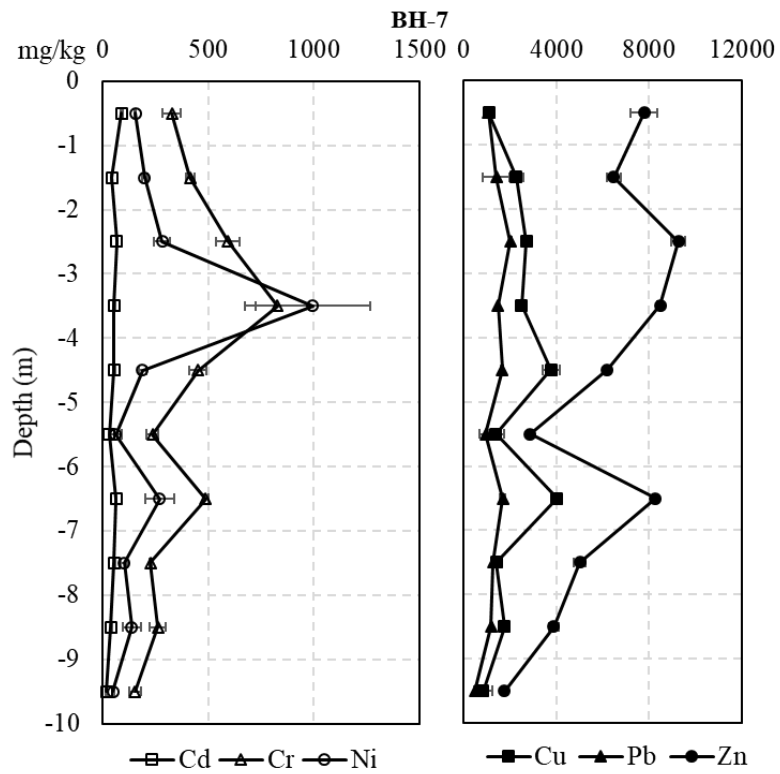


Figure 4-6 (7) Vertical distributions of heavy metals at BH7.

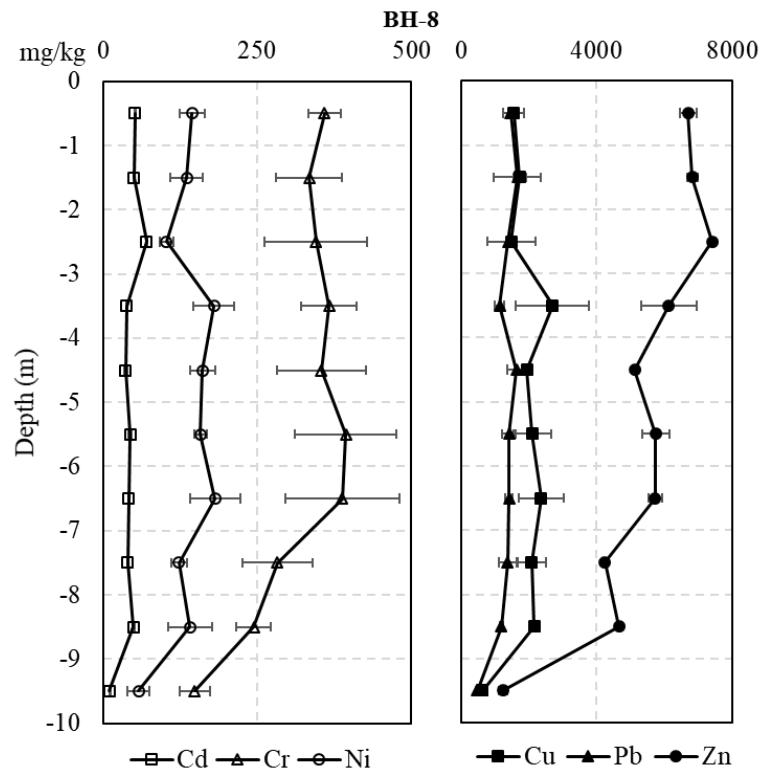


Figure 4-6 (8) Vertical distributions of heavy metals at BH8.

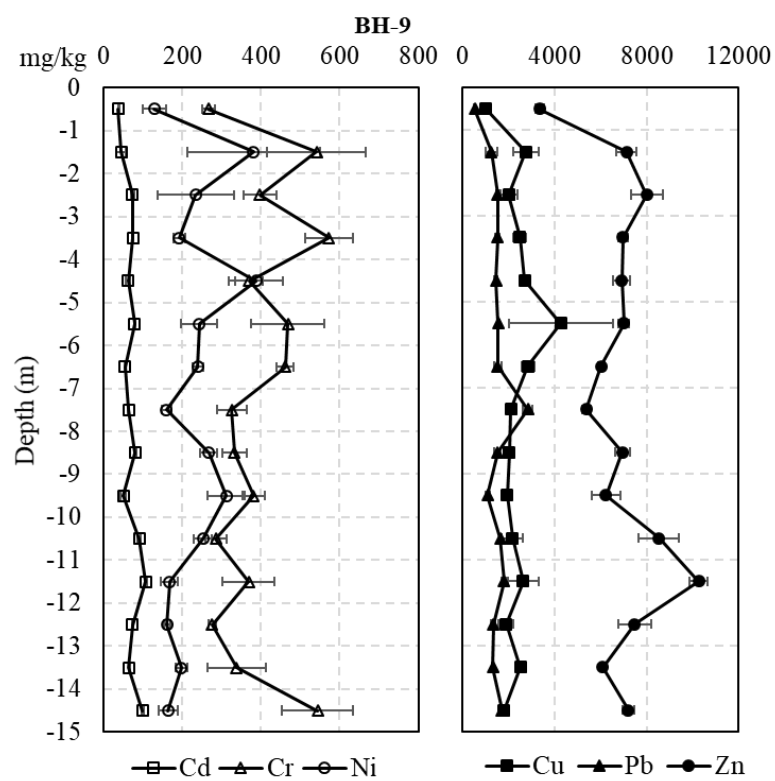


Figure 4-6 (9) Vertical distributions of heavy metals at BH9.

4.3.6 Analysis of heavy metal content with historical data

The better way to investigate heavy metal mobility is to compare the current contents with the raw contents of samples at specific positions. A similar comparison has been conducted in several studies^{15,31}, but the original contents in those studies were estimated through simulated waste data. We compare the measured sample data with corresponding yearly concentration data in Figure 4-7. If the heavy metal is stable, the points will be close to the 45° line or within the lower right area, which means that the contents in the waste samples are equal to or higher than the estimated value. If points occur in the upper left area, it means that the metal has positive mobility. As shown in the figure, almost all of the points for Cu, Pb, Cd, and Zn lie in the upper area (above the 45° line), whereas points for Cr are mostly in the lower area or on the 45° line.

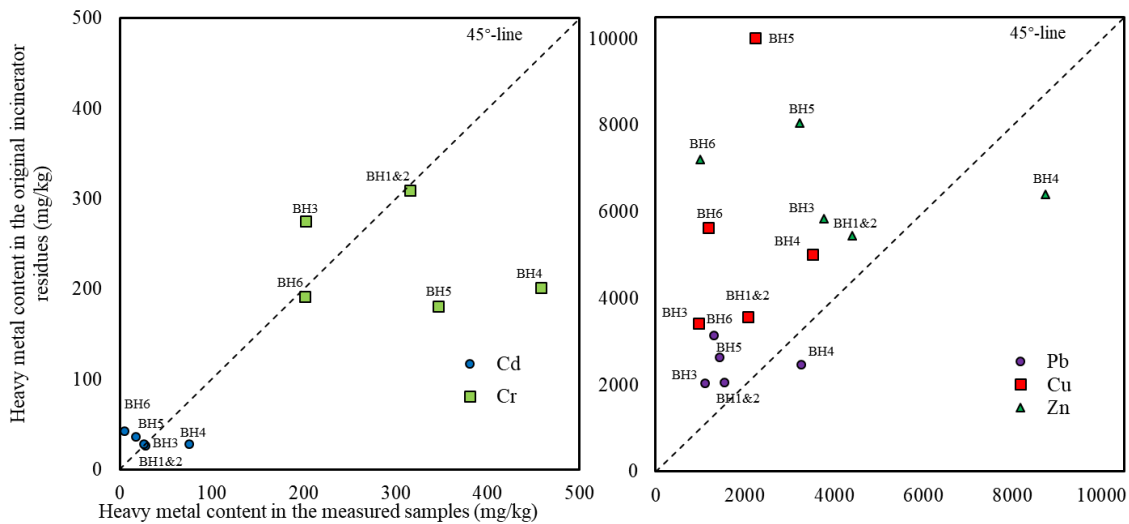


Figure 4-7 Heavy metal contents in measured samples versus concentrations in original incinerator residues.

We also calculated the total input mass of heavy metals and current storage of heavy metals (only includes the sections 2, 3, 4, 5, and 7, where we got samples). The total heavy metal mass was compared before and after the waste was landfilled at the study site (Fig. 4-8). The estimated current total mass of Cd and Cr is close to the original total mass landfilled, which means almost no leaching occurred. In comparison, the amounts of Pb, Zn, and Cu were decreased compared with those in the original landfilled incinerator residues, especially Cu. This implies that rainfall washed some Cu, Zn, and Pb from the landfill, whereas Cr and Cd remained mostly in the waste. This calculation was not accurate because of uncontrollable errors. However, the general trend is plausible.

Our findings disagree with those of He et al, who found that the mobility of almost all heavy metals was negative. This difference might be related to the difference in landfill waste. All metal contents, except for Cu, in the measured samples of BH4 were higher

than the original contents in the incinerator residues, which is unique among the core samples. BH4 had a very high pH in the leaching test, as did the leachate collected from the actual site (will be presented in later chapters), which might explain why it stands out among the BHs. Among the heavy metals, Cu and Zn exhibited relatively stronger mobility than the other metals, followed by Pb and Cd, and finally by Cr as the most stable metal.

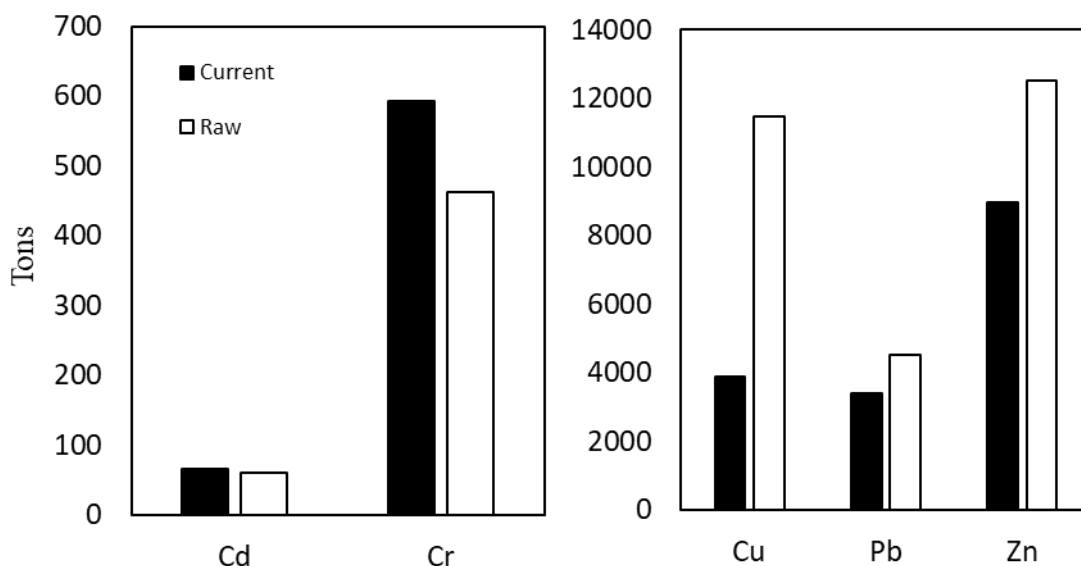


Fig. 4-8 Total mass storage of heavy metals in this landfill site (raw and current).

4. 4 Conclusions and future works

In this chapter, the elemental compositions and heavy metal content of samples from nine BHs (BH1–BH9) from two typical Japanese landfill sites were analyzed. The conclusions could be reached as follow:

- 1) The composition results showed significant differences between the layers with and without waste. High heavy metal contents occurred in waste layers, but it's strongly relative to the type of waste. Both sites have very high heavy metal content samples, and that means the waste layers still present a large potential source of environmental pollution.
- 2) Correlations between elements were estimated in this chapter, and we found strong correlation between Ca and heavy metals in the waste of site A. However, we didn't find the similar result in site B. As weathering process could remove most of the dissolvable salts, it's believed that the insoluble Ca salts might help to trap the heavy metals inside this kind landfill after long-term washing of rainfall.
- 3) Because incinerator residues are the main source of landfill waste in Japan, we could collect the data from the local governmental historical records. Therefore, it's possible

to compare the experimental data with data from records in this study, and it's more convincing. The results suggested that Cu, Zn, and Pb in the landfill could be washed out more easily by rainfall, whereas Cr and Cd tended to remain in the waste.

- 4) In this chapter, we analyze the data by using the PCA method to classify the samples. Fortunately, we could find three groups for the samples, which are fresh BA and FA, aged BA and FA, and Incombustible waste and soil. This result will support our next work in chapter 5.

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CHAPTER 5

HEAVY METAL SPECIATION DISTRIBUTION ANALYSIS IN LANDFILLS

5. 1 Introduction

After checking the basic composition of all samples, we found the heavy metal content is very high in the landfilled incinerator residues. However, the total content is not enough to judge the hazard level of the waste. In this chapter, we will further analyze the samples by other test methods.

Heavy metal as one adverse factor limits the utilization of incinerator residues¹, it's still the main environmental risk from monofill sites of incinerator residues. Researches related to the landfill of incinerator bottom ash have been well studied by many scholars²⁻¹³. Chimenos³ et al studied the short-term natural weathering process of MSWI bottom ash; Freyssinet⁵ focused on chemical changes and leachate mass balance; ... Heavy metals are reported that highly concentrated in both incinerator bottom ash and fly ash. However, the reports on heavy metals in the monofill of incinerator residues are nearly blank. It's necessary to investigate the heavy metal speciation for potential hazard evaluation as well as the landfill mining in the future.

Sequential extraction procedure (SEP) has been widely used for heavy metal species analysis¹⁴⁻¹⁸. The result could present the distribution, mobility, and bioavailability of heavy metals in the environment depend on the association form in the solid phase to which they are bound. The variations of the chemical or physical condition of the environment can accelerate the release of toxic heavy metals, which cause contamination from landfill sites. Fly ash and aerosol particles generated from municipal solid waste incinerators have been studied by the SEP method to characterize the metal mobility, therefore, the species analysis through the SEP method is necessary.

In addition, with the help of an X-ray absorption fine structure (XAFS) analysis¹⁹⁻²⁹, the chemical species could be also identified. However, it's believed that XAFS analysis is more accurate than wet extraction by SEP²⁵⁻²⁹ because of no speciation modification of target elements by the reagent. The result of XAFS is useful for understanding the chemical reactions of heavy metal inside diverse landfill conditions, while the result of SEP is more suitable for evaluation the potential environmental hazard level. Takaoka et al¹⁹ investigated the Pb and Cu species distribution by XAFS spectra in incinerator fly ash from Japan. It's found the main species of Pb and Cu is binding to chloride in the raw incinerator fly ash. Hsiao et al²² investigated the Cu in MSWI bottom ash through XAFS, and he suggested the main species of Cu presents as CuO. However, the report of species changing under natural landfill conditions is limited.

The purpose of this study is to analyze heavy metal speciation in the monofill of

incinerator residues through various methods and trying to estimate heavy metal hazard level in this kind of landfill site. Figure 5-1 presents the analysis pathway and pretreatment of the samples. The further analysis test includes sequential extraction procedure, X-ray diffraction (XRD), X-ray absorption fine structure measurement (XAFS), and scanning electron microscope observation (SEM). The results agree with several proposed hypotheses in the works of literature and could provide valuable data for future study. It's the first practice of evaluation of heavy metal hazard level in semi-aerobic type landfills for incinerator residues. Furthermore, it will benefit the future mining of old landfills of incinerator residues.

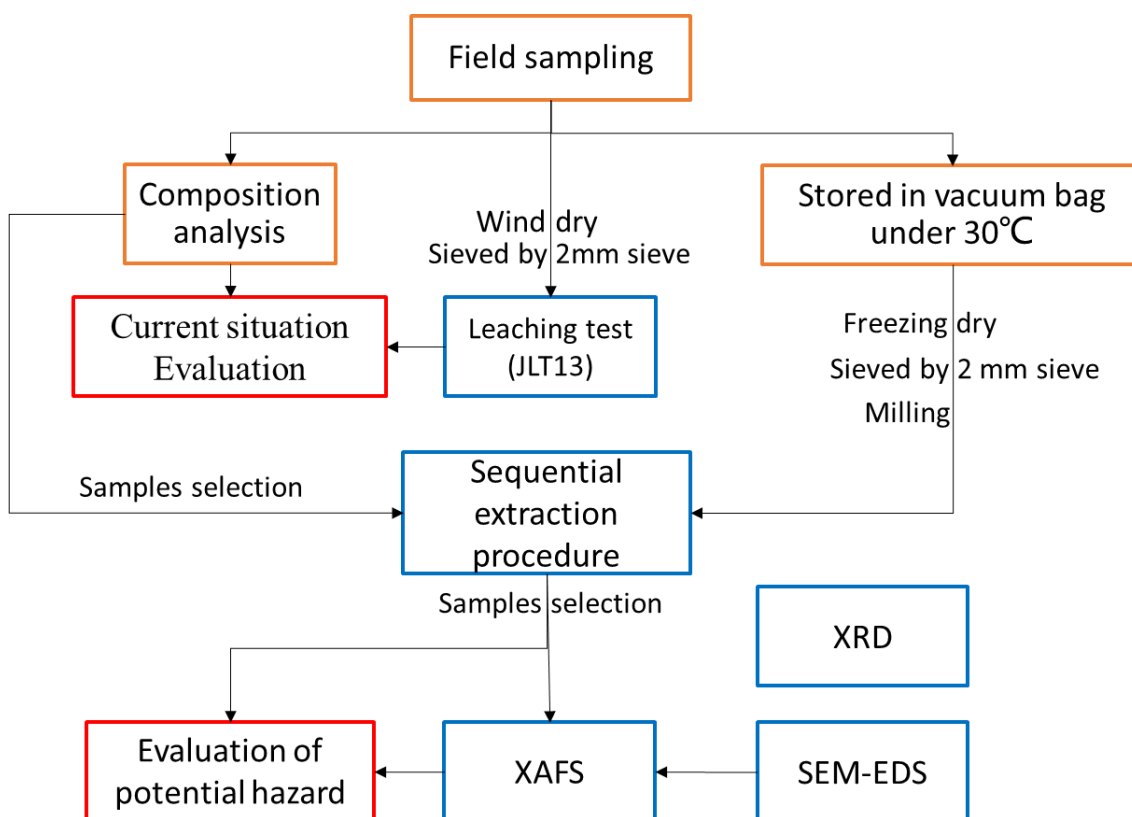


Figure 5-1 The research content and pathway of chapter 5.

5. 2 Material and Methods

5. 2. 1 Samples and its pretreatment for each analysis

The samples in landfill site A and B were collected on-site and stored with vacuum plastic seal bags, and then they were sent to -30 °C frozen storage room after brought back to the laboratory. After a series of pretreatments (including drying, sieving, sorting, milling,

microwave acid digestion et al), the samples were tested by several instruments. To narrow down the samples conducted speciation analysis, we applied principal component analysis (PCA) (Figure 4-5) and cluster analysis (Figure 5-2) to the samples for separation and selection. The detailed PCA process could be found in chapter 4. Cluster analysis was conducted by PAST software, Euclidean distance between points were calculated and the distance between clusters were computed using Ward's method. We selected the samples following the principals as follow:

- 1) Basically, we selected samples from each classified group;
- 2) Our key targets focused on the aged and fresh incinerator residues, and the samples cover all of the sampling points and landfill period.
- 3) The condition of the samples.

Twenty samples were selected out of a hundred samples for further analysis. The specific sampling position could be found in Figure 5-3 and a detailed description of the samples was presented in Table 5-1.

A freeze-drying process (at -50 °C) has been conducted to the selected samples before sieving through a 2 mm sieve. After that, the samples were milled to the fine powder. These samples will be tested by SEP and XAFS measurement.

In the cluster analysis, the samples could be classified into 3 groups: 1) cover soil (#1 and #2); 2) gypsum like a waste (#15); 3) various incinerator residues (fresh or aged incinerator residues). The samples covered a full-time scale of around 40 years (1975 to 2015), the detailed estimated buried year of each sample could be found in Table 5-1.

5. 2. 2 Leaching test

A leaching test was performed on the landfill incinerator residues samples according to the Japanese Leaching Test-13 (JLT-13) for three times. We used ultra-pure water to extract heavy metals from samples at a ratio of 1:10 (g/mL). The samples were mixed with the ultra-pure water in a polyethylene bottle, and the bottle was then shaken on a horizontal oscillator at 200 rpm for 6 h. Next, after standing for 6 h, the solution was centrifuged at a speed of $3000 \times g$ for 20 min. After filtration with a 1- μ m membrane filter, we obtained the leaching solution. The pH of the leaching solution was measured by pH meter (HM-30P, TAODKK, Japan), and the heavy metal concentrations were measured by ICP-MS.

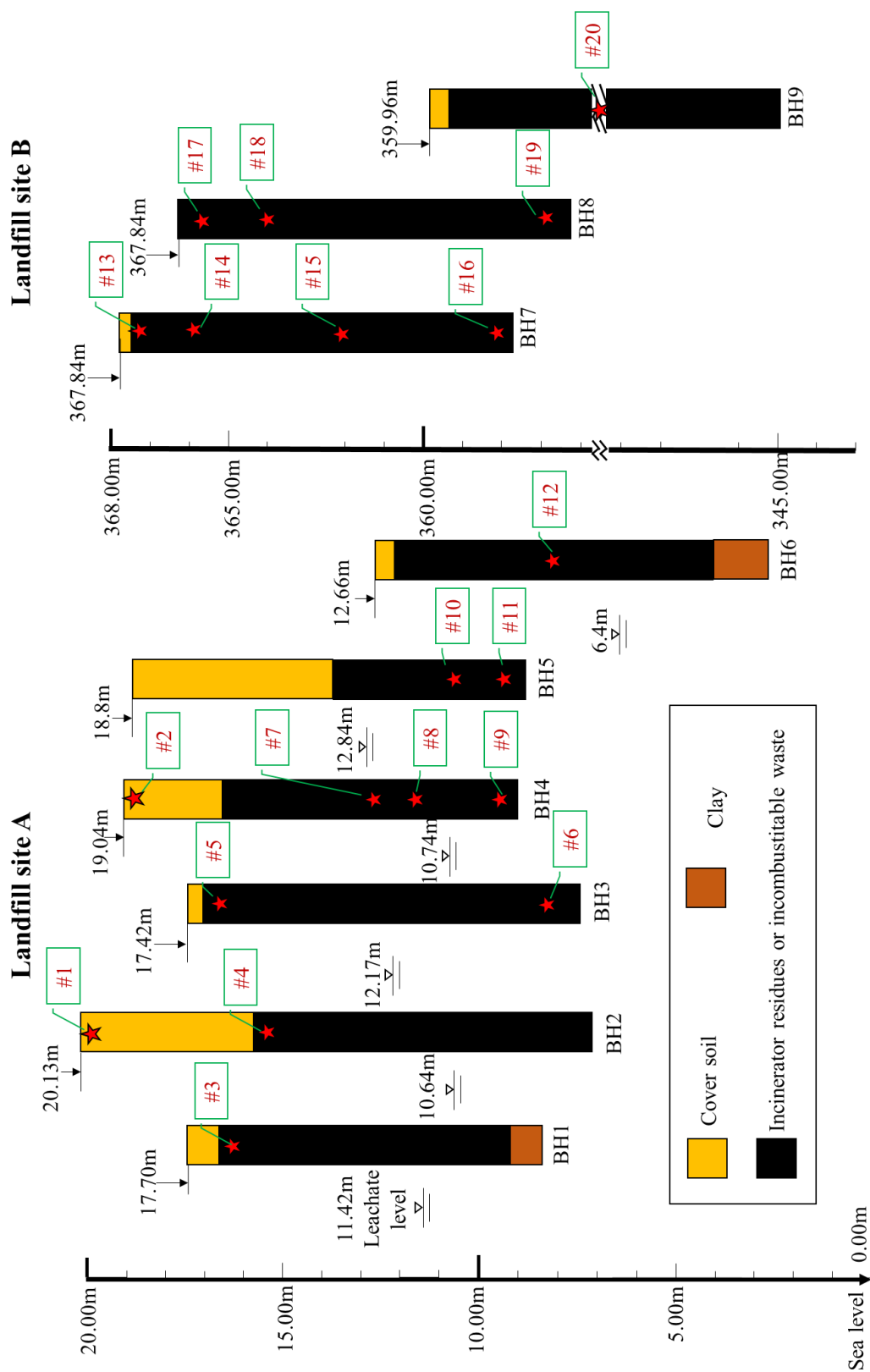


Figure 5-3 The positions of selected samples in this study.

Table 5-1 Description of each sample.

Point NO.	Position	Description	Estimated buried year
#1	0 ~ 0.5 m of BH2	Cover soil of BH2, yellow soil with plant roots.	--
#2	0 ~ 1 m of BH4	Cover soil of BH4, brown soil with stones.	--
#3	2 ~ 3 m of BH1	Black waste with brick and plant.	1984
#4	4.4 ~ 5m of BH2	Dark gray waste.	1985
#5	1 ~ 2 m of BH3	Black waste includes brick, glass and iron wire.	1985
#6	8 ~ 9 m of BH3	Black waste mud.	1978
#7	6 ~ 7 m of BH4	Dark gray waste with iron wire.	1987
#8	7 ~ 8 m of BH4	Dark gray waste with iron wire.	1986
#9	9 ~ 10 m of BH4	Dark gray waste with iron wire.	1985
#10	7 ~ 8 m of BH5	Dark gray waste with tiny stones.	1991
#11	9 ~ 10 m of BH5	Dark gray waste includes iron wire, tiny stones and pieces of ceramic.	1987
#12	4 ~ 5 m of BH6	Black waste.	1995
#13	0 ~ 1 m of BH7	Brown waste with tiny stones.	2005
#14	2 ~ 3 m of BH7	Gray waste with bricks.	2004
#15	5.5 ~ 6.0 m of BH7	White waste, gypsum.	2003
#16	9 ~ 10 m of BH7	Light gray, fiber and iron sheet.	2000
#17	0 ~ 1 m of BH8	Gray sand.	2015
#18	2 ~ 3 m of BH8	Brown waste.	2013
#19	9 ~ 10 m of BH8	Gray waste with stone.	2010
#20	7 ~ 8 m of BH9	Gray caking waste with iron wire.	2008

5. 2. 3 Sequential extraction procedure (SEP)

The freeze-drying samples were extracted by steps with chemical reagent shows in Table 5-2²⁷. Each samples were tested by three times. A 50mL plastic centrifuge tube was used as an extraction container. Each sample was tested with 1g and in triplicate experiments. The extraction procedure was conducted in a horizontal water-bath shaker. The final fraction was also used the microwave acid digestion. After each extraction step, the mixed solution was centrifuged and filtrated with a 0.45 um membrane filter, and the pH value was measured by pH-meter before and after the extraction period. After step 5, the residual sample was dried under 60°C in the oven and weighted. 0.1 g of residual sample was used to conduct step 6 by microwave digestion system, detailed information of each step could be found in Table 5-2. The solution from each step was measured by ICP-AES

and ICP-MS for the concentration of heavy metals.

Table 5-2 Sequential chemical extraction procedure steps.

Fractions	Procedure		
	Reagent	Time/h	Temp.
F1 Water soluble	20 mL Ultra-pure water	6	Room temp.
F2 Ammonium acetate extractable (Exchangeable)	20 mL 1.0 mol/L CH ₃ COONH ₄	6	Room temp.
F3 Acid soluble	15 mL 1.0 mol/L CH ₃ COONa (pH=5, adjustment by CH ₃ COOH)	6	Room temp.
F4 Reducing extractable	20 mL 0.2 mol/L NH ₂ OH·HCl (with CH ₃ COOH in 25 vol/vol%)	6	85°C
F5 Oxidizing extractable	1). 10 mL 30% H ₂ O ₂ (with 0.02 mol/L HNO ₃ , pH=2)	1). 2	1). 85°C
	2). 1.78 mol/L CH ₃ COONH ₄ (with CH ₃ COOH in 25 vol/vol%)	2). 6	2). Room temp.
F6 Residual	7.0 mL HNO ₃ + 2.5 mL HF + 0.5 mL 30% H ₂ O ₂ 0.1 g of residue sample from F5 was used		

Before the landfill samples, two standard samples were tested three times by the same procedure to evaluate the method, they are NIST SRM2711a (Montana soil) and JSAC 0401 (Forest soil). The result is shown in Table 5-3, it's found the sum of each extracted fraction is nearly equal to the certified value (except Ni), therefore, we considered the method is available for our analysis for Cd, Cu, Pb, and Zn.

Table 5-3 The SEP result of the standard materials. (mg/kg)

NIST	F1	F2	F3	F4	F5	F6	Sum	Certified value	Recovery rate
Cd	0.07	13	20	13	1.3	2.8	50	54	92.8%
Cr	0.02	0.0	0.49	2.9	2.6	69	75	52	144.5%
Cu	0.98	2.2	12	38	31	64	150	140	106.1%
Ni	0.00	0.10	0.92	5.0	2.7	35	43	22	197.0%
Pb	0.51	54	430	540	110	56	1200	1400	84.7%
Zn	0.09	2.9	25	150	44	180	410	410	97.8%
JSAC									
0401									
Cd	1.6	0.81	0.68	0.49	0.00	1.3	4.9	4.3	115.2%
Cr	0.62	0.17	0.50	3.1	2.3	69	76	50	149.8%
Cu	0.42	0.04	0.36	0.51	2.5	10	14	15	91.7%
Ni	0.32	0.08	0.78	2.0	1.8	42	47	19	251.0%
Pb	0.82	0.32	1.1	9.0	7.6	14	32	26	124.8%

Zn	0.60	0.07	0.71	8.5	6.8	40	57	67	85.0%
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To evaluate the potential risk of heavy metals, risk assessment code (RAC) was introduced to assess the hazard level of heavy metals in the landfill sites in this study³⁰⁻³⁵. Guido Perin³⁰⁻³¹ firstly introduced RAC in his report as the tool to assess the potential environmental risk based on the result of SEP testing. After that, researchers started to accept this concept and also applied a similar analysis in many research fields. Originally they considered RAC to evaluate the heavy metal releasing risk in the aquatic environment. The essential idea of RAC is to assess metal pollution was expressed as the percentage of water-soluble (F1), exchangeable (F2), and acid-soluble (F3) fraction in sediments. In this study, I would like to use it to estimate the hazard level under acid condition of landfill incinerator residues. It could be calculated through the equation below:

$$RAC = \frac{(F1 + F2 + F3)}{Total\ content} \quad Eq(5-1)$$

The total content is the sum of six fractions. If the RAC<1%, we consider the sample is at no risk level in the aquatic environment. The range of 1-10%, 10-30%, 30-50%, and >50% are identified as low risk, medium risk, high risk, and very high risk respectively. However, not only the RAC value but also the total content should be considered. The Japanese criteria of the content of Cd, Pb, and Cr(VI) for contaminated soil are 150, 150, and 250 mg/kg respectively. No limit value is set to Cu, Zn, and Ni. After comparing this limit value to the content in incinerator residues, we consider if the content of RAC fractions larger than these limit values, the potential hazard level will be quite high.

5. 2. 4 X-ray diffraction and SEM-EDS observation

To determine the weathering stage, XRD measurement of selected samples (1 cover soil (#2) and 6 incinerator residues (#4, #7, #8, #9, #12, and #20)) was conducted to identify the crystalline phases. Before the measurement, the samples were pretreated by drying under 105°C for 24h. Even though Saffarzadeh³⁶ concluded XRD was not effective to analyze several newly-formed crystalline phases and amorphous substances, it's still possible to determine the weathering stage by XRD result. Because the hydration process will change dissolvable salts to hydrates form under high pH conditions. Samples were measured by a powder XRD (RINT UltimaPC, Rigaku Corp., Tokyo, Japan) continuously with Cu-Ka radiation at 40kV and 20mA, with a speed and a data sampling interval of 10°/min and 0.02° from 5° to 90° at 2θ. The diffraction data were collected using a semiconductor detector (D/teX Ultra2; Rigaku Corp.). The XRD pattern was analyzed

using PDXL2 analysis software (Rigaku Corp.).

The selected powder samples (#4, #9, and #20) were pasted to carbon tape for SEM-EDS observation, however, it's not easy to find hot spots in all samples. Backscattered electron mode was performed with SEM (JSM-5600T, JEOL, Japan) under 15kV accelerating voltages and a low-vacuum mode. Element analysis and mapping were used EDS system (JED-2300M, JEOL, Japan).

5. 2. 5 X-ray adsorption fine structure measurement

XAFS spectra of selected 9 samples (1 cover soil (#2) and 8 incinerator residues (#4, #6, #7, #8, #9, #12, #18, and #20)) were obtained from beamline BL01B1 in the SPring-8 facility (Hyogo, Japan) and beamline BL12C in Photo Factory (Tsukuba, Japan). The samples were selected after the analysis of the SEP result. Cu-K edge (8680 - 9580 eV) and Pb-LIII edge (12700 - 13420 eV) spectra of the samples were measured. We didn't measure long range of Pb due to the presence of Br. The reference materials' spectra of Cu and Pb were listed in Table A5-1 and Figure A5-1 and A5-2, which were also obtained from these two facilities in the old time^{19, 21}. Multiple scans were collected for each sample and merging them after collection without a bad signal spectrum. The merged spectra were normalized by software Athena through the regular process carefully. Both X-ray absorption near edge structure (XANES) and extended structure (EXAFS) were analyzed in this study. The chi EXFAS functions were extracted by AUTOBK Algorithm featured in Athena with default Rbkg at k^2 -weighted. The principal component analysis (PCA) was performed to samples' spectra with software package Sixpack to determine the number of reference spectra required to conduct linear combination fitting (LCF) with an experimental error. We also conducted the PCA to samples' spectra with reference materials' spectra to check the distance between each sample and standard material. Through this process, we selected the most possible reference materials to do LCF for the samples. The final result of LCF comes out from XANES for Cu, and EXAFS for Pb, because of the shape of XANES of the Pb-LIII edge XANES of samples and reference materials are too similar. The whole process could be found in Figure A5-3.

5. 3 Results and Discussion

5. 3. 1 The leaching test result

Before we investigate the selected samples, we conducted the leaching test to all waste layer samples from both sites. The whole result of the leaching test could be found in the appendix Table A5-1. A total of 73 samples were tested by the Japanese leaching test

method NO. 13. The leaching concentration of only 10 samples and 27 samples could be detected for Cd and Ni respectively. A summary of the leaching test result is presented in Figure 5-4, all heavy metals had very low leaching concentration in this test, and no sample exceeded the limit of landfill waste regulation, which means that all of the landfill waste was still suitable for landfilling. Among the metals, Cu exhibited relatively higher leaching concentrations, and Cd and Ni could hardly be leached. Cr, Pb, and Zn have similar leaching concentration range. According to the average value, the leaching ability of heavy metals follows as $Cu > Zn > Pb > Cr > Ni > Cd$.

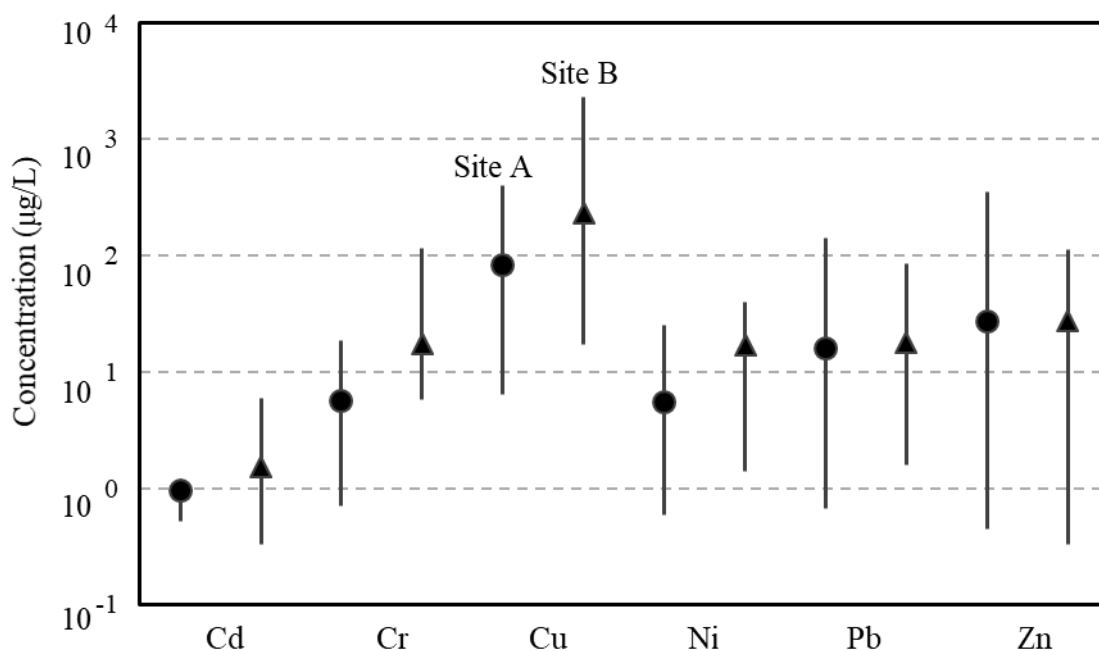


Figure 5-4 The leaching test result of landfill waste.

Table A5-1 also presents the pH of leaching liquor, it's could be considered as the raw pH of landfill waste. It's found the pH in site A ranged from 7.5 to 11.6. BH1, BH2, and BH6 have a lower pH than the other BHs. In site B, the pH of incinerator residues was almost more than 11, except for some waste plaster samples in BH7. More detailed information could be found in Figure A5-4.

When comparing the leaching result between site A and site B, there are some big differences that could be observed. For Cu, Cr, and Cd, the samples from site B showed higher leaching concentration. Ni in site A could release a little, but almost no Ni in site B (only 3 samples) could leach out. The leaching behavior of Pb and Zn is similar in sites A and B. As a conclusion, the leaching ability of Cu, Cr, and Cd from fresh incinerator residues are higher than aged ones, however, the behavior of Ni might be the opposite. Zn and Pb seem not to change so much.

Even though the leaching result shows low mobility of heavy metals in old and new landfill sites, the potential risk still exists when the total content of heavy metals is high in the buried wastes. Further analysis needs to proceed.

5. 3. 2 Element composition of the selected samples

The chemical composition of major elements was measured by XRF and C-H-N detector (Table A5-3). Heavy metal concentration was measured by ICP-AES and ICP-MS after sequential extraction process (we have evaluated the accuracy by testing standard materials), the total content was the summation of each fraction. Samples #1 and #2 contain a relatively low content of heavy metals, smaller than 100 mg/kg. #12, #15 and #16 also show low content of heavy metals. The other samples contain more than 1000 mg/kg of Pb or Cu, or both of them are high content.

It's pointed out that there's a significant composition change among landfill wastes with different landfill age, especially the samples between site A and site B. A decreasing of Ca and Cl could be observed through the timeline, which also was mentioned in our previous report. Cl also could be considered as the indicator of incinerator fly ash, because the Cl content in fly ash is usually very high. Zhu et al have demonstrated that more than 90% Cl in the fly ash is in soluble fractions. Therefore, it's believed that the Cl in the incinerator fly ash samples from site A have almost removed by the rainfall (proved by the low Cl content in the samples), while there is still fresh fly ash in site B (#14, #17 and #18 contain relatively high Cl, especially for #18 (14.95%)). In chapter 6, the monitor record from the administrator of site A shows the concentration of Ca and Cl in the leachate was very high during the landfill operation period and decreased immediately after the closure of the landfill. However, the annual amount of Cl and Ca in the leachate doesn't change so fast, which implies the rainfall washing process could last for years, even decades. A large amount of Ca and Cl fled away through rainfall to the leachate; therefore, the Ca and Cl have been considered as a part of the main mass loss fraction from landfill sites.

The result just suggests the full interaction between landfill waste and rainfall (hydration process), which could affect the mineral compounds and heavy metals' transformation and neoformation process in the landfill. When analyzing the Cl sourced from the wastes, it presents that the amount of Cl is much larger than the amount of Ca, which may indicate the Cl also came from other chlorides, like NaCl, KCl, and metal-Cl. However, the heavy metal concentration in the leachate has been detected as very low for these years. We concluded that the relatively high pH (10~12) inside the landfill area inhibited the dissolution of heavy metal salts.

Because the city government also allows the new site to receive some industrial solid wastes, there's quite an amount of waste gypsum was buried in site B. Therefore, #15 and #16 are selected waste gypsum contains high Ca and S, which could be identified as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, they are discussed separately.

5. 3. 3 Speciation distribution based on the SEP result

The result of sequential chemical extraction combined with RAC analysis is shown in Figure 5-5. As for the pH of each extraction, steps are shown in Table 5-5. It's known that #1 and #2 are cover soil type samples, #15 and #16 are waste gypsum, the others are incombustible waste or incinerator residues, therefore, cover soil samples and gypsum waste were discussed separately. As extraction behavior of heavy metal is strongly related to pH value, Table 5-5 shows the pH of landfill waste in F1 (water-soluble) and F2 (exchangeable) steps are quite high for non-amphoteric metals to dissolve. So, there isn't so much fraction ratio of F1 in all of the samples.

Cd's contents ranged from 1.0 to 77.8 mg/kg, it's quite lower than other heavy metals. In cover soil, Cd was almost in residual fraction (F6), over 98%. While in waste samples, the F6 ratios were 3% ~ 35%. The highest fraction was an acid-soluble fraction (F3) and reducing extractable (F4) in waste samples, it's 28% ~ 54% and 8% ~ 43%. However, the exchangeable fraction (F2) also presents a high ratio.

The content of Zn is the highest heavy metal, it ranged from 83.3 to 9679.8 mg/kg. F6 is the highest fraction in soil type samples (74% and 54%). But, in waste samples, F2, F3, and F4 are higher than F6. While comparing the speciation of Cd and Zn in time scale, it's found that fresh wastes from Site B had higher RAC than Site A.

The total content of Pb ranged from 21.3 to 3577.9 mg/kg (Table A5-3). In soil sample #1 and #2, the F4 (reducing available) and F6 (residual) are the highest two fractions of Pb. In sample #15, the highest fraction is F4 (86%), while F3 (acid-soluble) and F4 are two main fractions of Pb in the other waste samples. There is a large amount Pb in F3 like #5, #6, #7, #10, #13, #14, #17 and #18, which was acid extractable.

The content of Cu ranged from 35.7 to 5114.5 mg/kg. In soil type sample (#1 and #2), the highest ratio fraction is F6 (59% and 48%). The second highest is F4 (25% and 24%). But, it's different in the landfill waste samples. The highest ratio fraction in waste samples is F2 and F5. In samples like #3, #10, #12 and #13, the highest one is F5 (oxidizing available), while in samples like #5, #6 and #14, the F2 is higher. Figure 5-2 (a) also shows the RAC results through the timeline of the samples (except soil and gypsum), it's found no obvious trend of RAC changing. The oldest buried incinerator residues sample (#6) from site A could also have high RAC value, even is similar to the newest residue sample (#18).

The total concentration of Cr ranged from 9.7 to 677.1 mg/kg. The main fraction of Cr in

all samples is F6, except #15. The second highest fraction ratio is F4.

Ni's content ranged from 31.1 to 551.8 mg/kg. The species distribution is similar to Cr. The highest fraction is F6 in all samples except #15. The second highest fraction is F4. In #15, F4 is higher than F6.

As we have described earlier, the content of RAC should also be considered for potential hazard level estimation. We have estimated the Japanese regulation limits for landfill waste leaching tests before. If the RAC fraction content of Cd, Pb, and Cr is smaller than 150, 150, and 250 mg/kg respectively, we consider the potential risk is low. However, according to Figure A5-5, most of the samples have higher content of RAC fractions of Pb than the limit, which strongly suggests the high potential risk from currently landfilled incinerator residues.

We compared the RAC content between sites A and B in Figure 5-6. The Mann-Whitney test result shows that the RAC content of Cd, Cr, and Zn from site B is greater than site A significantly at $p=0.05$ level. However, the speciation changing of Ni, Cu, and Pb between sites A and B is not so significant. As we mentioned before, the SEP method is considered as a hazard level estimation method in this study. XAFS method is used as a species analysis method, so we selected samples according to the result of the SEP result.

Figure 5-7 shows the RAC of Pb and Cu distribution for all samples, the result presents most samples were still in the high-risk level (yellow zone), and even very high-risk level (red zone). Soil, waste gypsum and low heavy metal content samples (except #16) are in the relatively safe zone, while 87.5% waste samples with high heavy metal content are in the unsafe zone. These results could imply the highly potential hazard level from the buried incinerator residues. We have illustrated that the samples could all pass the leaching test in the former section. However, we only could conclude that the landfill is safe for the surrounding environment currently. When referring to decide to terminate the aftercare of this landfill (here we only talk about site A), it's obvious to find that the high potential risk strongly suggesting us to continue the work. We proceed with cluster analysis base on the SEP results of Pb and Cu (Figure 5-7). Soil and gypsum waste are quite different from the other samples. We selected samples (purple dots in Figure 5-6) from the safe zone and unsafe zone respectively to proceed XAFS measurement of Pb and Cu, the obtained spectra are presenting in Figure 5-10. Slightly difference could be found in the spectra of Pb, while obviously difference among the spectra of Cu. Further discussion could be found in the section of species analysis based on the XAFS result.

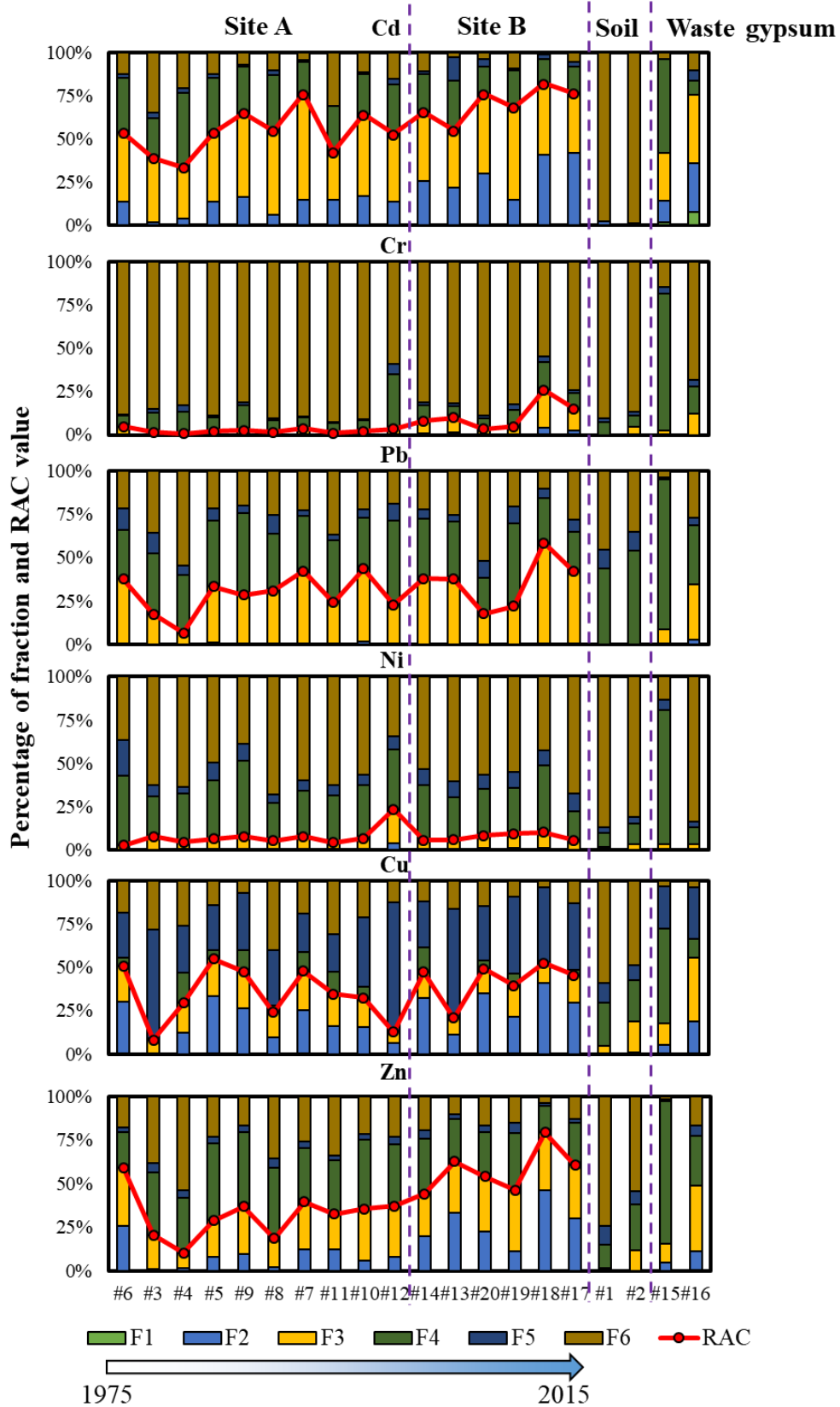


Figure 5-5 Sequential extraction result of selected samples, the RAC is also presented.

Table 5-5 pH value of each extraction step for the samples.

Point NO.	F1	F2	F3	F4	F5	F6
#1	7.41	7.00	5.00	2.00	--	--
#2	9.52	7.82	4.93	2.00	--	--
#3	9.28	7.67	4.96	2.00	--	--
#4	8.90	7.73	4.98	2.00	--	--
#5	11.3	7.98	5.00	2.00	--	--
#6	11.8	8.51	5.00	2.00	--	--
#7	11.9	8.45	5.00	2.00	--	--
#8	10.8	8.04	5.00	2.00	--	--
#9	11.1	8.26	5.04	2.00	--	--
#10	11.2	7.94	4.98	2.00	--	--
#11	11.5	8.08	5.01	2.00	--	--
#12	8.43	7.62	4.97	2.00	--	--
#13	11.9	8.84	5.00	2.00	--	--
#14	11.6	8.78	4.98	2.00	--	--
#15	8.62	7.12	5.03	2.00	--	--
#16	8.61	7.29	5.02	2.00	--	--
#17	11.9	8.88	5.01	2.00	--	--
#18	11.5	8.89	5.01	2.00	--	--
#19	10.9	8.33	5.02	2.00	--	--
#20	11.8	8.85	4.99	2.00	--	--

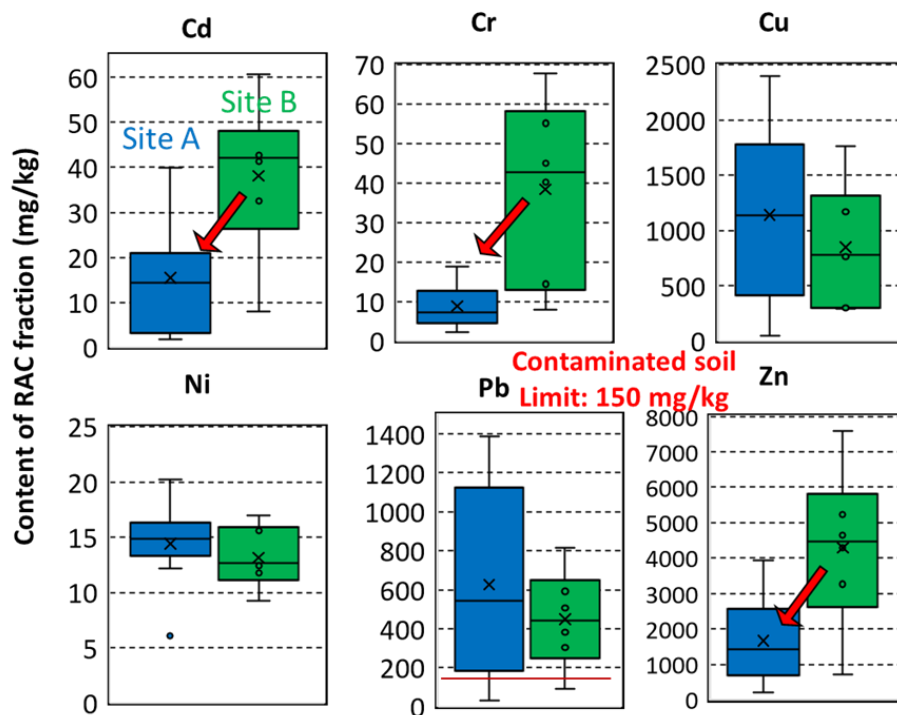


Figure 5-6 Comparison of RAC content between sites A and B.

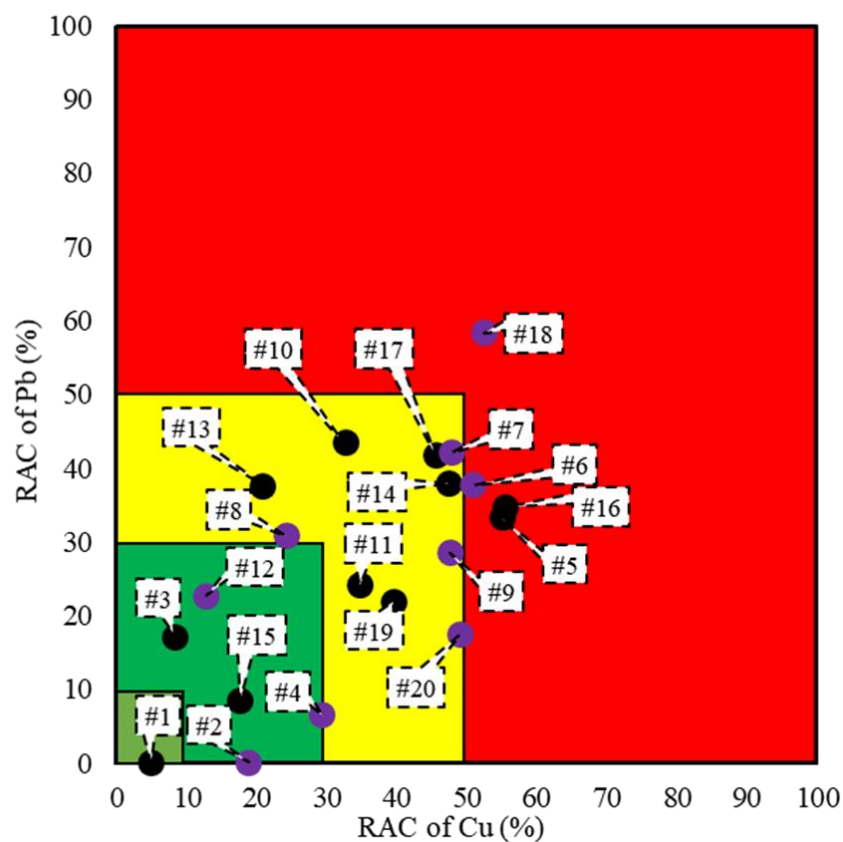


Figure 5-7 RAC result of Cu and Pb, purple dots are the selected samples for XAFS measurement.

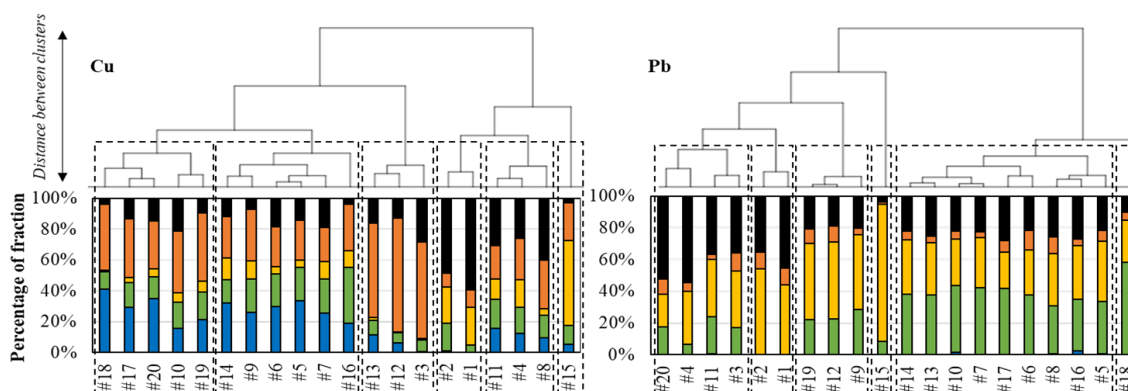


Figure 5-8. Cluster analysis based on the SEP results of Cu and Pb.

5.3.4 Weathering stage identification

The landfilled incinerator residues will experience hydration, carbonation, and oxidation weathering processes in the semi-aerobic landfill sites. The major mineral compounds

have changed and formed stable phases after these processes. According to the XRD measurement results in Figure 5-8, ettringite and gypsum were still detected in the samples from landfill sites A and B. The appearance of gypsum means the hydration and carbonation process wasn't completely finished. But the presence of calcite and magnetite indicates the occurrence of carbonation and oxidation process. Even though there are many secondary amorphous products generated that couldn't be measured by XRD, we could still identify the weathering stage of the samples by observing the mineral compounds of Ca. Ettringite has been reported could generate calcite through the formula as below³⁶:

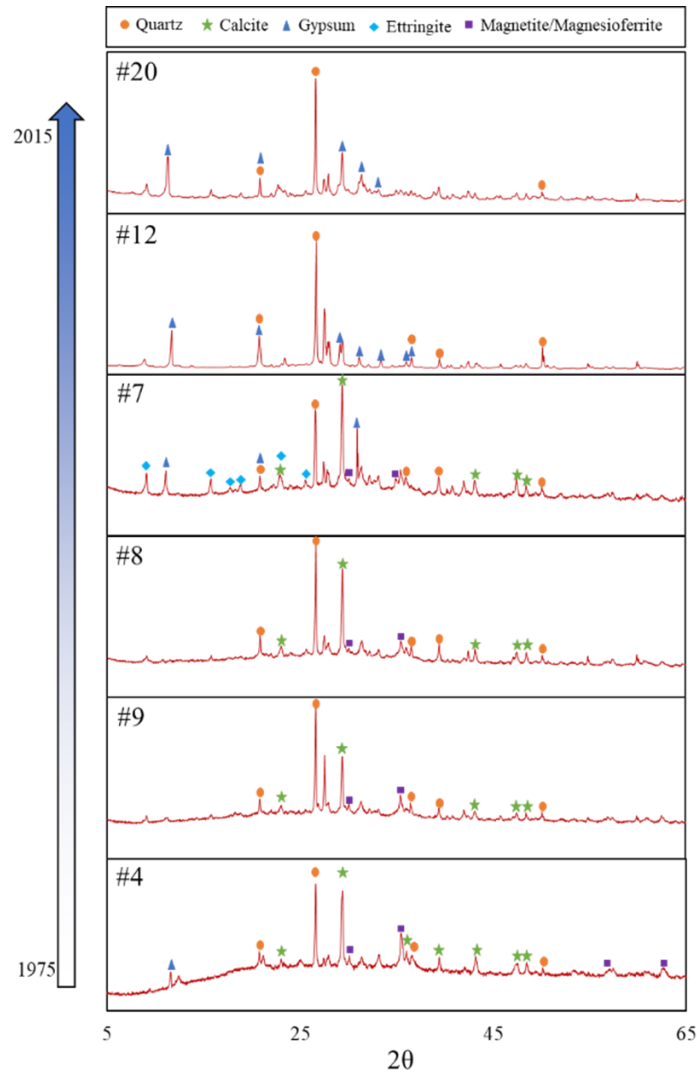
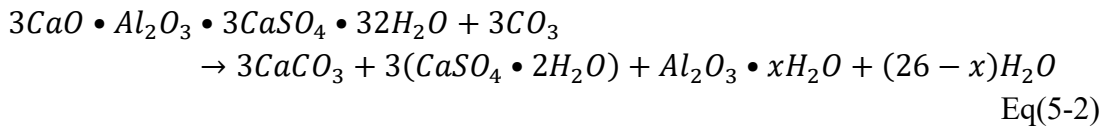


Figure 5-9. The XRD result of selected samples to identify the weathering stage of the buried incinerator residues.

So, samples like #7 might still not reach the most stable stage, yet. Calcite presents in

most samples from site A imply they have experienced the weathering processes and became relatively stable under current environmental conditions, while mineral compounds in the samples from site B are still available to change.

Through the XRD investigation, we determinate the weathering process did happen in the incinerator residues from site A and the presence of calcite means the incinerator residues will reach a relatively stable stage in the near future. However, the SEP result presented slightly changes in the samples from sites A and B. Does the weathering process affect the species distribution, chemical form of heavy metals in incinerator residues? The answer is still uncovered. Therefore, we introduced XAFS to identify the species of Pb and Cu in some samples.

5.3.5 Species analysis based on XAFS measurement

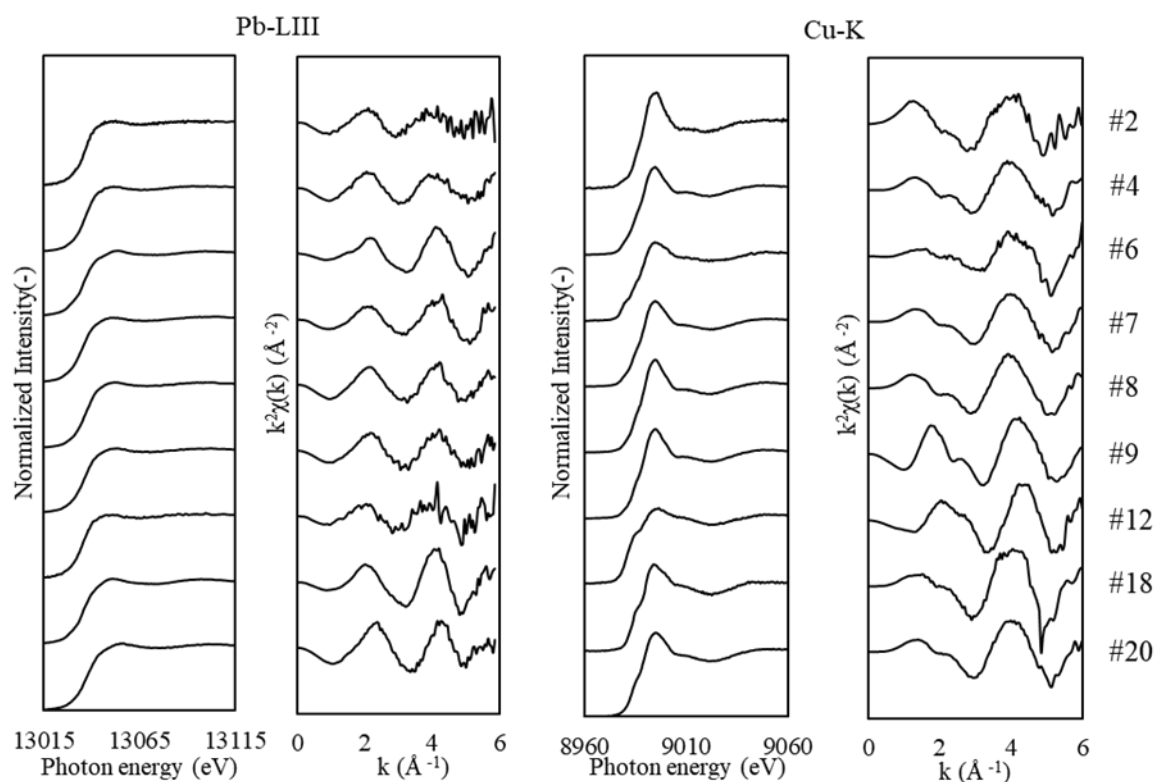


Figure 5-10 The Pb-LIII and Cu-K edge XANES and EXAFS spectra of the samples.

The process of analysis of XAFS data has been described in the former section, to determine the standard reference for linear combination fitting (LCF). We tested the spectra of reference material by PCA with samples' spectra. The test result could be found in the appendix (Figure A5-6, A5-7). The spectra of Cu show a lot of differences both in XANES and EXAFS. However, the XANES spectra of the Pb don't present much difference between the samples. According to the PCA result of XANES and EXAFS, we

could separate the samples into at least 4 groups.

For the XANES of Cu, PC1 accounts for more than 70.3% variance, therefore, we classified the samples into 4 groups mainly depending on the PC1. For EXAFS of Cu, similar groups could also be classified. It's found samples #4, #6 and #12 is quite different from the others. #4 has the highest peak height while #12 is the lowest one. However, the pre-edge of #12 is more significant. We also conducted the PCA procedure to the samples with the reference materials (XANES), the result is presented in Figure A5-6. The pre-edge of spectra could indicate the presence of Cu(I) in the samples, so #12 is close to the Cu(I) zone in Figure A5-6, while #4 most likely doesn't contain Cu(I).

Because the differences in XANES and EXAFS are both obvious for Cu, we decided to proceed linear combination fitting (LCF) to XANES spectra. And the final result is shown in Table 5-6. Cu speciation is quite different in different samples. Cu mainly presented in the form of CuFe_2O_4 , Turquoise, and $\text{Cu}(\text{OH})_2$ in sample #4. Copper carbonates, Cu_2S and CuO are the major species in #6. #12 shows higher ration of Cu(I) as we have described before, CuCl , Cu_2S , and CuO are mostly exist form in #12. The Cu in other waste samples was most likely in CuO , CuSO_4 , and CuCl . As it's known that the incinerator fly ash belongs to hazardous waste, it needs pretreatment before final landfilling. Pretreatment in Japan was stabilization with chelate reagents mostly, and most reagents worked through the function group with S. It may explain why so much Cu-S bond is observed in some samples. #18 and #20 from site B is relatively fresh incinerator residues, the most significant difference between site A and site B is the presence of Atacamite. However, the most common species of Cu in site A are CuSO_4 and CuCl . This result suggests the species changing inside the semi-aerobic landfill of incinerator residues.

Because the spectra of Pb LII-edge XANES is very similar to each other (including the reference materials), we determine to conduct fitting through EXAFS. However, the quality of EXAFS data is not good after $6 \text{ \AA}^{-1}$, therefore, we only analyze the data ranges from 2 to $6 \text{ \AA}^{-1}$. Obviously, the difference could be observed among the EXAFS data of Pb between the samples. As we mentioned before, we would like to analyze the data through the combination of XANES and EXAFS. The PCA procedure has also been applied to both XANES and EXAFS data. After seriously comparison the LCF results of XANES and EXAFS, we obtained the result presented in Table 5-6.

It's found the Pb LIII-edge EXAFS of the samples could be separated into 6 groups based on the shape of EXAFS spectra, while it's 4 groups for XANES spectra. Sample #12 presents especially again, the species of Pb in #12 are metallic Pb, PbHPO_4 and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. For the soil (#2), $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ also has the highest ration, but, Pb adsorbed to goethite was also found. Pb-Goethite was found in sample #4, PbSiO_3 and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ are also found in #4. From the XRD result, we know that the waste inside landfills did have experienced the weathering process from rainfall and iron is high content in some samples. The generation of goethite was possible, the adsorption between

Pb and goethite is acceptable³⁸⁻⁴⁰. The most common species of Pb in landfilled incinerator residues are PbO and PbSiO₃, which are already reported usually could be found in fresh bottom ash. As we couldn't detect the PbCl₂ and PbS in the samples, it's believed the chemical species of incinerator fly ash has changed after a short time landfilling. Because we also couldn't detect PbCl₂ in samples from site B, even though the Cl content is still high in the samples.

Combined with the results from Cu and Pb, it's believed that the species shifting did happen after the weathering process. However, the SEP result implies a slightly changing of speciation distribution.

A comparison between the result of Cu and Pb has been conducted. We identified the chemicals which is soluble in F3 according to the result of Funatsuki and Takaoka's^{19, 37} research (to check the chemicals in Table A5-4). The result could be found in Figure 5-11 and Figure A5-8. Generally the SEP result agrees with the result of XAFS. Due to the complicate composition in the wastes, it's acceptable to find some samples have higher acid soluble chemicals' content than the result of SEP.

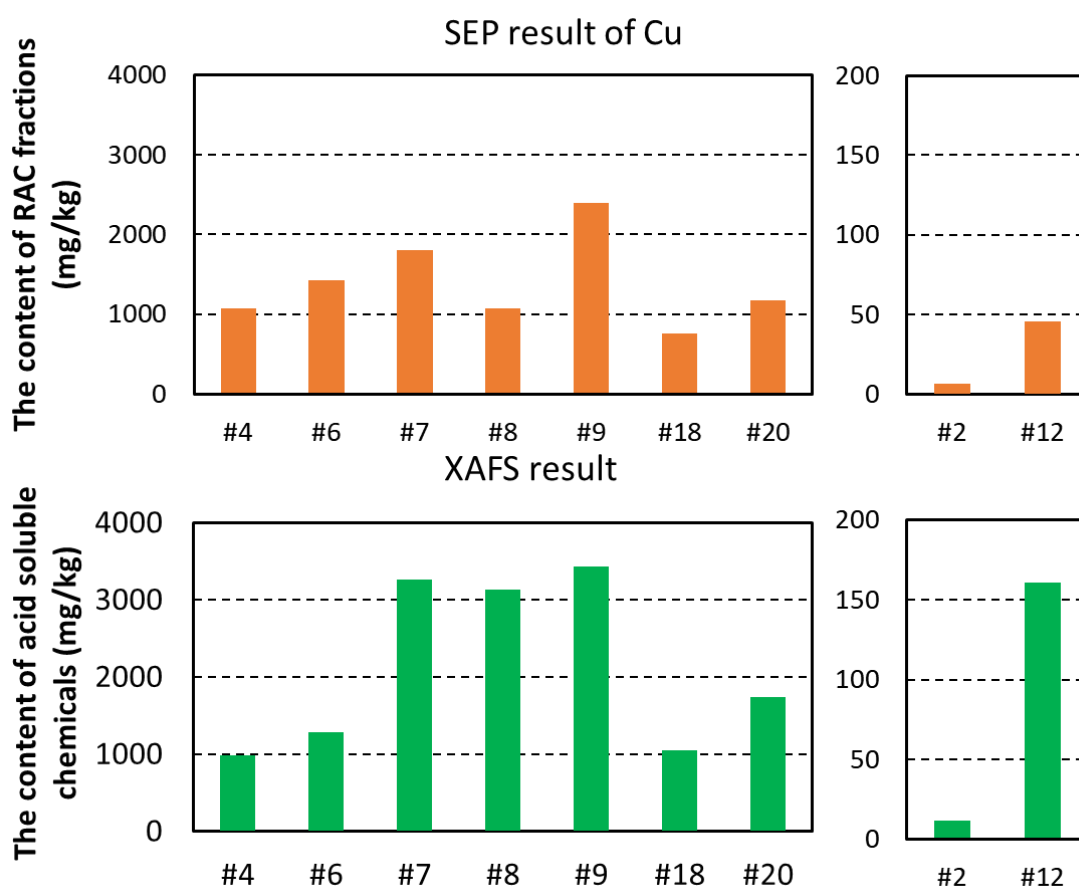


Figure 5-11 The comparison of the result of SEP and XAFS (Cu).

Table 5-6 Cu and Pb speciation in samples from the landfill sites, the result of Cu was analyzed through K-edge XANES spectra, while Pb was mainly from LIII-edge EXAFS spectra.

	CuO	CuCl	CuS	Cu ₂ S	CuCO ₃	CuSO ₄	Cu(OH) ₂	Turquoise	Atacamite	CuFe ₂ O ₄	R
#2				0.252			0.315	0.127		0.307	0.002
#4							0.27	0.257		0.473	0.011
#6	0.257			0.336	0.407						0.005
#7		0.223		0.133		0.383	0.261				0.006
#8	0.112	0.340				0.339				0.209	0.002
#9	0.176	0.309				0.337				0.177	0.002
#12	0.286	0.390		0.324							0.002
#18			0.279						0.721		0.008
#20	0.337	0.250				0.143			0.270		0.001
	Pb	PbO	PbSiO ₃	PbHPO ₄	3PbO·PbSO ₄ ·H ₂ O	Pb-Goethite	Pb ₃ (PO ₄) ₂			Red-χ ²	k range (Å ⁻¹)
#2					0.483	0.517				0.011	2~6
#4			0.417		0.236	0.348				0.004	2~6
#6		1.00								0.005	2~6
#7		0.51			0.490					0.007	2~6
#8		0.428	0.455				0.117			0.004	2~6
#9	0.269	0.447	0.283							0.004	2~6
#12	0.151			0.522	0.327					0.017	2~6
#18		0.898					0.102			0.017	2~6
#20*			0.761	0.239						0.002	2~6

5. 3. 6 Observation through SEM-EDS

For more specific analysis of heavy metals inside landfill waste samples, the observation through SEM was conducted. In our study, three samples were observed and several hot points of metal Pb, Cu, Cd, and Ni were found, the element composition result was shown in Table 5-7. Cr was found abundant in spot 1 and 11, Ni was a little bit higher in spot 1 and 11, too. In these two spots, Fe content is very high. So, maybe, they are a part of stainless steel. Cd was only found in spot 17 with a high concentration of Ag. Cu and Pb have been found had more hot spots than the other metals, but Cu and Zn seem to distribute in the samples evenly. Pb more likely appeared as small size particle or coated by some other mineral compounds (Figure 5-12). There're no significant correlations could be found between Cu and S in this result. However, the Cu and Fe could be found co-abundant in some spots, it may imply the presence of CuFe_2O_4 . Some spots of sample #4 and #9 contain Cl with a high Pb concentration, PbCl_2 might exist in these spots just like most reports mentioned PbCl_2 in incinerator fly ash.

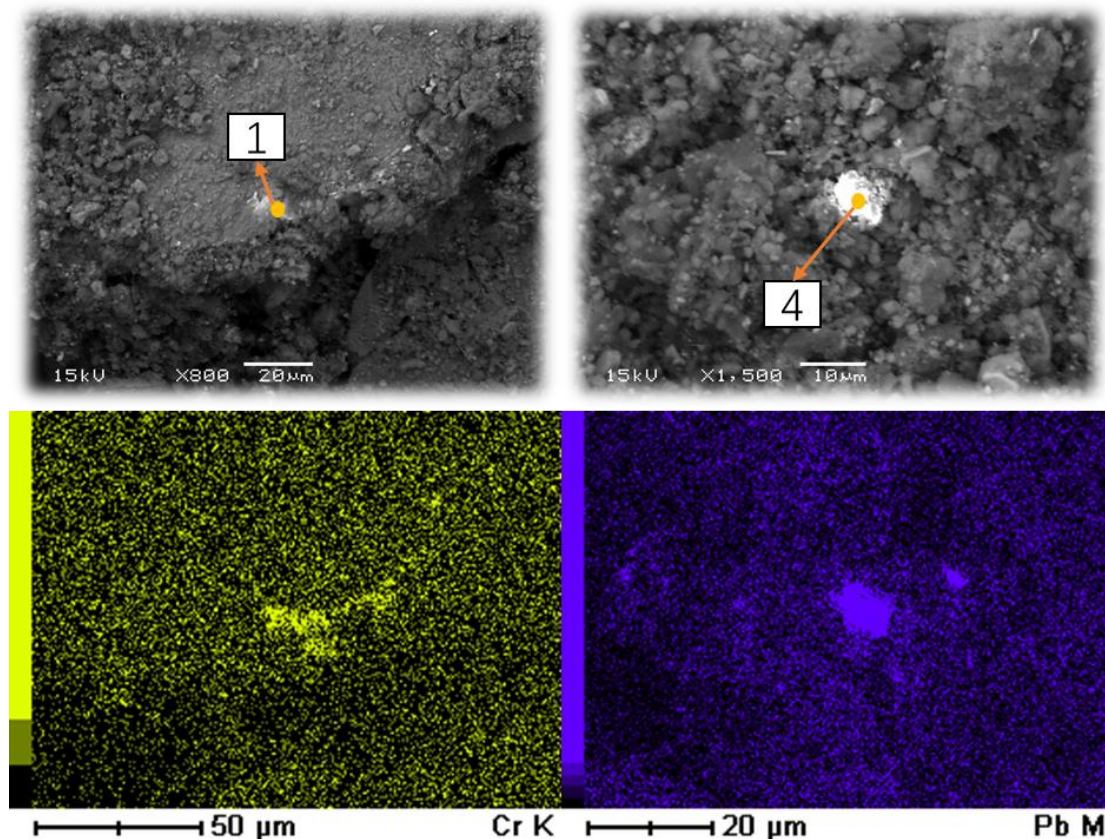


Figure 5-12 BSE image of “hot spot” 1 and 4, the concentration of Cr and Cu is high in spot 1, and spot 4 is probably a lead chemical compound particle.

Table 5-7 Result of SEM-EDS heavy metal “hot spots” in observed samples, w/w (%).

	#4					#9						#20		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
C	-	14.33	9.19	7.43	12.86	15	16.14	8.33	8.12	10.51	11.17	9.05	9.35	12.15
O	20.57	23.22	18.78	23.45	15.8	31.79	36.33	26.03	29.1	26.94	15.34	14.89	32.18	16.44
Na	-	-	-	-	-	-	1.71	-	-	-	-	-	0.91	-
Mg	1.18	0.93	0.63	0.59	0.82	0.82	1.03	0.53	0.81	0.82	0.78	0.83	0.84	0.72
Al	8.96	4.86	3.89	4.36	5.08	6.5	10.01	4.2	4.35	8.75	5.02	4.25	3.44	3.5
Si	5.66	3.64	3.51	3.04	3.39	5.04	17.07	7.21	4.8	6.42	4.09	5.85	9.61	5.3
P	0.55	-	-	0.4	0.34	0.38	-	-	0.46	0.44	-	-	0.73	-
S	0.52	0.35	2.48	2.97	0.96	2.06	-	2.14	-	1.4	0.55	0.79	1.14	1.09
Cl	-	-	1.47	-	-	-	-	0.67	-	-	-	1.39	1.55	1.42
K	-	-	-	-	-	0.42	2.36	-	-	-	-	0.72	-	0.47
Ca	4.83	3.19	4.27	3.36	3.04	9.8	5.58	6.89	6.29	10.51	5.91	8.64	12.59	8.86
Ti	0.85	-	0.43	0.37	0.41	0.27	-	0.24	-	-	-	-	1.44	-
Cr	<u>8.73</u>	-	-	-	-	-	-	-	-	-	<u>10.24</u>	-	-	-
Fe	40.31	5.12	6.69	6.26	9.07	5.66	4.58	8.8	29.62	18.48	40.2	1.11	1.47	1.07
Ni	<u>4.36</u>	-	-	-	-	-	-	-	-	-	<u>4.01</u>	-	-	-
Cu	<u>8.04</u>	<u>44.34</u>	2.23	-	<u>48.24</u>	2.11	-	2.1	2.24	2.38	2.69	<u>32.54</u>	-	<u>30.59</u>
Zn	1.44	-	1.9	1.52	-	1.92	-	1.4	-	1.35	-	<u>19.95</u>	-	<u>18.4</u>
Ba	-	-	-	-	-	-	-	0.98	2.11	1.89	-	-	-	-
Pb	-	-	<u>44.52</u>	<u>46.25</u>	-	<u>18.24</u>	<u>5.2</u>	<u>30.48</u>	<u>12.09</u>	<u>10.1</u>	-	-	-	-
Ag	-	-	-	-	-	-	-	-	-	-	-	-	12.66	-
Cd	-	-	-	-	-	-	-	-	-	-	-	-	<u>8.57</u>	-
Th	-	-	-	-	-	-	-	-	-	-	-	-	3.51	-

5.3.7 Discussion of chemical species changing in the semi-aerobic monofill of incinerator residues

We conducted SEP, XAFS and SEM-EDS measurement for landfill waste to investigate heavy metal speciation distribution in two semi-aerobic monofill of incinerator residues. The SEP result suggested high hazard level of Pb from both aged and fresh incinerator residues, however, the aged samples didn't show a decreasing trend of hazard level according to time-line. SEP result could predict heavy metal behavior under certain chemical condition, while XAFS result could tell us the exactly species changing in the landfills. We could know specific chemical species of heavy metals in our samples from XAFS result, but it's impossible to predict the behavior without SEP result. The chemical compounds won't simply appear in pure form, it's complexed or combined with another compound. SEM-EDS measurement is a good way to observe small particles with high heavy metal content, through this way it's possible to ensure the XAFS result and predict behavior of heavy metal more precisely.

This research investigates the heavy metal speciation distribution of heavy metals in monofills for incinerator residues by several method. The SEP results suggest a high potential environmental risk of heavy metals still exists after 20 to 40 years' weathering process. The major threaten comes from available fractions of Pb, which presented as acid extractable fractions' content is higher than the limit. The weathering process didn't reduce the hazard level. Therefore, it's still can't be sure about terminating the aftercare of the closed landfill. Rainfall only took away small amount of heavy metals in 20 to 40 years, and the Cu and Pb species did change after weathering process.

5. 4 Conclusion

In this chapter, we investigate the heavy metal speciation distribution of heavy metals in monofills of incinerator residues by several methods. The results could be concluded as follow:

- 1) The leaching test shows no samples exceed the limits for landfill waste, therefore, the landfill is safe to the surrounding environment currently. However, the high content of heavy metals inside buried incinerator residues is still a great threat to the communities near the landfill area.
- 2) The SEP results suggest a high hazard level of Pb still exists after 20 to 40 years' weathering process. The acid extractable fraction of Cu, Cd, Pb, and Zn is high. Ni and Cr presented a relatively stable fraction distribution than the other heavy metals. The speciation distribution doesn't change so much according to the result of the SEP

test.

- 3) Some samples were tested by XRD, and we could confirm the occurrence of the weathering process in the old sites. With the rainfall washing through the waste body, secondary mineral chemicals, like calcite, could be formed. So we could use these mineral chemicals to check the weathering stage of the samples in the future,
- 4) The XAFS measurement was conducted to several samples to measure the Pb-LIII and Cu-K edge spectra. After conducting a series analysis process, we could get the species distribution result of selected samples. Comparing the result to the SEP result, it's more reasonable. The species of Pb and Cu did have some changes after the weathering process, even though the SEP showed a similar result between fresh and aged incinerator residues.
- 5) Through the SEM observation, we could find some evidence for the XAFS result.

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CHAPTER 6

MASS BALANCE OF SEVERAL HEAVY METALS IN THE LANDFILL SITE A

6. 1 Introduction

Incineration technology for municipal solid waste (MSW) treatment is attracting attention from researchers in both developed and developing countries¹⁻². The high efficiency of volume reduction and energy recovery from waste are two major reasons for the utilization of incineration technology³⁻⁴. However, by-products from incinerators, such as bottom ash (BA) and fly ash (FA), must be handled carefully⁵. BA generally contains fewer pollutants than FA and it can be recycled as a material for construction purposes. However, there can be very high contents of some heavy metals (copper (Cu), chromium (Cr) and nickel (Ni)) in BA¹. FA is considered to be a hazardous material due to its high heavy metal and dioxin contents³, such that pretreatment is required prior to disposal or recycling. Treatment largely constitutes a stabilization process to reduce the mobility of heavy metals, but the content remains high in the treated FA. Recently, incinerator residues (BA and FA) have been widely studied; large amounts of incinerator residues are stored temporarily or landfilled at landfill sites^{2, 5}. Incinerator residue buried in landfill sites is subject to aging and weathering processes, which affect the mobility of heavy metals and even allow them to leach out and cause serious pollution. Therefore, it is necessary to study the heavy metals present in landfills.

In Japan, incineration has been widely used for MSW treatment since the 1970s, and landfill is the major method for disposing of incinerator residue⁶. Japan appears to be the first country to use monofill sites for incinerator residue disposal. Furthermore, most Japanese landfill sites are semi-aerobic⁷, which are markedly different from anaerobic sites⁸. Anaerobic landfill represents the earliest type of landfill and is widely used worldwide. Unlike anaerobic landfill, semi-aerobic landfill rain can pass through the waste body to enhance the decomposition of the waste⁸. This can dramatically reduce methane generation. Rain also removes most dissolvable salts from mono-filled incinerator residues. Heavy metals, as concentrated trace elements in incinerator residues, are among the most important environmental hazards posed by landfill⁹⁻¹⁰. The heavy metal content in incinerator residues from monofill sites is much higher than that in MSW in regular landfill sites¹¹, which obviously increases the hazard level. However, the low organic compound content of incinerator residue means that such landfill sites generate little landfill gas, with low chemical oxygen demand (COD) in the leachate¹²⁻¹³, which can be a serious problem for regular waste landfills. Currently, only the chemistry of inorganic compounds interacting with heavy metals in landfills containing incinerator residue is assessed¹⁴⁻¹⁶. It is necessary to determine the environmental risks posed by the high heavy metal contents of monofill sites.

The responses of heavy metals in incinerator residues in landfill environments, to aging and weathering processes, have been investigated using lab-scale experiments and short-term landfill simulations¹⁷⁻¹⁸. Changes in the mineral profiles of incinerator residue play

an important role in the trapping of heavy metals. However, it is still not clear how such changes affect full-scale landfills. Belevi suggested using a mathematical model for evaluation of the long-term behavior of MSW waste in landfills¹⁹⁻²⁰. Therefore, it's possible to predict when the "final storage quality" of one landfill could be achieved. Incinerator bottom ash samples were collected and analyzed for the prediction of incinerator bottom ash monofills. And it's reported laboratory experiments of samples can't predict the chemical behavior of bottom ash in monofills. The condition of a real landfill environment can't be simulated in the lab, the field sampling and monitor of a real landfill are necessary. Determining the mass balance of elements in a landfill is a good way to understand their general behavior²¹⁻²⁵. Cossu²⁵ discussed the role of mass balance work in a landfill site, several models have been proposed to estimate the different elements (carbon, nitrogen, sulfur and trace elements) inside one landfill. It is not easy to carry out systematic and accurate mass balance analyses in full-scale landfill sites. There have been few studies estimating the mass balance of elements in landfill sites²¹⁻²⁴. Chun²¹ focused on carbon, nitrogen, and sulfur in regular MSW landfill sites, while He and Øygard aimed to determine the mass balance of heavy metals in regular MSWs landfill sites and BA produced by landfill incineration. Øygard²²⁻²³ estimated heavy metal leaching from landfill municipal solid waste incineration (MSWI) BA and mixed construction waste. However, only 2 years' worth of data for anaerobic-type landfills were included. He²⁴ evaluated the mass balance of heavy metals based on data from MSW and anaerobic landfill core samples. In this study, we estimated the mass balance of heavy metals from a single full-scale, non-operational Japanese landfill for incinerator residues using field samples and data extracted from records. The data covered almost the entire operation period, up to 2015. To our knowledge, this is the first study of its type.

In our previous chapter, we analyzed the heavy metal distribution and leaching behavior of samples collected from the same landfill site studied herein. We presented the vertical distribution of the heavy metal content in the landfill layers and found that the heavy metal content of the incinerator residues was much higher than that of the cover soil and incombustible waste, which implied that the metals did not move vertically. We also compared the current heavy metal profile of the landfill site with previous records and detected high mobility of zinc (Zn), Cu, and lead (Pb), and low mobility of Cr and cadmium (Cd). In this paper, we focused on mass balance and compared our results to those of previous studies. With this study, we would like to understand general behavior of heavy metals inside a semi-aerobic landfill of incinerator residues during a relatively long time. It's also possible to predict the future behavior of heavy metals.

6. 2 Material and Methods

6. 2.1 Characteristics of the landfill site

The landfill site was in operation from 1975 to 2000 and received 4.07 million tons of waste in total (not including cover soil and soil waste derived from subway construction). Incinerator residue accounted for 75% of the landfill waste (3.04 million tons), while the other 25% comprised incombustible waste (mainly consisting of concrete, asphalt, glass, ceramics, etc.)¹¹. The source of the incinerator residue was MSW incinerators from the same city, and the characteristics of these incineration plants are summarized in Table 3-2. All of the incineration plants use continuous stoker-type furnaces, but two different air pollution control (APC) systems are in operation, namely lime spray plus an electrostatic precipitator (EP), and an EP with a gas scrubber; thus, FA neutralized by $\text{Ca}(\text{OH})_2$ and EP ash were both sent to this landfill site, in addition to BA. Consequently, dissoluble salts such as CaCl_2 contribute significantly to the mass loss from the waste body²⁶.

The sandwich-like structure of this landfill is detailed in chapter 3. Cover soil with a depth of at least 0.5 m was spread over the entire landfill site. A liner was installed at the bottom of the site. Rainfall could penetrate through the waste body and rinse away dissolvable fractions. Hume pipes for leachate collection were set up at the bottom of the landfill site. Almost all of the leachate was collected and sent to the treatment facility together with the runoff from the surface collection pit. Then, the treated leachate was discharged to the wastewater treatment plant. Figure 6-1 shows data on rainfall and leachate generation. The amount of rainfall was given by the annual rainfall volume multiplied by the capture zone surface area. The extent of the capture zone differs according to the operation period. The stage 1 capture zone is the initial area, the stage 2 capture zone includes the entire area of the original site, and the stage 3 capture zone includes the original landfill area plus an extended area. The leachate generation rate was obtained from the records of treated leachate held by the facility and is given by the leachate volume divided by the rainfall volume. The average leachate generation rate at this landfill site was 29%, from 1976 to 2013. As we have no data on the leachate generation rates in 2014–2015, we estimated them based on the average leachate generation rate, as shown in Figure 6-1. The bottom part of Figure 6-1 shows the ratio of leachate to total disposed waste (including incinerator residue and incombustible waste; L/gS). The highest ratio occurred in 1980 (0.00015), and the lowest was in 2002 (0.00002). The L/S did not vary significantly following the closure of the site. The effects of variation in L/S were not considered in this study.

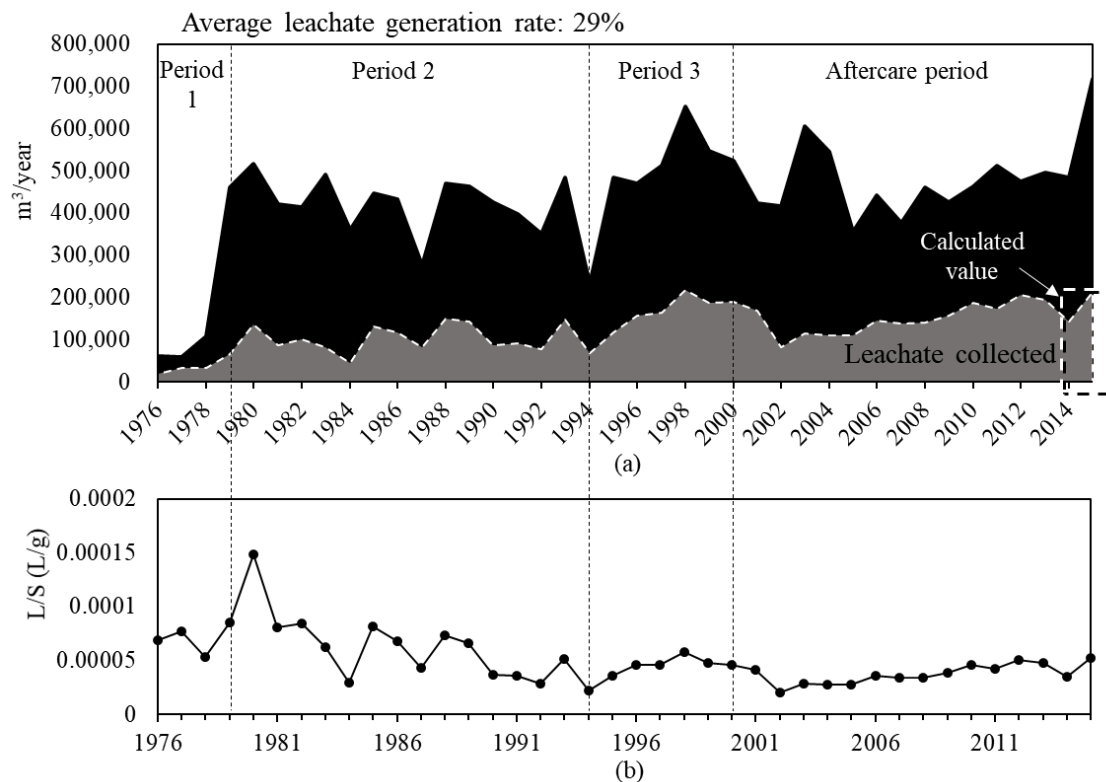


Figure 6-1 (a) Amounts of rain and leachate collected from a landfill area. (b) the ratio of annual leachate to total disposed waste (including incinerator residue and incombustible waste).

6. 2. 2 Description of the data collected

The data collected for the mass balance calculation included the annual weight of incinerator residue sent to the landfill site for the period 1975–2000 (tons/year), heavy metal content of the incinerator residue from each MSWI plant for the period 1981–2000 (mg/kg, dry basis) and moisture content, the treatment capacity of each MSWI plant (tons/day; Table 3-2), leachate generation from the landfill site for the period 1976–2015 (m³/year; Figure 6-1), and concentrations of heavy metals in the leachate for the period 1979–2015, as sampled at the influent of each leachate treatment facility (Figure 6-2). All data were extracted from documents published by the local government, and measured based on the methods prescribed by the Japanese Industrial Standards or Ministry of the Environment of Japan. In these methods, FA and BA are considered together as incineration residue. Figure 6-2 shows the data sources. There were several unexpected problems with the data. First, because several years' worth of incinerator residue heavy metal data (1975~1980) were missing, we used the average values from 1981 to 1985 to estimate the values for that period, and the heavy metal content from each MSWI plant

varied slightly over that time. We assumed that the heavy metal contents from the MSWI plants were similar to those in the years just before and after the period for which data were missing. Second, the concentrations of some of the heavy metals in the leachate were below the detection limit, such as Cd (presented as < 0.01 mg/L). In these instances, we took half the detection limit as the actual concentration in the leachate, in accordance with the Data Quality Assessment of the EPA²⁷.

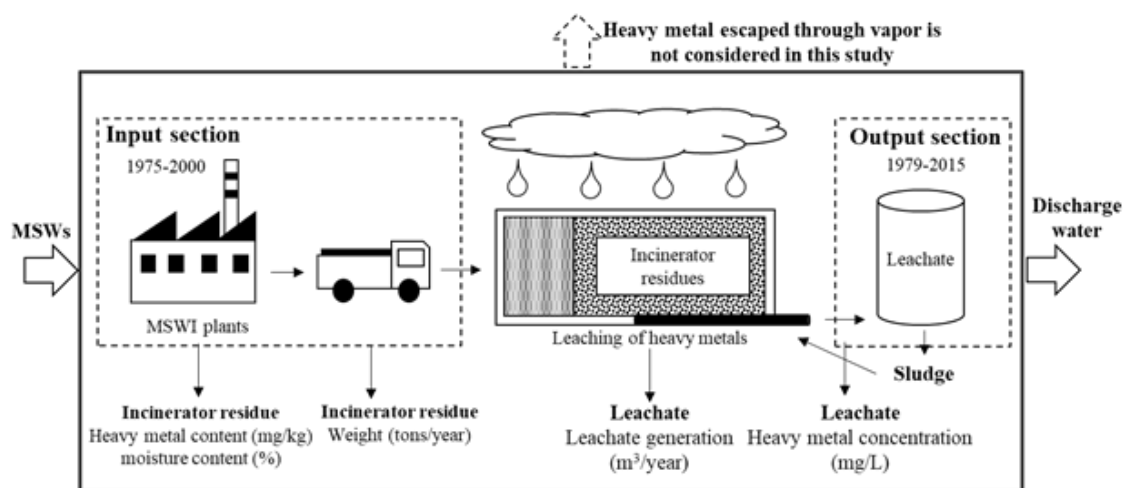


Figure 6-2 Sources of data used in this study.

6. 2. 3 Mass balance calculation process

The mass balance calculation includes an input section and an output section (Figure 6-2). The input is the total mass of heavy metals in the incinerator residue sent to the landfill site. The output is the total mass of heavy metals in the leachate collected from the site. During the calculation process, we assumed the following: 1) the heavy metal content in the incombustible waste was low compared to that in the incinerator residue, and 2) the target heavy metals in the incombustible waste did not leach out. These assumptions are supported by the findings of our previous study, which showed that the heavy metal content of the incinerator residues was much higher than that of the cover soil and incombustible waste. The leaching ability of the collected samples was weak. Therefore, based on our two assumptions, it is possible to calculate the mass balance specifically for the incinerator residue. However, it was not possible to estimate the mass of mercury (Hg) that had escaped in gas²⁸⁻³¹, because no gas-related calculations were carried out in this study.

Input section

The incinerator residue was collected and measured prior to being sent to the landfill site so that we could calculate the mass of heavy metals in the raw landfill waste. The total mass (TM, kg) of heavy metal from incinerator plant x was calculated using Eq. (6-1):

$$TM_{(M, x)} = \sum_{1975}^{2000} M_{(year)} N_{(x)} (1 - W_{(x, year)}) C_{(HM, x, year)} \quad (6-1)$$

where $M_{(year)}$ is the mass of incinerator residue (kg) for a given year, $N_{(x)}$ is the proportion of total incinerator residue generated by incinerator plant x (calculated based on the MSW treatment capacity, %), $W_{(x, year)}$ is the moisture content of the incinerator residue for a given year (%), and $C_{(HM, x, year)}$ is the heavy metal content of the incinerator residue (mg/kg).

The first year of operation was 1986 for incinerator plant C, and 1980 for incinerator plant E. Finally, the total mass of heavy metal was calculated by summing the results for all incinerator plants.

Output section

In the output section, we only considered heavy metals that escaped through the liquid phase, because the sludge generated in the leachate treatment facility was sent back to the landfill site prior to closure. After closure, sludge cannot be estimated because no further records are available. The discharged heavy metal mass (DM; through leachate) can be calculated using Eq. (2):

$$DM = \sum_{1976}^{2015} V_{(year)} C'_{(HM, year)} \quad (6-2)$$

where $V_{(year)}$ is the leachate generation volume of a given year (L), and $C'_{(HM, year)}$ is the heavy metal concentration in the leachate for that year (mg/L).

6. 3 Results and Discussion

6. 3. 1 General characteristics of the raw incinerator residue from different plants

The landfill site received incinerator residue from five incineration plants in the city. Therefore, it is also important to investigate the characteristics of the incinerator residue from all of these plants. Figure 6-3 shows the heavy metal content of incinerator residue generated from different plants for the period 1980–2000, and Table 6-1 shows the general statistical results. The average metal contents of plants D and E were higher than those of plants A and B, but the variance was similar. The furnaces at the various plants were large of the same type, such that the BA should also have similar characteristics (we also assume that the incinerated waste was similar among plants, as it all originated from the same city). The characteristics of FA clearly differed according to the APC system used, which may, in turn, have caused differences in heavy metal distribution. The differences

in heavy metal contents in incinerator residues among the various plants can be considered to have arisen largely from the differences in FA composition. In Table 3-2, we summarize the different APC systems used in the five plants. Plants A and B use a lime spray process prior to exposure of the pollution to the EP system, while in plants D and E gas flows directly into the EP system and then passes through a scrubber; plant C uses both systems. The addition of $\text{Ca}(\text{OH})_2$ may reduce the heavy metal content via dilution effects, and generate a considerable amount of CaCl_2 ²⁶. Therefore, it is reasonable to expect that the incinerator residue generated from plants D and E contained higher heavy metal levels than plants A and B. As plant C uses both types of APC system, the results are slightly more complicated. The low-content heavy metals (Cd, arsenic [As], Hg and Cr) showed a narrow distribution range, while those of Pb, Zn, and Cu were wider. Figure 6-3 shows many outliers for Zn and Cu, which may have been due to the generally higher variability in Zn and Cu content in MSW versus other heavy metals; their higher variance and RSD are also shown in Table 6-1. Generally, heavy metal content was relatively stable, but it was higher in some years according to the plant and type of metal. The heavy metal contents of the incinerator residues from different plants showed similar distributions, so we assumed that the heavy metal content of the landfill site would also be distributed similarly, regardless of whether the incinerator residue from the plants was landfilled together or separately.

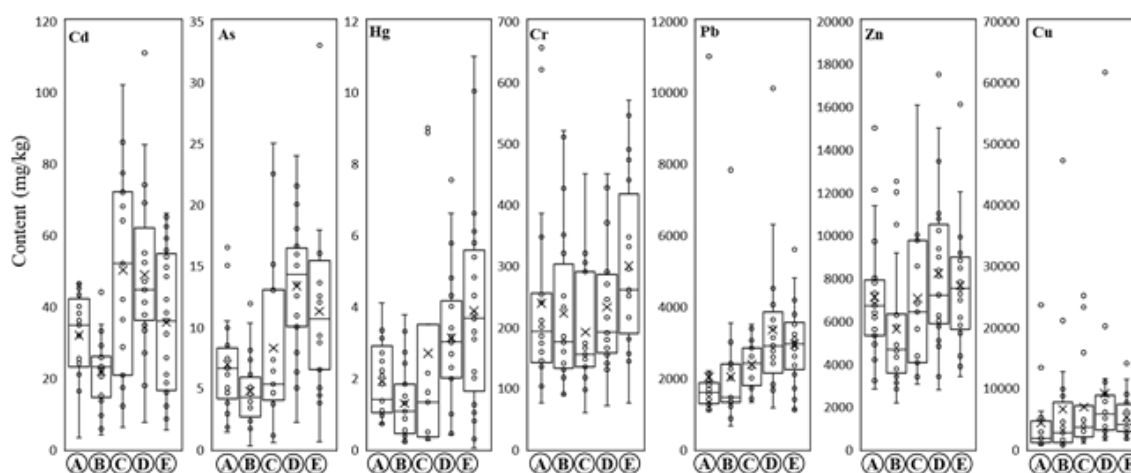


Figure 6-3 Heavy metal content of incinerator residue from different incineration plants.

Table 6-1 Heavy metal contents by incinerator plants

	Plant	Mean	Min.	Max.	Med.	S.D.	Variance	R.S.D.	Kurtosis	skewness
Cd	A	31.9	3.34	46.5	34.7	11.7	137	11.7	-0.11	-0.63
	B	21.8	4.04	44.0	23.0	9.49	90.1	9.50	0.59	0.13
	C	50.2	6.20	102	52.0	29.4	864	29.4	-1.14	0.04
	D	48.9	7.60	111	44.6	23.0	531	23.0	1.66	0.91
	E	35.6	5.40	66.0	36.0	20.4	415	20.4	-1.5	0.07

Pb	A	2030	1080	11000	1590	2080	4.34*10 ⁶	2140	19.7	4.38
	B	2030	661	7823	1450	1520	2.30*10 ⁶	1130	11.1	3.03
	C	2370	1310	3500	2400	667	4.44*10 ⁵	187	-0.76	0.06
	D	3340	1160	10100	2900	1950	3.80*10 ⁶	1140	6.96	2.33
	E	2940	1100	5600	2950	1130	1.28*10 ⁶	437	0.45	0.37
Zn	A	7100	2810	15000	6700	2930	8.58*10 ⁶	1210	1.62	1.15
	B	5620	2150	12500	4650	2970	8.83*10 ⁶	1570	0.79	1.3
	C	7040	3050	16050	6400	3520	1.24*10 ⁷	1760	1.63	1.13
	D	8210	2780	17500	7200	3760	1.41*10 ⁷	1720	0.63	0.94
	E	7640	3400	16100	7500	2960	8.74*10 ⁶	1140	2.17	1.04
Hg	A	1.90	0.720	4.10	1.4	1.04	1.08	0.568	-0.85	0.64
	B	1.30	0.200	3.77	1.06	1.04	1.08	0.843	0.39	1.08
	C	2.70	0.240	9.00	1.32	3.36	11.3	4.19	0.4	1.43
	D	3.10	0.400	7.54	3.00	1.89	3.59	1.15	0.35	0.74
	E	3.90	0.0300	11.0	3.66	2.92	8.54	2.20	0.88	0.99
As	A	6.90	1.40	16.5	6.60	3.86	14.9	2.16	1.35	1.06
	B	4.80	0.26	11.9	4.25	2.89	8.34	1.76	1	1
	C	8.30	0.56	25.0	5.30	7.36	54.1	6.55	1.09	1.41
	D	13.3	2.20	24.0	14.2	5.59	31.3	2.35	-0.29	-0.11
	E	11.3	0.61	33.0	10.7	6.96	48.4	4.29	4.1	1.47
Cr	A	240	76.0	656	193	156	2.45*10 ⁴	103	2.95	1.83
	B	222	88.0	520	175	134	1.79*10 ⁴	80.8	0.53	1.26
	C	191	60.0	450	155	104	1.08*10 ⁴	56.4	1.39	1.31
	D	232	71.0	450	191	109	1.18*10 ⁴	50.8	-0.09	0.93
	E	300	76.0	570	261	140	1.97*10 ⁴	65.6	-0.6	0.54
Cu	A	4270	703	23500	1780	5900	3.48*10 ⁷	8160	5.6	2.39
	B	6530	595	47200	2720	10800	1.17*10 ⁸	18000	10.9	3.15
	C	6910	1020	25100	3550	7850	6.17*10 ⁷	8920	1.74	1.74
	D	9070	1440	61600	5730	13100	1.71*10 ⁸	18900	15.2	3.75
	E	5260	1600	14000	4030	3350	1.12*10 ⁷	2140	1.18	1.33

The unit is mg/kg for heavy metal content.

6. 3. 2 General characteristics of the leachate

The leachate was monitored from the opening of the landfill site up to the present. Generally, the leachate was sampled and measured at least once every 2 months. The data used in this study are annual average values. Figure 6-4 shows the yearly change in pH and COD of the leachate, where the sampling point was the influence of the leachate

treatment facility. The figure shows a slight variation in the pH and a significant decrease in COD after the closure of the landfill. In comparison to regular landfills, it is clear that the COD of the leachate in this landfill was much lower, even at the beginning of its operation. The highest COD was detected in the period 1983–1985 and was approximately 150mg/L. The pH increased slightly after the closure of the site and has remained stable thereafter. The chloride (Cl) and calcium (Ca) concentration have been monitored since 1994; thus, Figure 6-5 shows their concentrations, and the Cl/Ca molar ratio in the leachate from 1994 to 2015. Before the closure of this landfill, the Cl and Ca concentrations varied markedly but remained at a high level. Following the closure of the site, the Cl and Ca concentrations decreased significantly every year, which indicates that the dissoluble fraction of the incinerator residue was disappearing. The similar shapes of the Cl and Ca curves suggest that CaCl_2 had dissolved, where this compound has been confirmed to be abundant in FA neutralized by $\text{Ca}(\text{OH})_2$. According to the change in the molar ratio, other chloride salts (NaCl , KCl and heavy metal chloride) were present in the leachate, in addition to CaCl_2 . However, it is also possible that the dissolved Ca precipitated by reacting with CO_2 or other chemicals. As the Cl and Ca concentration decreased every year, the ratio also decreased, to close to 2. In our previous chapter, we presented the Cl contents of the field samples. In this chapter, the average Cl content in the waste samples was 0.08–0.33%, which was very low compared to that of fresh FA. The low Cl content in the leachate and waste body implies that the dissolvable fractions inside the landfill incineration residues have saturated. The bottom part of Figure 6-5 shows the yearly mass loss of Cl and Ca from the leachate. The total discharged mass of Cl and Ca following the closure of the site be classified according to three stages. The first stage only included the first year after landfill closure (2001); the discharged mass of Cl and Ca was similar to that during the landfilling period. The second stage lasted about 9 years, until 2010, wherein the discharged masses of Cl and Ca were smaller but larger than those during stage 3. In stage 1, as the final landfill area had just been closed, it began to be covered with soil and planted over. Rainfall could fully penetrate the incinerator residues during this stage. After the final covering with soil, the penetration strength was lowered, so the heavy metal concentration and discharge mass decreased immediately. The dissoluble salts entered the leachate at a consistent rate during stage 2, after which the concentration and discharged mass decreased again. This may indicate that the dissolvable fractions in the incinerator residues had nearly washed out. Unfortunately, the sulfate was not monitored, so no data were available for the analysis.

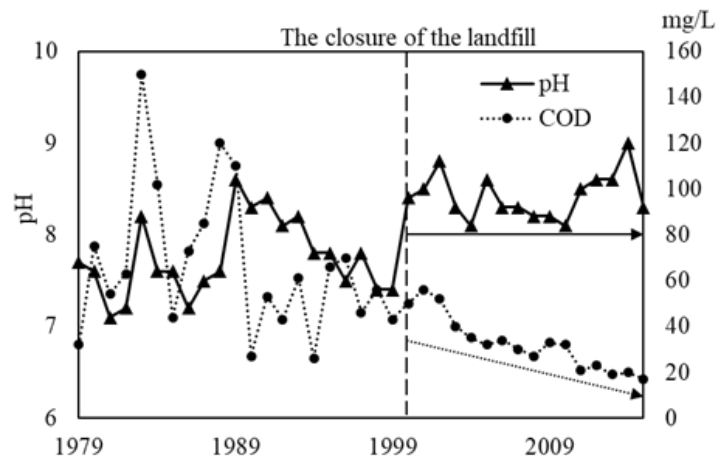


Figure 6-4 Yearly variation in the pH and chemical oxygen demand (COD) of leachate among leachate treatment facilities.

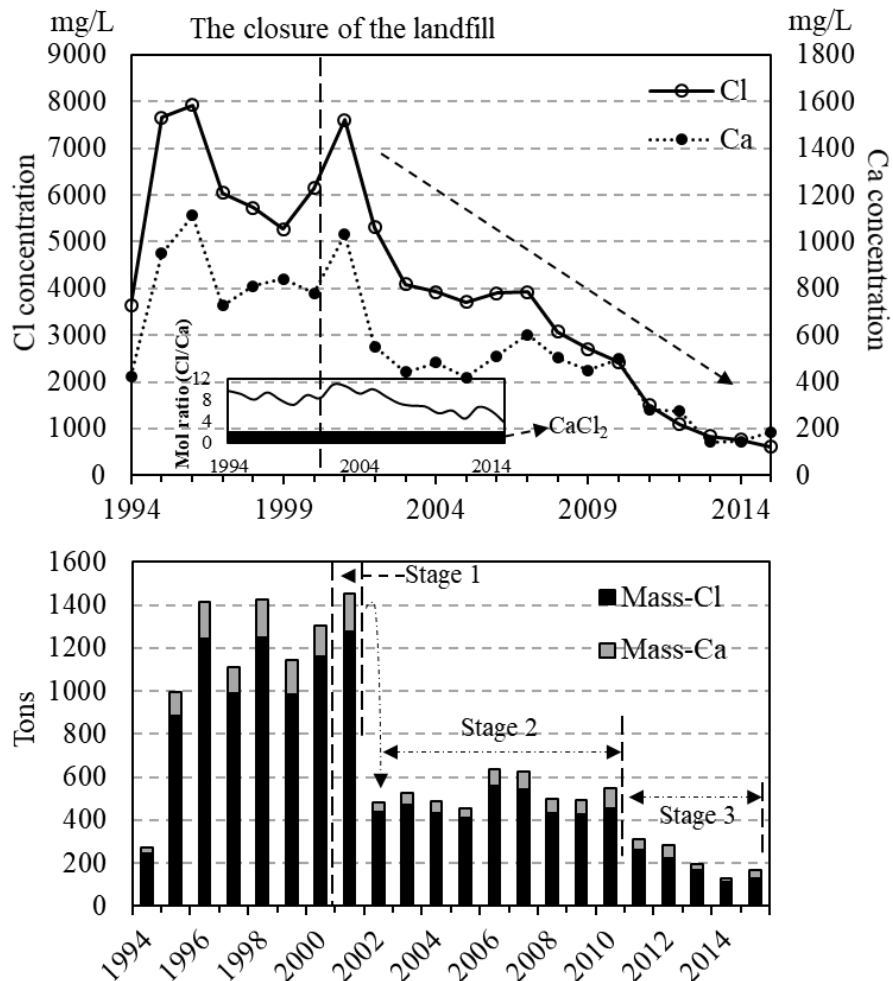


Figure 6-5 (a) The Cl and Ca concentration, Cl/Ca mol ratio in the leachate from 1994 to 2015. (b) The yearly mass loss of the Cl and Ca in the leachate.

6. 3. 3 Heavy metals in the leachate

The heavy metal concentration in the leachate has also been monitored since 1979. Figure 6-6 shows the measured concentrations of Cu, Zn, Cr and Pb in the leachate; the levels of Cd and Hg were always too low to be detected (i.e., lower than the detection limit). The figure shows that there was a relatively high heavy metal concentration in the early period of operation of this landfill; then, after 1994 (when the extended area of the landfill site began to be used), the heavy metal concentration decreased to a low level, at which it remained thereafter. This may be due to improvements in the technology used to stabilize FA, or to landfill management policies. In 1992, MSW FA was defined as specially controlled waste in Japan, and an intermediate treatment, such as chelate treatment, is required for landfill MSW FA. The Cu concentration of the leachate was slightly higher in 2006 than the other years, and the Cr concentration was slightly higher in 2005 and 2008. Compared to leachate from regular anaerobic-type landfill sites, the heavy metal concentration was not high, and was, in fact, lower than several previously reported values; this is because the leachate from anaerobic landfills is usually concentrated liquor, with a very high concentration of pollutants. Compared to similar landfill sites, which also contain incinerator residue, the heavy metal concentration measured in this study was not high. The differences in landfill types may have been responsible for this difference, as semi-aerobic landfills can generate more leachate than anaerobic landfills, which reduces the heavy metal concentration of the leachate. Another important factor is the pH; the pH of the leachate in this study was higher than that previously reported for other sites. The annual discharged mass of heavy metals is also presented in Figure 6-6, which shows that the mass strongly depends on the heavy metal concentration and leachate production rate. Therefore, the discharged mass of heavy metals varies similarly to the concentration. The heavy metal leaching behavior of incinerator residue is related to several factors; while the pH and L/S play important roles, other factors, such as the presence of anions and organics in the leachate, also influence the dissolution of heavy metals. High leaching concentrations of Zn and Pb ceased in 1989 and remained low thereafter. As shown in Figure 6-4, there was a sudden increase in the pH of the leachate due to the alkaline chemicals in the incinerator residues. We analyzed samples from the landfill layers, and leachates from different areas of the landfill site (Table 6-2), and found a significant difference in the distribution of the pH among different parts of the site. Thus, the original pH of the incinerator residue varied by plant, and among years. The pH of the leachate from inside the landfill was generally higher than 9, and in some regions, it exceeded 12. The high pH strongly affected the leaching of Pb and Zn. Relatively higher masses of Cu and Cr were discharged into the leachate, even after closure of the site. As shown in Figure 6-4, the COD of the leachate decreased significantly following the closure of the site, and the complexation effects of the organics also weakened. However,

the dissoluble fraction of the incinerator residues will become saturated, so the heavy metal concentrations in the leachate will decrease in the near future, assuming that the environmental conditions do not change.

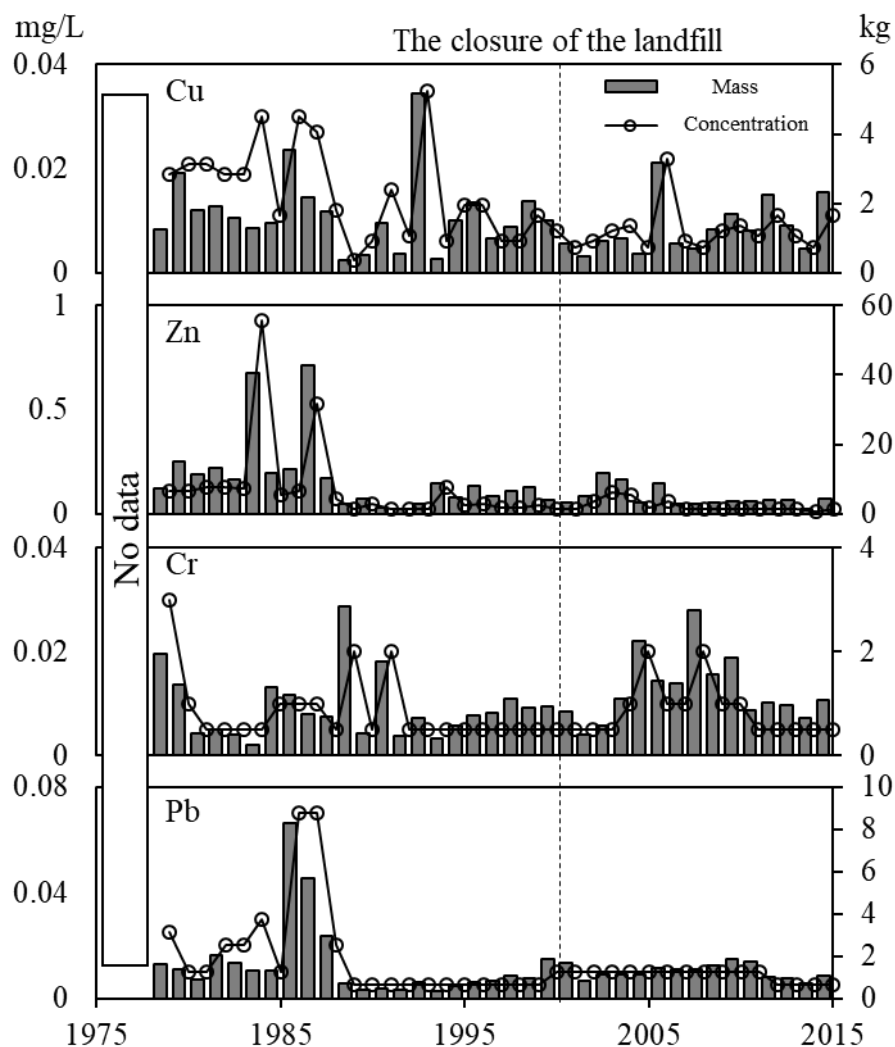


Figure 6-6 The heavy metal concentration and yearly discharged mass in the leachate.

Table 6-2 Leachate analysis results (samples obtained in 2016 by boring holes in landfill sites)

mg/L	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6
pH	10	11.9	12	12.72	9.52	6.8
ORP (mV)	-303	-352	-353	-378	-287	-123
Cd	N.D.	N.D.	N.D.	N.D.	N.D.	0.0013
Cr	0.0048	0.0061	0.0037	0.0063	0.0028	0.0009
Cu	0.0003	0.0090	0.0042	0.0019	N.D.	0.0093
Ni	0.0056	0.0105	0.0049	0.0145	0.0006	N.D.
Pb	0.0297	0.0661	0.0399	0.0139	0.0436	0.0360
Zn	0.0030	0.0087	N.D.	N.D.	0.0006	0.0558

6. 3. 4 Mass balance calculation results

Table 6-3 shows the results of the mass balance calculation of heavy metals in the landfill site considered in this study, and of two other reports on sites in Norway and China²³⁻²⁵. The total input masses of the heavy metals in this study for the period 1975–2000 were 83 t (Cd), 5,700 t (Pb), 14,000 t (Cu), 16,000 t (Zn), 6.6 t (Hg) and 600 t (Cr). The output masses of the heavy metals from leachate (1979–2015) were 3.5 kg (Cd), 55 kg (Pb), 57 kg (Cu), 300 kg (Zn), 1.5 kg (Hg) and 40 kg (Cr). The leaching rates of heavy metals over an almost 40-year period (1975–2015) were 0.0042% (Cd), 0.001% (Pb), 0.0004% (Cu), 0.0019% (Zn), 0.022% (Hg) and 0.0065% (Cr), respectively. The leaching rate calculated in this study was lower than that in the two previous reports. In the Norwegian study, the landfill site had been in operation since 1999, and there was no mention of its closure; also, only the total mass of input heavy metals in 2002 and 2003 was calculated, but the leachate from the landfill site may include leachate from old landfill waste (prior to 2002). Therefore, the conclusions that can be drawn from these results are limited. In the study of He, the heavy metal content of the MSWs was estimated based on landfill sampling performed after the site had closed. As mentioned above, the leachate from anaerobic landfills is usually highly concentrated liquor. He calculated the leachate rate based on historic leachate production rates, rather than actual data. Therefore, the mass balance analysis in that study was also limited.

Table 6-3 Mass balance data obtained in this study compared to those of two previous reports²³⁻²⁵

	This study (1975-2015), Japan			Øygaard's study (2002-2003), Norway			He's study (1993- 2003), China		
Waste	Incinerator residues with incombustible waste			MSWI bottom ash with construction waste			MSWs		
	Input (t)	Output (kg)	Leaching rate (%)	Input (kg)	Output (kg)	Leaching rate (%)	Input (t)	Output (kg)	Leaching rate (%)
Cd	83	3.5	0.0042	200	0.048	0.024	8.7	170	1.9
Pb	5700	55	0.0010	57000	0.72	0.001	550	820	0.15
Cu	14000	57	0.0004	64000	11	0.017	220	280	0.13
Zn	16000	300	0.0019	170000	2.2	0.001	810	1600	0.19
Hg	6.6	1.5	0.022	17	0.01	0.059	-	-	-
Cr	600	40	0.0065	3500	19	0.55	-	-	-

As shown in Table 6-3, the total masses of Pb, Cu, and Zn were much higher than those of Cd, Hg, and Cr in all studies. According to our results, the mobility of heavy metals can be ordered as follows: Hg > Cr > Cd > Zn > Pb > Cu. The leaching rates of Cd, Hg, and Cr were higher in all studies, although this could be due to calculation errors. As the concentrations of Cd, Cr, and Hg were too low to be detected, the results are mostly

presented as < 0.01 mg/L (Cd), < 0.001 mg/L (Cr) and < 0.0005 mg/L (Hg). We used the limit of detection (LOD)/2 as the leachate concentration in this study, which would certainly introduce some error into the calculation process. However, the concentrations of Cu, Zn, and Pb were detectable, so the results were more accurate than those for Cd, Cr, and Hg. Regardless of the likely calculation errors, Hg may still escape in gas; therefore, it may be released into the environment more readily. Zn, Pb, and Cu had high total masses, but low leaching rates, which implies that the efficiency of the FA stabilization treatment was excellent. In Section 6. 3. 2, we mentioned that the high pH inside the landfill is an important factor preventing heavy metals from escaping. Pb, Zn and Cu are easily affected by the pH, while Cr and Cd are not; this may be why the leaching rates of Cr and Cd were higher.

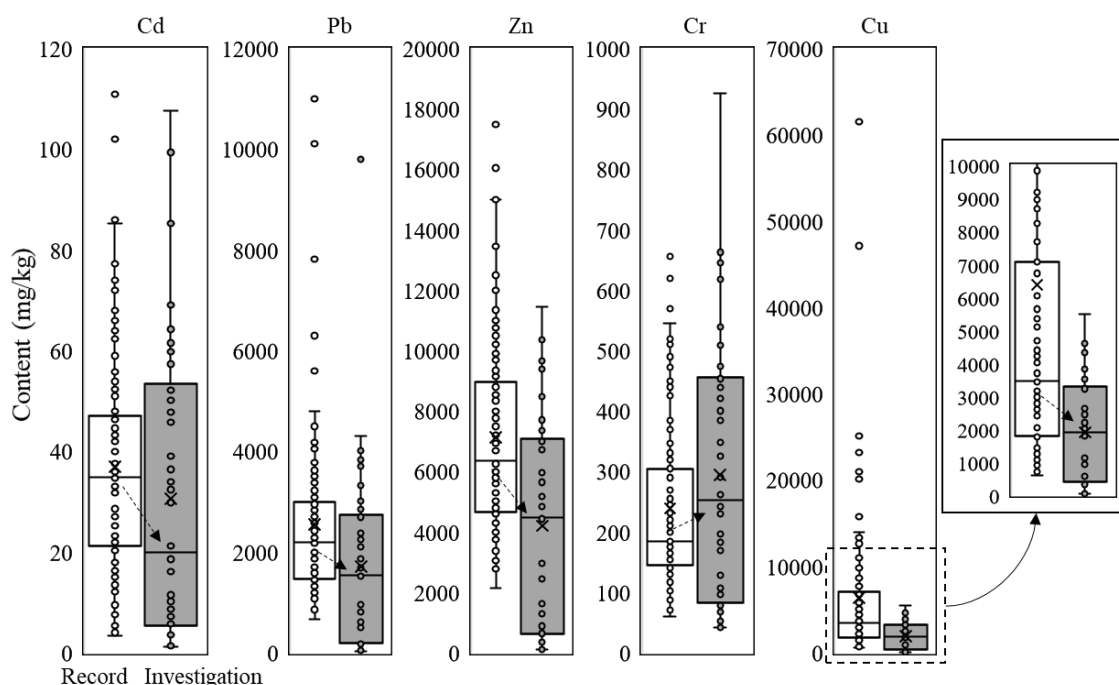


Figure 6-7 The comparison of heavy metal content in the record of incinerator residues and field sampling results.

Figure 6-7 shows a comparison between the data extracted from records and the field samples. The experimental procedure is described in detail in our previous chapter. A total of 42 field samples were included in this analysis. The median Cu, Pb, Zn, and Cd of filed samples do significantly less than the original record data at the $p=0.05$ level by using U-test (Mann-Whitney), while Cr is higher. The median Cd, Pb, Zn, and Cu contents decreased by 14.90, 657.3, 1880, and 1550 mg/kg, respectively. Only the median Cr content increased, by 67.10 mg/kg. In our previous chapter, we also calculated the heavy metal content at this landfill based on our collected data. The results were not in full agreement with the mass balance results presented herein, but the general trend was

largely similar. The analysis of the field samples suggested that Pb, Zn, and Cu had high mobility, while Cr and Cd had low mobility. This may have been because the leachable fractions in the incinerator residues had already been washed out. However, field samples allow only for limited, region-specific analysis, so the results from the mass balance calculation presented in this study are more accurate and reliable.

6.3.5 Changes in annual leaching rates of Cu, Zn, and Pb

To better understand the leaching behavior of Cu, Zn, and Pb at this landfill site, we introduced the “annual leaching rate” parameter, which is equal to the total mass of heavy metals in the leachate of a given year divided by the total amount of heavy metals disposed in the landfill up to that year, which can be calculated by Eq. (6-3):

$$LR_{year} = \frac{C_{year}V_{year}}{\sum_{1975}^{year} TM_{year}} \times 10^{-4} \quad (6-3)$$

Where LR_{year} is the leaching rate for a given year (%), C_{year} is the concentration of heavy metals in the leachate that year (mg/L), V_{year} is the leachate generation (L), and TM_{year} is the total amount of heavy metals disposed in that year (kg); the denominator remained almost constant after the year 2000.

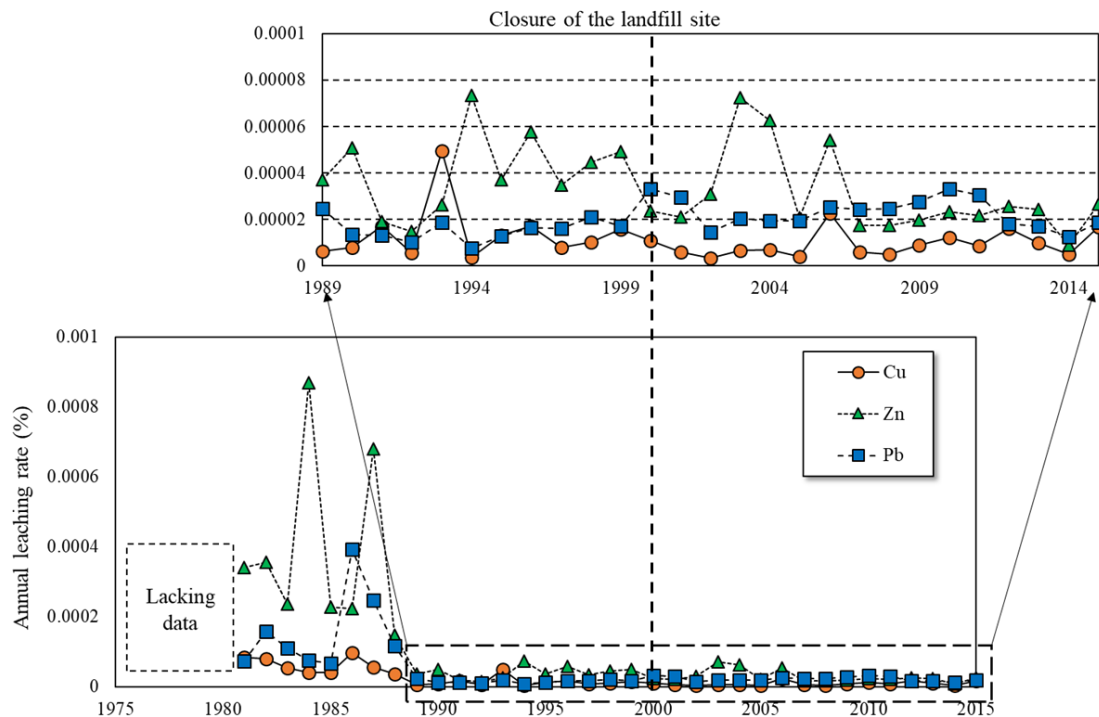


Figure 6-8 The annual leaching rates of Cu, Zn, and Pb.

Figure 6-8 shows the changes in annual leaching rates of Cu, Zn, and Pb at the landfill

site. Obvious changes occurred from 1989; before that date, the annual leaching rate fluctuated significantly, especially in the case of Zn. After 1989, the leaching rate remained below 0.0001%, and it remained below 0.00004% in the cases of Cu and Pb. Following the closure of the landfill site, the leaching rates of Cu, Zn, and Pb seemed to stabilize, at roughly 0.00002%. This could be due to several reasons. First, dilution effects of landfilled soil waste, derived from subway construction since 1989, are important; second, the high pH of the leachate also affects the leaching behavior of heavy metals; and third, the improved FA stabilization technology may prevent heavy metals from leaching. Finally, other possible factors, such as sulfide, anions, and organics, are not discussed in this study because we lack the necessary data.

6. 3. 6 A brief discussion on landfill mining

A closed landfill should be taken care of for the long-term to avoid any potential environmental pollution. The pollution factor is strongly connected to the wastes inside the landfill. In this study, we consider the wastes all come from the incineration plants, which is a mixture of incinerator bottom ash and stabilized fly ash. Therefore, if we want to conduct landfill mining to this kind of sites, the benefits we could achieve are 1) available space for a new landfill or other purposes, 2) the incinerator residues could be reused as the raw construction material, 3) and metals in the waste could be recovered. Figure 6-8 presents a brief idea of the landfill mining process in Japan.

For the first purpose, the most important one, Japan needs new spaces to bury the fresh incinerator residues in the near future. It's an emergency work to put on the schedule. There are cases that did similar works, it's reported the costs are very high. The work of comparing the cost of long time aftercare with a short time aftercare combined with a mining process could be conducted in the future.

The second purpose has been proposed by Shimaoka³². As it's reported that the Cl is not good for the cement industry, the rainfall washing could remove most of the Cl in the incinerator residues, so it's a good factor. And Shimaoka also illustrated this. However, the Ca also could release after a long-time weathering, this is not good for recycle incinerator residues in the cement industry. If we could stabilize the Ca in the waste, the benefit will become bigger. Shimaoka suggested to use carbonation process to stabilize heavy metals in fly ash. However, I think the carbonation process is also good for stabilize the Ca in incinerator residues.

Finally, the recovery of the metals. Currently, there's iron, aluminum, and other metals residues in the BA, and they were sent to the landfill without recovery. After extraction from the old landfill, we could obtain the metals directly by separation procedure. The metal elements inside residues could be extracted by acid reagents. As we have tested the samples by the SEP method, there's a considerable acid-extractable fraction of Zn, Pb, and Cu in the incinerator residues, this could be considered as a potential resource. We

calculated the potential mass which could be extracted by the acid in site A, the result is presented in Table 6-4. That's a large number of these metals' resources in the closed landfill site.

Table 6-4 The estimated mass of acid extractable of Pb, Zn, and Cu in site A.

Heavy metal	Mass of acid-extractable (tons)
Pb	1690
Zn	5460
Cu	4710

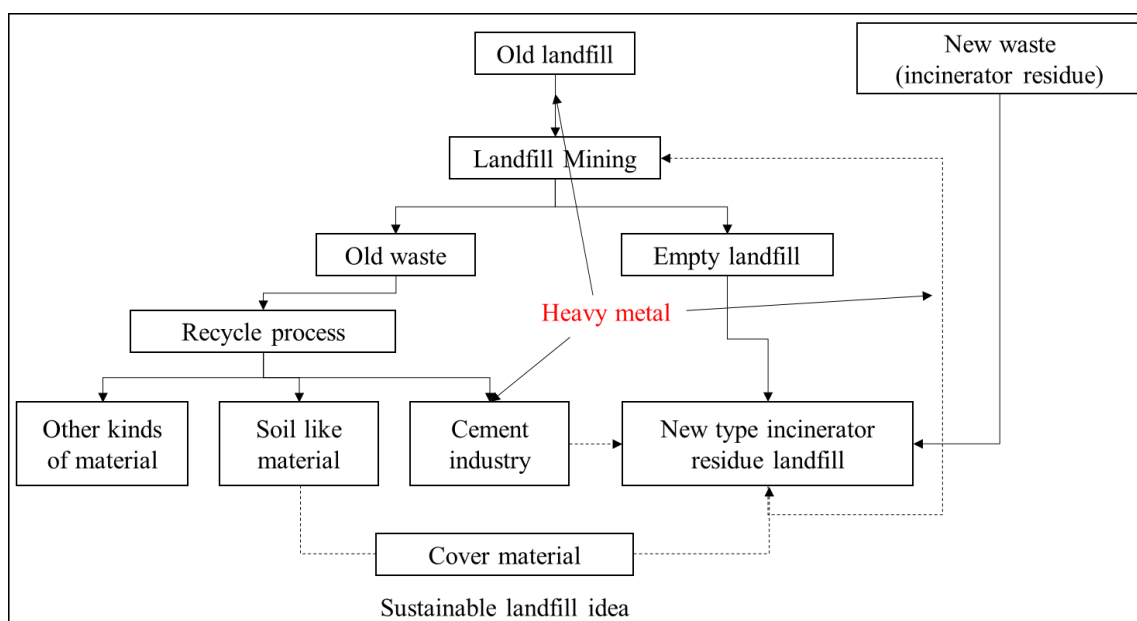


Figure 6-8 The idea of a sustainable landfill strategy in Japan.

The result of this study could be used as the fundamental material of landfill mining to site A in the future.

6. 4 Conclusion

In this chapter, the mass balance of heavy metals in a non-operational incinerator residue landfill site in Japan was estimated. Because the landfill waste is mainly incinerator residues, the COD was relatively low compared to values reported in the literature. And the pH increased in 1989 and remained above 8 following the closure of the landfill.

- 1) The Cl and Ca concentration of the leachate decreased significantly after the closure of the landfill, indicating that the dissolvable fraction of the incinerator residues had saturated.
- 2) The leaching rates from incinerator residues, for the period 1975–2015, were as follows: Cd, 0.0042%; Pb, 0.001%; Cu, 0.0004%; Zn, 0.0019%; Hg, 0.022%; and Cr,

0.0065%. Hg is considered to have the highest mobility due to the variety of routes via which it can be released. Cd and Cr had relatively high leaching rates compared to Pb, Zn, and Cu because the high pH inside the landfill largely prevented them from washing out. The total leaching rate was lower than that reported by Øygard and He. The calculation used in this study was based on raw data obtained from historical documents, so is more reliable than estimated values.

- 3) The annual leaching rates of Cu, Zn, and Pb varied significantly prior to 1989, gradually becoming more stable thereafter and remaining at approximately 0.00002% in the cases of Cu, Zn, and Pb. These heavy metals kept releasing from the landfill, but the amount is quite small for each year.
- 4) A mass balance of heavy metal inside landfills has been successfully conducted in this study. It's valuable for improving current landfill design and management. It's also could be used to evaluate the possibility of mining resources.

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CHAPTER 7

CONCLUSION AND FUTURE PERSPECTIVE

7. 1 Conclusion

A landfill is a final sink for the material flows into human society, It's necessary and can't be replaced by any other technology currently. In Japan, the landfill has been considered as the last step in the MSWs management system, because of the shortage of space for new landfill sites. To extend the period of using constructed landfills, the government encourage the cities to incinerate the MSWs before final disposal. Therefore, landfill waste in Japan is mainly a mixture of incinerator residues (including FA and BA) and a small amount of incombustible waste. "Semi-aerobic" type landfill was invented and widely applied in Japan since 1975, therefore, the typical Japanese landfill site is a semi-aerobic type monofill for incinerator residues.

We extracted boreholes samples from two typical Japanese type landfill sites to investigate the chemical properties in this study. Also, we asked the monitor data of one site from the administrators to proceed fully analysis of the landfill site. The result we obtained could improve our understanding of this type of landfills, and gives suggestions to reach a sustainable landfill strategy. The conclusions of each chapter have been summarized as below.

Chapter 2

It's found that the global MSW generation will reach 3.40 billion tonnes by 2050. Among these wastes, about 36.7% of them are landfilled in different countries by different methods. The rising awareness of "waste to energy" helps the spreading of incineration technology. Therefore, landfill wastes might become incinerator residues in other countries. At the meanwhile, "semi-aerobic" type landfill could decompose the waste faster than regular anaerobic type landfill, which will certainly shorten the period of aftercare. The combination of incinerator residues and semi-aerobic type landfills could be popular in the future. However, the research associated with this kind of landfill is limited, especially that focuses on the behavior of heavy metals.

Chapter 3

The geographic and weather condition of the two sampling landfill sites has been introduced in this chapter. Then, the detailed information and sampling process have been presented.

Chapter 4

The element composition and heavy metal content have been measured and presented. The contents of these heavy metals followed the order of $Zn > Cu \geq Pb > Cr > Ni > Cd$, revealing contents of Cu, Pb, and Zn of 100–10000, 500–5000, and 1000–20000 mg/kg, respectively. By checking the correlation between the elements, we found the insoluble

Ca salts may contribute to trapping heavy metals. The comparison of experimental data with historic data shows the Cu, Zn, and Pb in the landfill incinerator residues presents higher mobility than Cd, and Cr. In conclusion, the high heavy metal content implies a potential hazard to surrounding environment.

Chapter 5

The leaching test was conducted to the landfill incinerator residues, and no sample exceed the regulation limits of landfill waste. However, the potential environmental risk was suggested by the SEP result, the RAC fraction content of Pb in incinerator residues sample is higher than contaminated soil regulation. It seems the SEP result of Cu and Pb in site A and B isn't different significantly, while the XAFS result suggested there are some changes in chemical species of Pb and Cu after a 5-40 years weathering process. In conclusion, the potential hazard level of Pb in landfill incinerator residues is still high.

Chapter 6

The mass balance of heavy metals in site A showed a low leaching rate of Cd, 0.0042%; Pb, 0.001%; Cu, 0.0004%; Zn, 0.0019%; Hg, 0.022%; and Cr, 0.0065%. Therefore, the heavy metal storage is still high in the waste body. However, the leaching of heavy metals hasn't stopped, yet. Even though the rainfall removes the Cl from incinerator residues, the Ca is also lost, which is not good for the recycling of aged incinerator residues in the cement industry. The mass of acid-extractable Cu, Zn, and Pb is 4170, 5460, and 1690 tons respectively in site A, which could be considered as mining resources.

In this study, we investigated the heavy metals inside semi-aerobic landfills of incinerator residues. It's found the heavy metal content and storage in landfill area is still high after long time weathering process. The leaching loading of heavy metals is not much, however, the potential hazard level of Pb presents very high. The high content and storage of heavy metal Pb, Zn, and Cu could be a potential source of environmental pollution, however, they're also could be considered as potential mining resources. The monitoring data shows the leaching of heavy metals in site A will continue for a certain years, therefore it's hard to decide the termination of aftercare. The evaluation method we conducted in this study could be developed as part of the evaluation system to make decision of landfill graduation. However, I think It's better to reach landfill mining of old landfill sites in the future in Japan, due to the serious situation of landfill space crisis in the future.

7. 2 Future perspective

The general behavior of heavy metals in Japanese typical landfill sites was investigated in this study, and future investigations should be developed as follows:

- 1) Dioxins are also abundant in the incinerator residues, and they are more concerned by the citizens. We suggest an investigation on dioxins distribution and migration in typical Japanese landfill sites.
- 2) As the heavy metal content is still high in these landfills, it's hard to decide when to terminate the aftercare of old landfills. New testing methods and evaluation system should be developed. Our research could be used as a reference for this work. The new testing methods include SEP test as a potential risk evaluation process, XAFS measurement as the species analysis, XRD test for the weathering stage identification and SEM-EDS test as the further species analysis.
- 3) The XAFS data analysis procedure in this study hasn't been used by other schoolars. Complex environmental samples are difficult to get precisely result of species components. More samples and experiments should be conducted to check the reliable of this analysis procedure.
- 4) The heavy metal storage in site A has been calculated, and we also calculate the mass of acid-extractable fraction of Cu, Zn, and Pb. To conduct landfill mining in the future, our result could be considered as basic information.

APPENDIX

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Figure A5-7. XAFS data analysis of Pb-LIII edge EXAFS.

Figure A5-8. The comparison of result of SEP and XAFS (Pb).

Table A5-4. Identified extractable chemicals under F3 condition.

Table A4-1. The element composition results measured by XRF and CHN (dry basis).

Samples	Measured by XRF														Measured by CHN		
	O	Si	Ca	Al	Fe	K	Mg	Na	Ti	P	Mn	Ba	Cl	S	H	C	N
BH1-1	53.08%	24.36%	4.42%	5.27%	2.79%	2.61%	1.33%	0.64%	0.37%	0.14%	0.11%	0.05%	0.00%	0.33%	0.70%	1.79%	0.06%
BH1-2	52.87%	23.33%	5.91%	3.86%	4.08%	1.78%	1.03%	0.78%	0.33%	0.41%	0.06%	0.12%	0.10%	0.61%	0.53%	2.76%	0.06%
BH1-3	52.95%	22.64%	4.82%	4.68%	4.30%	2.08%	1.19%	0.77%	0.44%	0.34%	0.08%	0.06%	0.15%	1.02%	0.65%	2.48%	0.14%
BH1-4	53.29%	22.78%	4.58%	5.54%	3.51%	2.37%	1.53%	0.84%	0.42%	0.23%	0.07%	0.03%	0.04%	0.52%	0.53%	2.03%	0.09%
BH1-5	55.01%	25.82%	2.03%	5.15%	3.30%	2.08%	0.88%	0.40%	0.48%	0.10%	0.04%	0.00%	0.05%	0.22%	0.71%	0.95%	0.08%
BH1-6	54.15%	25.44%	1.11%	7.03%	5.02%	2.45%	1.87%	0.59%	0.57%	0.13%	0.18%	0.00%	0.04%	0.09%	0.75%	0.35%	0.06%
BH1-7	53.95%	24.98%	0.59%	5.97%	5.84%	2.48%	1.93%	0.53%	0.72%	0.13%	0.14%	0.04%	0.00%	0.05%	0.85%	0.15%	0.06%
BH1-8	54.27%	23.65%	1.57%	6.11%	5.51%	2.60%	1.93%	0.57%	0.60%	0.12%	0.16%	0.00%	0.00%	0.14%	0.77%	0.47%	0.07%
BH1-9	54.10%	26.47%	0.37%	7.25%	3.89%	2.72%	1.26%	0.64%	0.44%	0.09%	0.08%	0.02%	0.05%	0.08%	0.75%	1.36%	0.16%
BH2-1	54.99%	24.50%	0.73%	6.38%	2.60%	2.71%	1.07%	0.51%	0.35%	0.07%	0.07%	0.04%	0.00%	0.07%	0.95%	2.80%	0.20%
BH2-2	55.92%	25.22%	0.20%	6.72%	3.21%	3.13%	1.19%	0.00%	0.40%	0.08%	0.12%	0.00%	0.00%	0.09%	0.76%	0.26%	0.05%
BH2-3	56.30%	25.26%	0.14%	8.14%	2.82%	2.78%	0.99%	0.37%	0.37%	0.03%	0.06%	0.04%	0.00%	0.04%	0.77%	0.28%	0.04%
BH2-4	56.20%	23.06%	3.59%	6.33%	2.11%	2.20%	1.07%	0.65%	0.34%	0.05%	0.03%	0.04%	0.00%	0.12%	0.63%	0.55%	0.02%
BH2-5	54.82%	24.21%	5.03%	6.46%	2.83%	2.28%	1.09%	0.28%	0.34%	0.07%	0.07%	0.05%	0.00%	0.30%	0.70%	0.33%	0.02%
BH2-6	55.00%	26.49%	2.39%	5.85%	3.15%	2.61%	1.21%	0.28%	0.33%	0.08%	0.07%	0.04%	0.00%	0.17%	0.57%	0.31%	0.03%
BH2-7	49.46%	8.87%	10.87%	5.98%	15.34%	0.69%	2.47%	0.29%	0.79%	0.92%	0.18%	0.00%	0.11%	0.85%	1.15%	5.73%	0.16%
BH2-8	53.37%	23.78%	2.11%	6.21%	2.42%	2.21%	1.01%	0.90%	0.45%	0.19%	0.06%	0.00%	0.03%	0.58%	0.49%	3.74%	0.10%
BH2-9	55.33%	25.31%	1.80%	5.60%	2.60%	2.46%	1.20%	0.85%	0.43%	0.14%	0.07%	0.04%	0.00%	0.16%	0.47%	0.95%	0.05%
BH2-10	52.44%	16.93%	9.42%	4.51%	5.82%	1.22%	1.47%	0.75%	0.39%	0.49%	0.08%	0.05%	0.07%	1.32%	0.72%	3.71%	0.09%
BH2-11	45.86%	10.23%	10.36%	4.59%	12.37%	0.86%	2.71%	0.74%	0.59%	0.99%	0.13%	0.07%	0.16%	1.30%	1.06%	10.15%	0.35%
BH2-12	46.89%	9.37%	10.35%	5.20%	13.88%	0.80%	2.38%	0.98%	0.57%	0.98%	0.14%	0.07%	0.12%	1.23%	1.01%	9.19%	0.34%
BH2-13	49.01%	12.71%	10.17%	4.73%	12.41%	1.26%	1.92%	0.91%	0.49%	0.80%	0.14%	0.08%	0.12%	1.20%	0.83%	6.21%	0.18%

BH2-14	48.31%	11.36%	13.35%	4.78%	8.34%	1.12%	2.27%	1.48%	0.64%	1.16%	0.15%	0.09%	0.31%	1.69%	0.75%	5.41%	0.14%
BH2-15	48.42%	12.54%	10.67%	4.94%	14.21%	1.32%	2.29%	1.37%	0.62%	1.10%	0.42%	0.09%	0.21%	0.92%	0.52%	4.89%	0.13%
BH3-1	54.71%	25.34%	1.55%	6.08%	2.76%	2.33%	1.28%	0.00%	0.42%	0.11%	0.07%	0.04%	0.00%	0.09%	0.91%	3.28%	0.20%
BH3-2	54.03%	22.28%	8.74%	5.00%	2.36%	1.89%	1.20%	0.42%	0.32%	0.09%	0.07%	0.00%	0.00%	0.72%	0.67%	1.20%	0.04%
BH3-3	52.98%	24.51%	4.99%	5.91%	3.09%	3.06%	1.68%	1.02%	0.32%	0.10%	0.04%	0.05%	0.00%	0.16%	0.60%	0.74%	0.04%
BH3-4	49.03%	10.69%	14.26%	4.21%	4.46%	1.06%	2.34%	0.92%	0.79%	0.92%	0.12%	0.06%	0.34%	1.89%	0.91%	6.04%	0.15%
BH3-5	55.83%	25.29%	1.57%	6.29%	2.31%	2.28%	0.94%	0.83%	0.38%	0.17%	0.06%	0.00%	0.09%	0.08%	0.51%	1.06%	0.05%
BH3-6	53.40%	22.03%	5.01%	5.76%	2.83%	2.05%	1.52%	1.20%	0.46%	0.41%	0.08%	0.05%	0.25%	0.34%	0.39%	2.92%	0.06%
BH3-7	54.42%	24.50%	2.92%	5.79%	2.48%	2.12%	1.17%	1.05%	0.39%	0.22%	0.07%	0.00%	0.49%	0.34%	0.49%	1.52%	0.07%
BH3-8	51.44%	16.62%	12.33%	4.48%	3.84%	1.13%	2.11%	0.93%	0.47%	0.49%	0.08%	0.00%	0.33%	1.68%	0.71%	2.20%	0.05%
BH3-9	51.10%	16.73%	11.08%	5.16%	5.72%	1.34%	1.92%	0.84%	0.50%	0.56%	0.28%	0.00%	0.21%	1.09%	0.66%	3.12%	0.06%
BH3-10	46.07%	8.86%	13.62%	4.05%	7.68%	0.78%	2.43%	1.09%	0.59%	0.96%	0.30%	0.07%	0.39%	1.49%	1.00%	5.94%	0.16%
BH3-11	46.14%	9.25%	15.13%	3.36%	7.54%	0.60%	2.21%	0.70%	0.56%	0.71%	0.13%	0.10%	0.63%	2.15%	1.10%	3.89%	0.09%
BH3-12	51.58%	16.97%	5.99%	5.01%	9.31%	1.76%	1.50%	0.92%	0.46%	0.53%	0.12%	0.08%	0.28%	0.69%	0.76%	4.38%	0.16%
BH4-1	53.79%	25.28%	4.60%	5.52%	2.59%	2.50%	1.10%	0.53%	0.17%	0.38%	0.06%	0.00%	0.00%	0.08%	0.67%	0.57%	0.04%
BH4-2	54.23%	26.24%	3.96%	5.41%	2.89%	2.29%	1.14%	0.16%	0.22%	0.35%	0.05%	0.03%	0.00%	0.08%	0.67%	0.57%	0.04%
BH4-3	52.50%	21.18%	6.51%	5.09%	4.84%	1.72%	1.72%	0.30%	0.58%	0.58%	0.08%	0.03%	0.05%	0.40%	0.82%	1.74%	0.07%
BH4-4	47.73%	9.76%	14.67%	3.33%	6.67%	0.91%	2.66%	0.85%	2.39%	0.87%	0.16%	0.04%	0.22%	0.93%	1.08%	5.80%	0.16%
BH4-5	47.82%	9.69%	13.77%	4.72%	9.14%	1.34%	2.34%	0.77%	1.65%	0.83%	0.16%	0.05%	0.13%	0.92%	1.16%	6.01%	0.19%
BH4-6	47.92%	8.96%	13.09%	4.33%	9.08%	1.45%	2.38%	0.86%	1.02%	0.84%	0.17%	0.05%	0.13%	0.96%	1.24%	6.46%	0.19%
BH4-7	47.67%	8.70%	18.61%	2.36%	5.82%	0.33%	2.10%	0.67%	1.83%	0.69%	0.12%	0.05%	0.42%	0.65%	1.37%	5.34%	0.11%
BH4-8	48.47%	11.02%	12.74%	3.15%	7.79%	0.91%	2.95%	0.78%	1.18%	0.93%	0.13%	0.08%	0.18%	1.06%	1.01%	4.60%	0.12%
BH4-9	48.38%	10.87%	13.58%	3.38%	10.68%	0.85%	2.44%	0.84%	1.16%	0.74%	0.14%	0.06%	0.23%	0.95%	0.96%	4.16%	0.11%
BH4-10	47.80%	9.76%	16.76%	4.31%	9.31%	0.52%	2.23%	1.10%	1.51%	0.70%	0.15%	0.04%	0.65%	0.70%	1.04%	3.03%	0.06%
BH5-1	54.66%	28.59%	0.73%	5.11%	2.54%	2.46%	1.40%	1.06%	0.35%	0.12%	0.11%	0.00%	0.00%	0.04%	0.40%	0.22%	0.03%

BH5-2	53.69%	24.54%	4.45%	5.47%	2.67%	2.81%	1.45%	0.80%	0.37%	0.10%	0.09%	0.03%	0.00%	0.22%	0.58%	1.27%	0.06%
BH5-3	54.10%	25.92%	4.24%	4.93%	2.75%	2.27%	1.26%	0.32%	0.43%	0.13%	0.09%	0.03%	0.00%	0.29%	0.66%	0.51%	0.04%
BH5-4	54.08%	26.27%	3.67%	5.30%	2.36%	2.28%	1.40%	0.51%	0.48%	0.09%	0.05%	0.00%	0.00%	0.22%	0.51%	0.92%	0.05%
BH5-5	54.83%	26.74%	2.60%	4.47%	2.15%	2.34%	1.45%	0.00%	0.55%	0.09%	0.04%	0.00%	0.00%	0.15%	0.56%	0.88%	0.06%
BH5-6	53.46%	22.13%	7.15%	4.26%	3.22%	1.72%	1.08%	0.44%	0.44%	0.18%	0.06%	0.12%	0.26%	0.26%	0.57%	2.71%	0.08%
BH5-7	51.46%	21.45%	9.05%	3.69%	7.98%	1.44%	1.13%	0.96%	0.32%	0.39%	0.08%	0.05%	0.07%	0.79%	0.54%	1.60%	0.04%
BH5-8	50.07%	15.18%	10.40%	3.94%	7.03%	1.56%	2.38%	1.08%	0.70%	0.78%	0.14%	0.05%	0.14%	1.77%	0.66%	3.09%	0.12%
BH5-9	48.47%	16.26%	9.90%	3.21%	15.42%	1.08%	1.60%	2.14%	0.50%	0.85%	0.18%	0.05%	0.28%	1.15%	0.42%	0.96%	0.03%
BH5-10	48.34%	12.06%	12.13%	3.75%	19.32%	0.95%	1.72%	1.49%	0.73%	1.05%	0.19%	0.05%	0.38%	1.64%	0.52%	1.64%	0.57%
BH6-1	54.78%	24.96%	1.08%	6.36%	3.20%	3.07%	1.45%	1.02%	0.42%	0.09%	0.10%	0.05%	0.00%	0.06%	0.63%	0.50%	0.05%
BH6-2	49.23%	11.36%	12.80%	4.69%	5.25%	0.99%	2.14%	0.70%	0.70%	0.60%	0.12%	0.06%	0.14%	2.09%	0.89%	6.37%	0.13%
BH6-3	52.35%	19.07%	8.40%	5.26%	3.98%	1.38%	1.00%	1.35%	0.26%	0.17%	0.07%	0.00%	0.09%	3.05%	0.60%	3.37%	0.05%
BH6-4	53.86%	18.81%	5.83%	5.95%	3.86%	1.76%	1.44%	1.11%	0.38%	0.21%	0.08%	0.00%	0.08%	3.34%	0.53%	2.05%	0.11%
BH6-5	48.54%	6.77%	15.29%	2.71%	8.45%	0.55%	0.77%	0.31%	0.33%	0.07%	0.07%	0.00%	0.00%	9.41%	1.06%	7.48%	0.09%
BH6-6	52.61%	15.16%	10.86%	5.63%	3.91%	1.34%	0.87%	0.53%	0.34%	0.16%	0.07%	0.00%	0.16%	5.19%	0.56%	2.21%	0.05%
BH6-7	49.03%	17.73%	7.53%	4.85%	11.57%	1.46%	1.15%	0.62%	0.32%	0.15%	0.11%	0.00%	0.09%	2.34%	0.61%	2.99%	0.08%
BH6-8	53.13%	20.78%	6.91%	5.71%	3.47%	1.81%	1.02%	0.55%	0.36%	0.16%	0.07%	0.00%	0.10%	2.49%	0.64%	2.83%	0.11%
BH6-9	52.15%	15.30%	12.10%	5.13%	1.92%	1.32%	1.33%	0.42%	0.30%	0.09%	0.05%	0.00%	0.02%	8.26%	0.51%	1.41%	0.07%
BH6-10	52.98%	19.47%	7.40%	5.04%	2.86%	1.79%	1.03%	0.80%	0.30%	0.09%	0.06%	0.00%	0.03%	4.63%	0.48%	2.05%	0.00%
BH6-11	55.21%	26.19%	0.36%	6.23%	3.41%	2.50%	1.23%	0.68%	0.50%	0.06%	0.08%	0.00%	0.00%	0.14%	0.69%	0.71%	0.04%
BH7-1	50.34%	12.25%	16.93%	3.88%	4.30%	0.96%	1.64%	0.42%	0.57%	0.60%	0.09%	0.02%	0.47%	2.97%	1.16%	1.90%	0.08%
BH7-2	45.95%	6.55%	21.73%	4.05%	6.64%	1.30%	1.39%	1.39%	0.58%	0.70%	0.07%	0.01%	4.48%	2.32%	1.41%	2.36%	0.06%
BH7-3	44.88%	6.96%	19.54%	6.58%	6.60%	1.78%	1.75%	1.84%	0.70%	0.76%	0.09%	0.04%	4.69%	2.35%	1.22%	2.57%	0.05%
BH7-4	45.31%	7.55%	19.30%	3.97%	7.92%	1.68%	1.67%	1.88%	0.64%	0.83%	0.18%	0.04%	4.31%	1.63%	1.12%	2.09%	0.04%
BH7-5	45.39%	11.56%	17.58%	4.95%	6.04%	1.69%	1.31%	2.52%	0.49%	0.73%	0.10%	0.01%	4.62%	1.66%	0.97%	2.50%	0.07%

BH7-6	47.35%	4.77%	22.77%	2.48%	2.57%	1.03%	0.43%	1.10%	0.15%	0.31%	0.03%	0.00%	2.69%	13.02%	0.85%	2.17%	0.06%
BH7-7	45.21%	6.65%	18.22%	3.02%	9.21%	1.80%	1.14%	1.34%	0.42%	0.64%	0.11%	0.01%	3.72%	3.17%	1.16%	5.29%	0.11%
BH7-8	48.53%	12.82%	14.04%	3.80%	3.40%	1.56%	2.12%	0.99%	0.28%	0.30%	0.07%	0.01%	2.87%	7.66%	0.96%	2.52%	0.08%
BH7-9	46.37%	4.89%	21.87%	2.46%	4.74%	1.08%	0.75%	0.85%	0.36%	0.36%	0.06%	0.00%	2.41%	10.77%	1.08%	3.78%	0.11%
BH7-10	47.56%	2.65%	24.14%	1.55%	1.98%	0.73%	0.27%	0.50%	0.11%	0.15%	0.02%	0.00%	1.91%	16.75%	0.90%	1.88%	0.05%
BH8-1	43.09%	5.47%	21.86%	3.88%	4.30%	2.27%	1.65%	2.97%	0.81%	0.83%	0.07%	0.05%	7.75%	2.31%	1.01%	2.03%	0.03%
BH8-2	42.12%	5.19%	22.46%	2.98%	2.61%	2.25%	1.49%	2.54%	0.74%	0.71%	0.07%	0.05%	9.17%	2.26%	1.25%	1.81%	0.04%
BH8-3	37.01%	4.40%	21.47%	3.38%	1.85%	2.90%	1.31%	5.39%	0.59%	0.58%	0.07%	0.00%	14.95%	2.56%	1.27%	1.45%	0.05%
BH8-4	46.20%	8.33%	19.30%	3.63%	5.06%	1.23%	1.56%	1.24%	0.61%	0.95%	0.15%	0.03%	3.67%	2.17%	1.18%	3.07%	0.09%
BH8-5	42.67%	6.12%	22.69%	3.14%	4.60%	1.94%	1.36%	1.86%	0.58%	0.79%	0.10%	0.00%	7.34%	2.33%	1.12%	3.08%	0.09%
BH8-6	43.66%	5.97%	21.61%	3.81%	4.31%	2.04%	1.40%	1.96%	0.61%	0.63%	0.11%	0.00%	6.81%	3.12%	0.97%	2.62%	0.06%
BH8-7	44.62%	7.78%	19.94%	4.12%	5.25%	1.78%	1.50%	1.90%	0.58%	0.83%	0.11%	0.03%	5.27%	2.26%	0.94%	2.95%	0.07%
BH8-8	45.05%	7.79%	22.18%	2.31%	3.29%	1.34%	1.49%	1.73%	0.63%	0.72%	0.08%	0.03%	5.52%	2.39%	0.81%	2.14%	0.06%
BH8-9	45.39%	7.54%	20.50%	2.92%	3.59%	1.50%	1.50%	1.57%	0.71%	0.74%	0.07%	0.00%	4.35%	2.66%	1.27%	3.08%	0.08%
BH8-10	48.29%	13.50%	15.65%	3.41%	2.19%	1.93%	1.05%	1.21%	0.37%	0.24%	0.06%	0.00%	2.50%	5.35%	0.77%	3.13%	0.06%
BH9-1	50.97%	14.06%	13.79%	4.33%	8.29%	0.79%	1.61%	0.34%	0.49%	0.53%	0.12%	0.03%	0.58%	2.00%	0.93%	2.33%	0.11%
BH9-2	48.36%	7.38%	20.35%	4.52%	9.43%	0.53%	1.60%	0.65%	0.64%	0.81%	0.11%	0.00%	1.44%	1.76%	1.12%	3.10%	0.09%
BH9-3	49.63%	7.08%	19.98%	5.50%	6.50%	0.31%	2.15%	0.44%	0.81%	0.58%	0.09%	0.04%	0.83%	2.04%	1.43%	3.46%	0.08%
BH9-4	49.29%	11.04%	18.14%	3.73%	6.02%	0.81%	1.87%	0.78%	0.77%	0.71%	0.10%	0.04%	0.54%	2.31%	1.02%	2.48%	0.06%
BH9-5	48.32%	11.79%	16.64%	3.19%	5.52%	1.76%	2.00%	1.42%	0.84%	0.67%	0.12%	0.04%	1.26%	1.65%	1.01%	2.08%	0.05%
BH9-6	47.53%	10.73%	17.55%	4.25%	4.22%	1.85%	2.05%	1.33%	0.86%	0.70%	0.10%	0.04%	2.51%	2.04%	1.12%	2.40%	0.07%
BH9-7	47.88%	10.91%	16.91%	3.40%	5.35%	1.75%	1.92%	1.52%	0.78%	0.72%	0.12%	0.04%	2.29%	1.65%	1.02%	2.46%	0.06%
BH9-8	47.50%	13.22%	16.52%	2.84%	4.78%	1.54%	1.49%	1.30%	0.46%	0.54%	0.09%	0.03%	2.82%	1.62%	1.06%	2.83%	0.08%
BH9-9	44.16%	8.59%	19.36%	2.90%	4.35%	1.78%	1.97%	1.64%	0.73%	0.61%	0.08%	0.00%	5.71%	1.68%	1.06%	3.27%	0.13%
BH9-10	45.61%	8.92%	17.61%	2.91%	5.51%	1.79%	1.94%	1.94%	0.71%	0.64%	0.10%	0.04%	4.81%	1.46%	1.00%	2.91%	0.08%

BH9-11	45.50%	7.47%	20.34%	2.57%	3.03%	1.38%	2.05%	1.21%	0.67%	0.56%	0.08%	0.03%	4.19%	3.01%	1.17%	3.83%	0.10%
BH9-12	46.73%	11.89%	14.90%	3.57%	7.42%	1.96%	1.67%	1.62%	0.59%	0.55%	0.41%	0.03%	2.69%	2.13%	0.98%	2.22%	0.08%
BH9-13	45.72%	10.15%	16.36%	3.41%	2.86%	2.04%	2.10%	1.56%	0.84%	0.66%	0.10%	0.03%	4.05%	1.76%	1.07%	3.93%	0.12%
BH9-14	46.39%	9.78%	17.72%	3.03%	4.64%	1.53%	2.13%	1.35%	0.76%	0.75%	0.10%	0.08%	2.92%	1.95%	1.26%	3.34%	0.11%
BH9-15	46.23%	13.34%	13.82%	3.82%	5.88%	1.67%	2.05%	2.02%	0.72%	0.66%	0.10%	0.04%	2.08%	2.08%	0.97%	3.40%	0.12%

Table A4-2. Summarized result of the element composition (% , w/w, dry basis).

	Depth (m)	Type	O	Si	Ca	Al	Fe	K	Mg	Na	Ti	P	Mn	Ba	Cl	S	H	C	N	Num. of samples
BH1	0~0.8	Cover soil	53.08	24.36	4.42	7.22	2.68	2.61	1.33	0.64	0.37	0.14	0.11	0.02	0.00	0.33	0.70	1.79	0.06	1
	0.8-1.6	Waste	52.87	23.33	5.91	5.90	3.20	1.78	1.03	0.78	0.33	0.41	0.06	0.02	0.10	0.61	0.53	2.76	0.06	1
	1.6-4.25	Soil	53.12	22.71	4.70	7.04	3.14	2.23	1.36	0.81	0.43	0.28	0.08	0.02	0.10	0.77	0.59	2.25	0.11	2
	4.25-4.7	Clay	55.01	25.82	2.03	8.21	2.86	2.08	0.88	0.40	0.48	0.10	0.04	0.02	0.05	0.22	0.71	0.95	0.08	1
	4.7-8.2	Soil	54.12	24.69	1.09	8.17	4.63	2.51	1.91	0.57	0.63	0.13	0.16	0.02	0.01	0.09	0.79	0.32	0.07	3
	8.2-9.0	Clay	54.10	26.47	0.37	8.20	3.14	2.72	1.26	0.64	0.44	0.09	0.08	0.01	0.05	0.08	0.75	1.36	0.16	1
BH2	0	Surface soil	54.99	24.50	0.73	8.44	2.42	2.71	1.07	0.51	0.35	0.07	0.07	0.04	0.00	0.07	0.95	2.80	0.20	1
	0-4.5	Cover soil	55.65	24.85	2.27	8.77	2.63	2.60	1.11	0.32	0.35	0.06	0.07	0.04	0.00	0.14	0.69	0.35	0.03	5
	4.5-13	Waste	49.90	14.57	8.79	6.92	5.42	1.33	1.97	0.92	0.55	0.75	0.15	0.06	0.12	1.03	0.78	5.55	0.17	9
BH3	0	Surface soil	54.71	25.34	1.55	7.19	2.42	2.33	1.28	0.00	0.42	0.11	0.07	0.04	0.00	0.09	0.91	3.28	0.20	1
	0-0.4	Cover soil	54.03	22.28	8.74	5.92	2.26	1.89	1.20	0.42	0.32	0.09	0.07	0.00	0.00	0.72	0.67	1.20	0.04	1
	0.4-10	Waste	51.20	17.54	8.69	6.55	3.19	1.62	1.78	0.95	0.49	0.51	0.13	0.04	0.33	0.99	0.71	3.18	0.09	10
BH4	0-1.7	Cover soil	54.01	25.76	4.28	7.49	2.52	2.39	1.12	0.35	0.37	0.08	0.06	0.01	0.00	0.20	0.67	0.57	0.04	2
	1.7-10	Waste	48.54	11.24	13.72	7.15	3.99	1.00	2.35	0.77	0.77	0.82	0.14	0.05	0.25	1.41	1.08	4.64	0.13	8
BH5	0-1.2	Cover soil	54.66	28.59	0.73	7.28	2.48	2.46	1.40	1.06	0.35	0.12	0.11	0.00	0.00	0.04	0.40	0.22	0.03	1
	1.2-5.1	Soil	54.18	25.87	3.74	7.08	2.44	2.43	1.39	0.41	0.45	0.10	0.07	0.01	0.00	0.22	0.58	0.89	0.05	4
	5.1-10	Waste	50.36	17.42	9.73	6.45	5.62	1.35	1.58	1.22	0.54	0.65	0.13	0.06	0.23	1.12	0.54	2.00	0.17	5
BH6	0-0.5	Cover soil	54.78	24.96	1.08	8.81	2.84	3.07	1.45	1.02	0.42	0.09	0.10	0.05	0.00	0.06	0.63	0.50	0.05	1
	0.5-8.6	Waste	51.54	16.05	9.68	5.62	4.08	1.38	1.20	0.71	0.37	0.19	0.08	0.01	0.08	4.53	0.65	3.42	0.08	9
	8.6-10	Clay	55.21	26.19	0.36	8.50	3.06	2.50	1.23	0.68	0.50	0.06	0.08	0.00	0.00	0.14	0.69	0.71	0.04	1
BH7	0.3-10	Waste	46.69	7.67	19.61	3.67	5.34	1.36	1.25	1.28	0.43	0.54	0.08	0.02	3.22	6.23	1.08	2.71	0.07	10
BH8	0-10	Waste	43.81	7.21	20.77	3.36	3.70	1.92	1.43	2.24	0.62	0.70	0.09	0.02	6.73	2.74	1.06	2.54	0.06	10
BH9	0.5-15	Waste	47.32	10.42	17.33	3.60	5.59	1.43	1.91	1.27	0.71	0.65	0.12	0.03	2.58	1.94	1.08	2.94	0.09	15

Table A4-3. Heavy metals content in the BH samples (mg/kg, dry basis).

	Cd	Cr	Cu	Ni	Pb	Zn
BH1-1	5	82	89	61	49	231
BH1-2	7	85	376	48	193	646
BH1-3	10	116	713	66	227	983
BH1-4	6	84	290	45	208	724
BH1-5	4	68	95	48	47	216
BH1-6	3	113	80	81	23	118
BH1-7	4	141	78	112	21	108
BH1-8	4	122	84	90	23	106
BH1-9	1	79	51	62	23	82
BH2-1	1	58	27	62	24	85
BH2-2	1	67	52	80	25	110
BH2-3	1	61	21	69	22	66
BH2-4	1	46	32	36	26	84
BH2-5	1	63	55	62	25	96
BH2-6	2	71	57	60	28	100
BH2-7	62	539	3900	371	4015	9408
BH2-8	2	57	61	51	146	225
BH2-9	2	49	113	53	49	201
BH2-10	16	183	2008	87	705	2965
BH2-11	39	483	2494	188	1921	5966
BH2-12	36	440	3835	203	1781	5756
BH2-13	34	401	2064	206	1862	5166
BH2-14	50	462	2639	213	2882	6986
BH2-15	32	454	3226	223	1945	6718
BH3-1	1	70	50	72	38	103
BH3-2	2	63	60	53	75	201
BH3-3	1	68	40	64	35	103
BH3-4	52	326	1798	176	1693	5645
BH3-5	1	41	53	44	51	133
BH3-6	10	96	400	75	566	1619
BH3-7	2	53	178	48	120	358
BH3-8	46	191	649	88	1066	4436
BH3-9	30	262	935	121	1564	5706
BH3-10	48	405	2198	171	2697	9577
BH3-11	58	348	2290	195	2375	7709
BH3-12	16	230	1131	131	961	2448
BH4-1	4	59	35	46	20	86
BH4-2	5	64	44	41	27	114

BH4-3	69	173	939	86	2251	5771
BH4-4	108	474	2447	206	3702	10353
BH4-5	60	509	4770	247	2890	7398
BH4-6	57	389	4763	194	3330	7361
BH4-7	85	421	3533	266	3827	9659
BH4-8	99	385	3521	232	4299	11453
BH4-9	64	646	3537	205	3018	8481
BH4-10	62	663	4613	485	2858	9398
BH5-1	3	56	27	32	11	61
BH5-2	4	65	43	44	26	91
BH5-3	4	60	60	52	22	108
BH5-4	4	58	229	43	18	203
BH5-5	4	56	358	47	18	243
BH5-6	6	78	326	110	1008	435
BH5-7	7	197	1276	83	617	1285
BH5-8	35	291	2749	170	1945	5023
BH5-9	19	548	2449	338	1521	4533
BH5-10	21	618	4332	719	2107	4847
BH6-1	2	83	53	88	57	184
BH6-2	12	243	2254	152	817	2461
BH6-3	2	129	476	69	121	657
BH6-4	2	71	661	42	63	420
BH6-5	9	926	5498	210	498	1357
BH6-6	6	80	342	48	177	886
BH6-7	4	169	562	104	9806	2439
BH6-8	4	107	574	61	225	521
BH6-9	6	42	183	30	57	105
BH6-10	2	42	105	25	47	132
BH6-11	1	75	36	92	27	106
BH7-1	90	329	1075	157	1054	7775
BH7-2	43	415	2255	199	1411	6467
BH7-3	68	595	2687	281	2008	9259
BH7-4	55	827	2478	994	1481	8467
BH7-5	55	451	3760	189	1650	6193
BH7-6	31	237	1371	62	929	2863
BH7-7	64	487	4006	271	1667	8275
BH7-8	55	226	1402	101	1254	4999
BH7-9	40	262	1754	139	1161	3880
BH7-10	18	154	830	49	480	1757
BH8-1	51	359	1557	144	1461	6704

BH8-2	50	334	1731	136	1657	6835
BH8-3	71	345	1473	103	1382	7412
BH8-4	38	366	2698	179	1140	6136
BH8-5	37	354	1945	161	1625	5121
BH8-6	44	394	2100	158	1417	5745
BH8-7	42	388	2364	182	1410	5735
BH8-8	40	283	2086	123	1373	4247
BH8-9	49	244	2162	141	1182	4668
BH8-10	11	149	622	57	474	1233
BH9-1	36	266	1014	129	516	3349
BH9-2	44	541	2750	381	1245	7112
BH9-3	74	397	2010	234	1505	8009
BH9-4	75	572	2482	192	1508	6971
BH9-5	62	369	2685	387	1442	6907
BH9-6	78	468	4263	243	1539	7001
BH9-7	54	461	2841	239	1515	6026
BH9-8	64	325	2088	160	2822	5377
BH9-9	80	333	2030	267	1508	6943
BH9-10	50	381	1922	312	1075	6223
BH9-11	90	286	2160	252	1622	8527
BH9-12	107	368	2631	168	1783	10253
BH9-13	73	276	1874	161	1332	7476
BH9-14	64	338	2502	198	1303	6092
BH9-15	99	544	1793	164	1692	7187

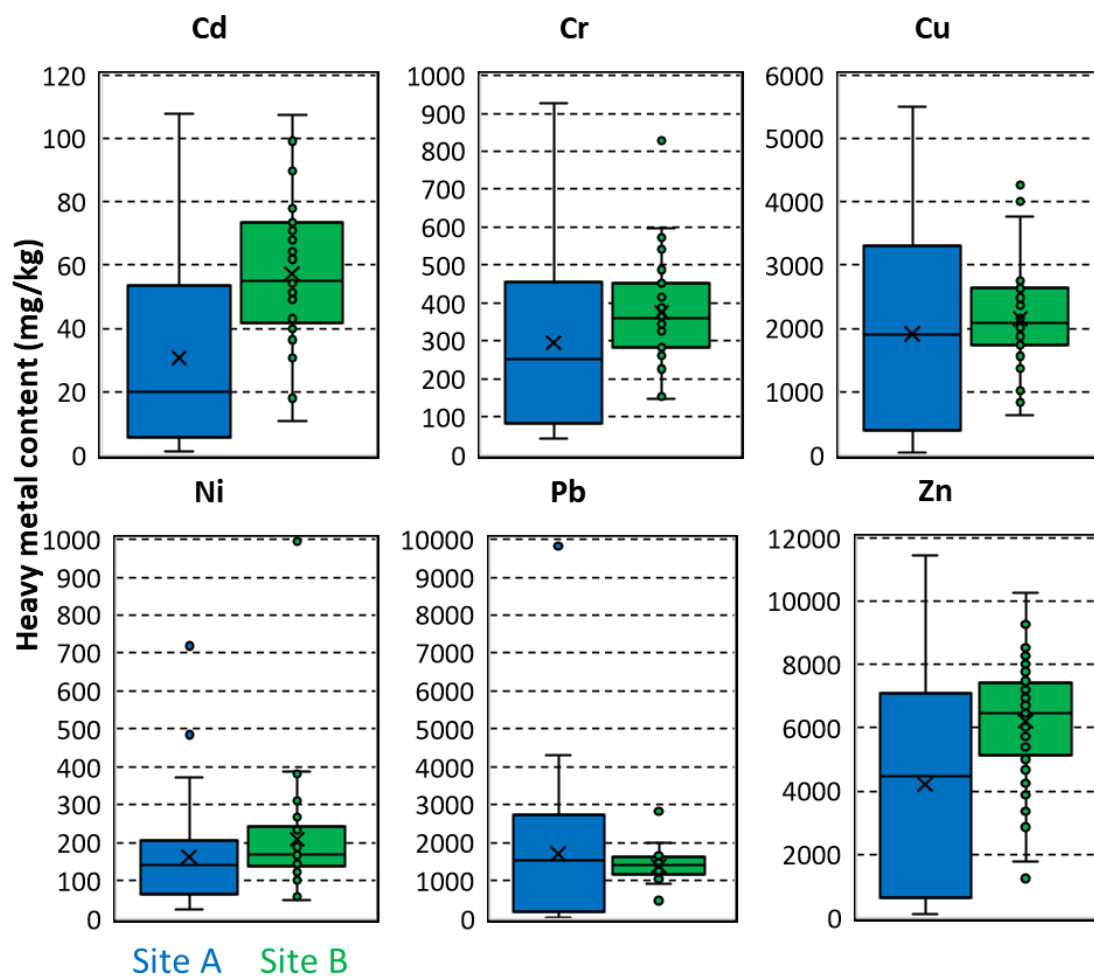


Figure A4-1. Comparison of heavy metal content in samples between site A and site B.

Table A4-4. Correlations between the content of elements (no-waste samples, site A).

P r	O	Si	Ca	Al	Fe	K	Mg	Na	Ti	P	Mn	Ba	Cl	S	H	C	N	Cd	Cr	Cu	Ni	Pb	Zn
O		0.25	0.01	0.00	0.25	0.19	0.05	0.09	0.39	0.00	0.21	0.23	0.04	0.00	0.40	0.08	0.35	0.00	0.03	0.02	0.74	0.01	0.01
Si	0.24		0.01	0.67	0.55	0.27	0.90	0.52	0.70	0.05	0.87	0.21	0.15	0.00	0.24	0.08	0.54	0.39	0.19	0.15	0.56	0.00	0.01
Ca	(0.50)	(0.54)		0.00	0.07	0.00	0.36	0.97	0.05	0.16	0.11	0.73	0.58	0.00	0.11	0.43	0.24	0.07	0.32	0.19	0.01	0.06	0.08
Al	0.74	0.09	(0.72)		0.33	0.00	0.61	0.84	0.55	0.02	0.61	0.18	0.35	0.00	0.07	0.08	0.75	0.01	0.93	0.07	0.04	0.13	0.09
Fe	(0.24)	(0.12)	(0.36)	0.20		0.49	0.00	0.40	0.00	0.15	0.00	0.74	0.35	0.63	0.11	0.26	0.80	0.43	0.00	0.76	0.00	0.79	0.74
K	0.27	0.23	(0.61)	0.60	0.15		0.44	0.56	0.97	0.15	0.06	0.45	0.13	0.00	0.40	0.38	0.85	0.07	0.78	0.08	0.05	0.15	0.10
Mg	(0.39)	(0.03)	(0.19)	(0.11)	0.77	0.16		0.21	0.00	0.19	0.00	0.38	0.74	0.49	0.97	0.42	0.91	0.42	0.00	0.71	0.01	0.96	0.91
Na	(0.34)	(0.13)	(0.01)	(0.04)	0.18	0.12	0.26		0.98	0.10	0.19	0.99	0.22	0.52	0.05	0.97	0.71	0.23	0.24	0.67	0.91	0.12	0.20
Ti	(0.18)	0.08	(0.39)	0.13	0.81	(0.01)	0.73	0.00		0.34	0.01	0.16	0.56	0.37	0.25	0.40	0.66	0.29	0.00	0.32	0.00	0.79	0.80
P	(0.71)	(0.40)	0.29	(0.46)	0.29	(0.30)	0.27	0.34	0.20		0.24	0.71	0.00	0.00	0.46	0.03	0.13	0.00	0.00	0.00	0.90	0.00	0.00
Mn	(0.26)	(0.04)	(0.33)	0.11	0.78	0.38	0.78	0.27	0.52	0.24		0.57	0.91	0.49	0.26	0.31	0.98	0.90	0.00	0.61	0.00	0.76	0.71
Ba	0.25	(0.26)	(0.07)	0.28	(0.07)	0.16	(0.18)	(0.00)	(0.29)	(0.08)	(0.12)		0.87	0.59	0.14	0.50	0.46	0.26	0.98	0.43	0.60	0.86	0.78
Cl	(0.41)	(0.30)	0.12	(0.19)	0.20	(0.31)	(0.07)	0.25	0.12	0.81	0.03	(0.03)		0.00	0.86	0.06	0.06	0.00	0.04	0.00	0.99	0.00	0.00
S	(0.57)	(0.61)	0.74	(0.61)	(0.10)	(0.56)	(0.14)	0.13	(0.19)	0.74	(0.15)	(0.11)	0.66		0.30	0.06	0.74	0.00	0.43	0.00	0.33	0.00	0.00

H	0.17	(0.25)	(0.33)	0.37	0.32	0.17	(0.01)	(0.39)	0.24	(0.15)	0.24	0.30	(0.04)	(0.22)		0.11	0.00	0.11	0.13	0.22	0.00	0.39	0.25
C	(0.36)	(0.35)	0.17	(0.35)	(0.24)	(0.18)	(0.17)	(0.01)	(0.17)	0.45	(0.21)	0.14	0.38	0.38	0.33		0.00	0.27	0.98	0.07	0.60	0.01	0.02
N	(0.20)	(0.13)	(0.24)	(0.07)	0.05	0.04	(0.03)	(0.08)	0.09	0.31	0.01	0.15	0.38	0.07	0.58	0.84		0.79	0.38	0.27	0.45	0.21	0.24
Cd	(0.72)	(0.18)	0.36	(0.49)	0.17	(0.37)	0.17	0.25	0.22	0.83	0.03	(0.24)	0.67	0.64	(0.33)	0.23	0.06		0.07	0.00	0.34	0.00	0.00
Cr	(0.44)	(0.27)	(0.21)	0.02	0.93	0.06	0.72	0.24	0.74	0.54	0.74	(0.00)	0.41	0.17	0.31	(0.01)	0.18	0.37		0.14	0.00	0.13	0.11
Cu	(0.45)	(0.29)	0.27	(0.36)	0.07	(0.36)	0.08	0.09	0.21	0.81	(0.11)	(0.17)	0.79	0.71	(0.26)	0.37	0.23	0.78	0.31		0.69	0.00	0.00
Ni	0.07	(0.12)	(0.50)	0.41	0.73	0.39	0.48	(0.02)	0.62	0.03	0.64	0.11	(0.00)	(0.20)	0.60	(0.11)	0.16	(0.20)	0.73	(0.08)		0.77	0.69
Pb	(0.49)	(0.59)	0.39	(0.31)	0.06	(0.30)	(0.01)	0.32	(0.06)	0.85	(0.06)	0.04	0.76	0.82	(0.18)	0.49	0.26	0.65	0.31	0.76	(0.06)		0.00
Zn	(0.53)	(0.49)	0.36	(0.35)	0.07	(0.33)	0.02	0.26	0.05	0.90	(0.08)	(0.06)	0.81	0.81	(0.24)	0.46	0.24	0.77	0.33	0.90	(0.09)	0.96	

“() ” means minus value.

Table A4-5. Correlations between the content of elements (waste samples, site A).

P r	O	Si	Ca	Al	Fe	K	Mg	Na	Ti	P	Mn	Ba	Cl	S	H	C	N	Cd	Cr	Cu	Ni	Pb	Zn
O		0.00	0.00	0.26	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.01	0.64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	0.90		0.00	0.18	0.01	0.00	0.00	0.79	0.00	0.00	0.00	0.03	0.02	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	(0.82)	(0.90)		0.04	0.33	0.00	0.00	0.81	0.00	0.00	0.01	0.06	0.00	0.03	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.01	0.00
Al	0.18	0.21	(0.31)		0.53	0.03	0.11	0.25	0.00	0.13	0.59	0.55	1.00	0.00	0.88	0.44	0.49	0.33	0.25	0.96	0.43	0.72	0.36
Fe	(0.50)	(0.38)	0.15	(0.10)		0.01	0.20	0.15	0.31	0.01	0.01	0.33	0.98	0.79	0.37	0.03	0.00	0.69	0.00	0.00	0.00	0.00	0.09
K	0.81	0.88	(0.88)	0.34	(0.38)		0.00	0.77	0.00	0.00	0.01	0.13	0.00	0.05	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Mg	(0.75)	(0.71)	0.62	0.25	0.20	(0.54)		0.42	0.00	0.00	0.00	0.00	0.02	0.07	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Na	(0.14)	0.04	(0.04)	0.18	0.22	0.05	0.13		0.66	0.02	0.02	0.18	0.05	0.05	0.03	0.28	0.35	0.62	0.36	0.67	0.04	0.59	0.67
Ti	(0.65)	(0.67)	0.59	0.44	0.16	(0.51)	0.87	0.07		0.00	0.00	0.00	0.02	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P	(0.79)	(0.72)	0.59	0.24	0.41	(0.60)	0.87	0.36	0.84		0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	(0.59)	(0.52)	0.41	0.09	0.37	(0.41)	0.58	0.36	0.50	0.70		0.02	0.05	0.20	0.11	0.03	0.04	0.01	0.00	0.00	0.00	0.02	0.00
Ba	(0.48)	(0.34)	0.29	0.09	0.16	(0.24)	0.52	0.21	0.45	0.60	0.36		0.02	0.01	0.05	0.01	0.04	0.02	0.05	0.03	0.06	0.26	0.00
Cl	(0.42)	(0.35)	0.46	0.00	0.00	(0.46)	0.37	0.31	0.36	0.41	0.31	0.35		0.17	0.07	0.79	0.34	0.01	0.04	0.09	0.00	0.18	0.00
S	(0.08)	(0.30)	0.34	(0.70)	(0.04)	(0.30)	(0.28)	(0.31)	(0.28)	(0.32)	(0.20)	(0.40)	(0.22)		0.76	0.60	0.54	0.31	0.29	0.49	0.59	0.43	0.20

H	(0.73)	(0.80)	0.73	(0.02)	0.14	(0.68)	0.68	(0.34)	0.67	0.55	0.25	0.30	0.28	0.05		0.00	0.05	0.00	0.00	0.00	0.01	0.00	0.00
C	(0.71)	(0.74)	0.51	(0.12)	0.33	(0.58)	0.58	(0.17)	0.49	0.58	0.34	0.38	0.04	0.08	0.73		0.00	0.00	0.00	0.00	0.13	0.05	0.00
N	(0.51)	(0.47)	0.26	0.11	0.51	(0.35)	0.42	0.15	0.46	0.59	0.32	0.31	0.15	(0.10)	0.31	0.50		0.14	0.00	0.00	0.00	0.18	0.03
Cd	(0.66)	(0.67)	0.68	0.15	0.06	(0.61)	0.83	(0.08)	0.84	0.72	0.40	0.37	0.40	(0.16)	0.78	0.45	0.23		0.00	0.00	0.00	0.00	0.00
Cr	(0.81)	(0.82)	0.72	(0.18)	0.56	(0.76)	0.54	0.15	0.59	0.67	0.50	0.30	0.32	0.17	0.63	0.58	0.46	0.56		0.00	0.00	0.01	0.00
Cu	(0.79)	(0.84)	0.73	(0.01)	0.47	(0.72)	0.61	0.07	0.70	0.71	0.48	0.34	0.27	0.11	0.73	0.61	0.52	0.60	0.91		0.00	0.01	0.00
Ni	(0.63)	(0.61)	0.56	0.12	0.56	(0.60)	0.47	0.32	0.61	0.65	0.46	0.29	0.48	(0.08)	0.38	0.24	0.65	0.45	0.77	0.76		0.01	0.00
Pb	(0.60)	(0.48)	0.42	0.06	0.50	(0.45)	0.48	(0.09)	0.49	0.44	0.37	0.18	0.21	(0.13)	0.48	0.30	0.21	0.55	0.41	0.42	0.39		0.00
Zn	(0.80)	(0.77)	0.73	0.14	0.26	(0.71)	0.88	0.07	0.86	0.84	0.62	0.44	0.48	(0.20)	0.77	0.51	0.34	0.94	0.68	0.71	0.60	0.63	

“() ” means minus value.

Table A4-6. Correlations between the content of elements (waste samples, site B).

P r	O	Si	Ca	Al	Fe	K	Mg	Na	Ti	P	Mn	Ba	Cl	S	H	C	N	Cd	Cr	Cu	Ni	Pb	Zn
O		0.00	0.00	0.43	0.06	0.00	0.46	0.00	0.43	0.10	0.72	0.44	0.00	0.38	0.21	0.58	0.24	0.98	0.72	0.77	0.95	0.12	0.26
Si	0.57		0.00	0.18	0.22	0.80	0.00	0.10	0.33	0.90	0.07	0.09	0.00	0.02	0.08	0.84	0.08	0.05	0.85	0.72	0.97	0.56	0.78
Ca	(0.50)	(0.93)		0.11	0.08	0.83	0.00	0.22	0.39	0.72	0.02	0.08	0.00	0.03	0.19	0.36	0.02	0.01	0.59	0.59	0.74	0.66	0.30
Al	0.14	0.23	(0.27)		0.00	0.74	0.02	0.89	0.04	0.02	0.29	0.24	0.58	0.01	0.07	0.76	0.48	0.18	0.00	0.08	0.18	0.18	0.01
Fe	0.32	0.21	(0.30)	0.51		0.07	0.20	0.11	0.32	0.01	0.00	0.37	0.02	0.01	0.27	0.12	0.24	0.26	0.00	0.00	0.00	0.20	0.01
K	(0.76)	(0.04)	(0.04)	(0.06)	(0.31)		0.48	0.00	0.15	0.25	0.38	0.65	0.00	0.06	0.84	0.49	0.22	0.39	0.81	0.50	1.00	0.07	0.18
Mg	0.13	0.51	(0.54)	0.40	0.22	0.12		0.97	0.00	0.00	0.13	0.00	0.53	0.00	0.08	0.44	0.14	0.00	0.05	0.09	0.09	0.03	0.00
Na	(0.89)	(0.28)	0.21	0.02	(0.28)	0.82	0.01		0.20	0.11	0.92	0.98	0.00	0.10	0.51	0.08	0.05	0.51	0.43	0.74	0.99	0.11	0.17
Ti	(0.14)	0.17	(0.15)	0.35	0.17	0.25	0.79	0.22		0.00	0.22	0.00	0.52	0.00	0.01	0.82	0.87	0.00	0.01	0.02	0.07	0.03	0.00
P	(0.28)	(0.02)	0.06	0.40	0.41	0.20	0.48	0.28	0.72		0.15	0.01	0.19	0.00	0.02	0.85	0.79	0.20	0.00	0.00	0.01	0.01	0.00
Mn	0.06	0.31	(0.39)	0.18	0.48	0.15	0.26	0.02	0.21	0.25		0.15	0.50	0.03	0.89	0.86	0.65	0.01	0.06	0.06	0.10	0.12	0.00
Ba	0.13	0.29	(0.30)	0.20	0.15	0.08	0.61	0.01	0.61	0.45	0.25		0.42	0.01	0.32	0.56	0.55	0.03	0.06	0.18	0.17	0.09	0.01
Cl	(0.96)	(0.51)	0.47	(0.10)	(0.38)	0.75	(0.11)	0.90	0.11	0.23	(0.12)	(0.14)		0.32	0.25	0.17	0.08	0.73	0.88	0.71	0.65	0.27	0.47
S	0.15	(0.40)	0.36	(0.46)	(0.41)	(0.32)	(0.74)	(0.28)	(0.79)	(0.77)	(0.37)	(0.45)	(0.17)		0.04	0.57	0.53	0.01	0.00	0.01	0.04	0.00	0.00

H	(0.22)	(0.30)	0.23	0.31	0.19	(0.04)	0.30	0.11	0.41	0.40	(0.02)	0.17	0.20	(0.34)		0.36	0.68	0.06	0.11	0.13	0.24	0.07	0.00
C	0.10	0.04	(0.16)	(0.05)	0.27	(0.12)	0.14	(0.30)	0.04	0.03	(0.03)	(0.10)	(0.24)	(0.10)	0.16		0.00	0.49	0.98	0.09	0.94	0.47	0.50
N	0.20	0.30	(0.38)	(0.12)	0.20	(0.21)	0.26	(0.34)	0.03	(0.05)	0.08	(0.10)	(0.30)	(0.11)	0.07	0.73		0.07	0.36	0.70	0.45	0.98	0.71
Cd	0.00	0.34	(0.42)	0.23	0.19	0.15	0.64	0.12	0.51	0.22	0.46	0.38	(0.06)	(0.46)	0.32	0.12	0.31		0.04	0.06	0.36	0.00	0.00
Cr	(0.06)	0.03	(0.10)	0.54	0.66	0.04	0.34	0.14	0.43	0.62	0.32	0.32	(0.03)	(0.49)	0.27	0.00	(0.16)	0.35		0.00	0.00	0.01	0.00
Cu	(0.05)	0.06	(0.10)	0.30	0.50	0.12	0.29	0.06	0.39	0.56	0.32	0.23	(0.07)	(0.44)	0.26	0.29	0.07	0.32	0.58		0.03	0.00	0.00
Ni	0.01	(0.01)	(0.06)	0.23	0.52	0.00	0.29	0.00	0.31	0.42	0.29	0.24	(0.08)	(0.34)	0.20	0.01	(0.13)	0.16	0.77	0.37		0.24	0.01
Pb	(0.27)	0.10	(0.08)	0.23	0.22	0.31	0.36	0.27	0.37	0.41	0.27	0.29	0.19	(0.49)	0.31	0.13	0.00	0.55	0.44	0.50	0.20		0.00
Zn	(0.20)	0.05	(0.18)	0.46	0.45	0.23	0.60	0.24	0.61	0.55	0.54	0.41	0.13	(0.61)	0.53	0.12	0.07	0.81	0.64	0.52	0.46	0.60	

“() ” means minus value.

Table A4-7. PCA result based on the element composition.

PC	Variance (%)
1	81.4
2	9.43
3	4.51
4	1.73
5	1.67
6	0.665
7	0.235
8	0.173
9	0.0694
10	0.0436
...	...

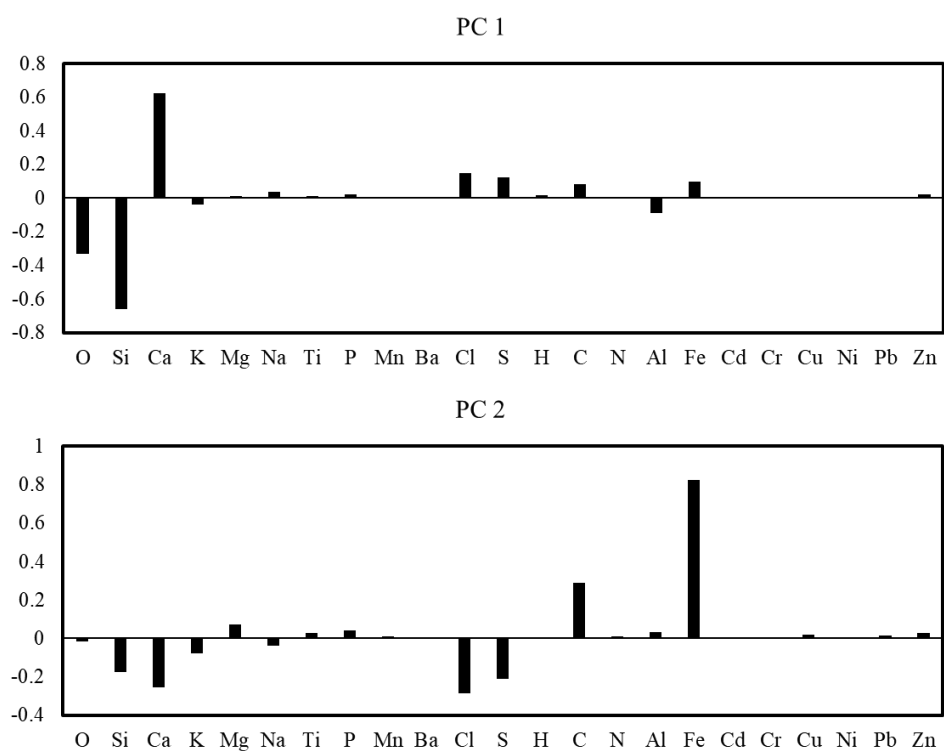


Figure A4-2. The loading of PC1 and PC2.

Table A5-1. The reference materials used in this study for XAFS data analysis.

Reference materials			
Cu	Metallic Copper	Pb	Metallic lead
CuO	Copper (II) oxide	PbO	Lead (II) oxide
Cu₂O	Copper (I) oxide	PbO₂	Lead (IV) oxide
CuS	Copper (II) sulfide	Pb₃O₄	Lead (II, IV) oxide
Cu₂S	Copper (I) sulfide	PbCO₃	Lead (II) carbonate
CuSO₄	Copper (II) sulfate	Pb(NO₃)₂	Lead (II) nitrate
CuCl₂ · 2 (H₂O)	Copper (II) chloride	PbS	lead sulfide
CuCl₂	Copper (II) chloride	PbSO₄	Lead (II) sulfate
CuCl	Copper (I) chloride	PbCl₂	Lead (II) chloride
CuBr	Copper (I) bromide	Pb₃(PO₄)₂	Lead (II) phosphate
CuBr₂	Copper (II) bromide	PbHPO₄	Lead (II) hydrogen phosphate
Cu₃(PO₄)₂	Copper (II) phosphate	Pb(OAc)₂	Lead (II) acetate
Cu(OH)₂	Copper (II) hydrates	PbSiO₃	Lead (II) silicate (alamosite)
CuCO₃	Copper (II) carbonate	PbCrO₄	Lead (II) chromate
Cu(OAc)₂	Copper (II) acetate	Ca₂PbO₄	Calcium plumbate
CuFe₂O₄	Cuprospinel	3PbO · PbSO₄ · H₂	Lead tribasic sulfate (TBLS)
CuAl₆(PO₄)₄(OH)₈ · 4H₂O	Turquoise	Pb₃(CO₃)₂(OH)₂	Hydrocerussite
CuSiO₃ · H₂O	Dioptase	Pb₅(PO₄)₃OH	Hydroxylpyromorphite
Cu₂Cl(OH)₃	Atacamite	Pb₅(PO₄)₃Cl	Chloropyromorphite
Cu(C₅H₁₀NS₂)₂	Cu(diethyldithiocarbamate)	Pb-Citrate	Lead (II) citrate
	) ₂	Pb-Goethite	(350 mmol/kg pH 6.5)
		Pb-Gibbsite	(300 mmol/kg pH6.5)
		Pb-Humate	(300 mmol/kg pH5)

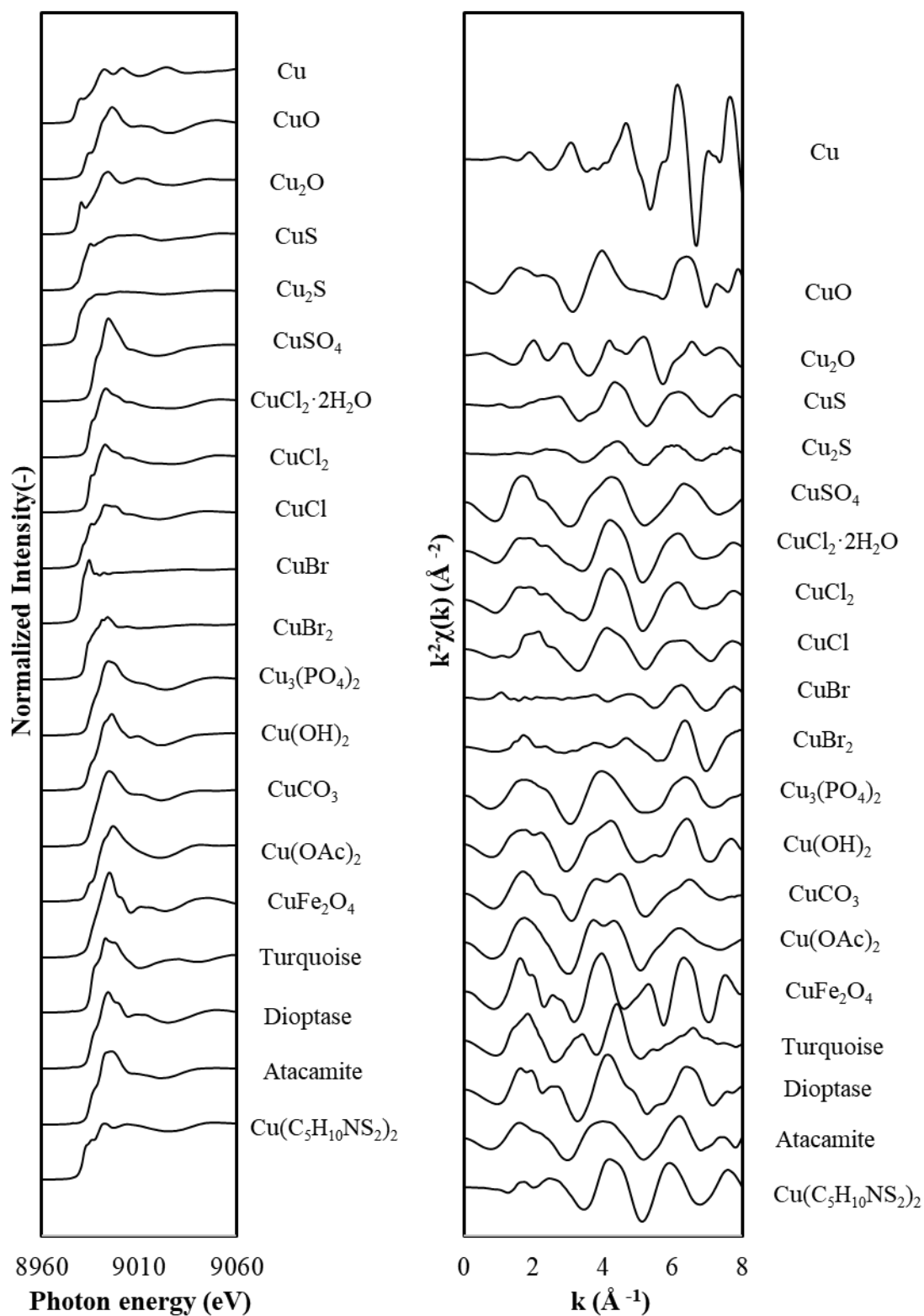


Figure A5-1. The spectra of Cu K-edge XANES and EXAFS (k^2 weighted) for reference materials.

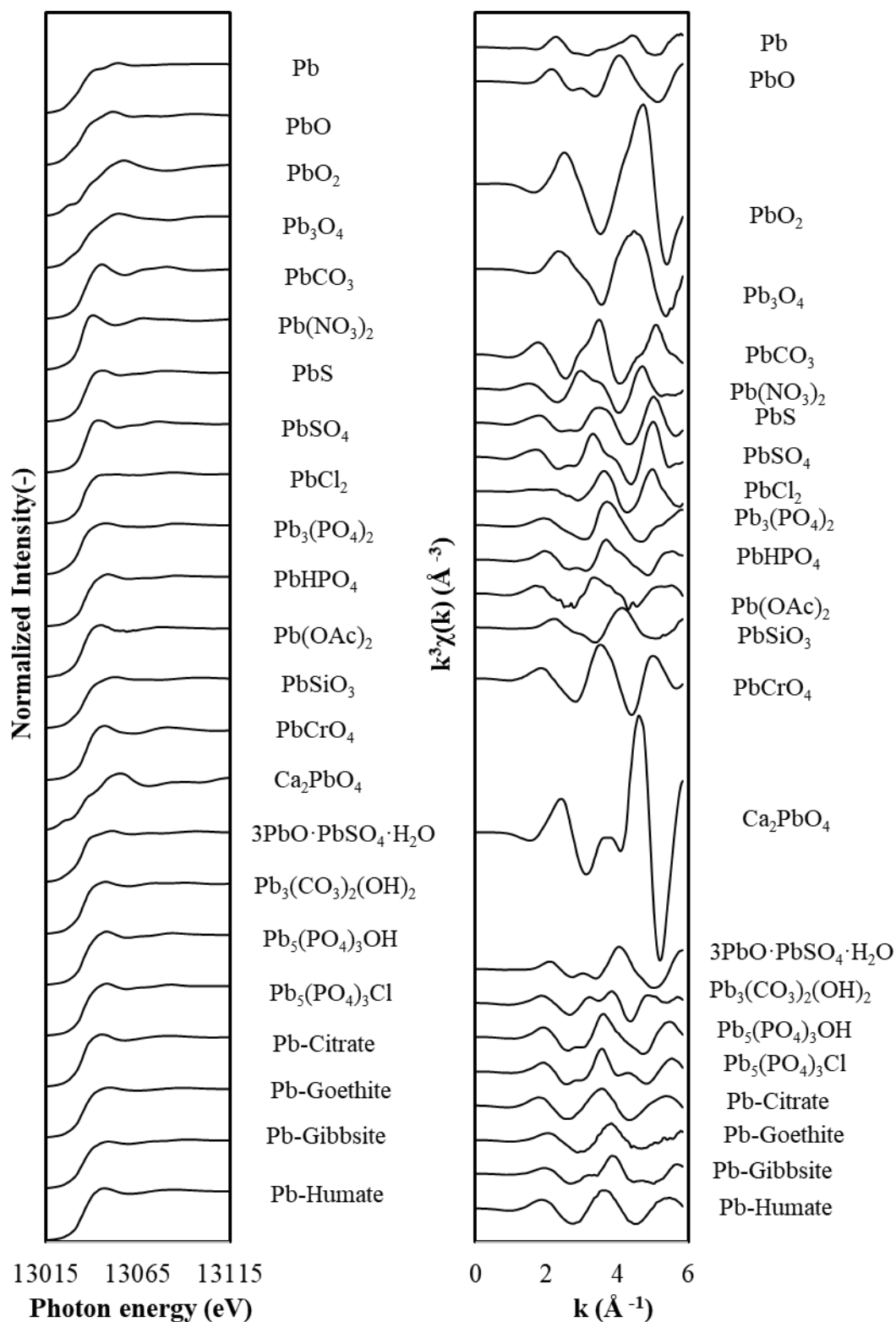


Figure A5-2. The spectra of Pb LIII-edge XANES and EXAFS (k^3 weighted) for reference materials.

Data collected from SPring-8 & PF

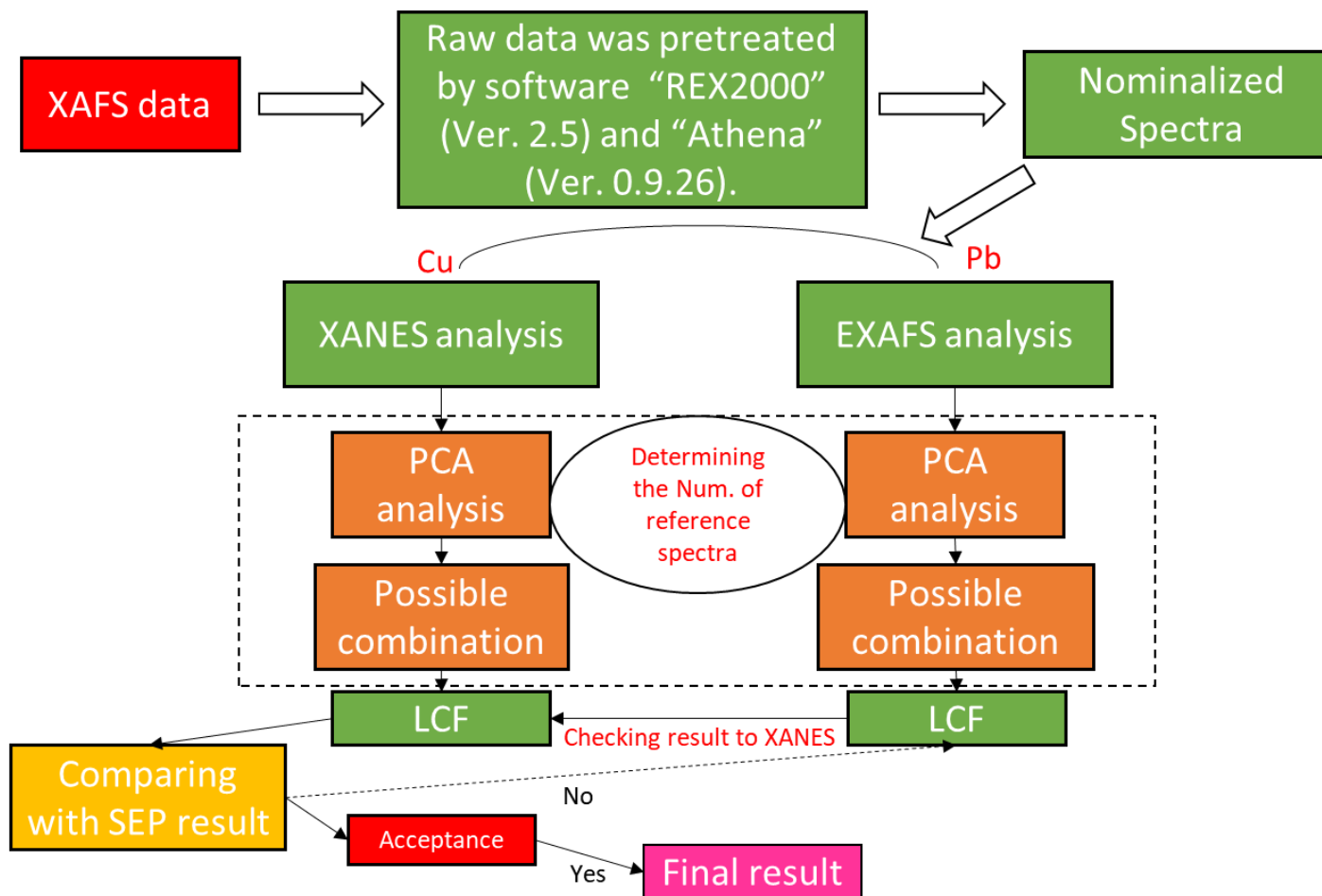


Figure A5-3. The treatment process of XAFS data in this research.

Table A5-2. Leaching test result.

	Depth (m)	pH	Leaching ($\mu\text{g L}^{-1}$)					
			Cd	Cr	Cu	Ni	Pb	Zn
BH1	1~2	9.7	1.11	8.26	141	4.96	72.8	206
	2~3	9.3	0.52	< LOD	73.7	1.93	16.9	40.4
	3~4	9.5	< LOD	5.11	16.2	0.96	15.4	47.63
BH2	4.4~5	8.7	< LOD	2.53	32.9	< LOD	0.670	0.530
	5~6	8.3	< LOD	4.13	13.3	< LOD	2.13	4.53
	6~7	8.9	< LOD	14.1	51.9	9.87	21.1	64.5
	7~8	10	< LOD	11.7	38.1	2.53	6.80	2.80
	8~9	9.6	< LOD	5.33	9.07	6.00	2.80	5.60
BH3	0.35~1	11.5	< LOD	9.60	6.40	< LOD	3.07	1.20
	1~2	11.2	< LOD	8.00	355	11.6	6.00	11.9
	2~3	9.4	1.20	18.4	208	19.9	143	353
	3~4	9.1	< LOD	7.60	37.5	4.93	10.7	29.5
	4~5	9.2	< LOD	6.40	21.1	2.93	1.33	9.87
	5~6	11.1	< LOD	9.87	67.7	3.20	1.73	41.3
	8~7	11	< LOD	11.6	260	5.33	6.53	32.8
	9~10	8.6	< LOD	8.67	19.7	12.3	13.1	30.9
BH4	3~4	11	< LOD	1.06	400	4.83	24.9	8.17
	4~5	11	< LOD	< LOD	197	< LOD	11.9	3.19
	5~6	11	< LOD	1.44	169	< LOD	5.00	3.81
	6~7	11.7	< LOD	< LOD	234	< LOD	68.0	15.3
	7~8	10.6	< LOD	0.70	136	0.590	9.48	1.59
	8~8.2	11.4	< LOD	< LOD	144	< LOD	19.8	4.89
	8.8~9.2	11.4	< LOD	3.63	42.5	0.590	1.33	0.890

	9.5~10	11.6	< LOD	2.26	40.5	2.15	< LOD	< LOD
BH5	5~6	10.6	< LOD	3.85	57.2	4.56	5.37	6.22
	6~7	11	< LOD	< LOD	16.3	0.670	1.19	< LOD
	7~8	11	< LOD	1.33	59.7	< LOD	7.39	3.17
	8~9	11.5	< LOD	1.41	24.6	1.96	< LOD	0.440
	9~10	11.4	< LOD	1.96	22.2	0.630	19.0	4.41
BH6	0.5~1	10.3	< LOD	6.13	57.9	< LOD	< LOD	12.3
	1~2	8.3	< LOD	3.07	20.5	< LOD	5.73	9.60
	2~3	7.9	< LOD	ND	13.5	< LOD	5.07	4.40
	3~4	7.6	< LOD	2.80	23.6	25.2	8.00	1.60
	4~5	8	< LOD	2.80	14.0	< LOD	5.87	2.53
	5~6	10.4	< LOD	5.60	32.1	2.93	9.00	4.13
	6~7	9.9	< LOD	5.87	89.7	1.20	5.87	4.40
	7~8	7.7	< LOD	1.87	9.47	< LOD	8.27	2.67
	8~8.6	7.6	< LOD	1.20	6.80	< LOD	9.60	2.40
BH7	0~1	11.6	< LOD	16.8	23.9	1.40	< LOD	< LOD
	1~2	11.7	< LOD	9.53	100	< LOD	31.9	33.1
	2~3	11.6	< LOD	16.2	27.7	< LOD	20.1	18.6
	3~4	11.6	< LOD	10.5	40.3	< LOD	11.2	14.3
	4~5	11.5	< LOD	7.93	66.8	< LOD	10.0	4.93
	5.4~6	8.7	1.00	5.80	70.2	< LOD	3.87	22.5
	6~7	9.1	0.87	5.93	49.6	< LOD	1.60	< LOD
	7~7.6	9.2	0.47	6.93	30.1	< LOD	4.60	< LOD
	7.6~8.3	11.0	0.93	8.40	63.3	< LOD	1.80	< LOD
	8.3~8.5	8.6	5.87	115	48.9	39.9	3.27	39.2
	8.8~9.2	10.2	0.33	6.87	79.5	< LOD	3.80	2.20
	9.5~10	8.2	1.07	6.40	17.3	< LOD	3.47	4.00

BH8	0~1	11.9	< LOD	24.7	40.5	<LOD	85.5	113
	1~2	11.8	<LOD	31.3	73.5	<LOD	21.1	91.6
	2~3	11.6	<LOD	42.4	64.6	<LOD	8.73	32.1
	3~4	11.6	<LOD	42.3	146	<LOD	6.93	26.6
	4~5	11.8	<LOD	15.5	241	<LOD	<LOD	2.20
	5~6	11.7	<LOD	18.7	81.8	<LOD	<LOD	1.67
	6~7	11.8	<LOD	11.6	159	<LOD	13.1	34.9
	7~8	11.8	<LOD	10.3	424	<LOD	29.5	27.3
	8~9	11.2	<LOD	11.1	71.7	<LOD	<LOD	0.33
	9~10	10.7	< LOD	8.07	75.3	<LOD	2.87	0.80
BH9	0.3~1	11.8	<LOD	20.6	52.5	<LOD	8.87	48.3
	1~2	11.7	<LOD	11.1	71.9	<LOD	<LOD	35.1
	2~3	11.7	<LOD	34.7	26.3	<LOD	<LOD	15.2
	3~4	11.4	<LOD	13.5	47.8	<LOD	3.13	11.1
	4~5	11.6	<LOD	16.7	17.1	<LOD	24.5	24.3
	5~6	11.7	<LOD	14.7	237	<LOD	31.9	22.5
	6~7	11.7	<LOD	9.73	105	<LOD	23.5	18.5
	7~8	11.7	<LOD	9.13	557	<LOD	63.2	50.2
	8~9	11.6	<LOD	11.7	2320	9.93	31.5	73.7
	9~10	11.5	<LOD	9.40	912	<LOD	29.2	33.1
	10~11	11.5	<LOD	9.73	613	<LOD	35.3	38.7
	11~12	10.5	<LOD	8.27	284	<LOD	5.53	6.73
	12~13	10.4	<LOD	11.5	913	< LOD	4.53	9.73
Limit for landfill			90	--	--	--	300	--

Limit for leachate	3	2000	3000	--	10	2000
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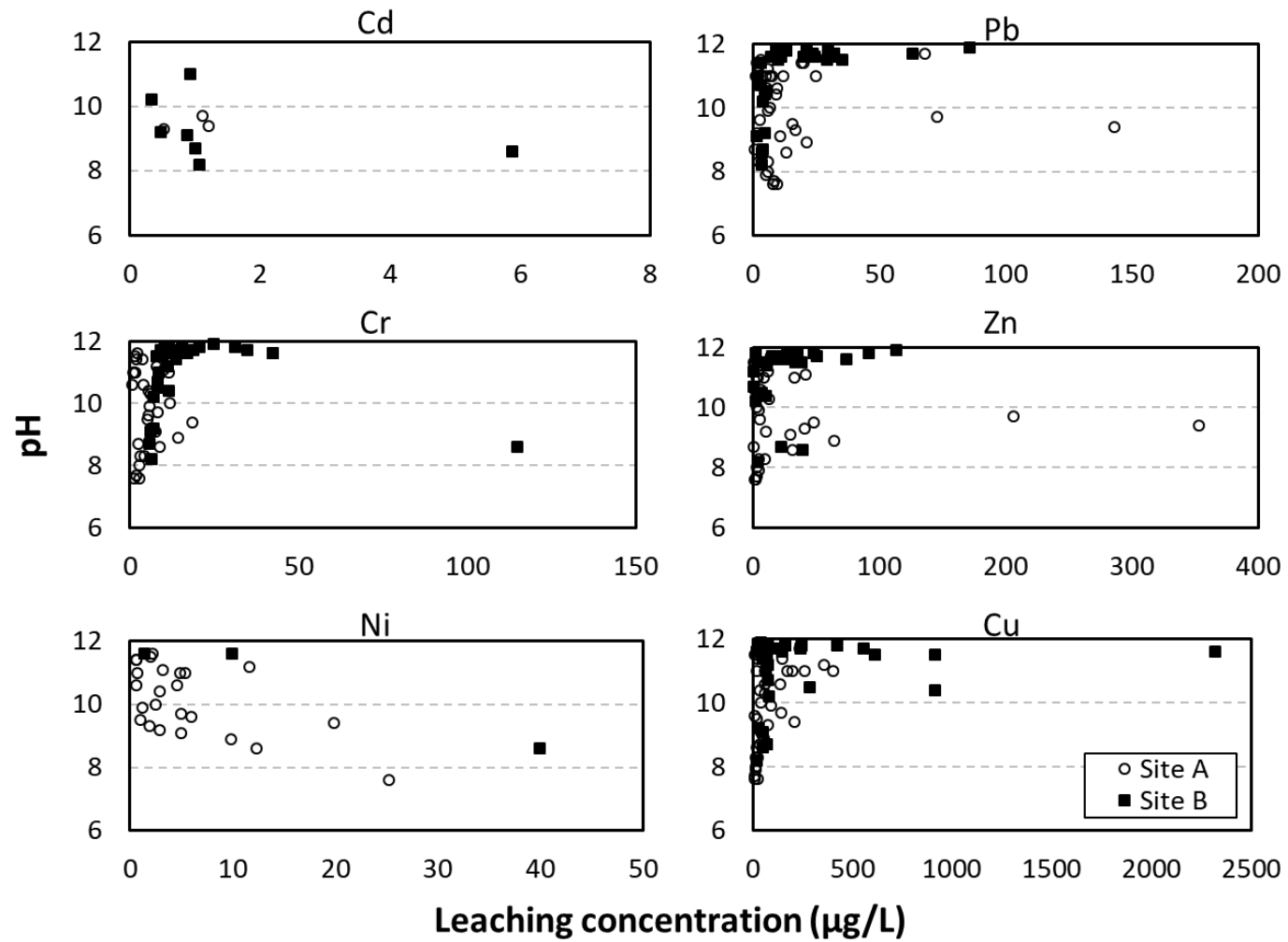


Figure A5-4. Leaching test result.

Table A5-3. Chemical composition of the selected samples measured by XRF and C-H-N detector, the content of heavy metals were measured by ICP-AES&MS.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17	#18	#19	#20
Major elements (wt %)																				
O	55.0	53.8	53.0	49.5	49.0	46.1	47.7	48.5	47.8	50.1	48.3	49.0	50.3	44.9	48.1	47.6	43.1	37.0	48.3	47.5
Ca	0.73	4.60	4.82	10.9	14.3	15.1	18.6	12.7	16.8	10.4	12.1	7.53	16.9	19.5	25.2	24.1	21.9	21.5	15.7	16.5
Si	24.5	25.3	22.6	8.87	10.7	9.25	8.70	11.0	9.76	15.2	12.1	17.7	12.3	6.96	1.24	2.65	5.47	4.40	13.5	13.2
Fe	2.42	2.48	3.20	7.86	2.58	2.81	2.86	4.06	4.73	3.89	8.13	9.27	2.69	3.01	0.22	0.98	1.29	0.94	2.00	2.49
Al	8.44	7.68	6.73	7.72	6.71	5.15	6.40	7.25	7.08	6.81	7.08	5.74	5.75	6.22	0.39	1.07	5.27	3.81	3.53	5.30
Na	0.51	0.53	0.77	0.29	0.92	0.70	0.67	0.78	1.10	1.08	1.49	0.62	0.42	1.84	0.35	0.50	2.97	5.39	1.21	1.30
Mg	1.07	1.10	1.19	2.47	2.34	2.21	2.10	2.95	2.23	2.38	1.72	1.15	1.64	1.75	0.00	0.00	1.65	1.31	1.05	1.49
K	2.71	2.50	2.08	0.69	1.06	0.60	0.33	0.91	0.52	1.56	0.95	1.46	0.96	1.78	0.76	0.55	2.27	2.90	1.93	1.54
Ti	0.35	0.38	0.44	0.79	0.79	0.56	0.69	0.93	0.70	0.70	0.73	0.32	0.57	0.70	0.00	0.11	0.81	0.59	0.37	0.46
Mn	0.07	0.06	0.08	0.18	0.12	0.13	0.12	0.13	0.15	0.14	0.19	0.11	0.09	0.09	0.00	0.02	0.07	0.07	0.06	0.09
P	0.07	0.08	0.34	0.92	0.92	0.71	0.65	1.06	0.70	0.78	1.05	0.15	0.60	0.76	0.06	0.15	0.83	0.58	0.24	0.54
S	0.07	0.17	1.02	0.85	1.89	2.15	1.83	1.18	1.51	1.77	1.64	2.34	2.97	2.35	18.6	16.7	2.31	2.56	5.35	1.62
Cl	0.00	0.00	0.15	0.11	0.34	0.63	0.42	0.18	0.65	0.14	0.38	0.09	0.47	4.69	1.91	1.91	7.75	15.0	2.50	2.82
C	2.80	0.57	2.48	5.73	6.04	3.89	5.34	4.60	3.03	3.09	1.64	2.99	1.90	2.57	2.17	1.88	2.03	1.45	3.13	2.83
H	0.95	0.67	0.65	1.15	0.91	1.10	1.37	1.01	1.04	0.66	0.52	0.61	1.16	1.22	0.85	0.90	1.01	1.27	0.77	1.06
N	0.20	0.04	0.14	0.16	0.15	0.09	0.11	0.12	0.06	0.12	0.57	0.08	0.08	0.05	0.06	0.05	0.03	0.05	0.06	0.08
Heavy metals (mg/kg)																				
Cd	1	1	5	41	28	38	52	63	25	19	8	4	78	49	3	5	57	74	12	54
Cr	92	74	157	631	368	398	516	582	414	363	677	135	413	559	80	10	447	213	170	430
Cu	42	36	1040	3630	2180	2790	3760	4460	5040	1620	5120	359	1390	3730	165	134	1750	1450	756	2380
Ni	66	59	78	340	245	552	261	225	218	217	316	69	219	306	33	31	222	115	98	191
Pb	22	21	224	3570	1240	3580	3290	3410	1910	1530	2220	139	1010	2150	169	46	1410	866	415	1730
Zn	83	95	1030	7820	5010	6640	8340	8970	6300	3480	4320	951	8340	9680	874	166	7680	9560	1540	6020

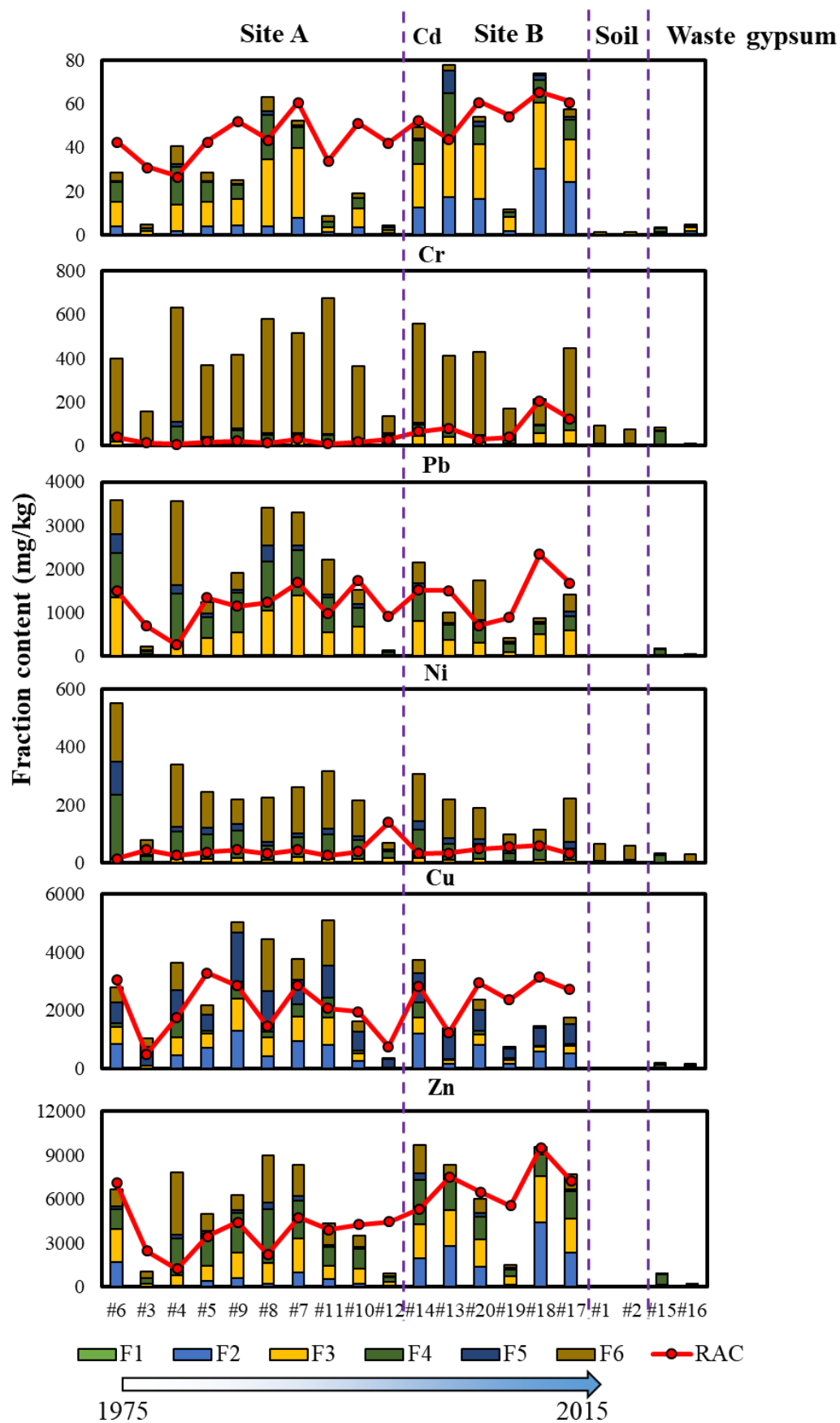


Figure A5-4. The SEP result by presenting the content of each fraction.

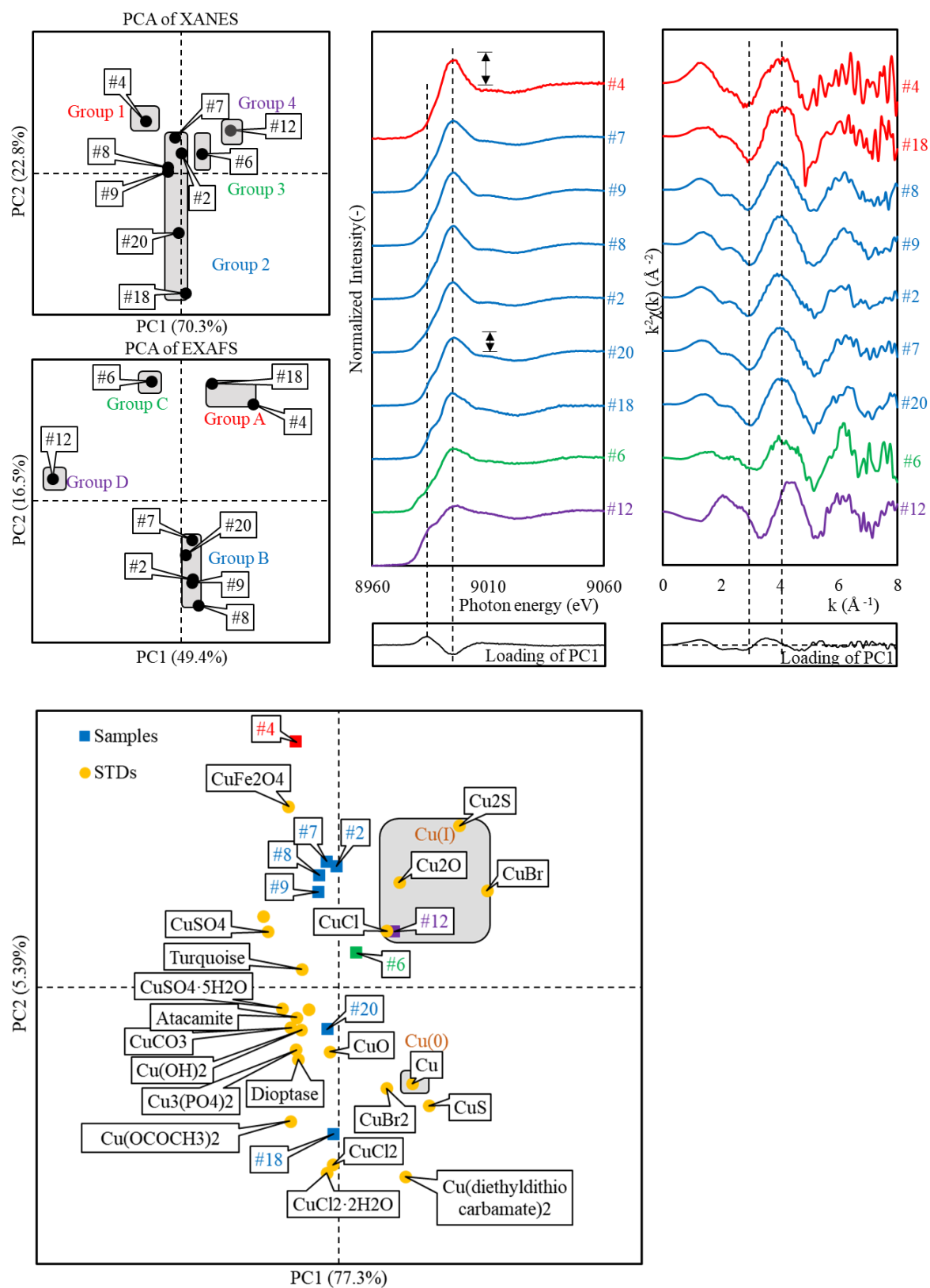


Figure A5-6. XAFS data analysis of Cu-K edge XANES.

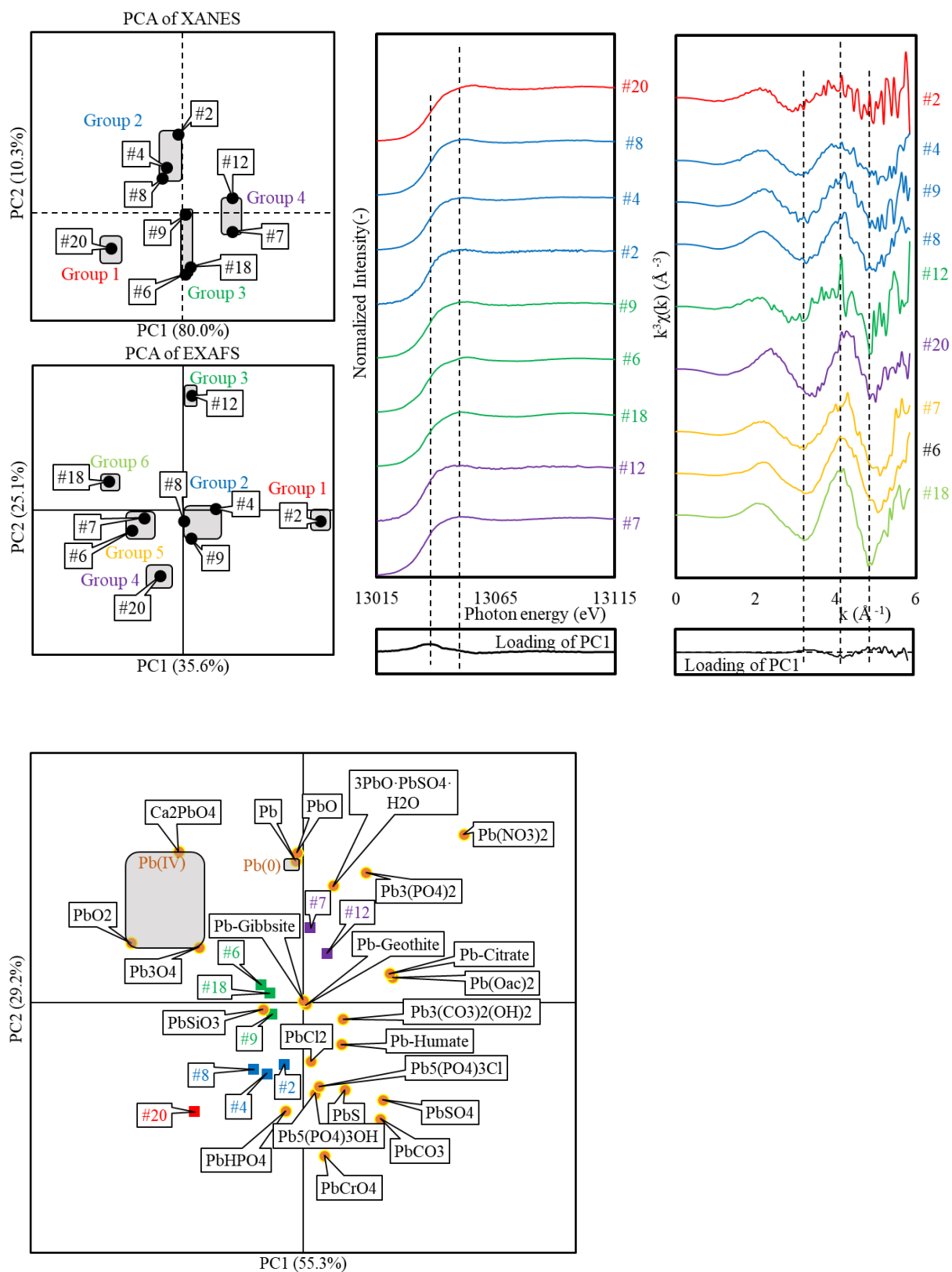


Figure A5-7. XAFS data analysis of Pb-LIII edge EXAFS.

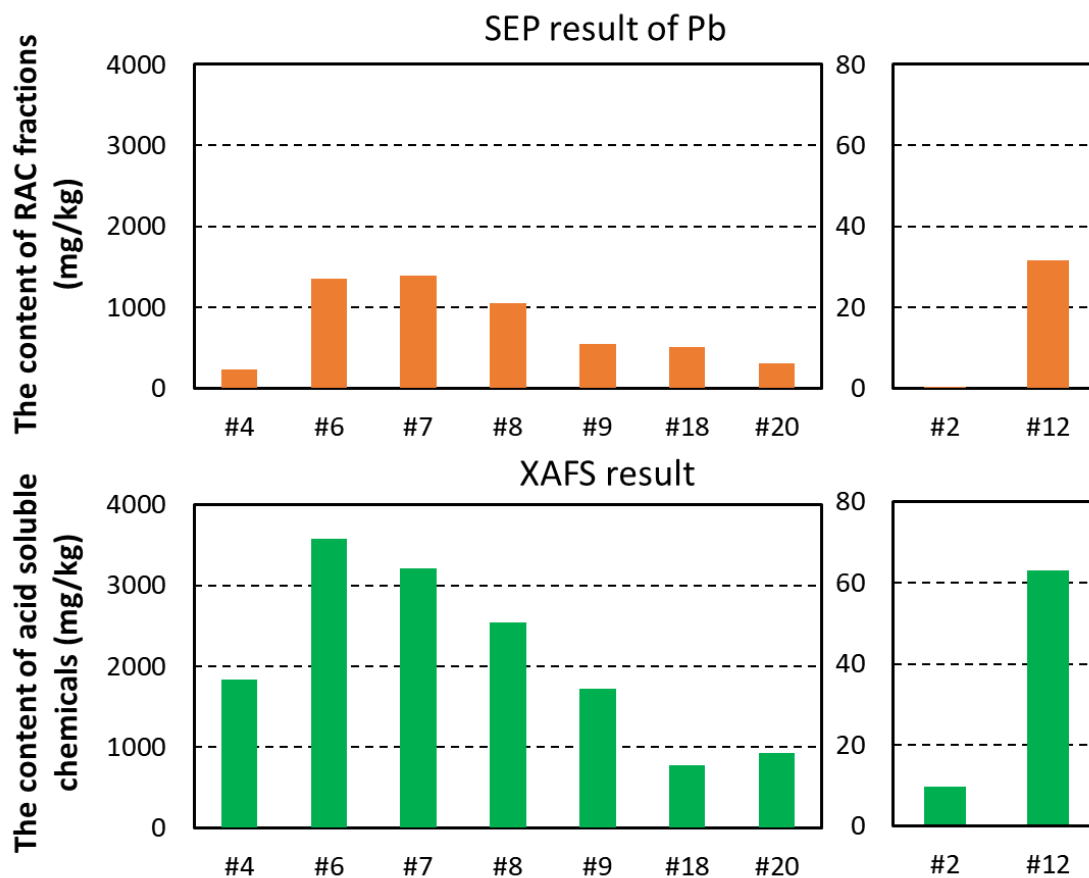


Figure A5-8. The comparison of result of SEP and XAFS (Pb).

Table A5-4. Identified extractable chemicals under F3 condition in XAFS result.

Cu		Pb	
CuCl	100%	Metallic Pb	95%
CuSO ₄	100%	PbO	100%
Cu(OH) ₂	100%	PbSiO ₃	70%
CuCO ₃	100%	3PbO·PbSO ₄ ·H ₂ O	95%
Acatamite	100%		
CuO	20%		

ACKNOWLEDGMENTS

I was always wondering what I'm going to write in this section, for this moment is so important in my entire life. The words aren't enough to express my gratitude to the people who have helped, supported and spurred me, while I want to hug all of them right now.

I owe my greatest thanks to my supervisor Prof. Masaki Takaoka, the professor of the department of environmental engineering at Kyoto University, and the guider to my research career. I want to thank him for his wise suggestions, kindly arrangements and, most important, strong patience on me. I still remember the first time when we met in Shanghai, and it's my first time to do a presentation in English. I received encouragement from him and learned a lot through communication with him. When I heard he could offer me a chance to study at Kyoto University, I was so excited. And finally, I am here to learn how to do researches under his instruction. I have got inspiration and confidence after each meeting with him. Every time when he invited me to join the experiments in PF or SPring-8, I won't hesitate to say yes. Because I enjoyed the discussion time in the experiment facility. Sometimes when I felt lost, he won't refuse to help me. I want to present my best thanks to Prof. Takaoka for taking care of me in these four and a half years. Also, I want to say sorry for those times I let him down. I could do better, but, I didn't. I'll remember this experience in my whole life just make sure I mustn't fall again.

To Prof. Kazuyuki Oshita, associate professor in our lab. Thank you for the advice you gave me in the seminars of our lab, thank you for the postcards you sent to me every year, and thank you for helping me revise the thesis content. You are so kind! We didn't communicate too much, but I know you are very nice to everyone. I also remember you went to the dining hall with us for lunch when you weren't so busy. It's such a pleasure to meet you in this lab.

To Kusakabe sensei, Fujimori sensei, I really thank you for all the support you gave me. Kusakabe sensei helped sampling in the landfill sites, and I still remember the fighting between us with the mosquito in the wild places. You also taught us more experimental skills while sampling process. After each sampling day, you took us to have meals and we enjoyed the talking. There's one time, it happened to be my birthday, you treated me for lunch as my birthday gift. I'm really touched because I hadn't received any gifts or greetings for birthday for a very long time. Thank you so much, and I hope you could find a good position in the near future. Fujimori sensei always gave me wise advice at the seminars. I also thank you for the help you supported me. Sometimes I didn't feel good to do the presentation in the seminar, you allowed me to delay my presentation. Thank

you for your kind consideration.

To Shiota san, the wise man in our lab. I couldn't finish most of my experiments without your help. The first time I learned XRF, ICP-AES & MS, ... you always taught me with patients. Sometimes I had problems with data treating, I also went to ask for your help, and you never said no. Each time we went to PF or Spring-8, we did the night shift together. And most of the time, we just struggled to not fall asleep, interesting moments. I always said, I really want a similar job as you are doing now, and I mean it. If possible, I want to achieve that goal.

Oosawa san always be there when I'm in trouble, and help me to get out of despair. Yamamoto san says she is my mother in Japan, and I do believe it. Not only the life in Japan, she always comforted me when my emotions are broken. I'm lucky to meet her in this place, and I really don't want to say goodbye to her. I know I behaved badly sometimes, she also accepted me. I promise I won't let you down again. Yamamoto san always smiles at me and makes sure I'm happy. Every time you say you are on my side, I really felt comfortable about that. It's you and Oosawa san helped my passing through those tough days, thank you so much!

To Sano san, thank you for your help for the landfill sampling and taught me how to get samples. I won't forget that.

To the graduate students of 2016. Aoki kun, Taniguchi kun, Toda kun, Nishimura san, Yamada kun, Matsuo kun, Lin kun, and Li (kiti) san. Aoki kun taught me using statistic methods, and XRF. Nishimura san taught me microwave digestion procedures and ICP-AES. Yamada kun taught me Japanese sentences and shared stories with me. Matsuo kun helped me moving house by rent a car. Lin kun helped me settle down in this place, Li san gave her furniture to me. Even after graduation, Nishimura san is still contacting me to help me. I'll never forget the times we have shared together.

To the graduate students of 2017. Ueura kun, Tainaka kun, Asako san, Matsui kun, and Anissa san. Ueura kun was my tutor when I just came here, and he supported me a lot at that time. Tainaka kun was kind to me, Asako san also taught me the experiments, Matsui kun always organized activities to let us get into this big family. Anissa san made delicious cakes, I like them.

To the graduate students of 2018. Mahazoun kun, Nakamura (syuta) kun, Nakamura (yuta) kun, Nishizono kun, Kojima kun, Ito kun, and Nitta kun. We also enjoyed beautiful moments when we had the lad traveling to Toba. The night, we counted stars by the coast, played table games.

To the graduate students of 2019. Yang san, Cao san, Aoki kun, Zhang kun, Miura kun, Miyahara san, Mukai kun, Paloma san, Wang Jin kun, and Guo kun. I like you all, just feel you are still here by my side.

To the students in the lab. Fatimah san, Sato kun, Li (chenchen) san, Wang kun, Zhang kun, Cheng san, Amanda san, Gem san, Anazawa kun, Uenishi kun, Kawasaki kun, Nishida kun, Yana kun, Yoo kun, Umemiya kun, Ogino san, Inoue kun, Kitatani kun, Takami kun, Tsujii kun, Mao san, Liu san, Aoba kun, Ike san, Egawa kun, Koide san, Terada san, and hayasaki kun. To the members, Zhang dong kun, Zhang (mengmei) san and Oleszek san.

Thank you all of you to make life here so colorful!

To my family, my father, mother, and sister, I can't walk so far without your support.

Finally, this research was funded by Environment Research and Technology Development Fund of Japan, grant number [3K143002 and 3-1701]. XAFS analyses at BL01B1 in SPring-8 and BL-12C in Photon Factory were conducted with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal No. 2015B1830, 2016B1534), with much help from Dr. Kiyofumi Nitta and the approval of the Institute of Materials Structure Science (IMSS) (Proposal No.2018G090). Also, I very much appreciate the support for the sampling in landfill sites and provisions of historical data from a local government.

I also want to thank the Ministry of Education, Science, Technology, Sport and Culture (Mombukagakusho) of Japan for providing the scholarship, thank you very much!

XIONG YIQUN