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공학박사학위논문

Production of plant growable soil
by acid washing and thermal treatment
of dredged marine sediment impacted
by petroleum and heavy metals

유류 및 중금속 오염 해양 준설토의 산세척 및
열처리를 통한 식물 생장용 토양 생산기술 개발

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**Production of plant growable soil
by acid washing and thermal treatment
of dredged marine sediment impacted
by petroleum and heavy metals**

by

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Abstract

Production of plant growable soil by acid washing and thermal treatment of dredged marine sediment impacted by petroleum and heavy metals

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Large amounts of dredged marine sediment is annually generated for management of navigational channel and harbor development. The ocean disposal of dredged sediment has been limited or/and prohibited due to national and international regulations and agreements in many centuries. The beneficial use of dredged sediment is considered as a sustainable alternative. However, the dredged sediment is often contaminated by heavy metals and petroleum due to anthropogenic activities. Those contaminants should be properly treated prior to the beneficial use of dredged sediment to minimize negative impacts on surrounding environment and

ecosystem.

The treated sediment with conventional treatments which mostly focus on the compliance of the regulatory standards without the consideration of sediment quality may be damaged or lost their original characteristics. Those treated sediments can be disposed at landfill facilities due to destruction of original characteristics or beneficially used within limited options such as backfill materials for construction due to its low qualities. It is important to design suitable treatment processes to produce the treated sediment with its enhanced qualities. A treatment process is needed to produce treated sediment with enhanced values that can provide not only physical function but also ecological function of soil. In addition, in order to address conventional problems of dredged sediment management which requires enormous spatial demand for storage and treatment, a treatment method with reliable removal efficiency for target contaminants within short treatment time is recommendable.

This research used the acid washing for the heavy metal removal and thermal treatment for removal of the petroleum to produce plant growable soil with enhanced values. In order to produce soil with enhanced fertility using treated sediment, changes in contents and mobility of contaminants, sediment physicochemical properties and newly formed negative byproducts during treatment were deeply investigated. In addition, changes in sediment salinity and salt compositions and those effects on plant growth in sediment before and after treatment were also researched in this study.

Firstly, changes in sediment fertility as plant growable soil during acid washing and neutralization depending on applied types of acid solutions (HCl, HNO₃, H₂SO₄) and neutralizers (CaO and NaOH) were investigated. The salts in dredged marine sediment was verified as critical plant stressors based on the barley

germination and growth test with water washing for the removal of sediment salinity. During acid washing and neutralization treatment, the salinity and salt compositions in sediment were changed depending on the applied acid solutions and neutralizers. The newly produced gypsum from treatment using CaO or sulfuric acid significantly affected the sediment salinity and salinity removal efficiency due to its low solubility. After acid washing and neutralization, the barley germination and growth were significantly improved by reducing the sediment salinity and heavy metal mobility without additional treatment for sediment salinity removal. The newly produced cation salts from neutralizers affected more plant growth than anion salts. CaO treated sediment showed the better agronomic performance than NaOH treated sediment by reclaiming the sodium abundant sediment, which causes soil structure deterioration, nutritional imbalance and toxic effects, with calcium containing neutralizer.

A low-temperature thermal treatment showed the successful production of plant growable soil using petroleum contaminated sediment. TPH content in sediment was efficiently removed with 93 percent of removal efficiency while most of the sediment physicochemical properties such as organic matter, nitrogen and minerals which are significantly related to product qualities as a plant growable soil were successfully preserved. The thermal treatment could also stabilize the mobility of heavy metals in sediment due to particle aggregation and newly produced carbonaceous materials. The thermally treated sediment was not enough to provide the plant growable environment due to newly generated soluble organics and increased salinity due to oxidation of sediment constituents. Those substances were simply removed with water washing post treatment after thermal treatment and the water washed sediment showed significantly improved sediment fertility as plant

growable soil. The suggested thermal treatment process with water washing successfully produced treated sediment with enhanced agronomic performance by controlling the existing and newly generated plant stressors and preserving original sediment characteristics.

In order to identify an optimized thermal treatment condition for the production of treated sediment as plant growable soil, the effects of heat temperature and oxygen availability on sediment fertility during thermal treatment were investigated. The pyrolytic treatment condition was successfully created by the physical control using a steel container with a lid and black carbonaceous matters under this environment were successfully produced without continuously providing nitrogen gas. The newly produced black carbonaceous matters in thermally treated sediment can support to preserve the sediment physicochemical properties with its strong adsorption of organic matter, nutrients and sediment minerals at higher heat temperature compared with thermally treated sediment under the oxygen moderate condition. Under all treatment condition, the mobility of heavy metals was successfully reduced and each heavy metal mobility was differently affected by the treatment conditions. The main reason for the reduction of heavy metal mobility after thermal treatment was caused by the increased residual fraction which is the non-labile fraction . It is highly suspected that the heavy metal mobility was dominantly reduced by particle aggregation under relatively oxygen abundant atmosphere or black carbonaceous materials under less oxygen available conditions.

The barley germination and growth under all thermal treatment conditions increased compared with its result of untreated sediment. It should be noted that the increased TPH removal efficiency and more reduced heavy metal mobility mainly contributed to the enhancement of barley germination and growth. The less produced

soluble organics considered as adverse plant stressors with the increase of heat temperature had positive effects on the enhancement of sediment fertility without additional treatment. Among various conditions, the thermally treated sediment under the highest temperature and least oxygen available conditions (500N) showed the best barley germination and growth. It is assumed that this result was caused by more preserved sediment characteristics and newly produced black carbonaceous materials compared with more oxygen available conditions at the same temperature. The thermally treated sediment fertility after water washing was more improved by removing the soluble organics and sediment salinity. The results of barley germination and growth in thermally treated sediment after water washing were similar to these results of thermally treated sediment without additional treatment. From this result, it was found that the changed sediment characteristics after thermal treatment cannot be improved by the water washing post. Therefore, it is important to remediate the sediment with the optimized treatment condition for the production of quality enhanced sediment with proper soil function.

Keyword : dredged marine sediment, salt, thermal treatment, heavy metals, plant growable soil

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CHAPTER 1

INTRODUCTION

1.1. General overview

The enormous amount of dredged marine sediment is generated due to development and management of navigational channel and harbor. The annual generation amount of dredged sediment in Korea is approximately twenty million cubic meters.¹ The ocean disposal of dredged sediment has been limited or/and prohibited in many countries^{2,3}, the management of dredged sediment has been a challenging issue. The land disposal of sediment at disposal facilities is a conventional treatment method in Korea. However, this treatment method is not considered as a sustainable treatment method due to its limited capacity. In addition, the construction and management for disposal facilities require huge cost and unpredictable threats to surrounding environment and ecosystems may occur due to contaminants leaching by heavy rainfall and flooding during operation of disposal facilities.⁴ In addition, the land disposal facilities are often constructed at the natural habitats such as mud flat, resulting in threatening the surrounding organisms and environment.

The beneficial use of dredged sediment is considered as a sustainable alternative. Beneficial use of dredged sediment has various economical and socioeconomic benefits by saving natural resources and reducing burdens to disposal facilities, especially countries with the lack of natural resources and shortage of

space. The dredged sediment can be beneficially used as construction materials such as coastal protection, construction filling materials and road subbase construction or ecological resources such as habitat creation, soil enhancement, agriculture and aquaculture farm.⁵ Sediment fertility is the capacity to support suitable environment for plant growth with the nutrients and organic matter. According to Table 1.1, the sediment in this study sufficiently has the organic matter and nutrients for barley growth compared with recommend soil for barley growth and general agricultural soil in Korea.

Table 1.1. Comparison of physicochemical properties in agricultural soil in Korea and recommended soil for barley growth and sediment in this study.

	pH	Organic matter (%)	TN (%)	TP (mg/kg)	CEC (cmol/kg)
Agricultural soil (Korea)	4.5-6	2-4	0.08-0.1	200-800	5-10
Recommend soil for barley growth	6.5-7.0	2-3	0.005-0.015 (N-NO ₃)	150-250 (Available P)	10-15
Sediment (This study)	7.66	6.75	0.635	1708	35.32

However, the dredged sediment is often contaminated with heavy metals and petroleum due to anthropogenic works such as industrial activities, accidental events, waste/wastewater discharge.⁶⁻⁸ Those contaminants are acknowledged as significant toxicants to environment and terrestrial receptors and could significantly affected

sediment fertility. The contaminants should be properly treated before beneficial use of dredged sediment to minimize negative effects on environment and ecosystems. The conventional treatment processes have generally been focused on the compliance of regulatory standards, resulting in the destruction of sediment characteristics without the consideration of the treated sediment quality. The treated sediment with low quality is disposed at land disposal sites or recycled as low quality construction materials such as backfill. The improved sediment qualities after proper treatment can be used as plant growable medium. In order to determine a sediment treatment method, the treatment should also have a reliable removal efficiency of target contaminants and rapid treatment time to address conventional problems of dredged sediment management due to considerable spatial demand for treatment and storage. The acid washing is an effective and efficient treatment method for heavy metal removal and thermal treatment can remove a wide range of organic contaminants in short treatment time.

Salts which are originated from the ocean as well as contaminants in dredged marine sediment could negatively also affect plant growth. The sediment salinity and its salt compositions can be changed during the treatment of contaminants in dredged sediment and these changes could significantly influence plant growth due to changes in osmotic stress to inhibit the water uptake of plants and specific ion toxicities and nutrition imbalances.⁹⁻¹¹ However, the change in sediment salinity and its salt compositions during the treatment has not been thoroughly investigated. Without the consideration of those changes, changes in sediment fertility after treatment may be misled with the only consideration of contaminants removal. Salts in sediment should be also carefully investigated and treated prior to beneficial use of sediment as plant growable soil.

In this research, changes in sediment physicochemical properties, petroleum and heavy metal contents and heavy metal mobility were investigated during acid washing for reduction of heavy metal and thermal treatment for petroleum removal with the consideration of changes in sediment salinity in order to produce the plant growable soil with enhanced fertility using treated sediment.

1.2. Background

1.2.1. Acid washing for reduction of heavy metal mobility

The dredged sediment is contaminated from a wide range of anthropogenic works such as industrial activities, mining, agricultural works.¹² The more labile heavy metals fractions (e.g., water soluble, exchangeable, carbonate bounded and reducible fractions) may have more risks to threat surrounding environment and ecosystems. These forms of heavy metals should be properly removed prior to beneficial use of sediment. The acid washing is one of the commonly used treatment for heavy metal removal in sediment to transfer heavy metals from sediment to extracting chemicals.¹³ The heavy metals in sediment are solubilized by ion exchange and dissolve soil minerals bounded heavy metals to aqueous solution with chemical additives.^{12,13} The acid washing may be a suitable treatment method for removal of liable forms of heavy metals in dredged sediment due to its reliable removal efficiency in short treatment time. In order to reduce mobile forms of heavy metals in dredged sediment, various parameters related to acid washing for heavy metal removal should be deeply understood. In Table 1.2, the parameters to affect removal efficiency of heavy metals by the acid washing are shown. Sediment characteristics such as distribution of sediment particles, organic matters and content of cation exchange capacity can affect the removal efficiency of heavy metals due to those higher surface area, adsorption and buffering capacity. The treatment conditions of acid washing such as chemical types, strength of solutions, treatment time and agitation methods can also significantly affect the heavy metal removal efficiency. Various organic and mineral acids such as hydrochloric (HCl), nitric (HNO₃) and sulfuric acid (H₂SO₄) can be used for chemical extractants. Among

mineral acids, the HCl show better performance for removal of Zn, Cu, Pb, Cd and Ni than HNO₃ and H₂SO₄.¹⁴⁻¹⁶ Forms of heavy metals in sediment critically affect the reduction of heavy metal mobility. The different heavy metals may have different dominant fractions. For example, the Zn is mostly bounded to carbonate and reducible forms and Cu is mainly bounded to organic matter. The Pb is dominantly bound to residual fraction which is known as a non-labile fraction. However, the fractions of heavy metals can be changed depending on the sediment characteristics, aging time and exposed environmental conditions.

Table 1.2. The parameters related to removal efficiency of heavy metals in dredged sediment by acid washing.¹³

Parameters	Description
Sediment physicochemical properties	Soil texture, cation exchange capacity (CEC), organic matter
Heavy metals	Heavy metal types (i.e., Cu, Zn, Cd, Pb etc.), fractionation, metal speciation
Extraction method	Chemical reagent types, solution strength, treatment time, agitation methods, liquid to solid ratios

1.2.2. Effects of salinity and salt compositions on plant growth

The dredged marine sediment is generated during the dredging activities of sediment for management of navigational channel and harbor development. The dredged sediment from the ocean includes high salinity and those salts dominantly consists of Na⁺ and Cl⁻. The high salinity and those salts in sediment could negatively

affect the plant growth due to osmotic stress, toxic effect of specific salt ions and nutrition imbalance.^{9,17} The high sediment salinity inhibits the plant growth due to osmotic effect.⁹ In osmotic phase, water uptake of plants is inhibited due to osmotic pressure of sediment solution with high salinity. The plant requires more energy for the water uptake with the increased of sediment salinity and the reduced water availability could negatively affect plant growth.^{9,18} The abundant Na^+ which is adsorbed on clay particles in sediment become sodic sediment and it leads to deteriorate the sediment structure by collapsing sediment structure with segregate clay particles and clogging of sediment pores with these collapsed sediment structure.¹⁸ This leads to hydraulic problems such as water logging, inhibited drainage and air availability.^{9,18} In waterlogged sediment, the sediment salinity can become higher due to accumulation of source originated or newly generated salts from irrigation water and fertilizers.¹⁹ The increased salts in waterlogged sediment could increase toxic effects on plant growth.

The salt compositions in sediment can also significantly affect the plant growth. Na^+ and Cl^- have toxic effects on plant growth such as leaf burn and dead tissue¹⁰ and it lead to restriction of plant growth^{20,21}. The nutrition imbalances which are induced by abundant of Na^+ and Cl^- in sediment also reduce the plant growth. The Na^+ and Cl^- inhibit the uptake of ions used as nutrients for plant growth such as K^+ , Ca^{2+} , Mg^{2+} and NO_3^- and these restrictions reduce plant growth.^{10,22} The negative effects of specific ions can be alleviated, by applying additives. For example, the calcium containing materials such as gypsum and lime can replace the sodium on the clay particles, resulting that the structural problems induced by sodium can be addressed. In addition, calcium addition can also alleviate toxic effects of Na^+ by inhibiting the uptake of Na^+ and enhance the uptake of K^+ , Ca^{2+} , Mg^{2+} in sodium

abundant environment.^{10,23} The changes in sediment salinity and salt compositions can be changed during the acid washing and neutralization treatment depending on the applied reagents. As discussed above, these changes should be thoroughly investigated and properly treated to enhance the sediment fertility.

1.2.3. Thermal treatment for organic contaminant

The thermal treatment is commonly used a treatment method to effectively remove various types of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and petroleum in dredged sediment and soil.^{24,25} The thermal treatment is suitable for the dredged sediment remediation due to its short treatment time for various organic contaminants with reliable removal efficiency. Based on the oxygen availability and heating temperature, the dominant thermal treatment reactions such as pyrolysis, degradation and oxidation are determined.²⁵ The thermal desorption mainly volatilize the organic contaminants in sediment and soil with other thermal reactions such as pyrolysis, degradation and oxidation.²⁵ Based on the heating temperature (300 or 350 °C), the thermal desorption is divided into low temperature thermal desorption and high temperature thermal desorption. Heating temperature and treatment time are commonly determined by the characteristics of contaminants and target treatment concentrations. The high heating temperature require relatively short treatment time to achieve the target removal efficiency but the treatment cost is expensive and treated sediment characteristics may be more destroyed. In addition, the sediment texture and physicochemical properties also influence thermal treatment efficiency. Some literature reported that the removal efficiency of PCBs and polybrominated diphenyl ethers (PBDEs) in fine particle showed lower than bigger particles²⁵ but

other literature also showed the opposite results^{26,27}. Those kinds of difference may be induced by the complexed soil matrix due to different organic matters contents and various compositions minerals.²⁵ Recently, pyrolytic treatment for petroleum impacted sediment has been researched.²⁸⁻³⁰ The pyrolytic treatment is generally conducted under the oxygen limited or absent condition by purging the nitrogen gas to remove the oxygen content in treatment atmosphere. By using the organic contaminants as feedstocks, production of black carbonaceous materials or recovery of petroleum depending on the dominant chemical reactions such as thermal cracking, polymerizing and transferring has been suggested.³⁰

1.2.4. Effect of thermal treatment on sediment physicochemical properties

Thermal treatment conditions significantly affect the sediment physicochemical properties such as pH, TN, TP and CEC. The changes in sediment physicochemical properties during the thermal treatment should be thoroughly investigated since those changes critically affect the sediment fertility as plant growable soil. During the thermal treatment, soil pH can be changed depending on the heating temperature. At lower than 250 °C, the formation of bicarbonate which is generated from mineralization of CO₂ during thermal treatment reduce the soil pH^{31, 32} but the soil pH was increased due to displacement of hydrogen on clay particle with base cations released from the combustion of soil organic matters^{31,32} and destruction of organic acids which can acidify the pore water in soil³³. These changes are also affected by the other sediment physicochemical properties depending on the contents of the organic matter and mineral buffers such as calcium carbonate. The soil organic matter which is an important source for plant growth can be also affected by the thermal treatment. The changes in organic matters c are also

differently influenced by the treatment conditions and constituents of sediment organic matters. During the thermal treatment, the organic matter in soil may be volatilized, chemically transformed or oxidized.^{34,35} The lignin, hemicellulose and volatile materials are degraded at low temperatures lower than 200 °C.^{36,35} The fulvic and humic acid are affected above 300 °C while the lipid and alkylaromatics is volatilized or chemically transformed to condensed carbon (e.g., char).^{36,37} Depending on the oxygen availability in the treatment atmosphere, the forms of organic matter after thermal treatment can be also changed. The nitrogen is influence by the reduced organic matter during thermal treatment by volatilization. According to the literature²⁸, the nitrogen was relatively more preserved due to the newly produced carbonaceous materials (e.g., char) during pyrolytic treatment. The phosphorous in soil is increased after thermal treatment due to it high thermal resistance and the reduced soil mass due to organic matter decomposition.³⁵ The constituent of phosphorous can be also changed from organic to inorganic phases during thermal treatment. These changes also affect the availability of phosphorous to plants. The CEC contents are influenced by the changed organic matter and minerals during thermal treatment.³⁴ each soil mineral is differently affected by the heat temperature. Kaolinite which is a relatively low thermal resistant mineral begins to decompose above 420 °C.³⁵ Other soil minerals such as montmorillonite and micas require higher temperature to be deformed but the longer treatment time less affected the destruction or deformation of clay minerals.

1.3. Objective and scope

The objective of this research aims at producing the fertility enhanced planting soil using petroleum and heavy metal impacted dredged marine sediment after acid washing and neutralization treatment and thermal treatment. The primary objectives of this research are as follows:

- i. To determine optimized acid solution and neutralization agents to produce the fertility enhanced sediment as planting soil with the consideration of changes in sediment salinity and its salt compositions, heavy metal mobility, TPH content and sediment physicochemical properties
- ii. To develop low thermal treatment technique to produce planting soil using petroleum contaminated sediment by understanding the changes in TPH, heavy metal mobility and sediment physicochemical properties by thermal treatment.
- iii. To identify newly generated byproducts as plant stressors during thermal treatment and propose the modified low thermal treatment process to minimize the identified plant stressors during treatment
- iv. To propose an optimized thermal treatment condition for the production of fertility enhanced sediment as planting soil by controlling the heat temperature and oxygen availability with the comprehensive consideration of TPH removal efficiency, mobility of heavy metals and sediment physicochemical properties

1.4. Organization of Dissertation

This dissertation consists of six chapters: Chapter 1 is the introduction and Chapter 2 is the literature review. Chapter 3 introduces the effects of acid solutions and neutralization agents on fertility of heavy metal impacted dredged marine sediment as planting soil during acid washing and neutralization treatment. Chapter 4 deals with the development of a low-temperature thermal treatment process for the production of planting soil using petroleum-impacted dredged sediment. Chapter 5 presents effect of heat temperature and oxygen availability during thermal treatment for the production of planting soil from petroleum-impacted sediment. Figure 1.1 is the scheme of this research.

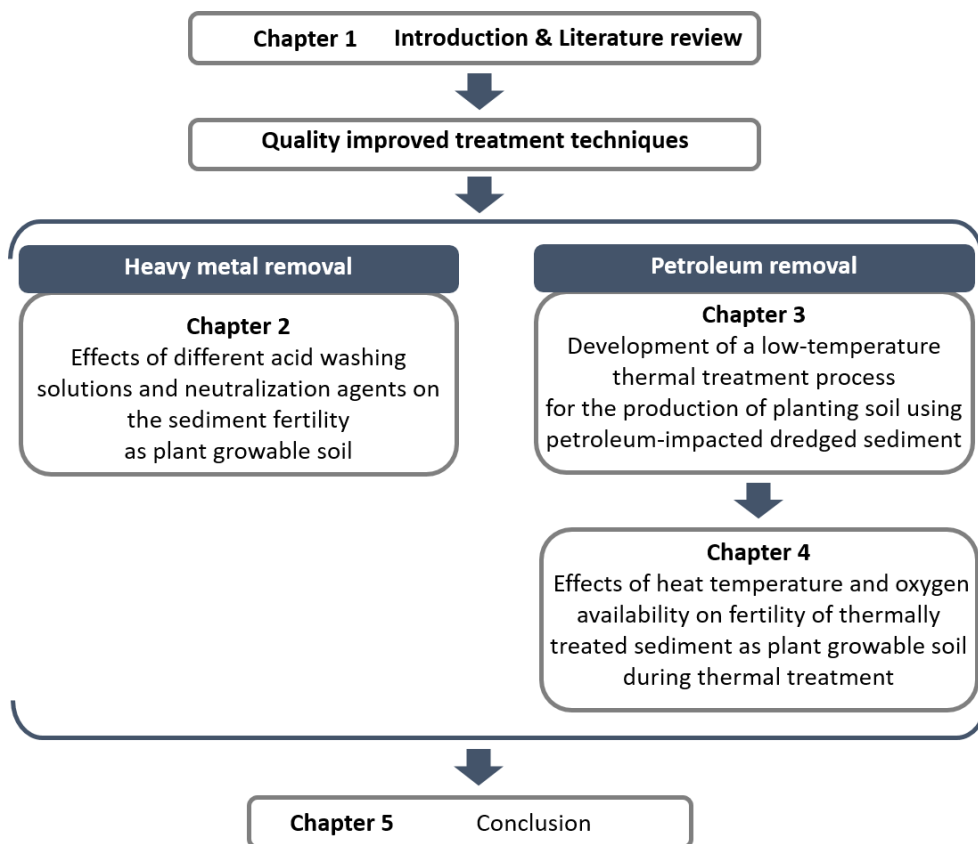


Figure 1.1. The structure of this study

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CHAPTER 2

Effects of treatment agents on fertility of heavy metal impacted dredged marine sediment as planting soil during acid washing and neutralization treatment

2.1. Introduction

Management of dredged marine sediment has been issued due to its substantial amount of annual generation.¹ The ocean disposal has been limited and/or prohibited due to international convention. Beneficial use of dredged marine sediment is considered as sustainable treatment method by minimizing environmental and socioeconomic problems related dredged sediment disposal. Dredged sediment is often contaminated by heavy metals from various anthropogenic works². Heavy metals, which have negative impacts on surrounding environment and ecosystem³, should be properly removed prior to beneficial use of dredged sediment as plant growable soil. Acid washing is acknowledged as a rapid and reliable treatment method for heavy metals treatment of soil and sediment⁴⁻⁶, resulting in addressing conventional problems of dredged marine sediment management such as enormous spatial demand. Acid washed sediment requires neutralization treatment to provide of suitable pH ranges for plant growable environment.

The dredged marine sediment contains enormous amount of salinity which can hinder plant growth by an osmotic effects to inhibit water uptake to plant⁷ and 85 % of the salts in dredged marine sediment consists of Na^+ and Cl^- which are considered as toxic ions and deteriorate sediment structure^{8,9}. In order to beneficially use dredged marine sediment as planting soil, not only typical contaminants but also source originated and newly produced salts during treatment should be monitored and properly treated to enhance the sediment fertility. Application of acid washing and neutralization treatment for removal of heavy metal in sediment could change the sediment salinity and salt compositions during treatment and those changes can significantly affect plant growth depending on applied types of acid solutions and neutralization agents. However, those changes during the acid washing and neutralization with various acid solutions and neutralizers has not been researched for the production of planting soil using dredged marine sediment with the consideration of comprehensive changes such as sediment characteristics and heavy metal mobility after treatment since most of acid washing studies has been mostly focused on removal efficiency of total contents and mobility of heavy metals¹⁰⁻¹². In this study, we investigated the changes in sediment salinity and salt composition in dredged marine sediment during acid washing and neutralization treatment depending on applied types of acid solutions and neutralizers with the changes in heavy metal mobility and sediment characteristics. In addition, the effects of those changes on sediment fertility were also evaluated using barley germination and growth test to produce the enhanced plant growable soil using dredged marine sediment after treatment.

2.2. Materials and methods

2.2.1. Sediment Sample Collection and Sediment Analyses

Heavy metal contaminated dredged marine sediment was collected from highly industrialized harbor area in Korea. After moving to the laboratory, the dredged sediment was air dried and then thoroughly hand mixed for hominization. Sediment total organic carbon (TOC) and total nitrogen (TN) contents were analyzed according to the Walkley-black method² and the Kjeldahl method³, respectively. The concentration of total phosphorus (TP) in sediment was extracted using aqua regia suggested by Chen and Ma⁴ and then TP in the extract was analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Technologies, Santa Clara, CA). EC_{1:5}, pH, and soluble salt contents (Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻ and NO₃⁻) were analyzed in a 1:5 (w:w) sediment slurry. In order to prepare the sediment slurry, 5 g dry weight (dw) sediment and 25 ml DI water were added in a 50-ml conical tube and the slurry was agitated on a horizontal shaker for 2 hours at 180 rpm. After agitation, the tube was centrifuged at 14,000 × g for 10 mins and then the supernatant was gently collected and filtered using a 0.45-μm syringe filter. EC_{1:5} and pH in were analyzed in extracts by a multi-parameter meter (Orion 5 star, Thermo Fisher Scientific, USA) equipped with a pH electrode and a conductivity cell. Soluble anion salt contents (SO₄²⁻, Cl⁻ and NO₃⁻) were measured by ion chromatography (DX-500, Dionex, US) equipped with an AS14 anion column and a CD20 conductivity detector and soluble cation salt contents (Ca²⁺, Mg²⁺, Na⁺ and K⁺) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Technologies, Santa Clara, CA). All analyses were carried out with triplicate samples. The crystalline minerals in sediment were

measured by X-ray diffraction (XRD; D8 Advance, Bruker Inc., Germany) with Cu-K α radiation at 40 kV and 40 mA in the range of 2θ scanning range from 5° to 90°. X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo VG Scientific) with an Al K α X-ray source (1486.7 eV) was applied to measure the sediment surface calcium containing complexes (Gypsum).

To investigate the plant growth effects of salt reduction, water washing was applied to reduce the sediment salinity till below 0.5 dS m⁻¹. Before and after water washing, the sediment physicochemical properties, TPH contents, heavy metal contents and fractionation of heavy metals were analyzed. The results were shown in Table 2.1, Table 2.2, Figure 2.1, respectively.

Table 2.1 pH, EC_{1:5}, TOC, TN, TP, CEC and SO₄²⁻ in untreated sediment before water washing and after water washing with deionized water.

	pH	EC _{1:5} (dS/m)	TOC (%)	TN (%)	TP (mg/kg)	CEC (cmol/kg)	SO ₄ ²⁻ (mg/kg)
Before water washing	7.06	17.5	3.91	0.67	1816	33.5	5018
After water washing	7.66	0.40	3.81	0.64	1708	35.3	220

Table 2.2. Total contents of TPH and heavy metals in untreated sediment before water washing and after water washing with deionized water.

	TPH	Ni	Zn	Cu	Pb	Cd
Before	4590±225	71.6±1.20	2630±120	316±3.32	126±4.58	5.66±0.67
water						
washing						
After	4920±328	72.1±1.41	2680±113	323±5.59	133±3	5.94±0.06
water						
washing						

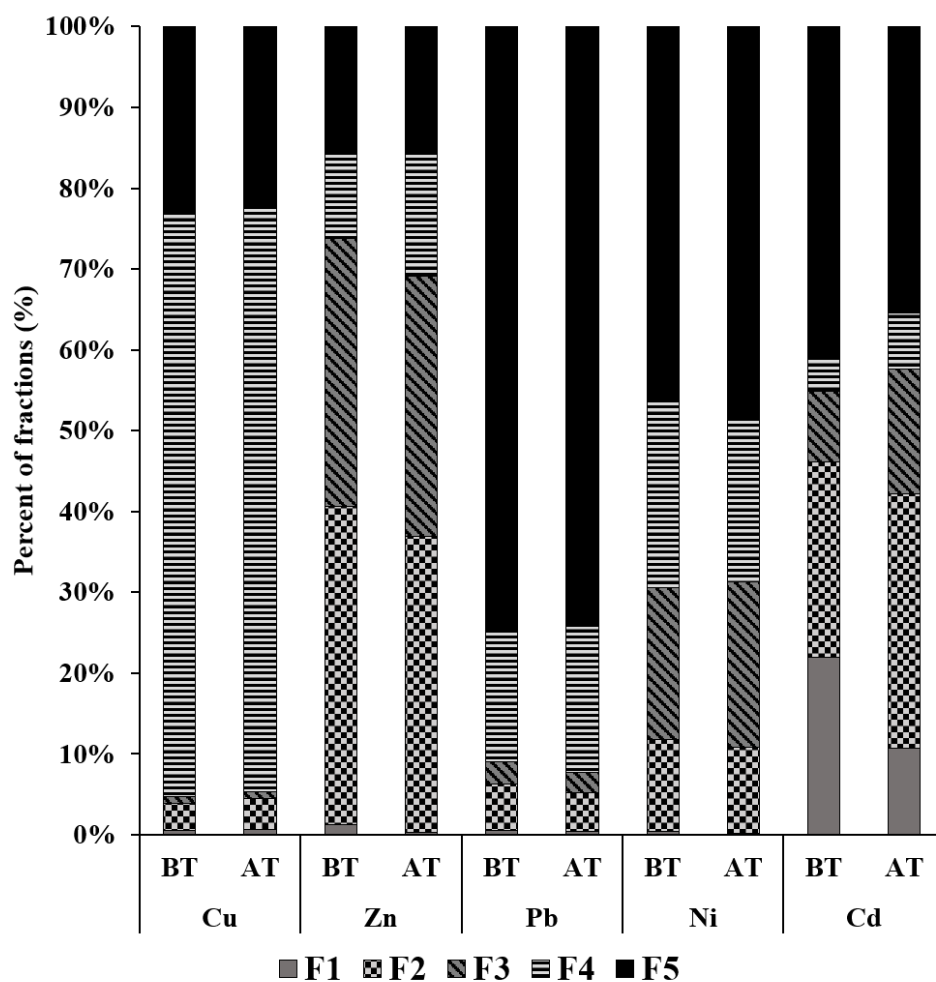


Figure 2.1. Composition of sequentially extracted fractions of heavy metals relative to the total amount in sediment before treatment (BT) and after treatment (AT) by water washing. Each fraction of heavy metals is represented as follows¹⁵: F1, exchangeable; F2, bound to carbonates; F3, bound to Fe/Mn oxides; F4, bound to organic matter; F5, residual.

2.2.2. Acid Washing, Neutralization Treatment and Water Washing

Acid washing was conducted with 50 g dry weigh (dw) of sediment and 250 ml of acid solutions using 0.5N HCl, 0.5N HNO₃ or 0.5N H₂SO₄ for 2 hours at 150 rpm using a horizontal shaker to reduce labile forms of heavy metals. After acid washing, neutralization treatment with calcium oxide (CaO) which has been known as a relatively high neutralizing value compared with the other calcium containing materials¹³⁻¹⁵ or NaOH was employed to neutralize acidified sediment neutral pH around or above 7. DI water was added to acid washed sediment to obtain 1:5 (w:w) sediment slurry and then neutralization agents was added. The slurry with neutralizing agent was agitated for 72 hours at 150 rpm and then centrifuged at 5,000 rpm for 20 mins to separate out the supernatant. The dosage of neutralizing agents and neutralization time were determined based on our preliminary study. Water washing was conducted to reduced sediment salinity till an electrical conductivity of the 1:5 (w:w) sediment slurry (EC_{1:5}) of around 0.5 dS m⁻¹. DI water was added to neutralized sediment to obtain 1:5 of liquid to solid ratio and the slurry was shaken for 2 hours at 180 rpm using the horizontal shaker. After water washing, the sediment was air dried for barley germination and growth test.

2.2.3. Heavy Metals and TPH Analysis

In order to investigate the effects of water washing on changes in fractionation of heavy metals in untreated sediment, sequential extraction procedure (SEP) was conducted based on Tessier's SEP¹⁶ with a modified last step of extraction. The last extraction step was modified to improve the residual heavy metal extraction followed by USEPA 3051A using a microwave digestion. The procedure of SEP method was detailly shown in Kim et al.¹. The total contents of heavy metal in

sediment was extracted using USEPA 3051A and the mobility of heavy metal before and after acid washing and neutralization treatment was analyzed by Toxicity characteristic leaching procedure (TCLP) according to USEPA Method 1311¹⁷. 2 g dry weight (dw) of sediment sample and 40 ml of an acetic acid solution (pH 2.88 ± 0.05) were added to in 50 ml polystyrene conical tube. The sediment slurry was mixed for 18 hr at 30 rpm using an end-over-end rotary mixer. The sediment slurry was centrifuged at $14,000 \times g$ for 10 mins and then the supernatant was collected passed through a 0.45- μ m syringe filter. The heavy metals in extracts for total contents, SEP and TCLP leached concentrations were measured by ICP-OES.

The concentrations of total petroleum hydrocarbon (TPH) in untreated and acid washed sediment were measured using Korea standard method for soil analysis.¹⁸ Anhydrous sodium sulfate (Na_2SO_4) for removal of water content in sediment was added and then thoroughly mixed. 100 ml of dichloromethane was added to extract TPH in sediment using a sonicator (Duty cycle 50%; Pulse mode 1 second) for 3 mins. This step was conducted twice. The collected extract was filtered through No. 5 filter paper (4 μ m pore size) and the mixed with Na_2SO_4 for removal of moisture content in the extract. Nitrogen purging was conducted to concentrate the filtered extract till 2 ml. The concentration of TPH in the concentrated extract was measured by gas chromatograph-flame ionization detection (GC-FID, Agilent Technologies, Santa Clara, CA) with DB-5 capillary column (30 m \times 0.32 mm \times 0.25 μ m) with helium as carrier gas (1–2 mL min⁻¹). The temperature of oven was initially set at 50 °C for 2 mins and then increased by 10 °C/min up to 320 °C for 10 mins. The injector and detector temperature were set at 300 °C and 320 °C, respectively. The content of sediment TPH was calculated by integrating the total area of n-alkanes (C8-C40).

2.2.4. Barley Germination and Growth Test

Barley (*Hordeum vulgare* L.) was used to assess to compare the effects of different types of acid solution and neutralization agents on phytotoxicity and sediment fertility after acid washing and neutralization treatment and water washing. Barley is one of the major ecotoxicity test species in international standards (i.e., International Organization for Standardization., ISO) and often used to assess the toxic effects of organic and inorganic contaminants in soil or sediment.^{19,20} Ten barley seeds were placed in each sediment sample (30 g) in 100 ml polyethylene dish. The DI water was added to achieve the field capacity of sediment. The barley was incubated in a growth chamber (E15, Conviron Inc., Canada) to maintain a constant experiment conditions (23°C, a light:dark photoperiod of 16:8) for 10 days. After the experiment, the root germination rate, the shoot development rate, and the lengths of root and shoot were measured.^{21,22}

2.3. Results and discussion

2.3.1. Barley Germination and Growth Test for Untreated Sediment after Salinity Removal.

The dredged marine sediment containing high salinity could have negative effects on plant growth without proper removal of salt prior to its beneficial use due to toxic effects, ion imbalance, water logging and poor permeability.^{7,8,21} In order to verify the effect of salts in dredged marine sediment on plant growth, the salts in sediment was removed through serial water washing till 0.5 dS m⁻¹ of sediment salinity and barley germination and growth experiment was conducted using water

washed sediment. After water washing, the sediment physicochemical properties, contents heavy metals and petroleum hydrocarbon (TPH) shown in Table 2.2 in the Chapter 2.2.1 was not significantly changed. In addition, the fractionation of heavy metals indicated in Figure 2.1 in the Chapter 2 was also not significantly affected by water washing. The results of barley germination and growth after water washing were shown in Figure 2.2. There was no germination of barley in untreated sediment due to extremely high salts contents originated from the ocean. However, the growth and germination of barley was gradually enhanced with the increase in the number of water washing by reducing residual salinity in sediment shown in Table 2.2. Even though the sediment still contained high contents of heavy metals and TPH, the barley germination and growth were significantly enhanced in only salinity removed sediment. From this result, it is verified that salts in sediment is also a critical plant stressor and the salts in dredged marine sediment should be carefully removed prior to beneficial use as plant growable soil.

Table 2.3. Changes in EC_{1:5} of untreated sediment, 1st water washed sediment, 2nd water washed sediment, 3rd water washed sediment, 4th water washed sediment

	Untreated	1 st water	2 nd water	3 rd water	4 th water
	sediment	washed	washed	washed	washed
		sediment	sediment	sediment	sediment
EC _{1:5}	17.24±0.12	4.15±0.28	1.11±0.03	0.72±0.01	0.51±0.09
(dS/m)					

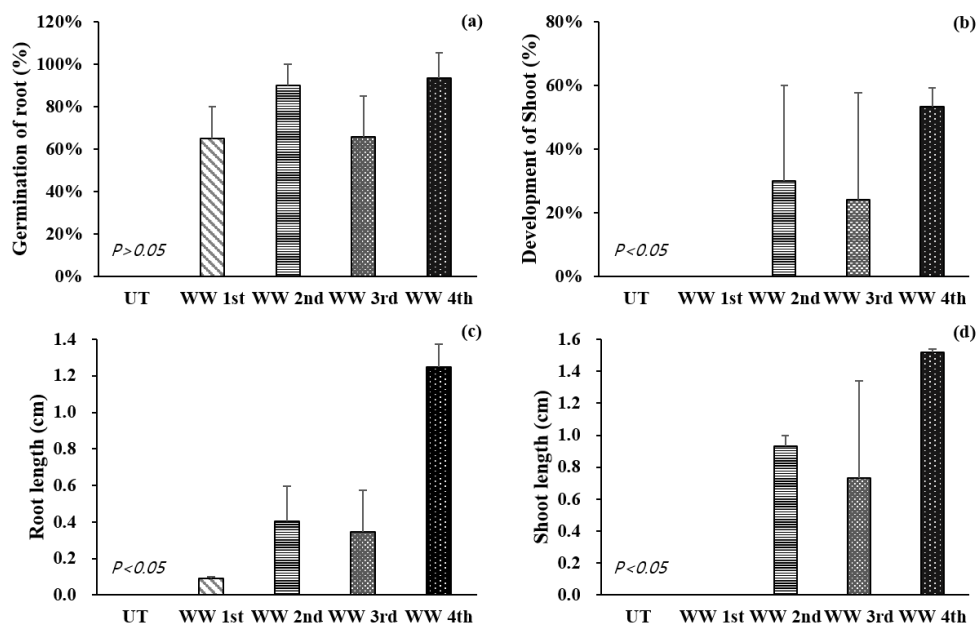


Figure 2.2. Barley (*H. vulgare*) germination and growth test results: (a) root germination, (b) shoot development, (c) root length, and (d) shoot length. UT: untreated sediment; UT: Untreated sediment; WW_{1st}: 1st water washing; WW_{2nd}: 2nd water washing; WW_{3nd}: 3nd water washing; WW_{4nd}: 4th water washing.

2.3.2. Changes in Heavy Metal Mobility and TPH after Acid Washing and Neutralization Treatment

The total contents of heavy metals which is shown in Table 2.2 in sediment were reduced after acid washing. The removal efficiency of Zn which was the highest concentration at $2742 \pm 41 \text{ mg kg}^{-1}$ in untreated sediment due to higher proportion of labile fractions was highest at 68-76% and the removal efficiency for the other heavy metals was 40-60%, except Pb and Cu by 0.5N H_2SO_4 . During acid washing with sulfuric acid, the formation of metal sulfate (i.e., PbSO_4), which is a insoluble form, could affect lower removal efficiency compared with the other acid solutions^{3,5}. The removal efficiency of Cu with H_2SO_4 was also lower than the other acid solutions.

This is line with the literature data.^{22,23} It is assumed that Cu which is dominantly bounded to less labile form such as organic matter bound^{1,2} is more difficult to be extracted by H₂SO₄ compared to by equivalent strength of HCl and HNO₃. The removal efficiencies of all heavy metals with HCl solution was higher than other solution, which can be attributed to the fact that the formation of aqueous complexes of Cl⁻ and heavy metals actively assists to extract heavy metals.²⁴ This is in agreement with other research.^{23,25-27} The Cd and Ni removal efficiencies by HNO₃ and H₂SO₄ were not significantly different but the removal efficiency was slightly higher (0.4-1%) with H₂SO₄. For Cu and Pb, HNO₃ showed higher removal efficiency than H₂SO₄. These is line with other studies.^{3,28}

Table 2.4. Total concentrations of heavy metals for untreated sediment, neutralization treated sediment with CaO or NaOH after acid washing with 0.5N HNO₃, 0.5N HCl and 0.5N H₂SO₄.

		Zn	Pb	Cu	Cd	Ni
UT		2742±41	133±2.4	350±4.5	6.35±0.14	146±0.7
CaO	0.5N	659±24	61±12	152±3.2	2.96±0.14	71±2.5
	HCl					
	0.5N	780±32	72±5.9	181±3.6	3.29±0.15	79±2.3
	HNO ₃					
NaOH	0.5N	857±31	107±4.6	222±10	3.25±0.09	79±3.0
	HCl					
	0.5N	761±36	71±2.6	172±6.0	3.45±0.06	83±0.5
	HNO ₃					
NaOH	0.5N	876±24	113±2.7	230±7.3	3.38±0.11	82±1.6
	HCl					
	0.5N	761±36	71±2.6	172±6.0	3.45±0.06	83±0.5
	HNO ₃					

According to TCLP test shown in Figure 2.3, most of heavy metal mobility after acid washing was reduced except Cu. The behaviors of TCLP leached amount for most of heavy metals after acid washing were similar to reduced total contents of heavy metal after acid washing, except Cu. The TCLP leached fraction of Zn which

was the highest mobile heavy metal was reduced 74-83%. It is believed that the toxic effects caused by highly mobile Zn were significantly reducing after water washing. The TCLP leached fraction of Ni which was the second largest mobile heavy metal was also reduced 75-82%. The TCLP leached amount of Cd decreased 42-55%. For Zn, Cd, Ni and Pb, reduction efficiency of TCLP leached amount by acid washing with HCl was most effective, followed by HNO₃ and H₂SO₄. The mobility reduction of Pb with H₂SO₄ was also much lowest due to the formation of lead complex during acid washing with H₂SO₄ whereas TCLP leached amount of Pb was almost completely removed by HCl and HNO₃. This trend is similar to the removal efficiency of total content of Pb. However, TCLP leached fraction of Pb was less than 2 percent of total content. Most of heavy metal mobilities effectively decreased after acid washing whereas the mobility of Cu increased after treatment. It is highly suspected that acid soluble forms of organic bounded Cu which are dominantly bounded to organic matter in sediment may be extracted and this result led to increase in Cu mobility, especially sulfuric acid treated sediment. There was no significant effect of neutralization agents on heavy metal mobility.

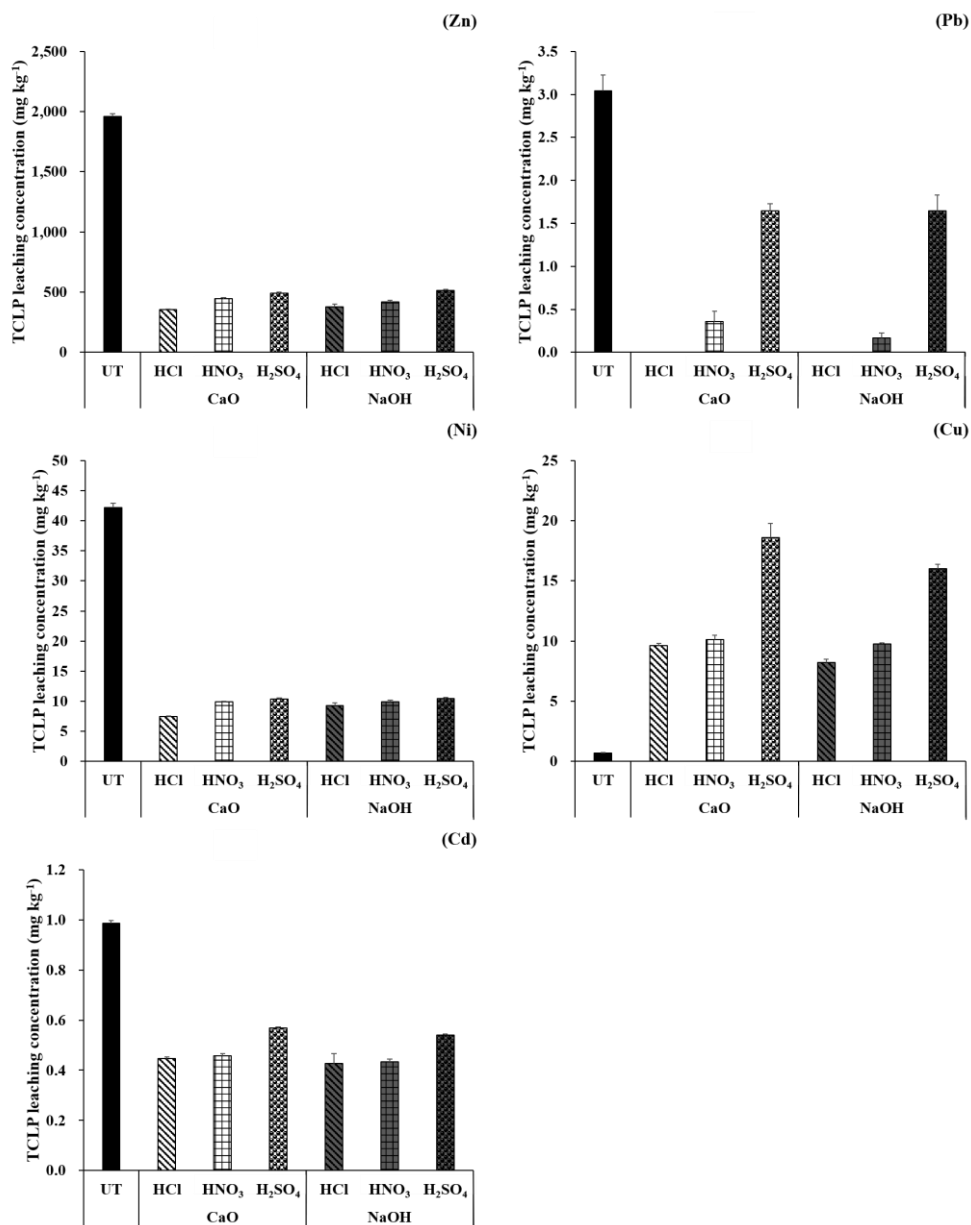
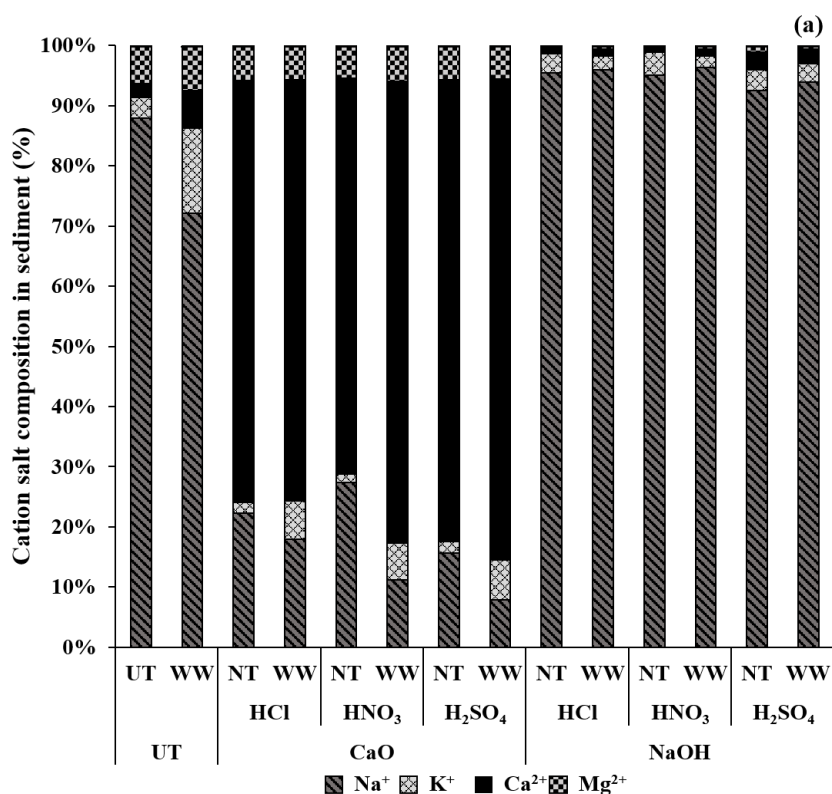


Figure 2.3. TCLP leaching concentrations of heavy metals for untreated sediment, treated sediment after acid washing with 0.5N HNO₃, 0.5N HCl and 0.5N H₂SO₄, Neutralization treated sediment with CaO or NaOH after acid washing with 0.5N HNO₃, 0.5N HCl and 0.5N H₂SO₄.

2.3.3. Salinity and Salt Ion Compositions after Acid washing and Neutralization treatment and water washing

The dredged marine sediment had high salinity and dominant salts in untreated sediment were analyzed Na^+ and Cl^- which were source originated salts from the ocean. During the acid washing and neutralization treatment, the salinity and salts composition of sediment were changed depending on applied acid solution and neutralization agents. The changed cation and anion salt compositions were shown in Figure 2.4. The $\text{EC}_{1:5}$ of acid and neutralized sediment shown in Table 2.3 was reduced 84-87% from $19.63 \pm 0.37 \text{ dS m}^{-1}$ to 2.07 ± 0.01 - $3.21 \pm 0.02 \text{ dS m}^{-1}$ by moving the original salt in sediment to acid and alkaline solutions during acid washing and neutralization treatments.



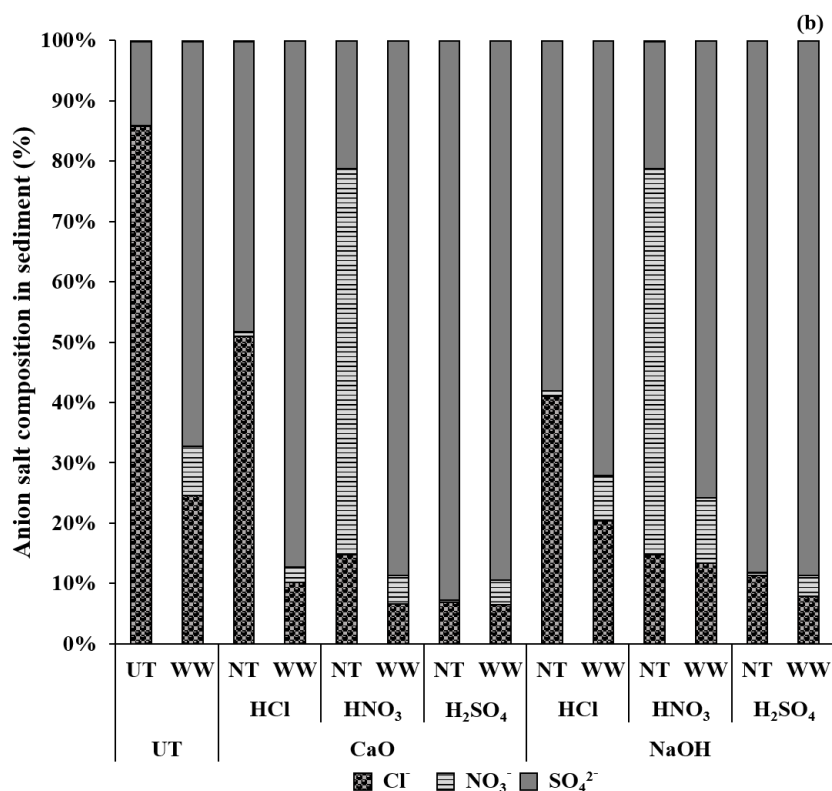


Figure 2.4. Compositions of salts in untreated sediment, acid washing and neutralization treatment applied sediment and acid washing and neutralization treatment applied sediment after water washing: Composition of (a) cation salts (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) and (b) anion salts (Cl^{-} , NO_3^{-} and SO_4^{2-}) for untreated sediment (UT), neutralized sediment (NT) with CaO or NaOH agent after acid washing with 0.5N HNO_3 , 0.5N HCl or 0.5N H_2SO_4 and water washed sediment (WW) after acid washing.

Table 2.5. Changes in pH and EC_{1:5} in acid washed and neutralized sediment before and after water washing.

		Before water washing		After water washing	
		EC _{1:5}	pH	EC _{1:5}	pH
UT		19.63±0.37	7.82±0.05	0.58±0.02	7.90±0.07
CaO	0.5N HCl	2.52±0.02	7.35±0.03	0.67±0.01	7.34±0.07
	0.5N	2.07±0.01	7.43±0.04	0.56±0.03	7.47±0.09
	HNO ₃				
	0.5N	3.21±0.02	7.13±0.03	0.50±0.01	7.20±0.08
	H ₂ SO ₄				
NaOH	0.5N HCl	2.61±0.12	7.21±0.06	0.36±0.01	7.46±0.09
	0.5N	2.17±0.21	7.47±0.02	0.36±0.01	7.58±0.01
	HNO ₃				
	0.5N	2.98±0.13	7.09±0.06	0.45±0.01	7.49±0.01
	H ₂ SO ₄				

The salinity was similar in the same acid washed sediment regardless of the type of neutralizer. The removal efficiency of salinity was relatively low using sulfuric acid due to formation of gypsum which is known as a sparingly soluble salt^{29,30}. Gypsum is associated with sulfate and calcium ion and it is often used as soil reclamation to address problems related to sodic soil.^{30,31} Unlike the other salts which are readily soluble, the values of EC_{1:5} in sulfuric acid washed sediment were analyzed relatively high due to newly generated gypsum which slowly released calcium and sulfate during acid washing and neutralization, especially treated

sediment with H_2SO_4 and CaO . According to XRD analysis shown in Figure 2.5, gypsum was identified in H_2SO_4 and CaO treated sediment. In addition, the newly formed peak at 348eV in H_2SO_4 and CaO treated sediment presented in Figure 2.6 was identified as gypsum by XPS analysis.³²

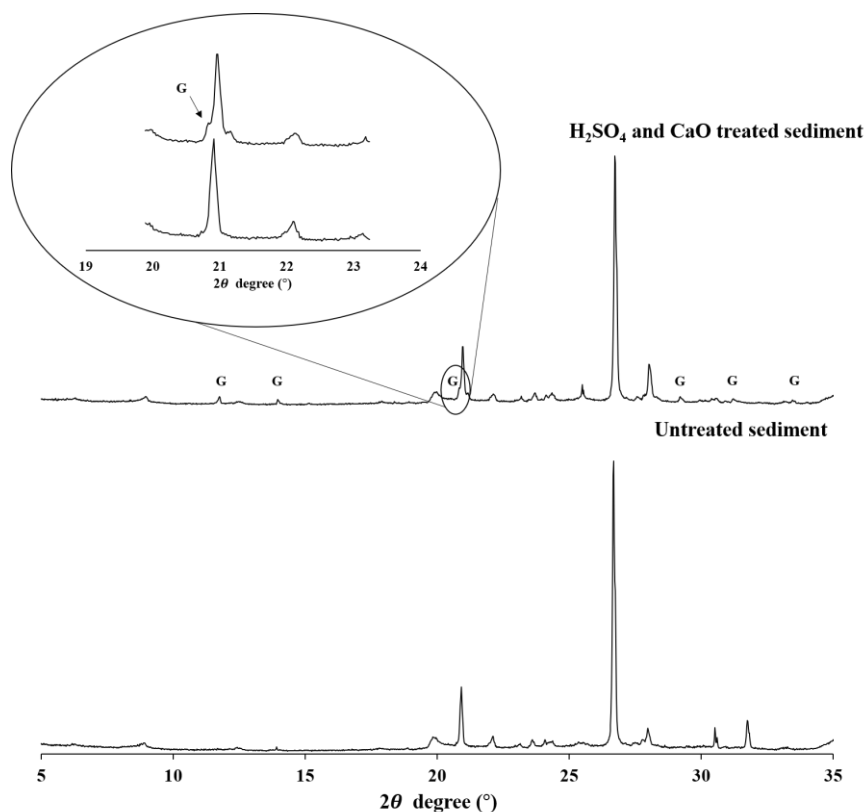


Figure 2.5. X-ray diffraction patterns of untreated sediment untreated and H_2SO_4 and CaO treated sediment. The peak labels are as follows: G, Gypsum.

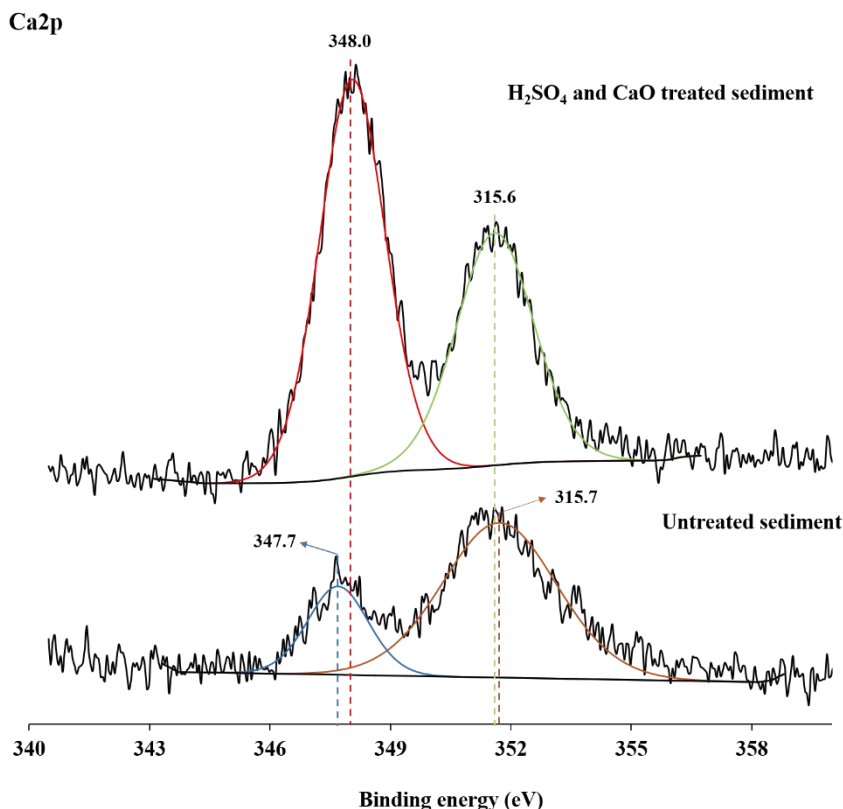


Figure 2.6. X-ray photoelectron spectroscopy of Ca₂p region spectra for untreated sediment and untreated and H₂SO₄ and CaO treated sediment for the identification of gypsum.

The salinity in HCl treated sediment was the second largest due to relatively content of high sulfate salt. The dominant anion salts were determined by applied types of acid solution but the Cl⁻ and SO₄²⁻ proportions in HCl treated sediment were similar. TOC content in HCl treated sediment was relatively lower than the other acid washed sediment, resulting that base cations such as Ca²⁺ and Mg²⁺ during decomposition of organic carbon may be relatively more released. These base cations were reacted with sulfate and formed minerals containing sulfate such as gypsum. The sulfate may be slowly released from the sulfate containing minerals. In addition,

release of sulfur or sulfide in organic³³ and inorganic phases (e.g., carbonate bounded)³⁴ by HCl were oxidized and then produced soluble sulfate during acid washing with HCl. In addition, sulfide from some extracted metal sulfide by HCl with highest heavy metal removal efficiency may be little contribute the formation of sulfate by oxidation reactions. Those may lead to increased sulfate in sediment after acid washing with HCl. HNO₃ treated sediment was the lowest salinity due to less possibility of formation of gypsum, regardless of neutralizer and dominant anion salt was nitrate which was generated from HNO₃ solutions. The dominant cation salts in acid washed and neutralized sediment were determined by applied types of neutralizer (see Figure 2.4). Mg²⁺ proportions were in CaO treated sediment were relatively higher than K⁺ whereas the K⁺ contents were higher in NaOH treated sediment than Mg²⁺ concentrations. It is believed that the affinity between the same valence of cations is higher than different valence cations.³⁵

As discussed above, salts which were identified critical stressors to barley germination and growth were removed by water washing around EC_{1:5} of 0.5 dS m⁻¹ to enhance the fertility of acid washed and neutralized sediment. The EC_{1:5} of water washed sediments with treatment of various acid solutions and neutralizers were shown in Table 2.3. The salinity removal efficiency and residual salt compositions were affected by applied types of acid solution and neutralizer after water washing shown in Figure 2.3. All treated sediments required twice water washing to achieve the targeted sediment salinity but H₂SO₄ and CaO treated sediment was needed three times water washing due to relatively more produced gypsum during treatment. The salinity of CaO treated sediments after water washing was relatively higher than NaOH treated sediment, especially sediment containing more gypsum before water washing. The salinity of H₂SO₄ and CaO treated sediment was the lowest among

CaO treated sediment due to one more water washing applied to meet the target salinity. The salinity of NaOH treated sediment with HCl and HNO₃ were the same and lowest among all treated sediment due to high proportion of readily soluble salts in those sediment before water washing whereas salinity of H₂SO₄ and NaOH treated sediment was relatively high due to relatively high proportion of low soluble salts such as gypsum due to high sulfate content generated from sulfuric acid. After water washing, the dominant cation salts were still determined depending on applied neutralizers but the dominant anion salts became sulfate salt for all cases regardless of applied acid solutions. Sulfate salt contents were relatively high at optimized conditions to form gypsum such as CaO or sulfuric acid treated sediment. HCl and HNO₃ treated sediment which are relatively more difficult to form gypsum may generate soluble sulfate during water washing due to sulfur oxidations using elemental sulfur or hydrogen sulfide.³⁶ The dominant anion salt in untreated sediment after water washing was also sulfate salt due to the same reactions such as sulfur oxidations and sulfate released from sulfate containing minerals.

2.3.4. Sediment Physicochemical Properties

The sediment physicochemical properties shown in Table 2.4 were not significantly changed after acid washing except TP. TOC was reduced 20-25% after acid washing but this reduction was relatively less than literature data³⁷. It is assumed that the abundant forms of organic carbons in sediment may be acid resistance forms such as humic acid and black carbon^{10,38}. The TN and CEC which can be affected by the changes in sediment organic matter³⁹ were not significantly changed after acid washing due to less changes of organic matter and minerals. The TP contents decreased 47-51% after acid washing. It is highly suspected that the leached

phosphorus by acid solutions is in labile forms of phosphorus such as water soluble, readily resorbable and low acid resistant phases of organic phosphorus.⁴⁰⁻⁴² However, the residual TP contents in acid washed sediment may be still sufficient for plant growth. The changes in sediment physicochemical properties after acid washing may be still fairly maintained to provide the environment for plant growth. TPH contents in sediment before and after acid washing with 0.5N HCl, 0.5N HNO₃ or 0.5N H₂SO₄ shown in Table 2.5 were not significantly affected by acid washing. This is in agreement with the literature.²²

Table 2.6. TOC, TN, TP, CEC and WHC in untreated sediment untreated (UT) and 0.5 N HCl treated sediment, 0.5 N HNO₃ treated sediment and 0.5 N H₂SO₄ treated sediment.

	TOC (%)	TN (%)	TP (mg kg ⁻¹)	CEC (cmol kg ⁻¹)
UT	4.85±0.02	1.13±0.01	2453±16	30.6±1.69
0.5 N HCl	3.64±0.08	1.22±0.01	1303±34	32.5±0.96
0.5 N HNO ₃	3.87±0.14	1.14±0.01	1235±16	34.8±1.62
0.5 N H ₂ SO ₄	3.85±0.18	1.13±0.01	1197±21	35.1±1.03

Table 2.7. TPH contents in sediment before and after acid washing with 0.5N HCl, 0.5N HNO₃ or 0.5N H₂SO₄.

	UT	0.5N HCl	0.5N HNO ₃	0.5N H ₂ SO ₄
TPH	7559±241	7485±379	6877±259	8334±98
(mg kg ⁻¹)				

2.3.5. Barley Germination and Growth test after Acid Washing and Neutralization Treatment

The barley germination and growth test was conducted to investigate the enhancement of sediment fertility before and after acid washing and neutralization treatment and the results were shown in Figure 2.7. The germination of root and shoot reached 100% in all treated sediment, which can be attributed that the sediment salinity and significantly decreased heavy metal mobility after treatment. As discussed above, the high contents of salts in dredged marine sediment is identified critical plant stressors. By reducing the sediment salinity during the removal of heavy metals and neutralization treatment, the treated sediment can provide the plant growable environment without additional treatment for salinity removal. From this result, it is verified that the dredged marine sediment with high salts contents can be beneficially used as plant growable medium after applying the suggested treatment processes in this study.

The different acid solutions and neutralizer differently affected on root and shoot growth (Root growth: ANOVA: $\alpha < 0.05$, $F = 55.76$, $df = 6$, $p < 0.001$; Shoot growth: ANOVA: $\alpha < 0.05$, $F = 19.01$, $df = 6$, $p < 0.001$). However, the different

removal efficiencies of total contents and mobility of heavy metals by depending on types of acid solutions and neutralizers were not significantly correlated to barley growth due to still high sediment salinity in acid washed and neutralized sediment. In addition, the sediment physicochemical properties after acid washing were also similarly changed regardless of applied treatment agents, resulting in no significant effect of sediment physicochemical properties on barley growth depending on types of acid solutions.

The barley growth in acid washed and neutralized sediment was influenced by changed sediment salinity and the compositions of salt ions. Firstly, the applied neutralizer showed significant impacts on root and shoot growth. Root and shoot growth in CaO treated sediment more improved in NaOH treated sediment. The dredged sediment originated from the ocean originally included enormous amount of sodium salt and the NaOH treated sediment solely contained sodium salt with less 7 percent of other cation salts. Abundant Na^+ , which is known as a toxic ion and deterioration of soil structure^{8,43} in NaOH treated sediment had negative effects on plant growth^{9,44}, indicating that root and shoot growth in NaOH treated sediment was more inhibited than CaO treated sediment. The excessive amount of Na^+ in sediment may occur deteriorate of sediment structure and it leads to hydraulic problems such as waterlogging and air availability.⁴⁵ Ca^{2+} released from the CaO can be used as plant nutrition¹³ and alleviate toxic effects of Na^+ by replacing Na^+ absorbed on clay particle and plant cell with Ca^{2+} .⁴⁶⁻⁴⁸ By replacing Na^+ with Ca^{2+} on clay particles, negative impacts of Na^+ on soil structure and its toxic effects on plant growth can be also addressed and alleviated. Inhibited K^+ uptake in Na^+ abundant dredged marine sediment can be also enhanced after applying the CaO treatment.^{47,49}

Among CaO treated sediment, the growth of root and shoot was enhanced

in the order of HNO_3 , H_2SO_4 and HCl . The salinity of CaO treated sediment with HNO_3 was relatively lower than the other CaO treated sediments. The essential nutrient intake of NO_3^- by plant can be restricted in high saline environment.^{50,51} The barley growth in nitric acid treated sediment would be more improved due to relatively more reduced osmotic stress from salinity and the increase of the availability of NO_3^- as a nutrient for barley growth.⁵² The barley growth in CaO treated sediment with H_2SO_4 was higher than in HCl treated sediment even though the salinity of CaO treated sediment with H_2SO_4 was higher than HCl treated sediment due to less toxic effects of SO_4^{2-} rather than Cl^- .²⁹ The abundant Cl^- in HCl treated sediment can inhibit the barley growth as a plant stressor with toxic effects^{44,51} and an inhibitor of NO_3^- uptake⁴⁹. The inhibition effect of Cl^- on NO_3^- uptake by plants can be also alleviated in divalent cation salt Ca^{2+} abundant environment rather than monovalent Na^+ sufficient environment.⁴⁹ In addition, the transport of Cl^- from root to shoot can be also reduced by Ca^{2+} , resulting in alleviation of negative effect of Cl^- on shoot growth CaO treated sediment.⁴⁹

The growth of root and shoot in NaOH treated sediment was enhanced compared with untreated sediment but these increases were lower than CaO treated sediment in all cases. Na^+ plays a role as a plant stressor and inhibits the plant uptake of essential cations such as K^+ and Ca^{2+} , resulting in reduced plant growth and nutrition imbalance.⁵¹ In addition, the sediment structure was negatively affected by excessive Na^+ content in NaOH treated sediment.⁴³ The root growth in NaOH treated sediment was not significantly different depending on applied acid solutions due to critical toxic effects of sodium salts but shoot growth was more sensitively affected by types of acid solutions. The barley growth in HNO_3 treated sediment was most improved among NaOH treated sediment. This result was the same as the result of

CaO treated sediment. HNO_3 treated sediment was lowest salinity among NaOH treatment due to lowest possibility of gypsum formation and the dominant NO_3^- originated from HNO_3 acid may be also used as nutrition for shoot growth. In addition, the dominant NO_3^- content in this sediment can also alleviate the toxic effect of Cl^- on plant growth.⁸ The shoot length in HCl treated sediment was slightly longer than H_2SO_4 treated sediment due to relatively low salinity and better reduction of heavy metal mobility. However, the difference of shoot length between both sediments was not significantly different.

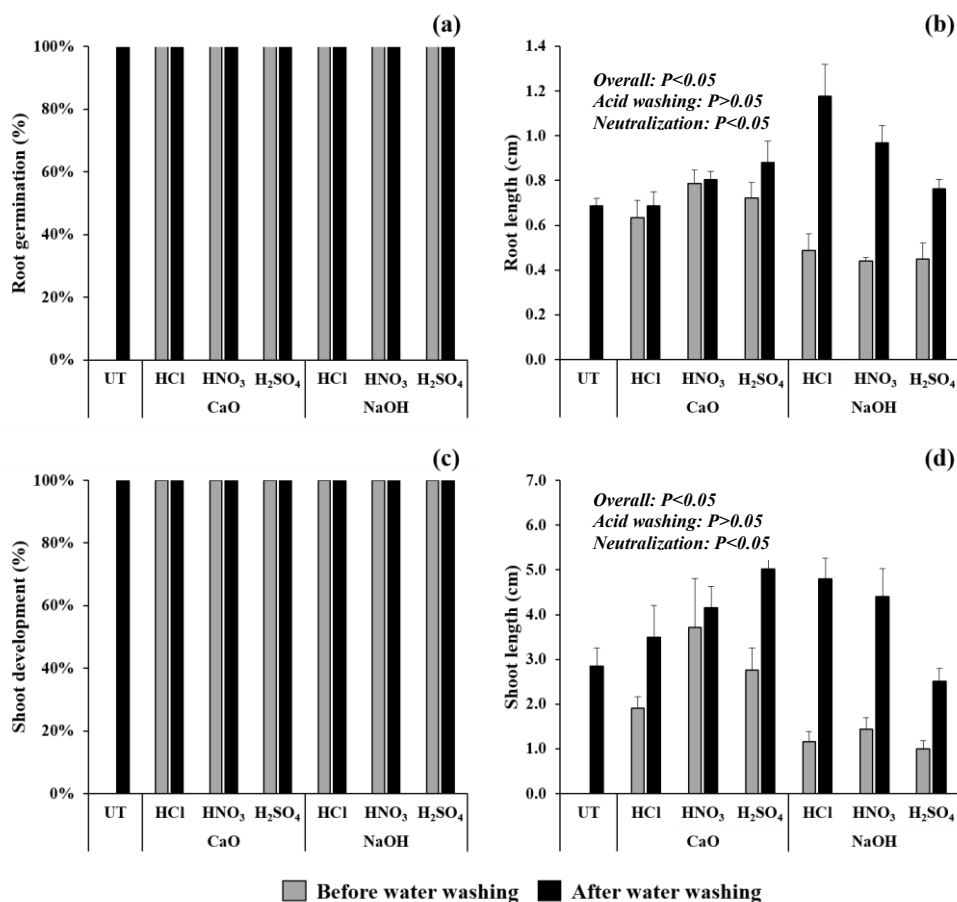


Figure 2.7. Barley (*H. vulgare*) germination and growth test results: (a) root germination, (b) shoot development, (c) root length, and (d) shoot length. UT: untreated sediment; HCl: Acid washed sediment with 0.5 N HCl solution; HNO₃: Acid washed sediment with 0.5 N HNO₃ solution; H₂SO₄: Acid washed sediment with 0.5 N H₂SO₄ solution; CaO: Neutralized sediment with CaO after acid washing; NaOH: Neutralized sediment with NaOH after acid washing.

2.3.6. Barley Germination and Growth test after Water Washing

After water washing, the root and shoot growth shown in Figure 2.7 increased 1.02-2.41-folds and 1.12-4.13 folds, respectively. From these results, the sediment fertility was effectively enhanced by water washing. The improved barley growth was attributed to reduced osmotic stress which require less energy for plant to uptake water.⁷ The reduced concentrations of specific toxic ions such as Na^+ and Cl^- also positively contributed the enhanced barley growth. In addition, the nutrition deficiency was also alleviated by reducing specific salts such as Na^+ and Cl^- that interfere with the uptake of nutrients such as K^+ , Ca^{2+} and NO_3^- .

Within the same neutralizer applied sediment, more reduced salinity for root and shoot lengths showed the more improved barley growth for all cases. The growth of root and shoot in NaOH treated sediment with HCl and HNO_3 was almost highest with the biggest growths rate after water washing due to the lowest sediment salinity which were least likely to form gypsum and the significant reduction of toxic ions such as Na^+ and Cl^- . Despite the similar salt ion compositions in NaOH treated sediment regardless of acid solution after water washing, the root and shoot growth in sulfuric acid treated sediment containing gypsum was lowest due to relatively high residual salinity after water washing. Between HCl and HNO_3 treated sediment with the NaOH treatment which were the same salinity, almost similar salt ion compositions and sediment characteristics after all treatment, root and shoot growth of HCl treated sediment was higher than HNO_3 treated sediment due to relatively higher removal efficiency of heavy metal mobility. It is highly suspected that the difference in the reduction of heavy metal mobility depending on acid solutions influenced barley growth by reducing strong plant stress effects from significantly reduced sediment salinity after water washing. In case of CaO treated sediment, the

barley growth was also most improved H_2SO_4 treated sediment due to the lowest salinity with the one more water washing in order to meet the target sediment salinity. The growth rate of root was relatively lower than those of shoot in CaO and NaOH treated sediment after water washing, which can be attributed that the root is more sensitive to plant stressors such as salinity and residual contaminants in treated sediment. Between NaOH and CaO treated sediment with H_2SO_4 treatment, the growth of root and shoot were in CaO treated sediment much higher than in NaOH treated sediment even though the salinity of NaOH treated sediment was slightly lower than CaO treated sediment. As mentioned above, the sodic soil which abundantly contains Na^+ in sediment can provide the negative environment on barley growth due to its toxicity, inhibition of other nutrition uptake and sediment structure deterioration. It should be noted that the CaO treated sediment with the proper sediment salinity treatment can provide better plant growable environment than NaOH treated sediment for the consideration of the long-term application of acid washed and neutralization treated sediment for planting soil.

2.4. Implications

In this study, we demonstrated that the dredged marine sediment can be beneficially used as inland plant growable resources by the suggested treatment processes in this study. The salts in dredged marine sediment was identified as critical plant stressors. The sediment salinity, salt compositions and sediment removal efficiency were changed depending on the applied acid solutions and neutralizers. The amount of newly produced gypsum significantly affected the sediment salinity after treatment. These changes significantly influence barely growth. After acid washing and neutralization treatment, the treated sediment can provide the plant growable environment due to significantly reduced sediment salinity without additional salinity removal treatment. In addition, the problems from the source-originated Na^+ in dredged marine sediment such as sediment structure degradation, toxic effects and nutrition imbalance can be alleviated by applying the Ca^{2+} from CaO neutralizers. From these results, it was found that the optimized treatment condition can improve the treated sediment quality with efficient removal of target contaminants.

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CHAPTER 3

Development of a low-temperature thermal treatment process for the production of planting soil using petroleum-impacted dredged sediment

3.1. Introduction

A substantial amount of dredged sediment is generated annually around the world to support human activities; for example, the management of navigational channels and the development of harbors.¹ Because disposal of dredged material may result in serious environmental and socioeconomic concerns, the beneficial use of this material is considered a sustainable alternative. Sediment that has been influenced by human activities may contain hazardous substances at significant levels, such that the application of remediation techniques is required to protect humans and the environment at the site where the dredged sediment is beneficially used. Most often, the potential human and environmental concerns caused by the presence of hazardous substances are addressed by treating dredged sediment to meet a preset regulatory limit. However, remediation techniques designed to meet the regulatory limit may fail to generate a product with properties desirable for beneficial use. For example, when dredged sediment is considered for use as a soil that supports plant growth (e.g., in agriculture, in recreational areas, for gardening), a negative impact on the physicochemical properties of sediment caused by the application of

harsh conditions for contaminant removal may be a significant concern.²⁻⁴

Thermal treatment offers several advantages for the treatment of petroleum-impacted dredged sediments to produce a planting soil. Thermal treatment deals with a wide range of petroleum hydrocarbons in soils and dredged sediments with high removal efficiency and reliability.³ It is a rapid process^{5,6} thus minimizing the spatial demand and costs involved in the storage of dredged sediment. Although thermal treatment applied under harsh conditions (e.g., incineration and smoldering) can negatively affect the soil/sediment properties related to their quality as planting media^{2,3} recent studies have suggested that the heat temperature and treatment time could be optimized to preserve the indigenous sediment properties favorable for plant growth, while maintaining a desired treatment efficiency for petroleum hydrocarbons.^{3,6,7} It has been reported that the mobility of heavy metals in soils or sediments changes after thermal treatment, often toward reduced mobility.^{8,9} The potential capability of thermal treatment to reduce the mobility of heavy metals may help improve the quality of the treated sediment as a planting soil when heavy metals exist as co-contaminants at relatively low level. Overall, thermal treatment has the potential to accomplish control over the source-originating plant stressors (i.e., removal of petroleum hydrocarbons and reduction in heavy metal mobility), while preserving the sediment physicochemical properties favorable to the fertility of the resulting medium. To take advantage of the potential of thermal treatment, a collective knowledge of the changes made by thermal treatment to sediment physicochemical properties and mobility of heavy metals in sediment is required. However, studies in the literature that comprehensively investigated such changes by thermal treatment and related the changes to the quality of treated sediments as planting media are rare. Previous studies have shown that the thermal treatment of

soils or dredged sediments may result in either increased or decreased ecotoxicity^{3,7,10}, suggesting the potential generation of toxicants during thermal treatment. However, studies in the literature that correlate the increased soil or sediment ecotoxicity by thermal treatment with the generation of toxicants are rarely found.

In this study, a bench-scale low-temperature thermal treatment process was employed to remove petroleum hydrocarbons from a dredged sediment and produce a planting soil. Sediment physicochemical properties were comprehensively evaluated, and the behavior of heavy metals in sediment was assessed to identify changes caused by the thermal treatment. Barley germination and growth tests were conducted using the treated sediment, and the results were analyzed along with changes in the observed sediment physicochemical properties, demonstrating that soluble organics and sulfate salts generated during the treatment act as major plant stressors for the treated sediment. We showed that the thermal treatment process could be modified to further improve the quality of the treated sediment as a planting medium.

3.2. Materials and methods

3.2.1. Sediment Collection and Pretreatment

Petroleum-impacted marine sediment used in this study was dredged from a highly industrialized harbor area in Korea. After transferring the sample to the laboratory, the sediment was air-dried and then thoroughly hand-mixed for homogenization. For the purpose of the current study, the sediment sample (Pretreated sediment with water-washing pretreatment, PT_{ww}) was pretreated by washing with deionized (DI) water to achieve an electrical conductivity of the 1:5 (w:w) sediment slurry (EC_{1:5}) of $<0.5 \text{ dS m}^{-1}$. This pretreatment was to rule out the potential contribution of source-originated salts on the barley germination and growth tests conducted in the current study. Our preliminary investigation revealed that source-originated salts have substantial adverse impacts on the germination and growth of barley and that this phytotoxic effect could be minimized by removing the salts to EC_{1:5} $<0.5 \text{ dS m}^{-1}$ by water washing. It was verified that the water washing did not significantly affect the sediment total petroleum hydrocarbon (TPH) and heavy metal concentrations (Table 2.2 in the Chapter 2), or the sediment physicochemical properties (Table 2.1 in the Chapter 2). The water-washed sediment was air-dried and then stored at $25 \pm 0.5 \text{ }^{\circ}\text{C}$ until use. Concerns related to the impact of source-originated salts on dredged marine sediment treatment and reuse are not within the scope of the current study. However, we note that these concerns should be thoroughly addressed in future studies.

3.2.2. Sediment Thermal Treatment and its Modification

Low-temperature thermal treatment was applied to the sediment that had

been pretreated by water washing. The regulatory requirement for the treatment was set as achieving a sediment TPH concentration of $<500 \text{ mg kg}^{-1}$. This TPH concentration is the Korean regulatory standard for soils in agricultural, residential, and recreational areas.¹¹ A 640-cm^3 heat-resistant glass container containing 50 g dry weight (dw) of sediment was placed in a muffle furnace, preheated to the target temperature. The thermal treatment was conducted at $300 \text{ }^{\circ}\text{C}$ for 30 mins without gas purging. This thermal treatment condition was determined after conducting a set of preliminary tests for thermal treatment at different temperatures and residence times, as shown in Table 3.1.

Table 3.1. TPH concentrations (mg kg^{-1}) in sediment before and after thermal treatment for preliminary study to determine heating temperature and treatment time. The TPH detection limit is 50 mg kg^{-1} . All treatment conditions meet the regulatory requirement of $<500 \text{ mg kg}^{-1}$. The thermal treatment condition of $300 \text{ }^{\circ}\text{C}$ for 30 min was selected in this study for its least intensiveness among the treatment conditions evaluated. Further reduction in heating temperature or treatment time is expected to result in potential failure of meeting the regulatory requirement.

	30 min	60 min	90 min	120 min
300 $^{\circ}\text{C}$	350	327	ND	ND
350 $^{\circ}\text{C}$	ND	ND	ND	ND

ND: Not Detected

As described below, the low-temperature thermal treatment of sediment resulted in the production of byproducts remaining in the treated sediment, which

exhibited phytotoxic effects. A modified laboratory thermal treatment process was employed to remove these byproducts. One method of modification was to apply enhanced ventilation during the thermal treatment to immediately discharge the generated off-gases using a customized ventilation machine. The ventilation machine had a nominal discharge rate of 10 m³/min, which was sufficient to immediately sweep out the off-gases released to the inner volume of the furnace (approximately 0.0045 m³). The other method was to apply a water washing post-treatment. DI water was added to the thermally treated sediment to obtain a 1:5 (w:w) sediment slurry. The slurry was agitated for 2 hours at 180 rpm and then centrifuged at 14,000 × g for 10 mins to separate out the supernatant. The procedure of water addition, agitation, centrifugation, and supernatant removal was repeated for a total of three events. The final supernatant collected was passed through a 0.45-μm syringe filter for EC_{1:5}, pH, sulfate, and total organic carbon (TOC) analyses. The settled solids were air-dried for use in the barley growth and germination experiment.

3.2.3. Physicochemical Property Analysis

TOC and TN concentrations were analyzed using the Walkley-black method¹² and the Kjeldahl method¹³, respectively. Phosphorus in sediment was extracted using aqua regia following Chen and Ma¹⁴ and then the extract was analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Technologies, Santa Clara, CA). Bulk elemental analysis was conducted using two elemental analyzers: Thermofinnigan Flash EA2000 (UK) for carbon, hydrogen, nitrogen, and sulfur content and Thermofinnigan Flash EA1112 (UK) for oxygen content. EC_{1:5}, pH, and SOC and soluble sulfate concentrations were analyzed in a 1:5 (w:w) sediment slurry. The slurry was prepared by adding 5 g dry

weight (dw) sediment and 25 ml DI water in a 50-ml conical tube and then agitating it on a horizontal shaker for 2 hours at 180 rpm. The tube was centrifuged at $14,000 \times g$ for 10 mins, and the supernatant was collected and passed through a 0.45- μ m syringe filter prior to analysis. A multi-parameter meter (Orion 5 star, Thermo Fisher Scientific, USA) equipped with a pH electrode and a conductivity cell was used for EC_{1:5} and pH measurements. Sulfate was analyzed using ion chromatography (DX-500, Dionex, US) equipped with an AS14 anion column and a CD20 conductivity detector. SOC was determined using a Shimadzu TOC analyzer (V-CPH, Shimadzu, Japan). All analyses were conducted using triplicate samples.

3.2.4. TPH, Volatile Organic Carbon, and Heavy Metal Analysis

The TPH in sediment was measured using Korea standard method for soil analysis.¹¹ Twenty-five gram dry weight of sediment was mixed with anhydrous sodium sulfate (Na₂SO₄) to remove water. The sediment was extracted with 100 ml dichloromethane using a sonicator (duty cycle of 50%, pulse mode of 1 second) for 3 mins. After repeating this step twice, the extract was filtered using No. 5 filter paper (4 μ m pore size). The filtered extract was mixed with Na₂SO₄ to remove the moisture content in the extract and then filtration was conducted again to remove Na₂SO₄ in the extract. The extract was concentrated to 2 ml using nitrogen gas. The TPH concentration in the concentrated extract was analyzed by a gas chromatograph with a flame ionization detector (GC-FID, Agilent Technologies, Santa Clara, CA) using a DB-5 capillary column (30 m \times 0.32 mm \times 0.25 μ m). The carrier gas was helium (1–2 mL min⁻¹) and the injection volume was 2 μ L. The oven temperature was initially set at 50 °C for 2 mins, increased at 10 °C/min to reach 320 °C, and then held at 320 °C for 10 min. The temperature of injector and detector were 300

°C and 320 °C, respectively. The TPH concentration was calculated by integrating the total area of n-alkanes (C8-C40) based on the calibration curve of an n-alkane mixture (C8–C40).

Volatile organics may be generated during thermal treatment, and these substances may adversely affect the quality of the product as a planting medium. For example, it has been reported that pyrolysis processes to convert biomass into biochars produced a significant amount of volatile organics, which exhibit toxicity to terrestrial organisms.^{15,16} Therefore, we analyzed the volatile organic carbon (VOC) content in the treated sediment. The analysis procedure followed US EPA 8260B (1996).¹⁷ Five grams of sediment in dry weight was placed in a pre-weighed 40 ml amber glass vial with 10 ml of methanol. An internal standard (fluorobenzene) was injected into the vial and then Na₂SO₄ was added in the vial to remove moisture. The vial was shaken for 2 mins to solubilize VOCs and the slurry was allowed to be settled. The supernatant was collected and analyzed using a purge and trap coupled to a gas chromatography with a mass selective detector (P&T GC-MSD, P&T; Teledyne Tekmar, Mason, OH, GC; Agilent 6890N , MSD; Agilent 5975, Agilent technologies, Palo Alto, CA) equipped with a DB-VRX column (60 m×0.25 mm× 1.4 µm).

Sequential extraction procedure (SEP) was applied to assess the changes in the chemical forms of heavy metals present in the untreated and treated sediments. A procedure proposed by Tessier¹⁸ was employed, which divides heavy metals in a solid medium into five fractions. A slight modification applied in the current study is to substitute the original procedure of digestion with HF-HClO₄ mixture with a microwave digestion procedure following USEPA 3052 for the final (i.e., 5th) extraction step. This modification was intended to enhance the exhaustiveness of the

final extraction step. The sum of the concentration of the five SEP fractions was assumed to be equivalent to the total heavy concentration determined by the USEPA 3052 method. More details on the modified SEP method are found in Kim et al.¹ The toxicity characteristic leaching procedure (TCLP) was conducted according to USEPA Method 1311 to assess the mobility of heavy metals in sediments before and after treatment.¹⁹ Two grams (in dry weight) of a sediment sample was mixed with 40 ml of an acetic acid solution (adjusted to pH 2.88 ± 0.05) for 18 hr at 30 rpm using an end-over-end shaker. The sediment slurry was centrifuged at $14,000 \times g$ for 10 mins for supernatant collection. The liquid samples obtained from either SEP or TCLP were passed through a 0.45- μm syringe filter and then analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Technologies, Santa Clara, CA).

3.2.5. Spectroscopic Analysis

Spectroscopic techniques were employed to identify the structural changes in organic and inorganic constituents in sediment after the thermal treatment. X-ray photoelectron spectroscopy (XPS; AXIS-Hsi, KRATOS, UK) with an Al K α X-ray source (1486.6 eV) was employed to identify changes in the carbon content on the sediment mineral surface. The Casa XPS program was used to deconvolute the XPS data. Attenuated total reflection Fourier transform infrared (ATR-FTIR) analysis was conducted to identify changes in the organic functional groups. A Nicolet FTIR spectrophotometer (model 6700, Thermo Scientific, USA) was used to obtain FTIR spectra ranging from 650-4000 cm^{-1} , with an 8- cm^{-1} -resolution at an average of 32 scans. X-ray diffraction (XRD; D8 Advance, Bruker, Inc., Germany) was used to analyze crystalline minerals with Cu-K α radiation, operated at 40 kV and 40 mA and

a scanning range of 5°-90°.

3.2.6. Barley Germination and Growth Test

Barley (*Hordeum vulgare* L.) was employed as a test species to evaluate the phytotoxicity and fertility of the sediment before and after the thermal treatment. *H. vulgare* L. is recognized as one of the representative ecotoxicity test species in international standards such as the International Organization for Standardization (ISO). This species is widely applied to evaluate the phytotoxicity of various organic and inorganic contaminants^{20,21} and allows for relatively easy management in the laboratory and a short test duration.²¹ In each 30-g sediment sample, prepared in a 100-ml polyethylene dish, ten barley seeds were placed, and DI water was added to the field capacity of the sediment. Triplicate samples prepared for each treatment were incubated in a growth chamber (E15, Conviron, Inc., Canada) at a constant temperature of 23 °C, with a 16:8 light:dark photoperiod for 10 days. The root germination rate, shoot development rate, and root and shoot lengths were measured after the incubation.

3.3. Results and discussion

3.3.1. TPH Removal Efficiency

The petroleum-impacted sediment, which had a moderate TPH contamination level ($4922 \pm 328 \text{ mg kg}^{-1}$), was successfully remediated to meet the regulatory standard of $<500 \text{ mg kg}^{-1}$ using the low-temperature thermal treatment. The TPH content of the treated sediment was $350 \pm 68 \text{ mg kg}^{-1}$, showing a TPH removal efficiency of 93%. The shape of the GC-FID chromatogram for the TPH extract of the sediment before the treatment indicated the dominance of a relatively heavier petroleum fraction and was close to that for weathered Bunker C oil (Figure 3.1)²², suggesting the influence of human activities at the sampling site (i.e., a highly industrialized harbor). The fact that the low-temperature thermal treatment showed a high efficiency in reducing the relatively heavier petroleum fraction demonstrates the applicability of the technique for a wide range of petroleum-impacted sediments.

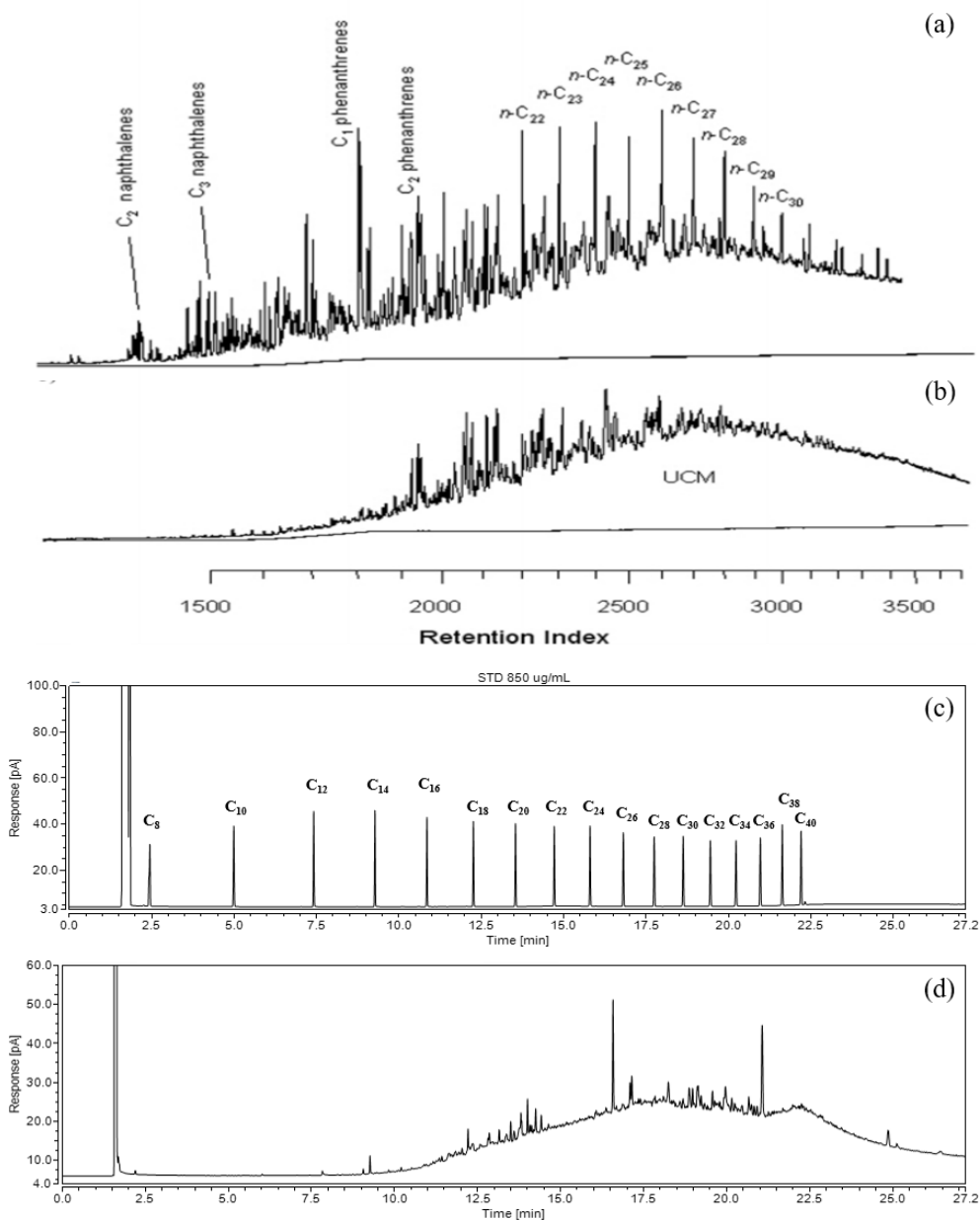


Figure 3.1. Gas chromatograms of extracts of sediment samples collected at a Bunker C oil spill site (a) 12 days and (b) 179 days after the spill presented in Nelson et al.²² and (c) a 850 $\mu\text{g mL}^{-1}$ TPH calibration standard and (d) an extract of the study sediment obtained in this work. GC chromatograms for (c) and (d) were analyzed by GC-FID. The retention index axis in panels (a) and (b) is indicative of the carbon number range from n -C₁₅ to n -C₃₇. Panels (a) and (b) were reprinted by

permission of the publisher (Taylor & Francis Ltd, <http://www.tandfonline.com>). Full bibliographic details of the figure source (Nelson et al.²²) are provided in the reference list at the end of this document.

3.3.2. Physicochemical Properties of Thermally Treated Sediment

Most of the sediment physicochemical properties were not significantly changed after the thermal treatment (**Table 3.2**). The conservation of sediment physicochemical properties can be attributed to the relatively low temperature and short heating time applied in the current study.⁵ The sediment TN and TP concentrations were slightly increased, which can be explained by the negligible mass removal of nitrogen and phosphorus from the sediment and a slight reduction in the bulk sediment weight due to organic matter decomposition and dehydration during the treatment.⁷ Sediment TOC content was not considerably changed, indicating that decomposition of sediment organic matter was not pronounced (discussed further in the following subsection). The sediment CEC value was also not significantly changed. Changes in CEC during thermal treatment of sediment result from the decomposition and deformation of sediment organic matter and the deformation of clay minerals.^{7,23} As stated above, the sediment TOC content was not significantly changed by the treatment, and the oxygen-containing functional groups of sediment organic matter were only slightly changed, as discussed in detail in the following subsection, along with the FTIR spectra. The clay contents were also only slightly changed (from 15.44% to 13.12% on the sediment dry wt basis; a 15.0% reduction; Table 3.3) by the thermal treatment. XRD analysis results presented in Figure 3.2 show that the sediment mineralogy was not significantly changed by the thermal treatment.

Table 3.2. Changes in pH, EC_{1:5}, TOC, TN, TP and CEC before and after thermal treatment.

	pH	EC _{1:5} (dS/m)	TOC (%)	TN (%)	TP (mg/kg)	CEC (cmol/kg)
Pretreated sediment	7.66	0.40	3.81	0.635	1708	35.32
Thermally treated sediment	7.04	1.58	3.54	0.688	1841	35.22

Table 3.3. Proportion of sand, silt and clays before and after thermal treatment.

Sample	Sand (%)	Silt (%)	Clay (%)
Pretreated sediment	39.32	45.24	15.44
Thermally treated sediment	62.64	24.24	13.12

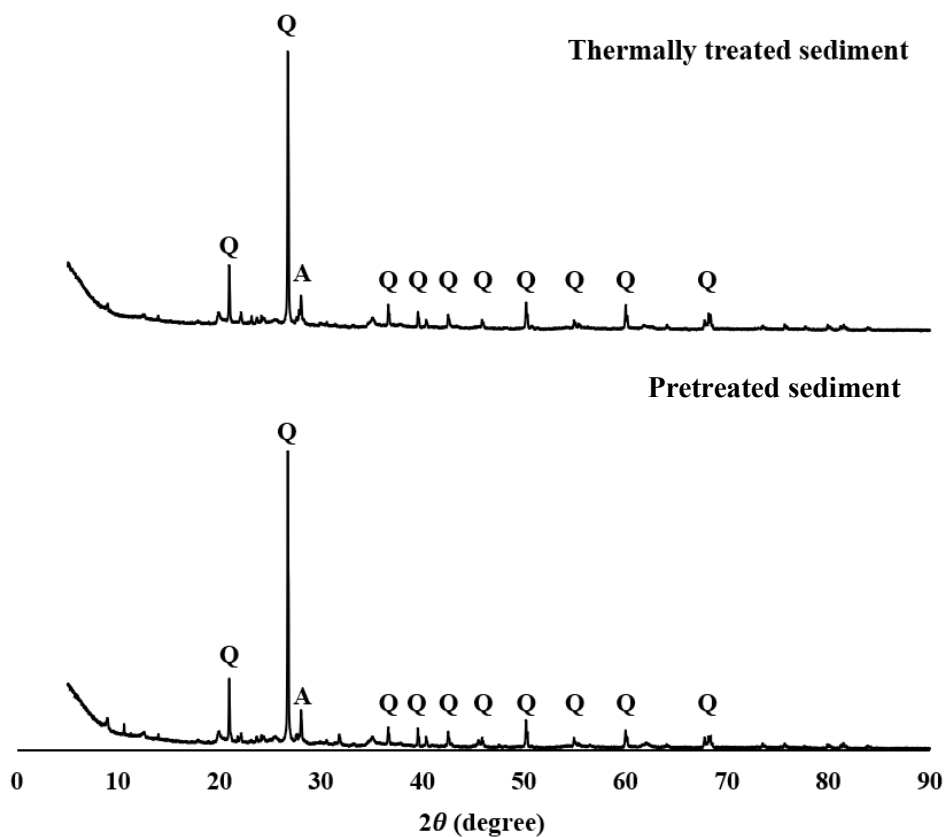


Figure 3.2. X-ray diffraction (XRD) patterns of pretreated sediment and thermally treated sediment. The peak labels are as follows: Q, Quartz; A, Albite.

Conventional soil and sediment thermal treatment techniques that employ high temperature (e.g., incineration and smoldering) have been reported to substantially change soil/sediment characteristics such as organic matter and nutrient contents.⁷ Pyrolytic treatment of soil and sediment has been suggested in the literature³ as a means to prevent loss of organic matter and to enhance its functions via conversion of organics (indigenous organic matter and/or petroleum) into char. However, pyrolytic soil/sediment treatment generally requires a long treatment time and a supply of a large volume of inert gas, which increases costs and energy

consumption for the treatment.³ The results of the current study show that the low-temperature thermal treatment, applied without gas purging or any other manner of manipulation of the gas composition in the thermal treatment unit, could successfully meet the regulatory treatment requirements, while minimizing changes in the sediment physicochemical properties.

One notable change in the sediment physicochemical properties resulting from the thermal treatment was a difference in the $EC_{1.5}$ value, which increased from 0.40 dS m^{-1} in the pretreated sediment to 1.58 dS m^{-1} in the treated sediment. This increase can mainly be attributed to the oxidation of reduced sulfur species in the sediment during the thermal treatment. The soluble sulfate concentration in the sediment increased by approximately 30-fold, from 220 mg kg^{-1} to 6565 mg kg^{-1} , by the thermal treatment. The thermal treatment also resulted in a reduction in sediment sulfur content from 1.03% to 0.63% (Table 3.4). This reduction in sediment sulfur content indicates the formation of gaseous sulfur oxides (e.g., SO_2 and SO_3), further verifying the significant occurrence of sulfur oxidation during the treatment. For the application of the thermal treatment for sediments or other sulfur-rich environmental media, the impacts of the oxidized sulfur species present in the treated product and the off-gas should be carefully considered.

Table 3.4. Changes in elemental composition before and after thermal treatment.

	C (%)	H (%)	N (%)	O (%)	S (%)	H/C ratio	O/C ratio
Pretreated sediment	6.25	1.15	0.43	7.16	1.03	2.21	0.86
Thermally treated sediment	5.06	0.73	0.3	6.12	0.63	1.73	0.91

The sediment pH was slightly reduced by the thermal treatment, but the pH of the treated sediment was still within the neutral range (a value of 7.04; see Table 3.2). O'Brien et al.⁷ compiled literature data to show that soil pH generally remains unchanged or decreases slightly upon heating at <250 °C, whereas heating above 250 °C results in a soil pH increase of 1 unit or even greater. The plausible mechanisms for the pH decrease are various oxidation reactions and carbon dioxide production, followed by its conversion into bicarbonate during the treatment.⁷ Increase in the soil pH, which is pronounced at higher temperatures, is mainly attributed to organic acid decomposition.⁷ The decrease in sediment pH by the thermal treatment at 300 °C observed in this study can be explained as follows: First, because of the richness of sulfur in the study sediment, the effect of proton-releasing sulfur oxidation reactions (e.g., oxidation of hydrogen sulfide or elemental sulfur into sulfate) was pronounced.²⁴ This potential pH-decreasing mechanism further highlights the significance of sulfur oxidation reactions on the treated sediment properties. Second, because of the relatively short heating time (30 min) applied, the decomposition of sediment organic matter, which is the major pH-increasing

mechanism, was insignificant. O'Brien et al.⁷ showed that the extent of soil organic matter decomposition is a strong function of the heating time, showing a much smaller reduction in the organic matter content at shorter heating times.

3.3.3. Changes in Organic and Inorganic Constituents

While the sediment TOC content did not change substantially, some notable changes in the characteristics of organics in sediment were observed after the thermal treatment. FTIR spectra (Figure 3.3) show that the signal for long-chain aliphatics (weak band at 2924 cm^{-1} present in the pretreated sediment, assigned as C-H bonds)²⁵ disappeared after the thermal treatment, which can be attributed to the removal of petroleum hydrocarbons. The reduced amount of sediment TPH content (4572 mg TPH kg⁻¹ or approximately 3980 mg C kg⁻¹, assuming a carbon weight percent of 87% in petroleum oils²⁶) is close to the reduced amount of sediment TOC content (0.27% or 2700 mg C kg⁻¹). Therefore, it is likely that the low-temperature thermal treatment could selectively remove petroleum hydrocarbons from the sediment. Previous studies have shown that thermal treatment at a heating temperature of 300 °C does not result in a significant reduction of sediment TOC of natural organic matter origin.^{7,27}

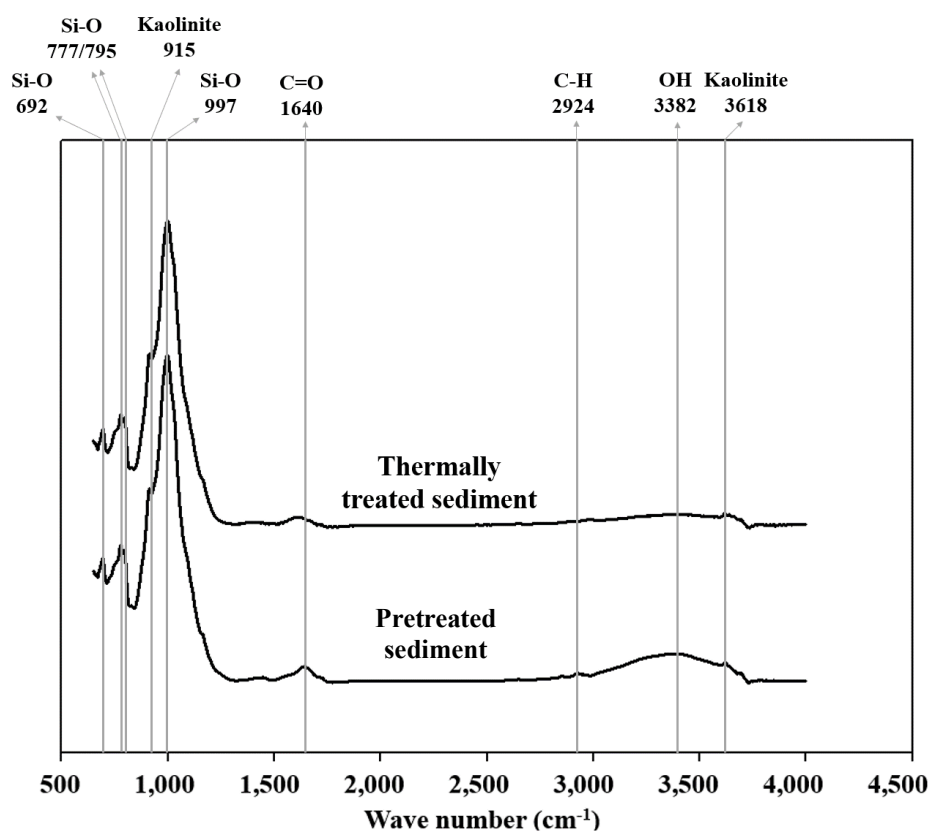


Figure 3.3. FTIR spectra for pretreated sediment and thermally treated sediment.

The surface carbon content was substantially increased (by 22%, relative to the value of the pretreated sediment) after the treatment. An increase in the surface carbon content by low-temperature thermal treatment of soils or sediments has been reported in the literature.^{27,28} This can be explained by the release of organics and their transformation products to the off-gas and the subsequent adsorption of these substances back onto the sediment during the treatment. When the laboratory thermal treatment process was modified by installing a ventilation device, the increase in the surface carbon content was less pronounced (a 3% increase with enhanced ventilation versus a 22% increase without enhanced ventilation), further verifying

this explanation. The soluble organic carbon (SOC) content in sediment was substantially increased, by 4.3-fold, after the treatment (Figure 3.4).

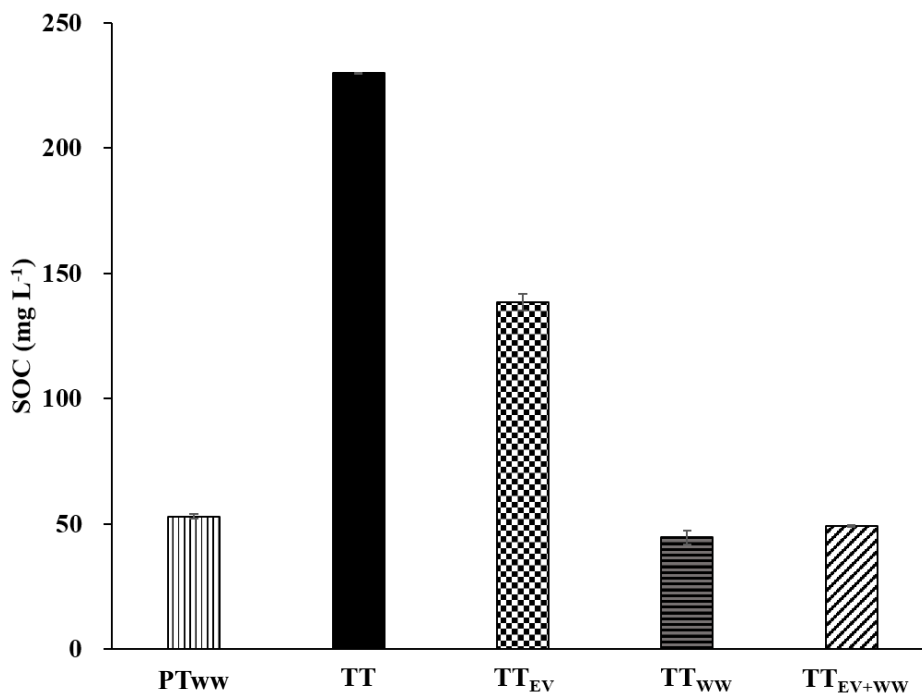


Figure 3.4. Soluble organic carbon (SOC) concentration of pretreated sediment with water washing (PTww), thermally treated sediment (TT), thermally treated sediment with enhanced ventilation (TTEV), thermally treated sediment with water washing (TTww) and thermally treated sediment with enhanced ventilation and water washing (TTEV+ww).

As observed for the surface carbon content, the increase in the SOC content was less pronounced when enhanced ventilation was applied. These results suggest that a portion of the transformation products that adsorbed onto the sediment was readily soluble in water. Chemical transformation of organic contaminants into water-soluble forms during thermal treatment has been reported in the literature.²⁹

Because no gas purging was applied for the thermal treatment in this study, the only external gas supply was from the air present at the beginning of the treatment in the treatment unit, which has an atmospheric composition. Presumably, the oxygen availability in the thermal treatment unit was neither sufficiently high to allow the chemical reactions occurring during the treatment to proceed toward mineralization nor sufficiently low for pyrolysis reactions to be predominant such that only sparingly soluble, condensed carbon remained as a residue in the sediment after the thermal treatment. The low heating temperature and short treatment time applied in the current study were also unfavorable conditions for the completeness of these reactions.^{27,28} However, pyrolysis reactions do occur during the thermal treatment, as evidenced by changes in the sediment elemental composition and a visual inspection of the treated sediment. The H/C ratio, which is indicative of the level of carbon condensation, decreased from 2.21 in the pretreated sediment to 1.73 in the treated sediment (Table 3.4). Darkening of the sediment color after the thermal treatment also indicated the formation of black carbonaceous matter on the sediment surface (Figure 3.5).



Figure 3.5. Photos of pretreated sediment and thermally treated sediment (heating temperature = 300 °C, heating duration = 30 min).

Minor changes in the chemical structure of the sediment organic matter identified by the FTIR spectra are as follows: The broad band near 3382 cm^{-1} arises from the stretching vibration of hydroxyl groups and indicates significant hydrogen bond interactions.³⁰ After the thermal treatment, the intensity of this band decreased due to dehydration reactions and organic matter decomposition.^{30,31} The band at 1640 cm^{-1} is assigned to C=O stretching vibrations of amides, and stretching vibrations of ester carbonyl groups, which are recognized as the hydrophilic portion of organic matter³², were slightly decreased and shifted to 1610 cm^{-1} . This change can be attributed to carbon condensation and dehydration reactions.³² Overall, the FTIR bands assigned to organic functional groups decreased slightly, but not substantially, after the thermal treatment. The elemental analysis results (shown in Table 3.4) indicate that the carbon, hydrogen, and oxygen contents and their ratios were only slightly changed after the treatment, further supporting the conclusion that the

structural changes in sediment organic matter were not substantial. Among the elemental compositions and elemental ratios examined, the changes in the hydrogen content (from 1.15 wt% to 0.73 wt%) and the H/C ratio (from 2.21 to 1.73) were relatively pronounced and were likely the result of the contribution of the carbon condensation reactions of the petroleum hydrocarbons in the sediment. XRD and FTIR results indicate that there was no significant change in mineral structures such as quartz and kaolinite after the treatment. The thermal treatment condition employed in this study is unlikely to affect sediment minerals.⁷

3.3.4. Changes in Heavy Metal Mobility

The fraction of heavy metals leached by TCLP relative to the total heavy metal content is used to assess the relative mobility of heavy metals present in sediment. The TCLP leached fraction was reduced by the thermal treatment for all heavy metals except Pb (Figure 3.6). A sequential extraction procedure (SEP) was employed to investigate the mechanism involved in the reduction of the heavy metal mobility by the thermal treatment. Figure 3.7 shows that the residual fraction (F5) of SEP, which represents the fraction of heavy metals strongly associated with sediment, increased after the treatment for all heavy metals except Pb. The sum of the two SEP fractions most weakly associated with sediment (i.e., F1 and F2) was reduced after the thermal treatment for all heavy metals except Pb (Table 3.5). These results suggest that for most of the heavy metals, repartitioning and/or chemical transformation occurred during the thermal treatment such that a portion of relatively labile forms of heavy metals was converted to less labile forms, resulting in reduced mobility. Previous investigations, conducted using soil and sludge, also reported decreasing labile fractions and increasing non-labile fractions of heavy metals in

response to thermal treatment.^{8,33}

Table 3.5. Concentrations in each sequential extraction fraction and total heavy metal contents (mg kg^{-1}) in sediments before and after thermal treatment. Data are shown as mean \pm standard deviation of triplicate measurements. PT: Pretreated sediment with water washing, TT: Thermally treated sediment.

		Ni	Zn	Cu	Pb	Cd
F1	PT _{ww}	0.10 \pm 0.02	9.11 \pm 0.97	2.16 \pm 0.11	0.55 \pm 0.13	0.55 \pm 0.02
	TT	0.82 \pm 0.05	58.0 \pm 1.3	1.58 \pm 0.14	0.47 \pm 0.12	0.85 \pm 0.01
F2	PT _{ww}	7.71 \pm 0.18	956 \pm 24	12.2 \pm 0.2	6.42 \pm 0.24	1.62 \pm 0.01
	TT	5.95 \pm 0.2	858 \pm 38	5.90 \pm 0.27	9.01 \pm 0.29	1.19 \pm 0.06
F3	PT _{ww}	14.8 \pm 1	869 \pm 10	2.66 \pm 0.26	3.32 \pm 0.21	0.79 \pm 0.01
	TT	12.3 \pm 0.7	1,220 \pm 22	13.8 \pm 3.6	12.0 \pm 3.1	1.03 \pm 0.01
F4	PT _{ww}	14.6 \pm 0.9	405 \pm 16	234 \pm 2	24.1 \pm 1.5	0.35 \pm 0.02
	TT	18.4 \pm 0.2	297 \pm 26	182 \pm 9	24.6 \pm 2.1	0.33 \pm 0.01
F5	PT _{ww}	34.9 \pm 0.4	402 \pm 7	71.6 \pm 3.5	98.8 \pm 1.7	1.82 \pm 0.07
	TT	40.0 \pm 0.7	860 \pm 247	127 \pm 2	90.7 \pm 4.0	2.66 \pm 0.27
F1+2	PT _{ww}	7.81 \pm 0.19	965 \pm 24	14.4 \pm 0.1	6.98 \pm 0.29	2.16 \pm 0.01
	TT	6.77 \pm 0.24	916 \pm 396	7.48 \pm 0.23	9.47 \pm 0.25	2.11 \pm 0.05
Total content	PT _{ww}	72.1 \pm 1.4	2,640 \pm 19	323 \pm 6	133 \pm 3	5.13 \pm 0.08
	TT	77.4 \pm 0.8	3,290 \pm 229	331 \pm 14	136 \pm 6	6.05 \pm 0.29

These changes in heavy metal fractionation can be attributed to the sediment particle aggregation and condensation of organic matter occurring during the thermal treatment. Sediment particle size analysis results (Table 3.3) indicate that the sand fraction increased significantly, while silt and clay fractions were decreased by the treatment. Particle aggregation has been reported to occur during thermal treatment of soils or sediments, resulting in an increased fraction of larger particles.⁷ Aggregation of sediment particles should result in the physical protection of heavy metals against leaching or extraction. As discussed above, carbon condensation occurred during the thermal treatment, as indicated by the increased H/C ratio (an indicator of aromaticity) and the changes in the FTIR spectra. Black carbonaceous matter produced by carbon condensation exhibits a high binding strength relative to heavy metals.³⁴ Therefore, heavy metals present in the sediment may be chemically protected against leaching or extraction, due to the partitioning of heavy metals to the newly formed carbonaceous matter. This explanation may be challenged by the fact that it is F5 (residual fraction) that showed an evident increase, whereas F4, representing the organic matter-bound heavy metal fraction, did not notably increase (or was even decreased) after the treatment. Thus, we analyzed the TOC content in the thermally treated sediment after conducting the SEP up to F4 to examine whether the fourth extraction procedure of the SEP could completely decompose the sediment organic matter, such that exhaustive extraction of organic matter-bound heavy metals was possible. The result showed that a significant amount of TOC remained in the thermally treated sediment (0.79 ± 0.02 wt%) after conducting the fourth extraction procedure. The fourth extraction procedure of the SEP was similar to the procedure decomposing amorphous organic matter in black carbon analysis, which is employed to enable the analysis of black carbon remaining in soils or sediments using TOC

analyzers.³⁵ Therefore, the TOC remaining in the sediment after the fourth extraction procedure of the SEP was expected to be contributed mainly by black carbon, substantiating our explanation of the chemical protection mechanism. The formation of black carbon may also result in an increased physical protection of sediment heavy metals. Black carbon produced during the thermal treatment is likely to be adsorbed onto the sediment surface, as indicated by the increase in surface carbon content after the thermal treatment. The heavy metals associated with sediment minerals are expected to be physically sequestered by the adsorption of black carbon on the mineral surface.

Unlike the other heavy metals, the TCLP-leached fraction exhibited a slight increase in Pb after the thermal treatment, suggesting that mechanisms contributing to the increase in heavy metal mobility may also be present during the thermal treatment. The slight reduction in organic functional groups during the thermal treatment is the likely mechanism that works toward increasing heavy metal mobility. Despite the increase, the TCLP-leached fraction of Pb remained less than 2% for the treated sediment.

In summary, the low-temperature thermal treatment of sediment is generally expected to result in the reduced mobility and increased stability of heavy metals. This additional benefit of the treatment is analogous to the role of stabilizing agents, which are often amended to soils and sediments to control heavy metal mobility and bioavailability.

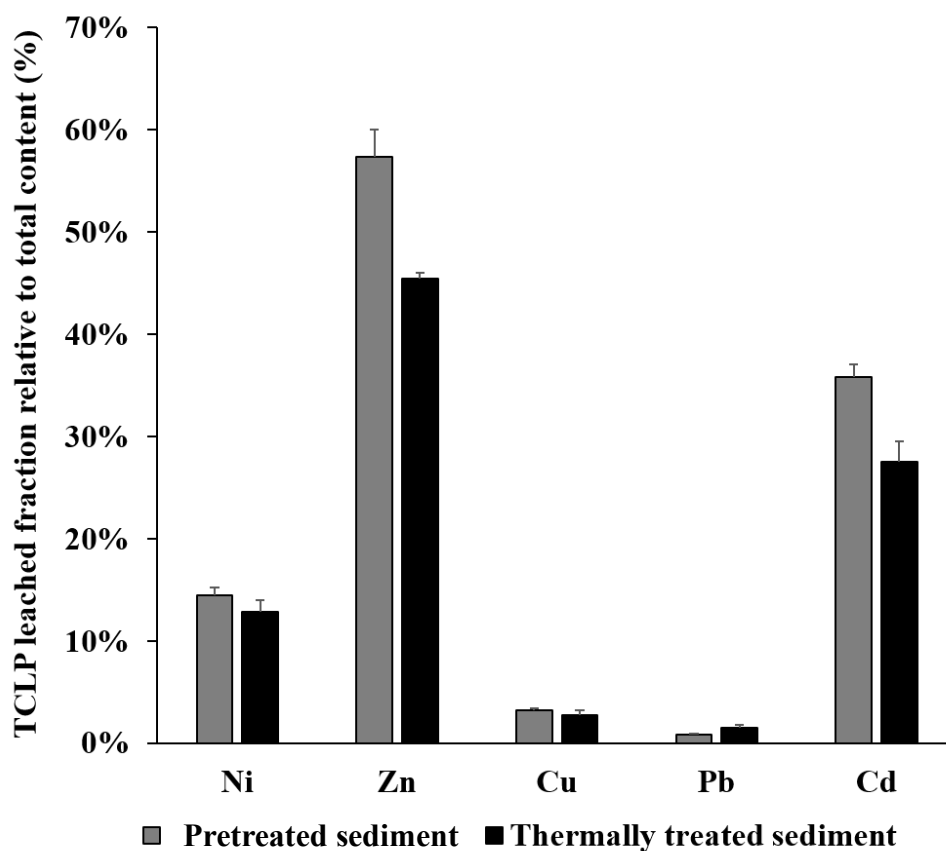


Figure 3.6. TCLP leached fraction of heavy metals relative to their total content in sediment for pretreated and thermally treated sediment. The total content of heavy metals in sediments is determined by summing the contents corresponding to the five fractions of sequential extraction procedure (SEP).

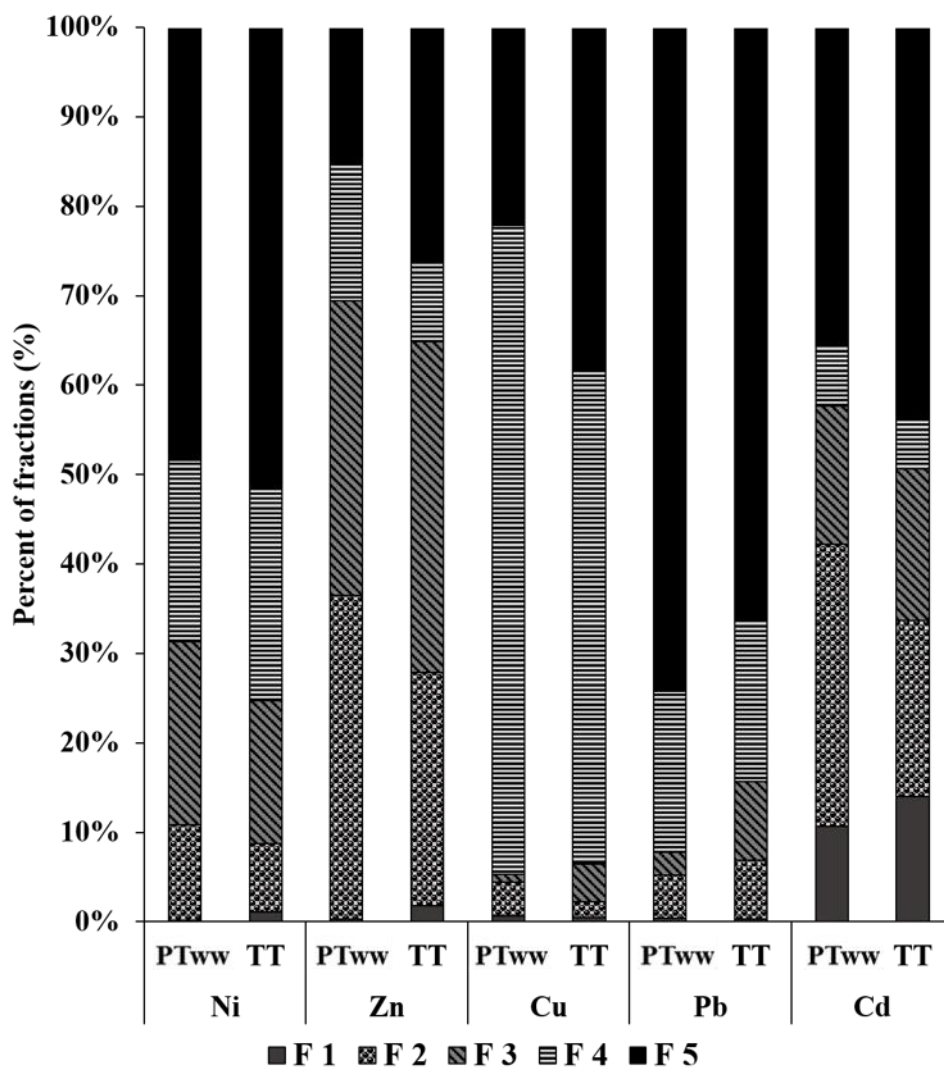


Figure 3.7. Composition of sequentially extracted fractions of heavy metals relative to the total amount in sediment. PTww: pretreated sediment with water washing, TT: Thermally treated sediment. Each fraction of heavy metals is denoted as follows¹⁵: F1, exchangeable; F2, bound to carbonates; F3, bound to Fe/Mn oxides; F4, bound to organic matter; F5, residual.

3.3.5. Effect of Thermal Treatment on Barley Germination and Growth

Despite the successful removal of petroleum hydrocarbons and the expected reduction in heavy metal bioavailability, the germination and growth of barley sown in sediment did not improve after the thermal treatment. Figure 3.8 shows that root germination, shoot development, and root length after a 10-d incubation were not significantly changed by the treatment. The shoot length after the 10-d incubation was significantly lower for the thermally treated sediment compared to the pretreated sediment. As discussed above, most of the physicochemical properties of the sediment analyzed in this study were not substantially changed by the thermal treatment except for SOC content and EC_{1:5}. None of the 54 VOCs analyzed in the thermally treated sediment were detectable, suggesting that the phytotoxicity exhibited by residual VOCs in the sediment was not significant (Table 3.6). Therefore, it is highly suspected that the soluble organics and the salts produced during the treatment exhibited negative effects on barley growth and germination, offsetting the beneficial effects of reducing the TPH content and heavy metal bioavailability.

Table 3.6. Volatile organic compounds (VOCs) of pretreated sediment and thermally treated sediment. The detection limit is 10 mg kg⁻¹ for all VOCs.

Volatile organic compounds (VOCs)	Pretreated sediment	Thermally treated sediment
Benzene	ND	ND
Toluene	ND	ND
Ethylbenzene	ND	ND

m,p-Xylene	ND	ND
o-Xylene	ND	ND
Trichloroethylene	ND	ND
Tetrachloroethylene	ND	ND
1,1,1-Trichloroethane	ND	ND
Methylene Chloride	ND	ND
Carbon Tetrachloride	ND	ND
Chloroform	ND	ND
Bromoform	ND	ND
Bromodichloromethane	ND	ND
Dibromochloromethane	ND	ND
1,2-Dichloroethane	ND	ND
1,1-Dichloroethene	ND	ND
1,1-Dichloroethane	ND	ND
cis-1,2-dichloroethene	ND	ND
trans-1,2-dichloroethene	ND	ND
Vinyl chloride	ND	ND
Acrylonitrile	ND	ND
Methyl Tertiary Butyl Ether(MTBE)	ND	ND
1,2-Dibromo-3-chloropropane	ND	ND
Naphthalene	ND	ND
Ethyl acetate	ND	ND
2-propanol	ND	ND
Nitrobenzene	ND	ND

Carbon disulfide	ND	ND
benzyl chloride	ND	ND
Acrolein	ND	ND
Methyl ethyl ketone	ND	ND
Allyl chloride	ND	ND
Allyl alcohol	ND	ND
Styrene	ND	ND
Methyl acrylate	ND	ND
Dichlorodifluoromethane	ND	ND
1,2-Dichloropropane	ND	ND
1,3-Dichlorobenzene	ND	ND
trans-1,3-Dichloropropene	ND	ND
cis-1,3-Dichloropropene	ND	ND
1,2-Dichlorobenzene	ND	ND
Trichlorofluoromethane	ND	ND
Bromochloromethane	ND	ND
1,2-Dibromoethane	ND	ND
1,2,3-Trichlorobenzene	ND	ND
Bromomethane	ND	ND
Chloromethane	ND	ND
Chlorobenzene	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND
1,4-Dichlorobenzene	ND	ND
1,1,2-Trichloroethane	ND	ND

1,1,2-Trichloro-1,2,2-trifluoroethane	ND	ND
1,2,4-Trichlorobenzene	ND	ND
Cumene (Isopropylbenzene)	ND	ND

ND: Not Detected.

3.3.6. Effect of Modification of Thermal Treatment on Potential Plant Stressors and Barley Germination and Growth

To improve the quality of the product of the thermal treatment of sediment as a planting soil, the treatment process was modified by employing either enhanced ventilation during the thermal treatment or post-treatment water washing (described in detail in the Materials and Methods section). Enhanced ventilation was expected to immediately discharge the oxidation products and radicals generated in the off-gas, thereby preventing the formation of the two suspected stressors for barley (i.e., soluble organics and salts) and their repartitioning to the treated sediment. Because both substances are water soluble, water washing after the treatment was expected to effectively remove these substances from the sediment.

For the thermal treatment with enhanced ventilation, only a 3% increase in the sediment SOC content was observed, indicating that the formation and repartitioning of soluble organics was successfully controlled. It should be noted that a 22% increase in the sediment SOC content was observed for the thermal treatment without enhanced ventilation. On the other hand, EC_{1:5} values were not substantially different between the treated sediments with and without enhanced ventilation, indicating that ventilation had a limited effect on preventing salt formation during the thermal treatment.

Water washing was effective at removing both soluble organics and salts

produced during the thermal treatment. The SOC content in the treated sediment was reduced by 81% after the water washing. $EC_{1.5}$ was substantially reduced from 1.58 $dS\ m^{-1}$ to 0.19 $dS\ m^{-1}$. The combined application of enhanced ventilation and water washing did not show additional benefits in terms of sediment SOC content or $EC_{1.5}$ reduction, suggesting that when water washing is employed as a post-treatment method, applying enhanced ventilation during the thermal treatment process may not be necessary. A less than 0.5% reduction in the sediment heavy metal content was observed upon water washing, indicating that the adverse effects of heavy metals on barley growth and germination, if there are any, may be exhibited similarly for the thermally treated sediment with and without water washing.

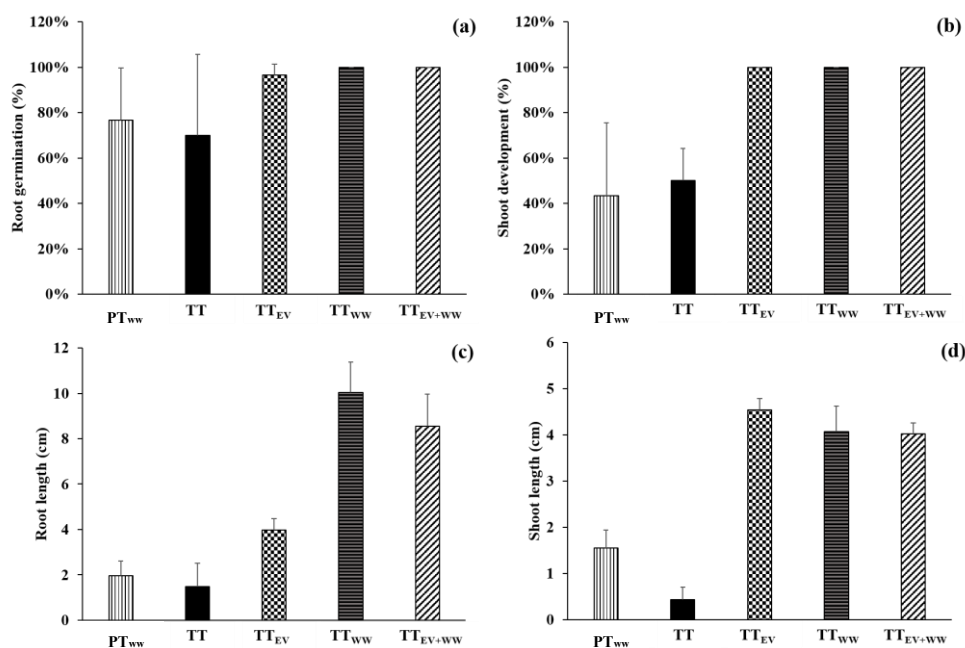


Figure 3.8. Barley (*H. vulgare*) germination and growth test results: (a) root germination, (b) shoot development, (c) root length, and (d) shoot length. PT_{ww}: pretreated sediment with water washing; TT: thermally treated sediment; TT_{EV}: sediment thermally treated under enhanced ventilation; TT_{ww}: thermally treated

sediment with water-washing post-treatment; TT_{EV+WW}: sediment thermally treated under enhanced ventilation with water-washing post-treatment.

The germination and growth of barley were considerably enhanced by modifying the treatment process using enhanced ventilation and/or post-treatment water washing (Figure 3.8). The percentage of root and shoot germination approached 100% when the modified processes were applied. For root length, the benefit of the process modification was much more pronounced for water washing than enhanced ventilation, whereas the other indicators examined showed comparable results between the two cases. It is likely that the significant removal of salts enabled by the water washing resulted in enhanced root growth. The cases where only water washing was employed and the combined application of enhanced ventilation and water washing showed similar results for all four indicators, which could be expected from the similarity in the sediment SOC contents and EC_{1:5} values between the two cases. Overall, the barley germination and growth test results could be reasonably explained by the SOC contents and EC_{1:5} values, strongly suggesting that soluble organics and salts acted as major stressors for the treated sediments. Therefore, a thermal treatment process applied to remediate petroleum-impacted sediments and to produce a planting soil should be designed to minimize the production of soluble organic or salt residues in the treated sediment and/or to remove these toxicants via post-treatment. Implementation of a post-treatment of water washing is a strong candidate for a process modification for this purpose.

3.4. Implications

The current study demonstrates that a low-temperature thermal treatment of petroleum-impacted, dredged sediment could successfully reduce the sediment TPH content to comply with regulatory standards, while preserving most of the physicochemical properties of the sediment related to the quality of the product as a planting soil. The thermal treatment could reduce the leachability and extractability of heavy metals, which would be an additional benefit when the risk associated with the presence of relatively low levels of heavy metals is of concern regarding the beneficial use of the product. However, the low-temperature thermal treatment employed in this study resulted in the production of soluble organics and salts as plant stressors. Fortunately, these substances can be easily removed from the thermally treated sediment using a simple process of water washing. In this study, a field-collected marine sediment sample was used for the experiments after washing with water to remove salts of indigenous origin because the presence of these indigenous salts was expected to mask any positive or negative effects of the sediment treatment processes on the barley germination and growth tests. Because water washing is not expected to precede the thermal treatment in field applications, a large amount of salts will remain after the treatment. Therefore, application of water washing prior to the beneficial use of the product as a planting soil may be necessary, regardless of the need to deal with the plant stressors produced during the thermal treatment. In this regard, a water washing post-treatment may not be an additional burden for the main treatment method for sediment remediation. However, the soluble organics-laden wastewater generated from the water washing process requires an appropriate treatment, incurring additional costs and resource

consumption. In this respect, optimization of the unit process of the thermal treatment to minimize the formation of soluble organics may still be beneficial. Studies are needed to further optimize the overall process of the low-temperature thermal treatment under consideration of the life cycle costs and environmental impacts and the quality of the product as a medium supporting the terrestrial ecosystem.

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CHAPTER 4

Effect of heat temperature and oxygen availability during thermal treatment for the production of planting soil from petroleum-impacted sediment

4.1. Introduction

Considerable amount of dredged sediment has been annually generated from development of harbor and navigational channel all over the world.¹ Beneficial use of dredged sediment is considered as an sustainable alternative, resulting in minimization of conventional problems related to sediment management such as environmental and socio-economic burdens for disposal of dredged sediment. Dredged sediment is often contaminated by petroleum due to anthropogenic works such as industrial, harbor activities and accidents (e.g. oil spills).² Petroleum, which potentially has negative impacts on environment and ecosystems, should be properly removed prior to beneficial use.

Thermal treatment, which is known as an reliable and rapid removal of wide range of petroleum hydrocarbons in soil and dredged sediment^{3,4} may differently affect sediment characteristics and residual heavy metal mobility depending on treatment conditions such as heat temperature and treatment time, thus these changes could also influence sediment fertility.^{4,5} According to Chapter 2, our proposed low thermal treatment technique provided additional benefits of preservation of original

sediment physicochemical properties and stabilization of heavy metal mobility during treatment of petroleum impacted dredged sediment with reliable petroleum removal efficiency. However, these advantages were offset from newly generated soluble organics and salts which substantially exhibited phyto-toxicity even though simple water washing post treatment could easily remove these plant stressors after thermal treatment. In addition, it was difficult to verify an optimized thermal treatment condition to reduce these negative byproducts since the treatment was conducted under only one condition. Such limitations have increased the need for the study of minimization of newly generated plant stressors during thermal treatment under various treatment conditions as well as changes in the other factors related to sediment fertility.

The heat temperature and treatment time are conventionally considered as predominant factors to influence on soil physicochemical properties during thermal treatment.⁵ However, the oxygen availability in treatment atmosphere, which is also an important factors to determine dominant thermal reactions such as oxidation and pyrolysis, also significantly affects not only petroleum removal but also the sediment characteristics, heavy metal mobility and sediment fertility during thermal treatment. However, a lack of literature deals with the comprehensive investigation and suggestion of optimized thermal treatment conditions depending on heat temperature and oxygen availability for the production of improved planting medium. It is common to manipulate gas compositions using purging gases to determine dominant thermal reactions.^{3,6} Formation of carbonaceous matter and oil recovery using organic matter or organic contaminants during pyrolysis of petroleum-impacted soil with the supply of inert gas has recently been reported.^{3,7,8} However, the production of black carbon or oil recovery with continuous inert gas supply during thermal

treatment may be less cost-effective and low energy-efficient using relatively little amount of indigenous organics in soil compared with carbon-rich resources (i.e., biomasses). In addition, continuous gases supply to manipulate desirable gas compositions for a field-scale thermal treatment may be required enormous capital and substantial resources. In reality, air compositions during thermal treatment is more manipulated by physical control such as physically making a closed treatment environment or application of ventilation than inert gas supply. In addition, char produced from a biomass is often pyrolyzed in a closed container with a lid without purging inert gas.⁹ However, such studies have not been reported for soil and sediment treatment with organic contaminants with the consideration of the comprehensive changes in factors related to sediment fertility.

In order to find an optimized treatment condition for the production of planting soil using petroleum impacted dredged sediment, the effects of heat temperature and oxygen availability on TPH removal, sediment physicochemical properties and heavy metal mobility during thermal treatment was investigated. The favorable air compositions during the thermal treatment were manipulated by creating open system or closed system using a lid of the container with or without nitrogen gas supply to only remove the residual oxygen content without continuous inert gas supply. The Barley germination and growth test was also conducted using thermally treated sediment which were treated at different heat temperatures and oxygen availabilities. We demonstrated the pyrolytic environment was successfully created without additional gas supply and more pyrolyzed sediment can enhance more sediment fertility as planting soil.

4.2. Materials and methods

4.2.1. Sediment Collection and Pre-Treatment

Petroleum-contaminated sediment used in the current study was collected from a highly industrialized harbor area in Korea. Upon arrival to the laboratory, the sediment was air-dried and thoroughly hand-mixed for homogenization. The sediment was then washed using deionized (DI) water to reduce its salt content. The water washing was conducted until an electrical conductivity of the 1:5 (w:w) sediment slurry ($EC_{1:5}$) of less than 1 dS m^{-1} was obtained. This water washing pre-treatment was necessary because the source-originated salts could substantially inhibit germination and growth of barley according to Chapter 2, which was used as an indicator of the sediment quality as a planting media in the current study. As discussed previous chapters, it was demonstrated that the application of the same sediment sample that the water washing did not significantly change sediment physicochemical properties and total petroleum and heavy metal contents. After the water washing, the sediment was air-dried and stored at $25 \pm 0.5 \text{ }^{\circ}\text{C}$ until use.

4.2.2. Thermogravimetric Analysis for the Determination of Thermal Treatment Conditions.

Thermogravimetric analysis (TGA) was conducted to determine the range of treatment temperature by monitoring of the sediment weight loss using a Discovery TGA analyzer (TA Instrument, New Castle, DE).^{3,6} Untreated sediment was heated under nitrogen or air gas (including oxygen content 21%) purging to compare the difference of weight loss depending on oxygen availability and changes in heat temperature for the determination of a range of heat temperature. The heat

temperature range was from 45 °C up to 1000 °C at heating rate of 10 °C/min. The results of TGA analysis, presented in Figure 4.1, showed that drastic change in sediment weight occurred at lower than 100 °C due to the loss of sediment moisture under both air and nitrogen purging conditions. The other largest peak was detected between 230- 600 °C due to a variety of reactions such as dehydration, dehydroxylation, decarboxylation, decomposition, transformation and vaporization of organic and inorganic constituents under both air and nitrogen purging conditions.^{5,10} The highest peak within these range under air and nitrogen gas purged environment were detected at 446 °C and 473 °C, respectively. According to O'Brien et al.⁵, the heavier hydrocarbon containing fuel oil is decomposed from 300 °C to 500 °C and thermal treatment at above 500 °C is prone to decompose or destructure of sediment original characteristics such as organic matter, nutrient and minerals. According to our previous study, we confirmed that thermal treatment for petroleum-impacted sediment at 300 °C using a muffle furnace without any gas purging successfully meet the Korean regulatory standard for soils in agricultural or residential areas. Therefore, the range of thermal treatment temperatures in the current study was determined at 300 °C, 400 °C and 500 °C for the reliable petroleum removal efficiency and the consideration of original sediment characteristics.

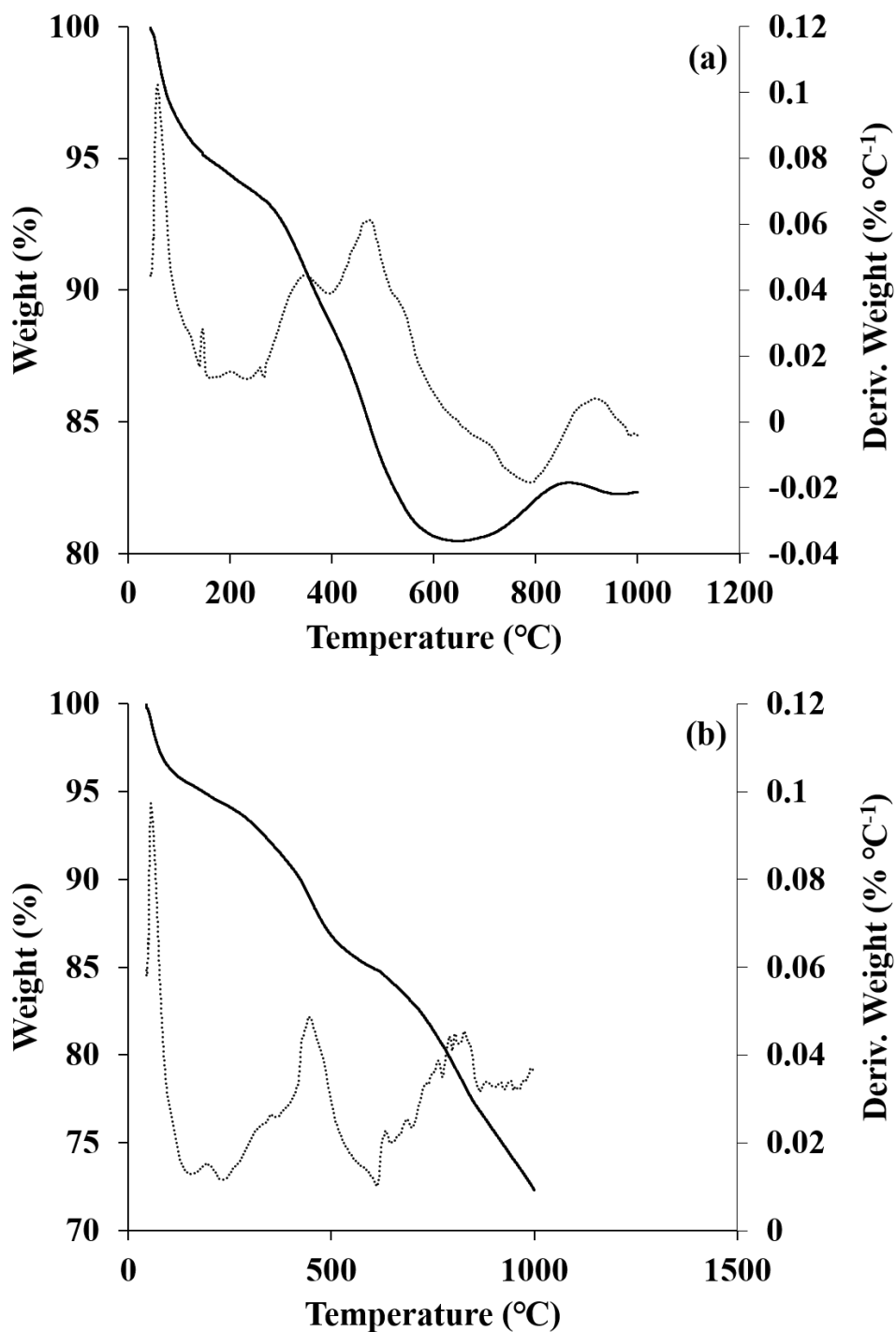


Figure 4.1. TGA-DTA curves for petroleum impacted sediment (a) under purging air gas at 10 °C/min, (b) purging nitrogen gas at 10 °C/min. The solid line stands for the weight loss of sediment and the dot line stands for the change in derivate weight

of sediment.

4.2.3. Thermal Treatment

Sediment thermal treatment was conducted in the laboratory using a muffle furnace under various temperatures and oxygen availability conditions. Three heating temperatures, 300, 400, and 500 °C, were applied. Thermogravimetric analysis result and TPH removal efficiencies observed under various thermal treatment temperatures using the same sediment sample in the previous chapter suggested that a heating temperature of 300 °C or higher is required to accomplish nearly complete removal of TPHs in the sediment. Previous studies reported that heating above 500 °C largely decomposes organic matter and essential nutrients in sediments, and substantially alters the sediment mineralogy.^{3,5} The oxygen availability condition during thermal treatment was varied as follows. (Figure 4.2) The first is a moderate oxygen availability condition for which a sediment sample was placed on a steel container without a lid such that the oxygen present in the inner volume of the furnace (approximately 0.0045 m³) was available during the treatment. The second is a low oxygen availability condition for which the steel container was closed using a lid after placing a sediment sample such that only the oxygen present inside the steel container (approximately 0.0022 m³) was available. The last one is no oxygen availability condition. For this condition, the oxygen in the inner volume of a closed steel container is filled with pure nitrogen gas prior to conducting thermal treatment.

A sediment dry weight of 50 g was used for each thermal treatment run. The sediment placed in the container was inserted to the furnace which was pre-heated to a target temperature. A relatively short treatment time of 30 mins was applied for

an energy-efficient, high-throughput thermal processing of sediment as well as for low impacts on original sediment characteristics. For the moderate oxygen availability condition, a ventilation machine with a nominal gas discharge rate of 10 m³/min was connected to the furnace to immediately discharge off-gases generated during the treatment. Because the steel container was closed using a lid for the other oxygen availability conditions, the off-gases could not be discharged from the container regardless of the presence or absence of any gas control measures in the furnace. The thermal treatment conditions or the thermally treated sediments are henceforth identified by a combination of the heating temperature and the oxygen availability condition, represented by M, L, and N for the moderate, low, and no oxygen availability conditions. For example, 300M represents a heating temperature of 300 °C and the moderate oxygen availability condition.



Figure 4.2. Controlled oxygen content in headspace of treatment environment during thermal treatment: (a) a steel container without a lid (Moderate oxygen available condition, M, using present oxygen in the headspace of a furnace), (b) a steel container with a lid (Low oxygen available condition, L, only using present oxygen in the headspace of the steel container), (c) a steel container with a lid and nitrogen purging into a closed container till complete removal of oxygen in the headspace of steel container (No oxygen available condition, N, no oxygen in the treatment atmosphere in a closed steel container)

4.2.4. Sediment analyses

pH, EC_{1:5}, soluble salt ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻ and NO₃³⁻) and SOC were analyzed in a 1:5 (w:w) sediment slurry. In a 50-ml conical tube, 5 g weight of sediment and 25 ml of deionized water were mixed for 2 hours at 180 rpm using a horizontal shaker. The tube was centrifuged at 14,000 × g for 10 mins and then the supernatant was gently decanted and was filtered using 0.45-μm syringe filter. pH and EC_{1:5} were measured using A multi-parameter meter (Orion 5 star, Thermo Fisher Scientific, USA) equipped with a pH electrode and a conductivity cell. Concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃³⁻ and SO₄²⁻ were measured using ion chromatography (DX-500, Dionex, US) equipped with an AS14 anion column and a CD20 conductivity detector for anions and ICP-OES for cations. SOC was analyzed using a Shimadzu TOC analyzer (V-CPH, Shimadzu, Japan). All analyses were conducted using triplicate samples.

Sediment physicochemical properties (total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), cation exchange capacity (CEC)) were analyzed the same methods which were introduced in the Chapter 3.2.4.

TPH content in sediment was measured according to the Korean standard method for soil analysis¹⁰. Volatile organic carbon (VOC) concentration in sediment was analyzed based on U.S. Environmental Protection Agency (USEPA) Method 8260B¹¹. Sediment heavy metals were characterized using the toxicity characteristic leaching procedure (TCLP) following USEPA Method 1311¹² and a sequential extraction procedure (SEP) developed by Tessier et al.¹² with a slight modification¹. Details on the extraction and analytical procedures for TPH, VOC, and heavy metals are provided in Chapter 3.2.4.

Spectroscopic analyses were also employed for sediment characterization.

X-ray photoelectron spectroscopy (XPS; AXIS-Hsi, KRATOS, UK) with an Al K α X-ray source (1486.6 eV) was used to measure the sediment surface carbon content. The Casa XPS program was applied to de-convolute the XPS data. X-ray diffraction (XRD; D8 Advance, Bruker Inc., Germany) with Cu-K α radiation at 40 kV and 40 mA in the range of 2θ scanning range from 5° to 90° was employed to analyze crystalline minerals in sediment.

4.2.5. Barley Germination and Growth Test

Barley (*Hordeum vulgare* L.) was used to investigate the ecotoxicity of sediment constituents and sediment fertility. Barley is one of the widely used ecotoxicity test species to evaluate ecotoxicological effects of organic and inorganic substances in soils and sediments.^{13,14} Ten barley seeds were placed in 30 g of sediment prepared in a 100 ml polyethylene dish. The sediment moisture content was adjusted to its water holding capacity using DI water. The barley seeds were then incubated in a growth chamber (E15, Conviron Inc., Canada) providing a constant temperature of 23°C and a light:dark photoperiod of 16:8 for 10 days. After the incubation, the root germination rate, the shoot development rate, and the lengths of root and shoot were measured. Triplicate runs were conducted for sediment samples treated by each thermal treatment condition.

4.3. Results and discussion

4.3.1 Effect of Thermal Treatment Conditions on the Characteristics of Sediment Organic Constituents.

The effect of thermal treatment on the characteristics of sediment organic constituents was strongly dependent on the heat temperature and the oxygen availability. Reduction in the sediment TOC content, which is the result of organic matter decomposition during thermal treatment, was more pronounced at higher heating temperature and higher oxygen availability. The relatively smaller reduction in sediment TOC contents observed for low (L) and no (N) oxygen availability conditions can be attributed to the dominance of pyrolysis reactions over oxidation reactions and the absence of ventilation, which favors the formation of organic intermediates that remains in the sediment or resorbs from the off-gas to the sediment during the treatment. Several evidences demonstrate that pyrolysis reactions occurred under L and N conditions, resulting in the formation of black carbonaceous matter. According to Table 4.1, H/C ratio in sediment, which indicates the degree of organic matter carbonization and aromaticity, was decreased from 2.21 in the pretreated sediment to 1.55 and 1.44 in 300N and 500N sediments, respectively. The decrease in the H/C ratios was more pronounced at higher heating temperature and for lower oxygen availability conditions.

Table 4.1. Elemental composition of pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under no oxygen-available condition (300N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under no oxygen-available condition (500N).

	C (%)	H (%)	N (%)	O (%)	S (%)	H/C ratio	O/C ratio
PTww	6.25	1.15	0.43	7.16	1.03	2.21	0.86
300M	3.41	0.52	0.46	5.64	1.17	1.83	1.24
300N	5.27	0.68	0.59	6.13	1.34	1.55	0.87
500M	0.31	0.16	0	1.42	0.98	6.19	3.44
500N	3.58	0.43	0.37	4.47	1.25	1.44	0.94

Visual inspection of the thermally treated sediments clearly indicates the dramatic difference in the contents and characteristics of sediment organic matter depending on the treatment conditions (Figure 4.3). The sediment color gets darker as the heating temperature increases for L and N conditions. At the same heating temperature, sediment treated at N condition is apparently darker than that treated at L condition. For 500M condition, the sediment color changed from yellow-gray

(pretreated) to red (treated), indicating a substantial decomposition of organic matter. The surface carbon contents, measured using XPS (Figure 4.4), increased with the decrease in oxygen availability, suggesting that the pyrolysis products formed in the off-gas were repartitioned onto the surface of sediment particles during the treatment. Overall, the results suggest that pyrolysis reactions occur significantly during thermal treatment conducted using closed containers (i.e., L and N conditions), which results in smaller change in the sediment TOC content compared to the treatment conducted with ventilation (i.e., M condition).

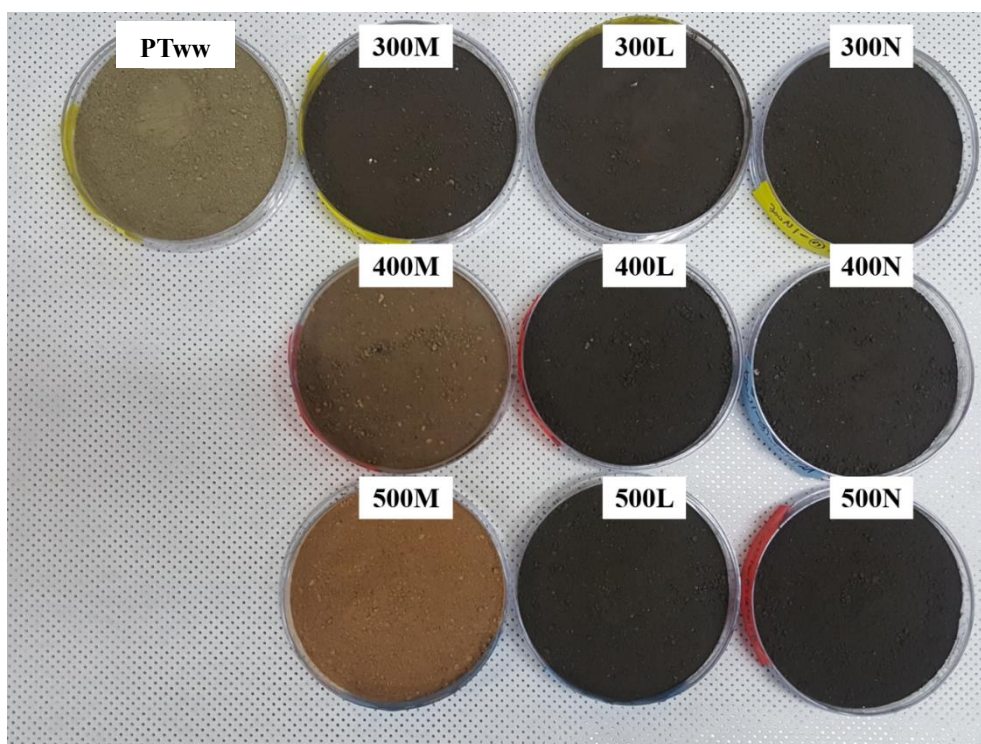


Figure 4.3. Changes in sediment color of pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available

condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

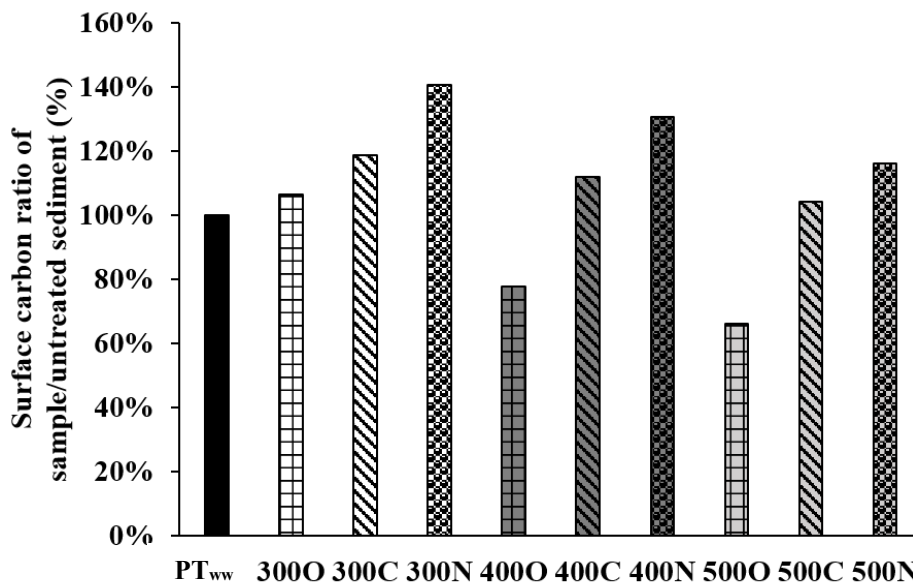


Figure 4.4. Surface carbon ratio sediment sample relative to pretreated sediment on sediment sample analyzed by XPS for pretreated sediment with water washing (PT_{ww}) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

The sediment TPH contents were effectively reduced from $5108 \pm 94 \text{ mg kg}^{-1}$ in the pretreated sediment to lower than the quantification limit of 50 mg kg^{-1} at temperatures and oxygen availability conditions applied in the current study. Chapter 3 reported using the same sediment sample that application of a heating temperature of 300°C without any physical control of the furnace atmosphere successfully reduced the TPH content to less than 500 mg kg^{-1} . A notable difference between the results of the current and the previous study is that the sediment TOC content was substantially decreased at 300°C in the current study (from 6.02% to 1.72-3.51) whereas only a slight decrease (from 3.81% to 3.54%) was observed in the previous study.

In Chapter 3, it was demonstrated that water-soluble organic intermediates produced during low-temperature (300°C) thermal treatment were one of the major plant stressors in thermally treated sediments. Therefore, soluble organic carbon (SOC) content is regarded as a key indicator of the quality of a thermally treated sediment as a planting soil. Because soluble organics are produced by partial oxidation of volatile organics in the off-gas during thermal treatment⁷, the increase in the sediment SOC content is more pronounced under conditions of limited ventilation during the treatment, which allow the products of the partial oxidation to be repartitioned to the sediment. The sediment SOC analysis results presented in Figure 4.5 show that the increase in the sediment SOC content after thermal treatment is evident when closed containers were used (i.e., L and N conditions). For 300L and 300N conditions, the sediment SOC content increased by 5.2- and 4.9-folds, respectively, compared to the pretreated sediment. The fact that the sediment SOC content was notably increased for the no oxygen availability condition (i.e., N) suggests that oxygen available in the sediment itself was involved in the reactions

that produce soluble organics. The results also indicate that the production of soluble organics can be effectively prevented by increasing the heating temperature. At 500L and 500M sediments, the SOC content was significantly lower than that for the pretreated sediment. The reduction in the sediment SOC content at higher heating temperatures can be attributed to the dominance of pyrolytic reactions such as thermal cracking and polymerization, which occurs at a temperature range of 400-500 °C.¹⁵ Li et al.⁷ reported that a considerable increase in the sediment SOC content was observed by pyrolytic treatment of petroleum-contaminated soil at relatively low temperatures, whereas a decrease was observed at temperatures of 500 and 600 °C.

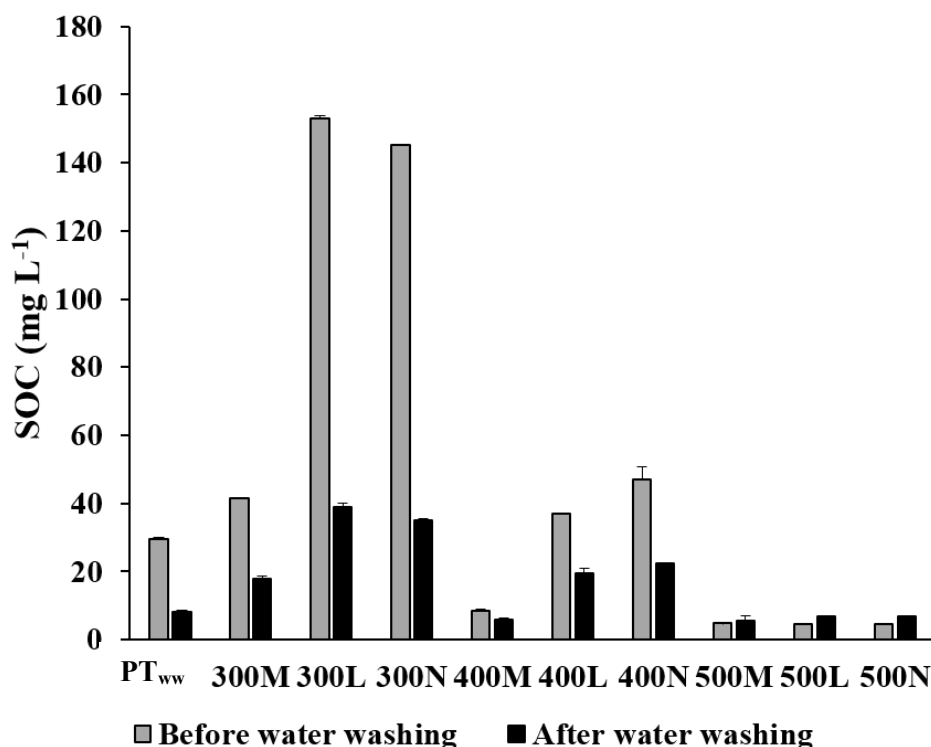


Figure 4.5. Soluble organic carbon (SOC) concentrations before and after water washing in pretreated sediment (PT_{ww}) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen

condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

4.3.2. Changes in sediment salinity and salt compositions after thermal treatment Physicochemical Properties

The production of oxidized matter, soluble sulfate salt generated from sulfur oxidation reactions, during thermal treatment also substantially affected $EC_{1:5}$ and sediment pH depending on treatment conditions. The sediment $EC_{1:5}$ values shown in Table 4.2 after thermal treatment were increased by 2.1 to 4.4-folds attributed to newly generated sulfate salts. According to Chapter 3, the sulfur oxidation reactions may be occurred using hydrogen sulfide, elemental sulfur in sediment during thermal treatment.¹⁶ The newly generated SO_4^{2-} shown in Table 4.3 during thermal treatment for all treatment conditions was mainly attributed to approximately 68-79% of sediment salinity increase and the positive correlation coefficient value between SO_4^{2-} and $EC_{1:5}$ showed also substantially high of 0.997 (see Figure 4.6), indicating that increased sediment salinity was mostly determined by the newly generated SO_4^{2-} contents during thermal treatment. The sulfate under moderate oxygen available condition was more generated using relatively more abundant oxygen in treatment atmosphere than under limited oxygen available conditions. There was no substantial difference in sulfate concentrations after thermal treatment under moderate oxygen available conditions regardless of temperature, which can be supported by the fact that the $EC_{1:5}$ values in thermally

treated sediment under M conditions were similar at all heat temperatures. On the other hand, sulfate contents under limited or no oxygen available conditions were also increased with the increasing temperature due to the increased available oxygen from sediment. Under these conditions, it is highly suspected that source originated oxygen become more available during thermal treatment due to increased organic matter decomposition, water loss and clay mineral dehydration with increased heat temperature. The R^2 between TOC and SO_4^{2-} contents under L and N conditions showed negatively moderate correlation value of 0.785 (see Figure 4.7), indicating that the generated oxygen from the decomposition of TOC may be attributed to the sulfur oxidation reactions under oxygen less available conditions. In addition, the decreasing elemental oxygen in thermally treated sediment at higher temperature under oxygen-free condition could be also supported the fact that the sulfur oxidation reactions could be occurred by using source originated oxygen. (Table 4.1). The salinity increase rates were reduced from 400 °C under oxygen less conditions due to reduced relevant thermal reactions to increase oxygen availability from sediment, which can be attributed to the decrease in the reduction rate of TOC contents from 400 °C under such atmospheres. It should be noted that newly generated sulfate from sediment or sulfur-rich materials during thermal treatment should be carefully monitored and properly managed before beneficial use due to its potential negative effects on plant growth. The impact of the other anion salts on increasing salinity after thermal treatment was negligible.

Table 4.2. pH, EC_{1:5}, TOC, TN, TP, CEC and WHC in pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

	pH	EC _{1:5} (dS m ⁻¹)	TOC (%)	TN (%)	TP (mg kg ⁻¹)	CEC (cmol kg ⁻¹)	WHC (%)
						1)	
PTww	7.76±0.01	0.96±0.02	6.02±0.15	0.74±0.01	1824±6	32.6±2.55	44±7.78
300M	7.48±0.18	3.70±0.03	1.72±0.07	0.47±0	2077±185	23.7±0.94	52±0.89
300L	8.06±0.13	1.99±0	3.45±0.05	0.65±0.01	1979±40	24.3±1.38	50.6±2.12
300N	7.60±0.04	2.01±0.03	3.51±0.03	0.66±0.01	2027±206	24.3±0.86	48.6±0.95
400M	7.11±0.03	4.20±0.02	0.58±0.03	0.19±0	2023±109	18.6±0.03	61.6±8.85
400L	7.71±0.10	3.11±0.13	2.52±0.03	0.47±0	1989±128	20.9±0.27	55.4±3.19
400N	7.61±0.04	3.14±0.05	2.74±0.02	0.48±0	2024±17	22.1±0.90	55.1±4.19
500M	6.87±0.11	3.64±0.05	0.21±0.02	0.03±0	2240±144	16.2±0.64	62.7±2.12
500L	6.81±0.03	3.45±0.02	1.81±0.02	0.34±0	2081±53	18.1±0.22	60.6±2.86
500N	7.02±0.01	3.12±0.04	1.45±0.02	0.34±0.01	2217±117	17.1±0.83	57±2.07

Table 4.3. Salt ion concentrations in pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

	Ca ²⁺ (mg kg ⁻¹)	Mg ²⁺ (mg kg ⁻¹)	Na ⁺ (mg kg ⁻¹)	K ⁺ (mg kg ⁻¹)	Cl ⁻ (mg kg ⁻¹)	NO ₃ ⁻ (mg kg ⁻¹)	SO ₄ ²⁻ (mg kg ⁻¹)
PTww	226±25	195±10	468±24	129±4.5	57±0.9	5.0±0.6	1960±2
300M	2380±17	1330±1.6	583±3.9	270±0.4	166±0.4	4.0±0.4	15316±523
300L	1131±21	596±12	560±53	160±11	222±2.3	4.6±0.4	5360±19
300N	1161±61	604±37	496±3	149±1	211±0	5.1±0.5	5401±128
400M	2790±89	1517±23	394±1.1	514±3.3	93±4.7	3.1±0.6	18025±230
400L	2090±16	988±4.5	504±4.1	199±9	174±1.9	3.7±0.4	11912±677
400N	2140±113	1006±59	540± ±5.9	206±4.1	171±1.4	3.6±0.4	12024±128
500M	2620±144	1485±77	306±8.8	495±11	63±1.7	2.6±0.3	15388±650
500L	2330±26	1065±20	395±7.5	374±8.7	117±0.2	3.0±0.2	14141±157
500N	2150±41	945±20	380±12	323±8.5	127±0.9	2.8±0.1	12411±120

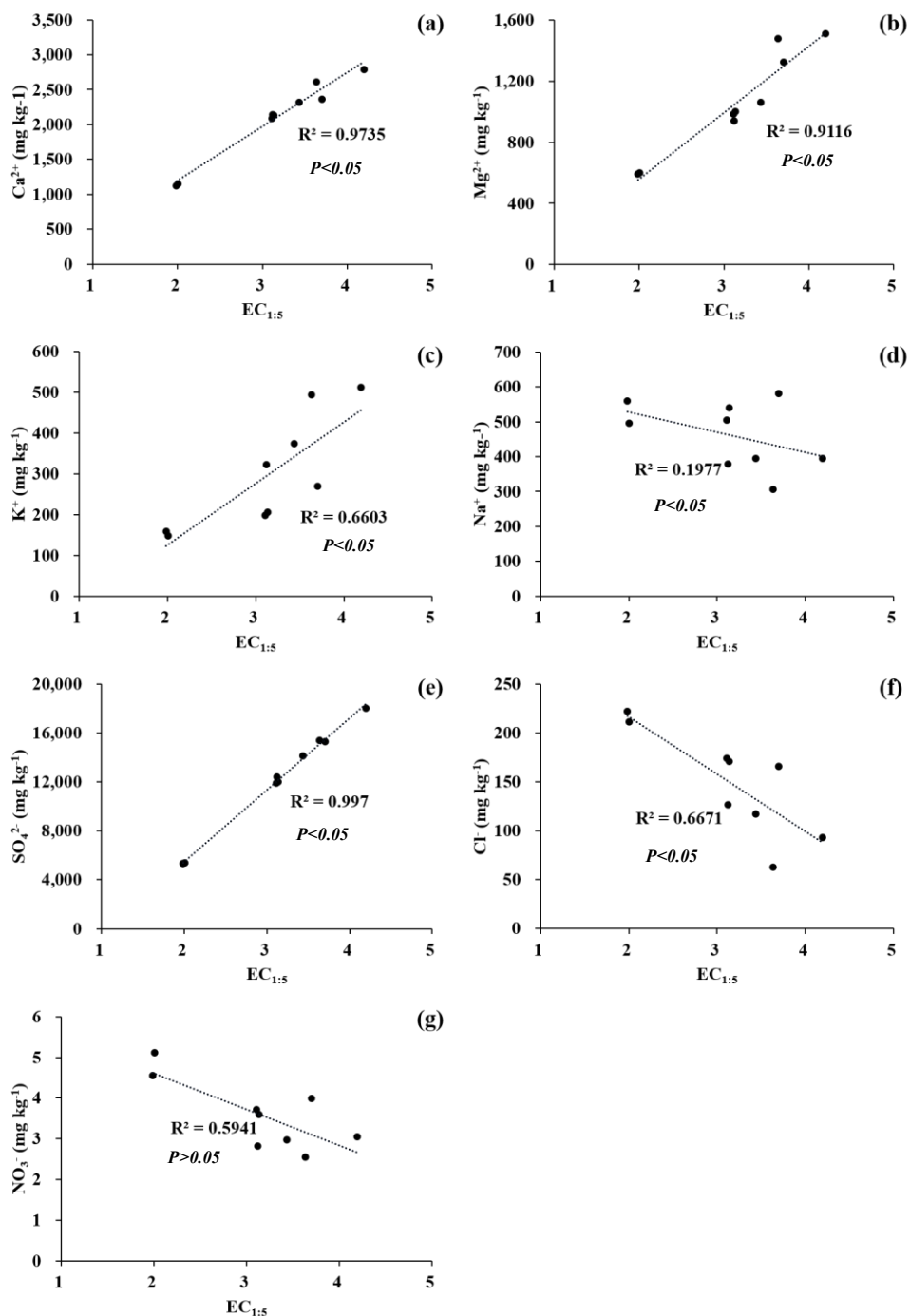


Figure 4.6. Correlation among Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , Cl^- or NO_3^- and $EC_{1:5}$ results of thermally treated sediment before water washing: (a) Ca^{2+} and $EC_{1:5}$, (b) Mg^{2+} and $EC_{1:5}$, (c) K^+ and $EC_{1:5}$, (d) Na^+ and $EC_{1:5}$, (e) SO_4^{2-} and $EC_{1:5}$, (f) Cl^- and $EC_{1:5}$, (g) NO_3^- and $EC_{1:5}$.

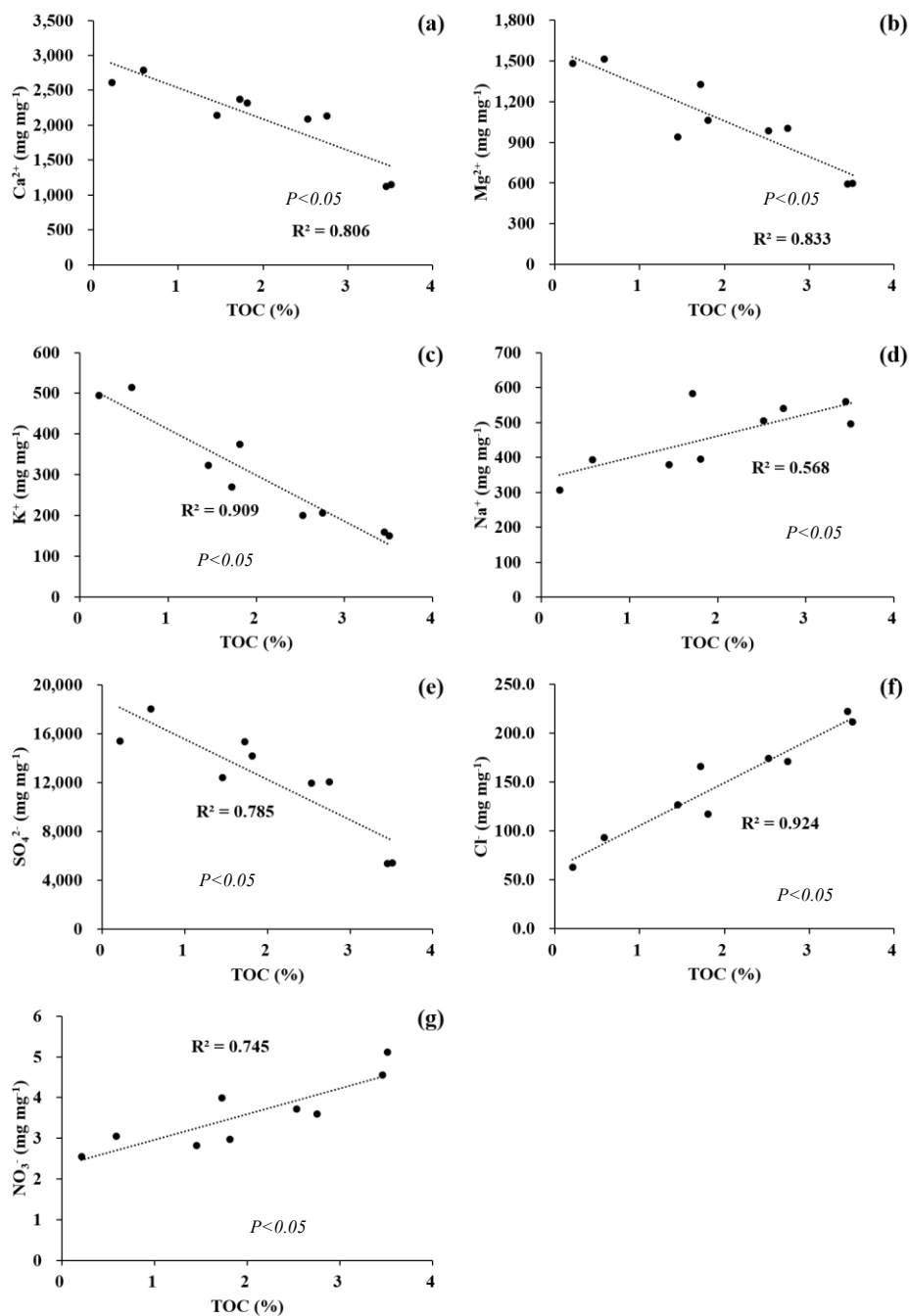


Figure 4.7. Correlation among Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , Cl^- or NO_3^- and TOC results of thermally treated sediment before water washing: (a) Ca^{2+} and TOC, (b) Mg^{2+} and TOC, (c) K^+ and TOC, (d) Na^+ and TOC, (e) SO_4^{2-} and TOC, (f) Cl^- and TOC, (g) NO_3^- and TOC.

As discussed in the manuscript, Ca^{2+} , Mg^{2+} and K^+ were increased during thermal treatment, especially Ca^{2+} content. The increases in Ca^{2+} and Mg^{2+} accounted for 13-14 percent and 6-8 percent of increased concentration of total salt ions, respectively while the increased concentration of K^+ after thermal treatment only contributed to less than 2 percent of increased total salt concentrations. These increases could be occurred by release of Ca^{2+} , Mg^{2+} and K^+ from the decomposition of organic compounds containing calcium and magnesium^{17,18} and/or the release of Ca^{2+} , Mg^{2+} and K^+ , or SO_4^{2-} from clay minerals during thermal treatment. The Ca^{2+} , Mg^{2+} or K^+ and TOC shows negative correlation with a high correlation coefficient value (R^2) of 0.806, 0.833 and 0.909 (see Figure 4.7), respectively, indicating that the release of those salts was occurred from decomposition of organic matter. In addition, the positive correlation coefficient values of Ca^{2+} , Mg^{2+} or K^+ and SO_4^{2-} also were obtained 0.984, 0.909 and 0.681 (see Figure 4.8), suggesting that decomposition of mineral complexes containing Ca^{2+} , Mg^{2+} or/and SO_4^{2-} may also contribute to the increases in those salt ions. However, according to the XRD result, Ca^{2+} , Mg^{2+} or/and SO_4^{2-} containing minerals were not detected by the XRD analysis. It is assumed that those complexes, which were in amorphous phases or tiny and evenly distributed, were difficult to be detected. The soluble form of salt ions could be reduced due to particle aggregation.¹⁹ The Na^+ content was reduced with the increase in heat temperature and oxygen availability. This reduction may be affected by physical protection by particle aggregation and Na^+ may be not released from the decomposition of organic matter or minerals unlikely the other salt cations, which can be explained by the low R^2 value of 0.568 for Na^+ and TOC which is negatively correlated shown in the Figure 4.7.

From the previous study, salts in sediment were identified as plant stressors to barley germination and growth, thus increased sediment salinity after thermal treatment could also be a plant stressor. In order to enhance the thermally treated sediment fertility, the salinity in sediment was reduced at around 0.5 dS m^{-1} by water washing with deionized water and then the $\text{EC}_{1:5}$ and concentrations of salt ions in extracts were analyzed. The value of $\text{EC}_{1:5}$ were analyzed at $0.20\text{-}0.62 \text{ dS m}^{-1}$ and the compositions of salt ions in sediment after water washing shown in Table 4.4 were also not significantly changed compared with their compositions before water washing. The SO_4^{2-} in all water washed sediments under all treatment conditions was still the dominant salt ion, followed by Ca^{2+} and Mg^{2+} . The sum of Ca^{2+} , Mg^{2+} and SO_4^{2-} concentrations accounted for approximately 90% of the total content of salts in all water washed sediment. One notable change was that fraction of Ca^{2+} relative to total salt contents was increased from 12-14% to 19-23% after water washing. Salts generally have high water solubility while gypsum consisting of Ca^{2+} and SO_4^{2-} is known as a sparingly soluble salt. During serial water washing, Ca^{2+} may be consistently released from calcium containing substances such as gypsum while other salts are easily removed at the initial washing stage, which can be attributed to higher contents of Ca^{2+} in water washing completed sediment. However, it is assumed that there are no considerable effects from the changes in salt ion composition on sediment fertility after water washing.

Table 4.4. Salt ion concentrations (mg kg^{-1}) after water washing in pretreated sediment (PT_{ww}) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
PT _{ww}	27±0.8	22±0.6	31±2.2	29±0.4	5.3±0.1	ND	249±1.5
300M	205±9.6	83±6.3	39±0.2	31±0.1	8.3±0	ND	743±32
300L	164±16	85±12	47±0.3	27±0.5	13±0.2	ND	495±33
300N	164±14	84±6.6	49±3	28±1.8	13±0.2	ND	529±43
400M	276±22	87±10	29±1.5	54±3	6.4±0.3	ND	1020±13
400L	205±1.3	78±0.8	39±1.4	24±0.7	10±0.2	ND	636±21
400N	206±1.8	80±3.8	42±2.3	26±0.6	9.4±0.1	ND	695±36
500M	454±27	120±4.6	28±0.1	65±0.4	2.5±0.1	ND	1750±54
500L	273±5.8	66±2.3	29±0.1	38±0.9	7.5±0.1	ND	920±39
500N	268±5.8	37±0.6	29±0.7	48±4.8	7.8±0.2	ND	759±67

ND: Not Detected.

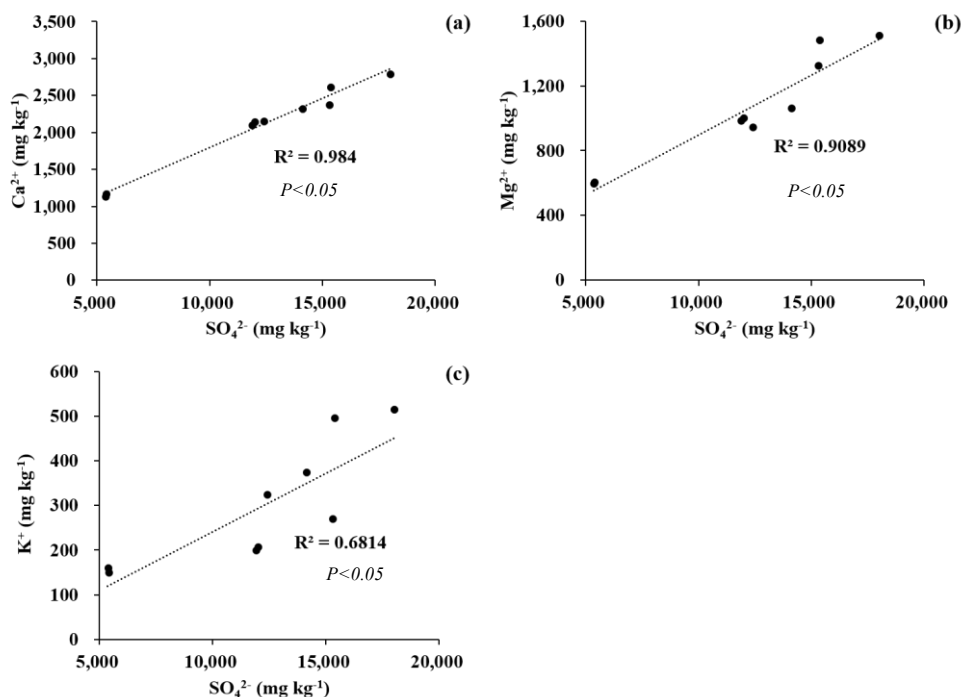


Figure 4.8. Correlation among Ca^{2+} , Mg^{2+} or K^+ and SO_4^{2-} results of thermally treated sediment before water washing: (a) Ca^{2+} and SO_4^{2-} , (b) Mg^{2+} and SO_4^{2-} , (c) K^+ and SO_4^{2-} .

4.3.3. Changes in sediment physicochemical Properties after thermal treatment

The pH of thermally treated sediment was decreased but these values were still within suitable pH ranges for plant growth and close to neutral (see Table 4.2; changed pH values from to 6.81 to 8.06). This result is the opposite of the fact that soil pH is increased after thermal treatment at above 250 °C⁵, indicating that increase in soil pH is induced by the release of alkali cations such as Ca^{2+} and Mg^{2+} from organic matter decomposition and the decomposition of organic acid. However, the hydrogen released from sulfur oxidation reactions during thermal treatment of sulfur-rich sediment was attributed to decrease in sediment pH. The increased sulfate content in thermally treated sediments was 2.6-4.1-folds larger than the sum

of increased calcium and magnesium concentrations, resulting in the decrease in sediment pH, especially under oxygen abundant environment and higher temperature. In addition, the newly formed bicarbonate from mineralization of CO_2 ⁵, which may be more produced during thermal treatment under oxygen more available atmosphere due to increased oxidation of carbon containing substances, could be also another reason to decrease sediment pH. which can be attributed by the fact that the increased sulfate concentrations under M condition, which were the main source for decreased in sediment pH during thermal treatment, were not significantly different regardless of temperature. The sediment pH was more decreased under higher heat temperature and oxygen more available conditions, resulting that these treatment conditions activated relevant reactions such as sulfur oxidation reactions and formation of bicarbonate for pH decrease.

According to Chapter 3, sediment physicochemical properties were not significantly changed during the thermal treatment under 300 °C for 30 min using the same muffle furnace but these properties as well as TPH removal efficiency in this study under the same treatment condition showed considerably different results. It is assumed that these differences were induced by the enhanced thermal conductivity during the relatively short treatment time from the additionally used the steel container, which is shown in Figure 4.2, for control the air composition, indicating the thermal conductivity is a critical factor which can change most of thermally impacted factors.

The oxygen availability and heat temperature during thermal treatment also influence on TN and CEC. The sediment organic matter loss via thermal treatment can affect contents of TN and CEC.⁵ The tendency of changes in TN contents after

thermal treatment was similar to loss of organic matter during thermal treatment under all treatment conditions. TN in thermally treated sediment were decreased at 12-96% due to its relatively low volatile temperature and organic matter loss^{17,20}, which can be explained by positive correlation coefficient value (R^2) of 0.926 for TN and TOC contents (see Figure 4.9).

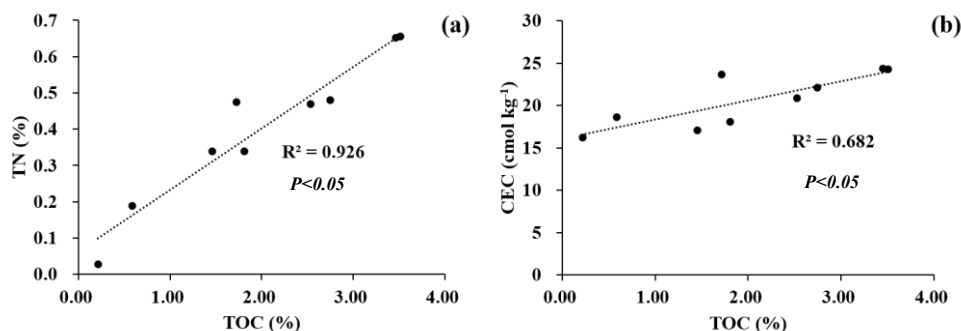


Figure 4.9. Correlation among TN, CEC and TOC results of thermally treated sediment: (a) TN and TOC, (b) CEC and TOC.

Sediment CEC contents, which is influenced by changes in organic matter and sediment minerals due to their decomposition and deformation^{5,17}, were also reduced by 25-50% after thermal treatment. From the XRD analysis presented in Figure 4.10, the sediment minerals were not significantly changed under all treatment condition.

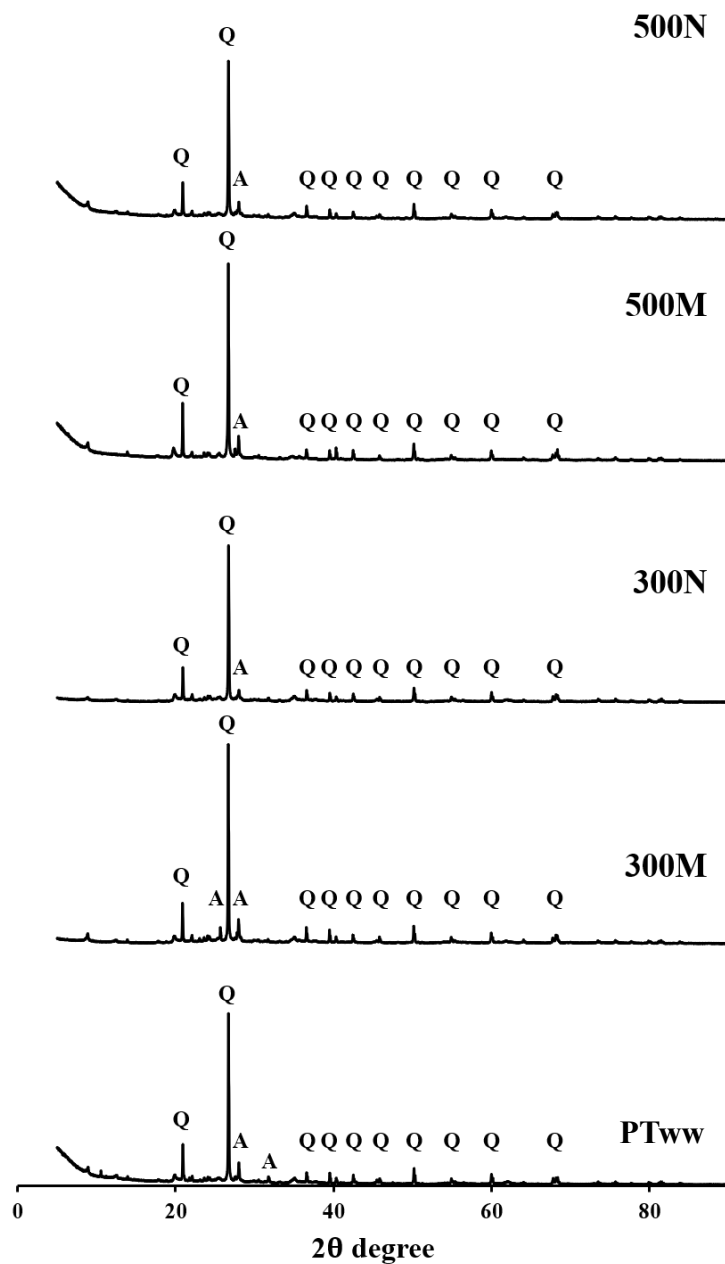


Figure 4.10. X-ray diffraction patterns of pretreated sediment (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under no oxygen-available condition (300N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under no oxygen-available condition (500N). The peak labels are as follows: Q, Quartz; A, Albite.

According to sediment particle distribution shown in Table 4.5, the proportion of clay in sediment were reduced 30-38% after thermal treatment but changes in clay fraction were not considerably different depending on treatment conditions. CEC content was less affected via thermal treatment compared with TOC and TN due to relatively less changes in clay minerals and relative less influenced from organic matter loss, which can be attributed to the moderate correlation coefficient value between CEC and TOC of 0.682. The fact that CEC content was not significantly changed by oxygen availability at the same heat temperature, indicating that this was caused by the nature of clay minerals, which is not substantially affected by oxygen availability within our temperature ranges. Sediment TP concentrations were slightly increased after thermal treatment under all treatment conditions, which can be explained by negligible mass loss of TP in during thermal treatment and the reduction of bulk sediment weight due to organic matter, losses of water TN. The sediment WHC (see Table 4.2), which is an essential factor for crop yields by influencing water availability to plant²¹, was increased by 9-30% after thermal treatment with increases in temperature and oxygen availability. The soil WHC was decreased or not substantially changed after thermal treatment in literature³, but our result showed improved WHC under all treatment conditions without addition of soil amendment (e.g. biochar). The WHC of thermally treated sediment under M condition was higher than L and N conditions due to their relatively lower hydrophobicity and higher polarity (see Table 4.1). In addition, thermally generated pores from condensed carbon under less oxygen condition which are the same function of soil amendment (i.e., biochar)⁹ and increased water retention from ash, which is more generated from the decomposition of organic matter under oxygen abundant condition²², may increase sediment WHC after

thermal treatment.

Table 4.5. Proportions of sand, silt and clays in pretreated sediment (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under no oxygen-available condition (300N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under no oxygen-available condition (500N).

Sample	Sand	Silt	Clay
	(%)	(%)	(%)
PTww	39.3	45.3	15.4
300M	63.1	27	9.9
300N	49.9	38.4	11.7
500M	61.9	27.8	10.3
500N	55.8	34.2	10

4.3.4. Changes in heavy metal mobility

The heavy metal extracted by TCLP relative to the total content of heavy metal (see Figure 4.11) was investigated in order to assess the effects of heat temperature and oxygen availability on changes in heavy metal mobility after thermal treatment. The TCLP leached fraction in thermally treated sediment was decreased for all heavy metals without Pb under all treatment conditions. The TCLP leached fractions of Ni, Zn and Cd were reduced at 18.2-85.4%, 11.2-68.3% and 21.2-45.3%, respectively. The mobility of Ni, Zn and Cd was reduced with increase in heat temperature and oxygen available conditions, especially 85.4%, 29.9% and

63.3% respectively under 500 M condition. On the other hand, the leached fraction of Cu by TCLP in all thermally treated sediment was also reduced at 29.9-91.3% but the tendency of decreased mobility of Cu were differently affected by oxygen availability depending on temperature. At 300 °C, the TCLP leached fraction of Cu was lowest at 91.3% under moderate oxygen available condition but from 400 °C Cu mobility under this oxygen condition was relatively higher than under oxygen limited conditions. In order to investigate the changes in fractions of heavy metal for the better understating of stabilization of heavy metal after thermal treatment depending on oxygen availability and heat temperature, sequential extraction procedure (SEP) was conducted. According to Figure 4.12, the residual fraction (F5) of SEP, which is known as the most strongly bounded fraction to sediment, for all heavy metals was increased under all treatment conditions, especially under moderate oxygen available atmosphere with increasing temperature. The organic bounded fraction of SEP (F4) was reduced in thermally treated sediment for heavy metals due to decomposition of organic matter, especially under M atmosphere and the F4 of Cu which dominantly accounted for 73% in pretreated sediment. This result was supported by the fact that R^2 values for F4 of heavy metals and TOC in thermally treated sediment showed positively high (see Figure 4.13). The iron/manganese oxide bounded fraction (F3), which was also decreased after thermal treatment with increased in temperature and oxygen availability. This result is line with literate data.²³ It is assumed that repartitioning and/or chemical transformation during thermal treatment affected the conversion of the iron/manganese oxide bounded fraction (F3) and organic bounded fraction (F4) into residual fraction (F5), which can be explained by the sum of those fractions (F3, F4 and F5) were almost similar or slightly increased after thermal treatment due to increased residual fraction under

all treatment conditions (see Table 4.6). These results may result in the reduction of TCLP leached fraction of heavy metals after thermal treatment under all conditions, especially M condition for some heavy metals.

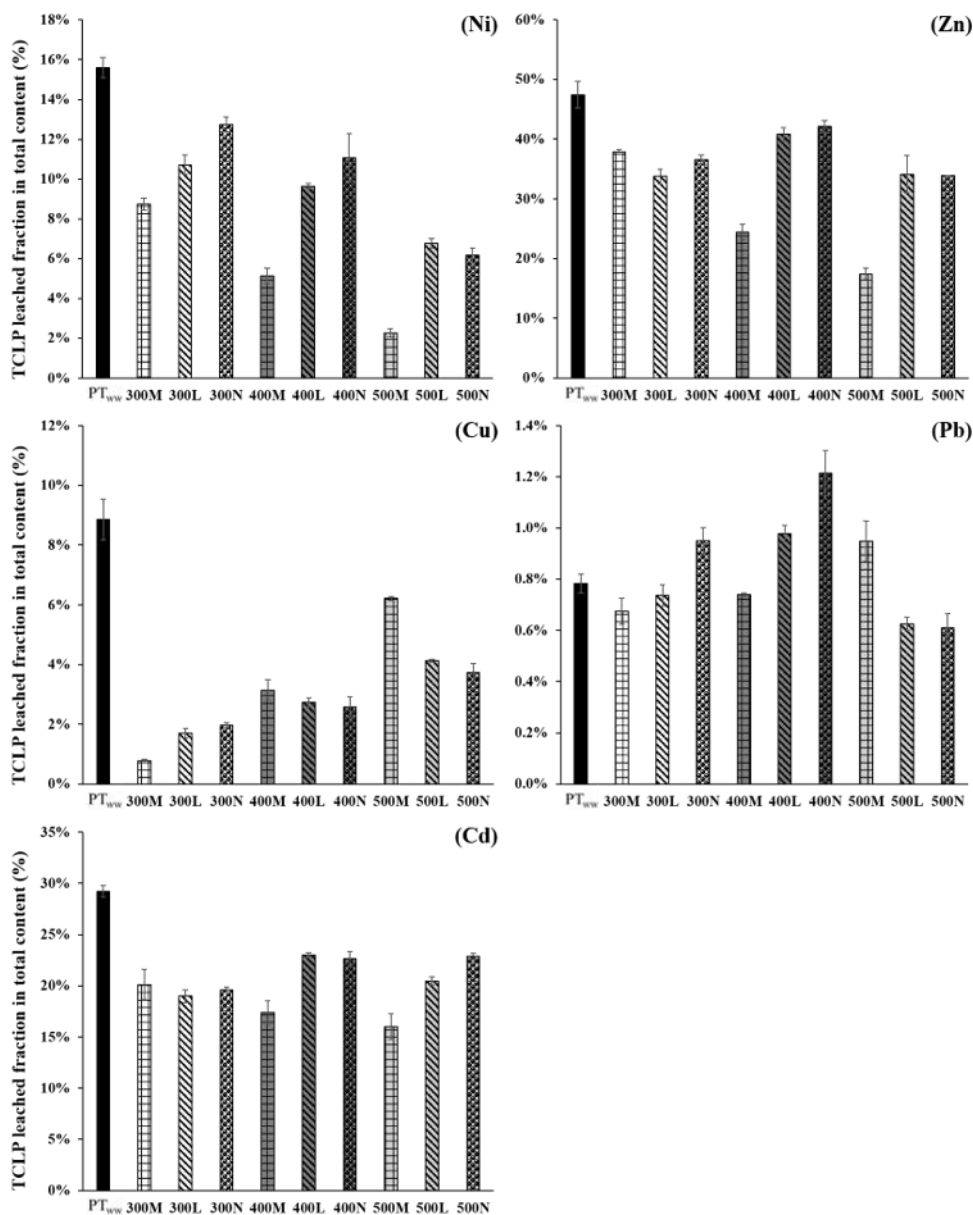


Figure 4.11. The TCLP leached fraction in total content (%) for pretreated sediment with water washing (PT_w), thermally treated sediment at 300 Celsius in moderate oxygen-available condition (300M), 300 Celsius in low oxygen condition (300L), 300 Celsius in no oxygen-available condition (300N), 400 Celsius in moderate oxygen-available condition (400M), 400 Celsius in low oxygen-available condition (400L), 400 Celsius in no oxygen-available condition (400N), 500 Celsius in

moderate oxygen-available condition (500M), 500 Celsius in low oxygen-available condition (500L), 500 Celsius in no oxygen-available condition (500N)

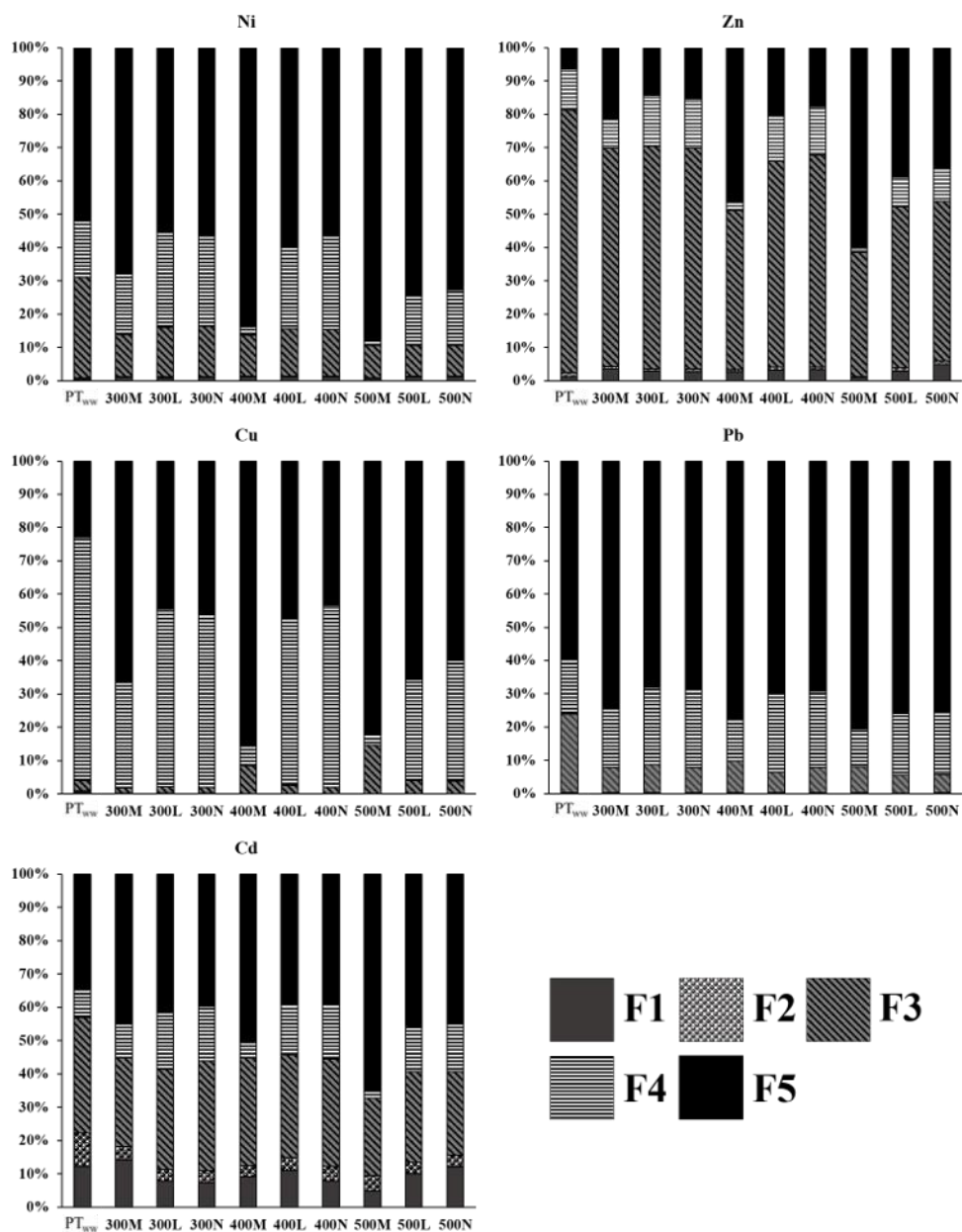


Figure 4.12. Composition of sequentially extracted fractions of heavy metals in total amount for pretreated sediment with water washing (PT_{ww}), thermally treated sediment at 300 Celsius in moderate oxygen-available condition (300M), 300 Celsius in low oxygen condition (300L), 300 Celsius in no oxygen-available condition (300N), 400 Celsius in moderate oxygen-available condition (400M), 400 Celsius in low oxygen-available condition (400L), 400 Celsius in no oxygen-

available condition (400N), 500 Celsius in moderate oxygen-available condition (500M), 500 Celsius in low oxygen-available condition (500L), 500 Celsius in no oxygen-available condition (500N)

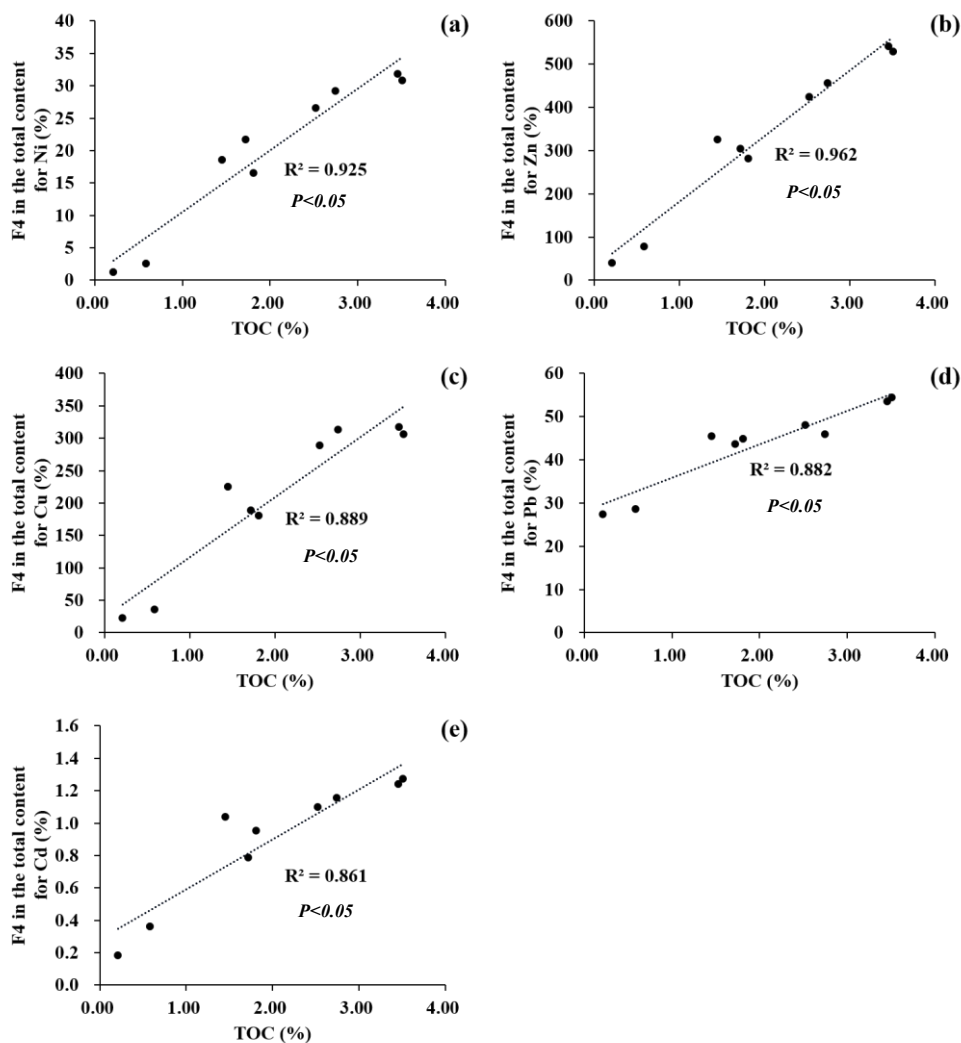


Figure 4.13. Correlation among F4 of SEP and TOC results of thermally treated sediment: (a) F4 of the SEP for Ni and TOC, (b) F4 of the SEP for Zn and TOC, (c) F4 of the SEP for Cu and TOC, (d) F4 of the SEP for Pb and TOC, (e) F4 of the SEP for Cd and TOC. F4 concentrations of the SEP for all heavy metals were divided by the total heavy metal content in sediment

Table 4.6. Concentrations in each sequential extraction fraction and total heavy metal contents (mg kg^{-1}) in pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

(a) Ni

	F1	F2	F3	F4	F5	Sum
	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
PTww	0.60±0.15	0.30±0.02	30.1±1.47	17.2±0.57	51.5±0.50	99.7±2.56
300M	1.20±0.02	0.37±0.01	14.9±1.59	21.9±1.13	79.7±1.84	118±4.58
300L	1.10±0.04	0.37±0.02	16.7±0.43	32.0±2.12	62.6±1.15	113±3.75
300N	1.10±0.01	0.27±0.02	16.9±1.01	30.9±0.46	62.8±2.08	112±3.57
400M	1.34±0.18	0.30±0.01	13.3±0.49	2.66±0.24	91.6±3.61	109±4.53
400L	1.28±0.07	0.34±0.02	15.1±1.02	26.7±0.07	63.6±0.78	107±1.95
400N	1.26±0.08	0.30±0.01	14.7±0.45	29.3±0.27	58.7±2.53	104±3.33
500M	0.74±0.06	0.25±0.02	10.5±0.87	1.33±0.10	94.8±0.27	108±1.33
500L	1.37±0.12	0.26±0.02	10.1±0.60	16.7±1.43	81.2±1.04	110±3.21
500N	1.41±0.06	0.31±0.02	10.4±0.51	18.7±1.61	82.5±6.96	110±9.17

(b) Zn

	F1	F2	F3	F4	F5	Sum
	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)
PTww	40.2±0.34	34.5±1.26	2414±94	383±4.33	193±6.7	3065±107
300M	125±4.72	24.5±1.0	2324±81	306±24	760±13	3540±123
300L	98.6±0.37	30.4±0.92	2351±19	542±34	499±29	3521±82
300N	96.6±2.3	32.5±2.09	2369±55	531±9.02	548±16	3576±84
400M	98.7±11.6	24.3±2.10	1738±27	80±4.92	1693±65	3634±110
400L	105±8.38	27.6±1.05	1956±59	425±2.0	652±7.9	3165±79
400N	106±5.73	25.6±0.95	1987±67	458±25	552±19	3129±116
500M	34.3±2.79	11.1±0.66	1275±55	41±3.48	2066±65	3427±127
500L	94.3±5.46	31.2±1.90	1568±116	283±8.51	1261±43	3237±175
500N	161±9.46	35.0±2.73	1581±74	327±0.82	1192±58	3297±146

(c) Cu

	F1	F2	F3	F4	F5	Sum
	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)
PTww	2.80±0.15	2.03±0.09	15.2±1.27	360±20	113±4	493±26
300M	1.10±0.14	0.15±0.01	9.60±1.22	189±17	394±13	594±31
300L	1.65±0.10	0.27±0.02	11.3±1.08	317±14	264±8	594±23
300N	1.31±0.07	0.27±0.02	10.5±0.36	306±9	274±16	592±25
400M	0.51±0.04	0.14±0.01	51.6±2.34	36±2	520±28	608±32
400L	0.63±0.03	0.12±0.0	14.6±0.82	289±7	276±4	581±11
400N	0.68±0.07	0.11±0.01	10.5±0.09	313±21	248±3	572±25

500M	0.50±0.02	0.30±0.01	94.5±1.95	22.8±1.23	530±12	648±16
500L	0.55±0.05	0.18±0.02	23.3±2.40	180±10	391±8	595±20
500N	0.52±0.01	0.17±0.01	22.8±1.13	225±2	373±35	622±38

(d) Pb

	F1	F2	F3	F4	F5	Sum
	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)
PTww	0.35±0.03	0.34±0.01	46.1±4.08	32.4±1.72	1167.24	195±13
300M	0.37±0.03	0.27±0.01	19.3±0.43	43.7±2.27	188±10	251±13
300L	0.26±0.01	0.24±0.01	19.9±1.05	53.5±2.91	158±6	232±10
300N	0.27±0.03	0.25±0.01	17.9±1.03	54.5±1.20	161±14	234±16
400M	0.22±0.01	0.31±0.01	21.0±1.40	28.5±1.98	171±1	221±4
400L	0.20±0.02	0.29±0.01	12.2±0.82	48.1±0.62	139±9	200±10
400N	0.19±0.01	0.24±0.01	15.1±1.33	46±1.45	138±2	200±9
500M	0.20±0.02	0.30±0.01	18.5±1.43	27.4±1.12	192±4	238±7
500L	0.21±0.01	0.25±0.02	12.8±1.30	44.8±2.31	182±4	241±7
500N	0.21±0.02	0.27±0.01	13.3±0.77	45.5±0.78	183±1	242±3

(e) Cd

	F1	F2	F3	F4	F5	Sum
	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)
PTww	0.87±0.03	0.71±0.06	2.47±0.12	0.63±0.04	2.44±0.06	7.13±0.32
300M	1.08±0.06	0.29±0.03	2.01±0.01	0.79±0.06	3.37±0.09	7.54±0.25
300L	0.57±0.02	0.24±0.02	2.16±0.02	1.24±0.07	2.95±0.09	7.17±0.21

300N	0.57±0.03	0.28±0.01	2.58±0.02	1.27±0.05	3.10±0.18	7.80±0.29
400M	0.75±0.07	0.26±0.01	2.63±0.09	0.36±0.02	4.11±0.15	8.10±0.33
400L	0.79±0.02	0.29±0.03	2.21±0.09	1.10±0.03	2.81±0.05	7.19±0.22
400N	0.56±0.03	0.31±0.03	2.30±0.04	1.15±0.03	2.81±0.03	7.13±0.14
500M	0.34±0.01	0.34±0.03	1.66±0.0	0.18±0.02	4.62±0.17	7.14±0.23
500L	0.71±0.04	0.23±0.02	1.91±0.11	0.95±0.09	3.22±0.12	7.03±0.37
500N	0.88±0.03	0.26±0.01	1.83±0.13	1.04±0.05	3.28±0.17	7.28±0.40

The stabilization of heavy metals during thermal treatment were attributed to particle aggregation, formation of metal oxide and carbonaceous matter. Under relatively oxygen abundant atmosphere (M), the particle aggregation and formation of metal oxide were assumed to be dominant stabilization mechanisms. Particle aggregation plays an important role as a physical protection against heavy metals leaching and extraction. The analysis of sediment particle size presented in Table 4.5 showed that the fraction of sand particle was increased 21-38 % after thermal treatment while silt and clay fractions were decreased, especially under moderate oxygen available condition. There was no substantial difference in sand fraction under moderate oxygen available atmosphere regardless heat temperature whereas sand fraction was increased with the increase in heat temperature under oxygen free condition, suggesting that heavy metal stabilization by particle aggregation was more influenced under more oxygen available atmosphere and this mechanism could be one of the critical reasons for the increased least labile fraction (F5). The formation of metal oxide during thermal treatment may result in the reduction of heavy metal mobility. According to literature^{24,25}, newly generated metal oxides (i.e., CuO, PbO and CdO) during thermal treatment may be against heavy metal leaching and

extraction due to physical sorption, precipitation and chemisorption on sediment minerals, suggesting that this mechanism was also attributed to the increase in the least labile fraction and the reduction of heavy metal mobility. Presumably, these forms of heavy metals are more generated under the higher temperature and abundant oxygen available atmosphere. However, newly generated metal oxides were not detected by XRD analysis, suggesting that these were not in crystalline phases, which were difficult to be formed in short time or too tidy and evenly distributed on sediment particles.²⁴ On the other hand, the newly produced black carbonaceous matter during thermal treatment under oxygen limited environment could provide more sorption sites to heavy metals, which can be explained that heavy metals are chemically or physically protected against extraction and leaching by reappportioning heavy metals to newly formed black carbon, which may be one of the main reasons for the increase in the residual fraction (F5). The increase in sediment surface carbon due to newly coated carbonaceous matter on sediment particle after thermal treatment can be also physical and chemical barriers against heavy metal extraction and leaching. The decreased contents of SOC, which can increase heavy metal mobility⁷, may also have a positive effect on decrease in heavy metal mobility. It should be noted that the dominant mechanisms of heavy metal stabilization during thermal treatment were explained depending on oxygen availability but these mechanisms cannot be equally applied to all cases due to complicated sediment matrix and different binding forms of each heavy metal. In addition, some stabilization reactions could be occurred at the higher temperature regardless of oxygen availability with increased thermal energy and use of source originated oxygen.

Pb mobility were differently affected by oxygen availability depending on

heat temperature range. For example, from 300 to 400 °C, Pb was more leached by TCLP under L and N atmosphere rather than M atmosphere whereas TCLP leached fractions of Pb under 500 L and N were less than under 500 M. Despite the changes in the behavior of pb mobility depending on heat temperature and oxygen availability, Pb fractions leached by TCLP under all treatment conditions were still less than 1.2 percent, indicating that there is no significant effect on plant growth from changes in Pb mobility.

As noted above, the changes in heavy metal mobility after thermal treatment could be differently occurred depending on treatment conditions but the thermal treatment of sediment under most of treatment conditions in this study had mostly positive effect on reduction of heavy metal mobility without additional energy and resources. It is expected that the sediment fertility could be improved after thermal treatment by reducing the mobility of heavy metals.

4.3.5 Effect of heat temperature and oxygen availability on barley germination and growth

The barley germination and growth results for all thermally treated sediments were enhanced (see Figure 4.14) but this result is the opposite to our previous study. According to previous Chapter 3, the result of barley germination and growth in thermally treated sediment (300 °C, 30 mins) was not improved compared with in pretreated sediment due to substantially increased salinity and soluble organics but this result was enhanced after removing those plant stressors. The enhanced fertility of thermally treated sediment more in this study than in previous study can be attributed to completely removed TPH contents and more reduced heavy metal mobility which were considered as main plant stressors and less

produced plants stressors in overall, resulting in improved germination and growth results without additional treatment after using our proposed thermal treatment technique with the use of the steel case. Root germination was increased 9-45% and shoot development was enhanced 0-36%. Root and shoot lengths were also increased 8.33-23.04 folds and 1.79-7.04 folds, respectively. At the same heat temperature, the barley germination and growth was relatively more improved under less oxygen availability due to relatively more preserved sediment physicochemical properties from newly produced black carbonaceous matter and relatively less production of critical plant stressors such as SOC and salinity in oxygen limited atmosphere. At the same oxygen availability, germination and growth of barley was mostly improved with the increase in heat temperature except under 500M, indicating that conversion of relatively more labile fractions of heavy metals to the least labile fraction and the increased water availability from improved aggregation and increased WHC.^{7,26} For example, the results of barley germination and growth for thermally treated sediment under 500L and 500N conditions showed the most enhanced fertility for all evaluation factors whereas these results for thermally treated sediment under 500M exhibited the almost lowest values. The contents of salinity and SOC in thermally treated sediment at 500 °C regardless of oxygen availability were not significantly different whereas the organic matter and TN contents, which are indicative of essential factors for sediment fertility, were substantially low in thermally treated sediment under 500 M condition compared with 500 L and 500N conditions due their increased decomposition with relatively more oxygen availability. It is highly suspected that the destroyed essential sediment physicochemical properties provided poor environment for plant germination and growth. According to Song et al.⁸, fertility of thermally treated soil with efficient

organic contaminant removal was enhanced after applying fertilizer. For the production of greening soil, essential elements such as sediment physicochemical properties as well as potential plant stressors including negative byproducts should be also importantly considered, monitored and properly managed. 54 of VOCs, which can be generated during production of black carbonaceous matters such as biochar and may have phyto-toxic effects on plant, was not detected in pretreated and thermally treated sediment under 300M, 300N, 500M, 500N conditions (Table 4.7), indicating that plant stress was not induced from VOCs. It should be noted that the more pyrolyzed sediment produced under highest temperature and least oxygen available condition can provide better vegetation environment by minimizing indigenous and newly generated plant stressor and preserving or improving sediment fertility related properties.

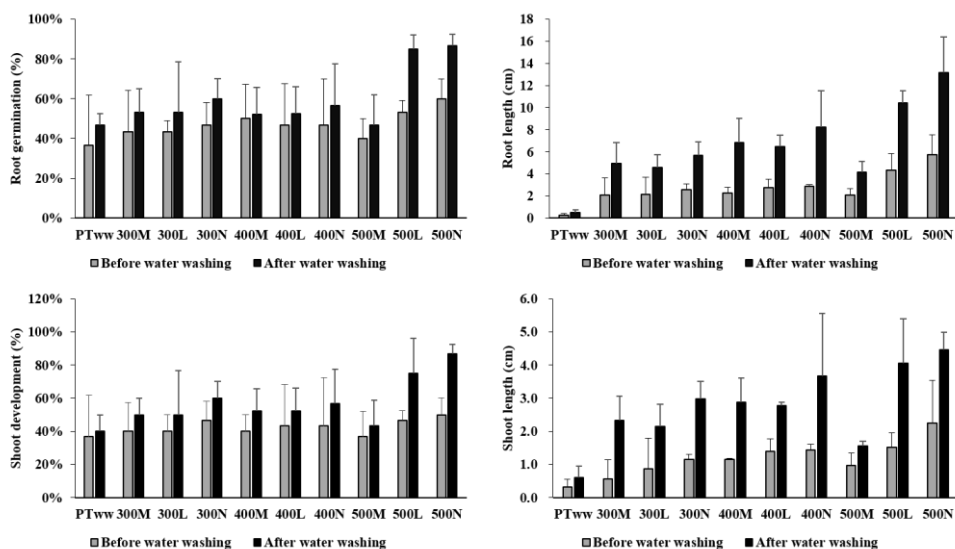


Figure 4.14. Results of barley germination and growth test before and after water washing for pretreated sediment with water washing (PTww), thermally treated sediment at 300 Celsius in moderate oxygen-available condition (300M), 300 Celsius in low oxygen condition (300L), 300 Celsius in no oxygen-available condition (300N), 400 Celsius in moderate oxygen-available condition (400M), 400 Celsius in low oxygen-available condition (400L), 400 Celsius in no oxygen-available condition (400N), 500 Celsius in moderate oxygen-available condition (500M), 500 Celsius in low oxygen-available condition (500L), 500 Celsius in no oxygen-available condition (500N)

Table 4.7. Volatile organic compounds (VOCs) in pretreated sediment with water washing (PTww) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under no oxygen-available condition (300N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under no oxygen-available condition (500N).

Volatile organic compounds (VOCs)	PTww	300M	300N	500M	500N
Benzene	ND	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	ND
Ethylbenzene	ND	ND	ND	ND	ND
m,p-Xylene	ND	ND	ND	ND	ND
o-Xylene	ND	ND	ND	ND	ND
Trichloroethylene	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND
Methylene Chloride	ND	ND	ND	ND	ND
Carbon Tetrachloride	ND	ND	ND	ND	ND
Chloroform	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND
Dibromochloromethane	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND
1,1-Dichloroethene	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND

cis-1,2-dichloroethene	ND	ND	ND	ND	ND
trans-1,2-dichloroethene	ND	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	ND	ND
Acrylonitrile	ND	ND	ND	ND	ND
Methyl Tertiary Butyl Ether(MTBE)	ND	ND	ND	ND	ND
1,2-Dibromo-3-chloropropane	ND	ND	ND	ND	ND
Naphthalene	ND	ND	ND	ND	ND
Ethylacetate	ND	ND	ND	ND	ND
2-propanol	ND	ND	ND	ND	ND
Nitrobenzene	ND	ND	ND	ND	ND
Carbon disulfide	ND	ND	ND	ND	ND
benzyl chloride	ND	ND	ND	ND	ND
Acrolein	ND	ND	ND	ND	ND
Methyl ethyl ketone	ND	ND	ND	ND	ND
Allyl chloride	ND	ND	ND	ND	ND
Allyl alcohol	ND	ND	ND	ND	ND
Styrene	ND	ND	ND	ND	ND
Methyl acrylate	ND	ND	ND	ND	ND
Dichlorodifluoromethane	ND	ND	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND

Trichlorofluoromethane	ND	ND	ND	ND	ND
Bromochloromethane	ND	ND	ND	ND	ND
1,2-Dibromoethane	ND	ND	ND	ND	ND
1,2,3-Trichlorobenzene	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND
Chloromethane	ND	ND	ND	ND	ND
Chlorobenzene	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND
Cumene (Isopropylbenzene)	ND	ND	ND	ND	ND

ND: Not Detected.

4.3.6. Changes in barley germination and growth after water washing.

Even though thermally treated sediment showed improved agronomic performance under all treatment conditions, increased salinity and soluble organics, which exhibit phyto-toxic effects, after thermal treatment may inhibit barley germination and growth by offsetting the benefit of thermal treatment to sediment. In order to improve thermally treated sediment fertility, water washing, which was verified as an excellent removal method for salinity and soluble organics without significant changes in sediment characteristics and the other contaminants, was conducted. After water washing, the EC_{1:5} values of sediment shown in Figure 4.15

became low or similar to 0.5 dS m^{-1} and SOC contents shown in Figure 4.5 were also reduced at 34-72% in sediment treated at 300 °C and 400 °C. SOC contents in thermally treated sediment at 500 °C regardless of oxygen availability were not changed but still showed lowest values. Barley germination and growth results after water washing shown in Figure 4.14 was considerably enhanced. The root germination and shoot development were increased at 27-59% and 9-73%, respectively and the lengths of root and shoot were also improved by 2.02-3 folds and 1.91-4.06 folds after water washing. From these results, newly generated phytotoxicants exhibit negative effects on barley germination and growth and thermally treated sediment can show better performance with the reduced those stressors. As discussed above, it is found that sediment fertility with the similar contents of SOC and salinity could show different agronomic performance due to differently changes in sediment characteristics after thermal treatment. The barley germination and growth results before and after water washing were also shown similar patterns based on thermal treatment conditions even though the increased rates of barley germination and growth after water washing were slightly different, suggesting that water washing had no substantial impact on enhancement of or changes in sediment physicochemical properties which were more influenced by treatment conditions during thermal treatment. Therefore, it is important to optimize thermal treatment conditions by considering the thermally treated sediment physicochemical properties, which can play a major role for sediment fertility, and minimizing negative effects from indigenous and newly produced plant stressor. According to the result of correlation analysis, there were no critical factors related to barley germination and growth. It should be note that only one or two predominant factors cannot represent overall changes in sediment fertility after thermal treatment due to complicated

sediment complexes and closely related each factor to sediment fertility. In order to produce a greening soil, optimized thermal treatment conditions should be determined based on the comprehensive analysis of changes in sediment physicochemical properties as well as indigenous and newly produced plant stressors.

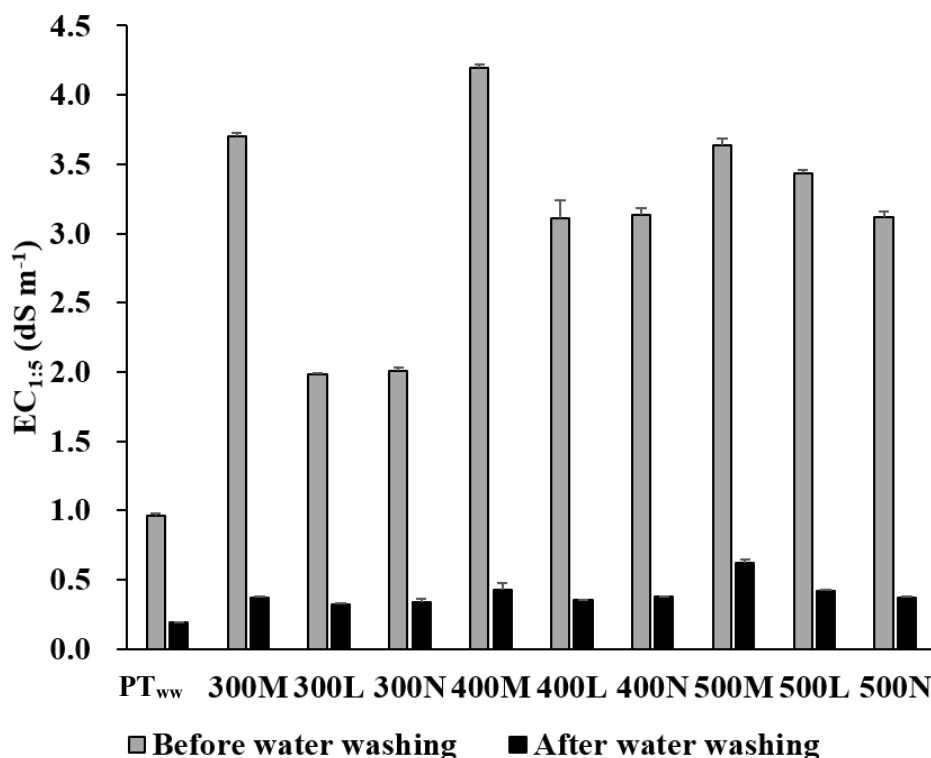


Figure 4.15. EC_{1:5} values before and after water washing for pretreated sediment (PT_{ww}) and thermally treated sediment at 300 °C under moderate oxygen-available condition (300M), at 300 °C under low oxygen condition (300L), at 300 °C under no oxygen-available condition (300N), at 400 °C under moderate oxygen-available condition (400M), at 400 °C under low oxygen-available condition (400L), at 400 °C under no oxygen-available condition (400N), at 500 °C under moderate oxygen-available condition (500M), at 500 °C under low oxygen-available (500L), at 500 °C under no oxygen-available condition (500N).

4.4. Implications

The current study demonstrates that the proposed thermal treatment technique can produce planting soil using petroleum impacted sediment based on the investigation of heat temperature and oxygen availability on TPH removal efficiency, sediment physicochemical properties, motility of heavy metals and sediment fertility. The SOC content, exhibiting a significant phyto-toxic effect, was successfully removed without additional treatment by only controlling the heat temperature and oxygen availability as thermal treatment conditions, suggesting that this resulted in the reduction of environmental and economical burdens and minimization of additional treatment process for removal of adverse treatment intermediate. In addition, pyrolytic treatment under oxygen-limited or -free atmospheres, which was successfully created with the use of a lid of a container without continuous inert gas supply, could minimize the generation of organic intermediate and produce black carbonaceous matter using source-originated organic matter, suggesting that newly produced black carbon can give additional benefits of better conservation of sediment physicochemical properties at relative high heat treatment and supply of more sorption site to contaminants. However, the sediment salinity, which can be a plant-stressor, was increased during thermal treatment at high temperature regardless of initial oxygen availability in the treatment environment. Manipulation of treatment conditions such as oxygen availability or heat temperature has a limit to addressing all relevant problems of production of negative byproducts during thermal treatment. The increased sediment salinity after thermal could be rapidly and easily removed by water washing, thus thermally treated sediment after water washing could provide better environment for plant germination and growth. But the

effluent, generated from water washing, may be still environmental and socio-economic burdens but water washing should be inevitably included as an essential part of a treatment process to remove indigenous salt in dredged sediment to produce a greening soil applicable to terrestrial ecosystems. By reasonably reorganizing sequence of treatment processes for co-contaminated sediment with heavy metals and petroleum, potential increase in sediment salinity during each treatment process could be reduced after finishing all treatment processes without post treatment. A further study is required to optimize sequence of treatment processes for mixed contaminated sediment to minimize newly generated salts during treatment for production of enhanced sediment fertility as planting medium.

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CHAPTER 5

Conclusion

This study demonstrated potentials to beneficial use of dredged marine sediment as inland plant growable soil after acid washing and thermal treatment. It is believed that the significant removal of sediment salinity and reduced heavy metal mobility after acid washing and neutralization treatment were dominant reasons to enhance the barley germination and growth. The effectively removal of petroleum and reduced heavy metal mobility by thermal treatment had positive effect on the barley grow.

Salts in dredged marine sediment were identified as critical plant stressor by conducting the barley germination and growth test after water washing for salinity removal in sediment. By lowering the sediment salinity, the germination and growth were gradually increased even though the contents of heavy metals and TPH contents in sediment were not removed after water washing. In order to beneficially use dredged marine sediment as inland plant growable soil, the salts which are originated from the ocean or the byproducts during treatment should be properly treated to provide the proper soil function for plant growth.

Treatment conditions differently influenced the treated sediment fertility as planting soil. The sediment salinity and salinity removal efficiency after acid washing and neutralization treatment were significantly affected by the amount of newly formed gypsum depending on types of acid solutions and neutralizers, especially H_2SO_4 and CaO . These changes also led to sediment fertility. In addition,

the salt compositions in treated sediment were also changed by the applied acid solutions and neutralizers. The cationic salts generated from neutralizers had more effects on barley growth than anionic salts produced from acid solutions. The CaO treated sediment showed the better agronomic performance than NaOH treated sediment. The CaO treatment can reclaim structural, hydraulic and toxicological problems caused by the source originated sodium salts in dredged marine sediment by replacing the exchangeable sodium. For thermal treatment, more activated pyrolytic treatment under higher and less oxygen available conditions can produce more black carbonaceous materials during thermal treatment, resulting in the better preservation of sediment physicochemical properties compared to the more oxygen available condition at the same heat temperature. In addition, the formation of sulfate salts which increase the sediment salinity were less occurred under oxygen limited conditions due to less available oxygen for sulfur oxidation reactions and soluble organics which were identified critical plant stressor were less formed at the higher temperature. From these results, the more pyrolyzed sediment at higher temperature can provide the better plant growable environment than more oxidized sediment.

The treated sediment fertility can be enhanced by the post treatment such as water washing by reducing the negative byproducts such as increased salinity and soluble organics. However, the post treatment cannot enhance the changed characteristics of treated sediment which were main factors for sediment fertility and were determined by the treatment conditions. Therefore, for the production of quality enhanced sediment which can provide suitable soil function for plant growth, dredged marine sediment should be treated under the optimized treatment conditions.

국문초록

유류 및 중금속 오염 해양 준설토의 산세척 및 열처리 통한 식물 생장용 토양 생산기술 개발

해마다 엄청난 양의 준설토가 항만 개발, 해안 수심 유지 및 관리를 위해 발생하고 있다. 이를 해양 투기하는 방법으로 처리해왔으나 국제적인 협약 및 규제로 인해 해당 방법의 적용이 제한 및 금지됨에 따라 이를 지속가능한 방법으로 처리하기 위해 준설토 유효활용에 대한 관심이 증대되고 있다. 하지만 상당한 경우에 준설토가 인간의 활동에 의해 중금속 및 유류로 오염되었다. 준설토를 유효활용하기 전 적용되는 환경 및 생태계에 미치는 영향을 최소화하기 위해 이를 적절한 방법으로 처리 후 유효활용하는 것이 중요하다. 기존의 정화처리 방법은 법적 기준을 맞추는데 초점이 맞춰져 있어 정화 후 준설토에 대한 가치가 크게 고려되지 않아 정화 후 준설토의 가치가 낮아져 이를 폐기처분 하거나 단순한 건설재료로 유효활용하는 것이 일반적이다. 본 연구에서는 오염물질의 적절한 제거뿐만 아니라 정화 후 준설토의 가치 향상을 통해 이를 생산성이 향상된 식물생장용 토양으로 유효활용할 수 있는 정화기술을 개발하는 것이 목적이다. 기존 준설토 처리의 경우 투기 또는 정화를 위해 막대한 공간이 필요한 것이 문제점이었다. 이러한 단점을 극복하기

위해 목표로 하는 오염물질을 신속하고 효율적으로 제거함과 동시에 정화 후 준설토의 가치를 향상시킬 수 있는 정화방법을 선택하고자 한다. 본 연구에서는 산세척을 통해 준설토 내 중금속을 제거하고 산세척 및 중화하는 과정에서 적용되는 다양한 산과 중화제의 종류가 정화 준설토의 식물 생장용 토양으로서의 가치에 미치는 영향 대해 알아보았다. 저온 열처리를 통해 준설토 내 유류를 제거하고 이를 식물 생장용 토양 생산 기술을 개발하고자 한다. 이를 토대로 다양한 온도와 산소조건에서 열처리를 수행하여 정화 준설토의 식물 생장용 토양으로서의 가치에 미치는 영향을 확인하여 생태가치가 향상된 식물 생장용 토양을 생산하는 최적의 열처리 조건을 도출하고자 한다. 이를 확인하기 위해 정화하는 과정에서 달라지는 오염물질 농도 및 이동성, 준설토의 물리화학적 특성 그리고 최종적으로 제안되는 기술을 통해 정화된 준설토를 이용하여 보리 발아 및 생장 실험을 수행하여 정화 전후로 달라진 생태가치를 확인한다.

첫 번째로 산세척 및 중화 처리 시 다양한 산용액과 중화제의 종류가 정화 준설토의 식물 생장용 토양으로서의 생산성에 미치는 영향 대해서 알아보았다. 염이 식물생장에 미치는 영향을 알아보기 위해 3차 종류수를 이용해 준설토 내 염을 단계별로 세척 후 보리 발아 및 생장 실험을 수행해본 결과 준설토 내 염의 농도가 낮아질수록 보리 발아 및 생장이 향상되는 것을 확인하였다. 염을 세척하는 과정에서 준설토 내 유류 및 중금속의 농도와 중금속의 결합형태가 염세척 전후로 크게 달라지지 않았음에도 불구하고 준설토 내 염만 제거되었을 때 보리 발아 및

생장이 증대되는 것으로 보아 염이 식물에 생장에 미치는 상당한 저해
 요인임을 확인할 수 있었다. 같은 세기의 HCl , HNO_3 , H_2SO_4 를 이용한 산
 세척을 수행한 결과 준설토 내 중금속의 이동성이 전반적으로 유사하게
 저감되었고 대부분의 물리화학적 특성도 산종류와 관계없이 산세척 후에
 크게 변하지 않는 것을 확인할 수 있다. 산세척 및 중화 처리 완료 시
 준설토 내 염이 정화하는 과정에서 세척되는 효과를 통해 정화 전에 비
 해 84-87%가 저감되었다. 적용되는 산용액과 중화제의 종류에 따라 준설토
 의 중화 후 염농도와 염세척 효율에도 영향을 미쳤다. 황산 또는 lime
 (CaO)으로 처리된 준설토의 경우 gypsum (CaSO_4)이 생성됨에 따라
 gypsum의 낮은 용해도로 인해 다른 산용액 및 중화제로 처리한 정화 준
 설토에 비해 중화 후 준설토 내 잔류 염이 상대적으로 높은 것으로 분석
 되었다. 뿐만 아니라, gypsum이 가장 많이 형성되는 H_2SO_4 와 CaO 로 처리
 된 준설토의 경우 목표로 하는 염농도인 0.5 dS m^{-1} 수준으로 정화하기 위
 해 3회의 세척이 필요했지만 다른 정화 준설토의 경우 2회에 세척을 통
 해 이에 근접하는 염농도를 달성할 수 있었다. 중화까지 완료된 준설토
 를 대상으로 보리 발아 및 생장 실험을 수행한 결과 정화 전 준설토 내
 높은 염농도로 인해 보리가 전혀 발아되지 않았지만 산세척과 중화 후
 준설토 내 염이 상당히 낮아지고 중금속의 이동성 또한 효과적으로 저감
 됨에 따라 모든 정화 준설토에서 뿌리 및 줄기 발아가 이루어졌으며 뿌
 리 및 줄기 생장 또한 크게 향상되었다. 적용된 중화제에 의해 발생한
 염 양이온(Ca^{2+} , Na^{+})이 산세척을 통해 증가된 염 음이온(Cl^{-} , NO_3^{-} , SO_4^{2-})보
 다 보리 생장에 더 큰 영향을 미쳤으며 특히 CaO 로 정화된 준설토에서

더 큰 생장을 보였다. 준설토 내 Na^+ 는 식물 생장에 독성영향을 미치며 토양의 구조를 파괴하고 다른 영양분의 섭취를 방해한다. CaO 의 적용을 통해 증가하는 Ca^{2+} 는 토양 표면에 흡착된 Na^+ 를 교체함으로써 토양의 특성을 개선하고 Na^+ 로 인해 발생하는 독성영향 저감 및 영양분 섭취 불균형 해결, 그리고 식물 생장에 영양분으로 사용됨에 따라 CaO 로 정화 준설토에서 식물생장에 더 유리한 환경을 제공하는 것으로 사료된다.

본 연구에서 제시하는 저온 열처리를 통해 준설토 내 유류를 효과적으로 제거하고 정화 후 대부분의 준설토의 물리화학적 특성을 보존할 수 있음을 확인하였다. 뿐만 아니라, 열처리 후 준설토 내 잔류하는 중금속의 이동성이 저감되는 효과를 보였다. 이는 토양 입자의 응집 (Particle aggregation)을 통해 중금속을 이용하기 힘든 형태로 안정화시키고 준설토 내 존재하는 유기오염물질 및 유기물을 이용하여 열처리 과정에서 탄화생성물 (Char) 생성을 통해 중금속의 흡착력을 증가시킴으로서 중금속의 이동성이 저감되었다. 이러한 장점에도 불구하고 열처리 후 준설토를 대상으로 보리 발아 및 생장 실험을 수행해본 결과 정화전에 비해 발아 및 생장이 크게 향상되지 않거나 저감되는 결과를 보였다. 이는 정화하는 과정에서 발생하는 soluble organics와 황의 산화를 통해 증가하는 황산염(SO_4^{2-})이 준설토의 염농도를 높이는 것이 원인이 된 것으로 사료된다. 열처리 준설토를 대상으로 3차 증류수를 이용한 세척을 통해 준설토 내 염 및 soluble organics를 쉽게 제거할 수 있었으며 해당 준설토를 대상으로 보리 발아 및 생장 실험을 수행한 결과 발아 및 생장이 매우 크게 증가함을 확인하였다. 이를 통해 본 연구에서 제시하는 열처리 정

화 공정을 통해 생태가치가 향상된 정화 준설토를 생산할 수 있음을 확인하였다.

열처리 정화를 통해 생태가치가 향상된 준설토를 생산하였으며 열처리 정화 조건 중 온도와 산소이용성을 달리하였을 때 달라지는 보리발아 및 생장 결과와 준설토의 물리화학적 특성, 잔류 중금속 이동성, 유류의 제거효율을 종합적으로 분석하여 생태가치가 향상된 최적의 열처리 정화조건을 도출하고자 한다. 열처리하는 과정에서 철통을 이용하여 산소의 이용성을 물리적으로 통제한 결과 지속적인 질소가스 주입 없이도 충분히 열분해 조건을 만들어 온도가 증가할 수록 더 많은 탄화생성물(carbonaceous materials)을 생산할 수 있음을 확인하였으며 해당 조건에서 생성된 탄화생성물의 흡착력을 이용하여 높은 온도에서도 상대적으로 산소가 더 많은 조건보다 준설토의 물리화학적 특성을 더 잘 보존할 수 있음을 확인하였다. 뿐만 아니라, 열처리 후 모든 조건에서 중금속의 이동성이 저감됨을 확인하였으며 온도 및 산소 이용성에 따라 각 중금속 별로 준설토의 이동성이 달라지는 것을 확인하였다. 전반적으로 열처리 정화 후 가장 이용하기 힘든 형태인 residual fraction의 증가가 이동성 저감에 주요한 원인인 것으로 사료된다. 산소 이용성이 높은 환경에서는 준설토 입자응집(particle aggregation)으로 인한 안정화가 이동성 저감에 긍정적인 영향을 미친 것으로 사료된다. 산소 이용성이 낮은 환경에서는 온도가 높아질수록 탄화생성물의 증가 및 준설토 입자응집(particle aggregation) 증가가 중금속 이동성 저감에 긍정적인 영향을 미친 것으로 사료된다. 다양한 조건에서 처리된 준설토를 대상으로 보리발아 및 생장

실험을 수행한 결과 모든 조건에서 보리밭아 및 생장이 정화 전에 비해 증가한 것으로 분석되었다. 이는 주요한 오염물질인 유류가 100% 수준으로 제거되고 중금속 이동성 저감이 향상된 것이 보리 밭아 및 생장 증대에 기여한 것으로 사료된다. 뿐만 아니라, 정화 후 발생하는 상당한 식물 생장 저해요인인 *soluble organics*도 추가적인 정화없이 열처리 조건 중 온도를 증가시켜 생성을 저해함에 따라 보리 밭아 및 생장에 긍정적인 영향을 미친 것으로 사료된다. 열처리 조건 중 산소가 적고 온도가 높은 환경 (500N)에서 열분해 처리된 준설토에서 가장 큰 밭아 및 생장을 보였다. 이는 열분해를 통해 생성된 탄화생성물의 흡착력과 산화 반응이 적게 발생하여 식물 생장에 필수요소인 물리화학적 특성이 같은 온도에서 산소가 더 많은 조건에 비해 더 잘 보존되고 상대적으로 염이 적게 생성된 것이 식물 생장에 긍정적인 영향을 미친 것으로 사료된다. 열처리 준설토를 대상으로 염세척을 수행한 결과 염 및 *soluble organics*의 저감을 통해 보리 밭아 및 생장이 증대되었다. 하지만 염세척을 통해 밭아 및 생장이 증가되는 양상이 열처리 후 온도와 산소 이용성에 따라 달라지는 준설토의 보리 밭아 및 생장 결과와 유사하다. 이를 통해 염세척을 통해 부정적인 저해요인 저감을 통해 준설토의 생산성을 향상시킬 수 있지만 열처리 후 변화된 준설토의 특성을 개선시키지는 못한다. 따라서, 정화 후 달라지는 준설토의 전반적인 특성이 식물 생산성을 결정하는 주요한 원인이므로 식물 생장용 정화 준설토 생산 시 이를 고려한 최적화된 열처리 조건으로 정화하는 것이 중요하다.

Keywords : dredged marine sediment, salt, thermal treatment, heavy metals,
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