

Applied and Environmental Soil Science

Soil Pollution Prevention and Remediation

Guest Editors: Ezio Ranieri, Fabian Bombardelli, Petros Gikas, and Bernardino Chiaia





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Contents

Soil Pollution Prevention and Remediation

Ezio Ranieri, Fabian Bombardelli, Petros Gikas, and Bernardino Chiaia
Volume 2016, Article ID 9415175, 2 pages

Integrated Nanozero Valent Iron and Biosurfactant-Aided Remediation of PCB-Contaminated Soil

He Zhang, Baiyu Zhang, and Bo Liu
Volume 2016, Article ID 5390808, 11 pages

Phytoremediation of Gold Mine Tailings Amended with Iron-Coated and Uncoated Rice Husk Ash by Vetiver Grass (*Vetiveria zizanioides* (Linn.) Nash)

F. S. Tariq, A. W. Samsuri, D. S. Karam, and A. Z. Aris
Volume 2016, Article ID 4151898, 12 pages

Dissolution of Metals from Biosolid-Treated Soils by Organic Acid Mixtures

Won-Pyo Park, Bon-Jun Koo, Andrew C. Chang, Thomas E. Ferko, Jonathan R. Parker, Tracy H. Ward, Stephanie V. Lara, and Chau M. Nguyen
Volume 2016, Article ID 9858437, 14 pages

Oil and Gas Production Wastewater: Soil Contamination and Pollution Prevention

John Pichtel
Volume 2016, Article ID 2707989, 24 pages

A Rationale for Pollutograph Evaluation in Ungauged Areas, Using Daily Rainfall Patterns: Case Studies of the Apulian Region in Southern Italy

Angela Gorgoglione, Andrea Gioia, Vito Iacobellis, Alberto Ferruccio Piccinni, and Ezio Ranieri
Volume 2016, Article ID 9327614, 16 pages

Role of Inorganic and Organic Fractions in Animal Manure Compost in Lead Immobilization and Microbial Activity in Soil

Masahiko Katoh, Wataru Kitahara, and Takeshi Sato
Volume 2016, Article ID 7872947, 9 pages

Cadmium Phytoremediation Potential of Napiergrass Cultivated in Kyushu, Japan

Yasuyuki Ishii, Kotomi Hamano, Dong-Jin Kang, Sachiko Idota, and Aya Nishiwaki
Volume 2015, Article ID 756270, 6 pages

Editorial

Soil Pollution Prevention and Remediation

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In this special issue we have invited authors who are scientists and engineers to contribute original research as well as review articles on recent advances made on techniques and methodologies for the soil pollution prevention and remediation. This journal is in the field of soil science and reflects its multidisciplinary nature including treatments for soil treatment and reclamation.

Soil pollution probably represents the most faced problem in environmental pollution. This is because soil is a point of concentration and recovery of toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health. Soil pollutants can contaminate water: water infiltration is the movement of water from the soil surface into the soil profile and soil is a valuable resource that support cultures and plant life. Soil pollution is the decrease in the productivity of soil due to the presence of soil pollutants. Moreover soil pollutants have an adverse effect on the physical, chemical, and biological properties of the soil and reduce its productivity.

Main causes of soil pollution are as follows: industrial activity, especially since the amount of mining and manufacturing has increased; agricultural activities, pesticides and fertilizers which are full of chemicals that are not fully degradable in nature and are widely utilized around the world; waste disposal, where there is also a large amount of industrial and municipal waste that is dumped directly into landfills without any treatment; and accidental oil spills, where oil leaks can happen during storage and transport of chemicals.

Main effects of soil pollution are *effect on health of humans; effect on growth of plants; decreased soil fertility; and toxic dust.*

Through expanding our understanding and development of innovative techniques to analyze and treat polluted soils, scientists and engineers can play a crucial role in bringing models and technologies to deal with the environment pollution problem effectively.

The relevant fundamental principles of soil quality management and treatment have been covered. However, the main focus is on assessing sustainable treatment technologies and current case studies related to soil remediation, natural and conventional water treatment, and sustainable drainage systems applied for diffuse pollution treatment.

Academics, professionals, and students in the soil, water, and environmental engineering, science, and management areas, as well as the geologist and hydrological engineers, should be interested in the detailed design, operation, management, and process control for soil and water quality monitoring and applied modeling issues presented in this issue.

This special issue presents a comprehensive collection of timely, novel, and innovative research case studies in the area of soil remediation. It demonstrates to practitioners how natural and innovative systems can be integrated into traditional soil remediation, which are predominantly applied for the treatment of diffuse pollution. Also, it assesses the design, operation, and management of soil remediation technologies and water treatment performance of sustainable drainage systems including hydrology and modeling.

Topics of interest include soil remediation, clogging and soil hydraulic conductivity, phytoremediation and soil remediation technologies, storm water management, urban runoff treatment, and soil quality parameters.

Specifically papers included in the special issue are related to role of inorganic and organic fractions in animal manure compost in lead immobilization and microbial activity in soil; cadmium phytoremediation potential of Napier grass cultivated in Kyushu, Japan; phytoremediation of gold mine tailings amended with iron-coated and uncoated rice husk ash by vetiver grass (*Vetiveria zizanioides* L.); oil and gas production wastewaters: soil contamination and pollution prevention; a rationale for pollutograph evaluation in ungaged areas, using daily rainfall patterns: case studies of Apulia region; the analysis of arsenic speciation in *Pteris vittata* L. and ash; dissolution of biosolid-borne metals of soils; and immobilization of As, Mn, Cu, and Pb in gold mine tailings amended with empty fruit bunch and rice husk biochars pyrolysed at different temperatures.

Particularly urban runoff and phytoremediation have been discussed in the special issue.

Storm water runoff from paved streets, sidewalks, and parking lots, and through lawns and storm drains flows, collects and transports waste, salt, pesticides, fertilizer, oil and grease, and other pollutants [1]. This water drains directly into rivers and sea, without receiving treatment. During their flow through soil pores, the pollutants are subjects to a series of interactions such as adsorption, volatilization, and plant uptake. Polluted storm water therefore can harm soil plants, fish, and wildlife, while degrading the quality of soil and water.

Phytoremediation is an environmentally friendly and low-cost approach for the decontamination of polluted sites and has been greeted with a high degree of public acceptance [2, 3]. Therefore research using phytoremediation technology has been encouraged. In particular, metal hyperaccumulation in different species is investigated with the aim of determining the mechanisms associated with the accumulation and detoxification of heavy metals and using these macrophytes and their rhizomes, roots, stems, and leaves for the decontamination of polluted sites.

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References

- [1] C. Van Lienden, L. Shan, S. Rao, E. Ranieri, and T. M. Young, "Metals removal from stormwater by commercial and non-commercial granular activated carbons," *Water Environment Research*, vol. 82, no. 4, pp. 351–356, 2010.
- [2] E. Ranieri, U. Fratino, D. Petruzzelli, and A. C. Borges, "A comparison between *Phragmites australis* and *Helianthus annuus* in chromium phytoextraction," *Water, Air, & Soil Pollution*, vol. 224, no. 3, article 1465, pp. 1–9, 2013.
- [3] P. Gikas and E. Ranieri, "Effects of plants for reduction and removal of hexavalent chromium from a contaminated soil," *Water, Air, and Soil Pollution*, vol. 225, no. 6, article 1981, pp. 1–9, 2014.

Research Article

Integrated Nanozero Valent Iron and Biosurfactant-Aided Remediation of PCB-Contaminated Soil

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Polychlorobiphenyls (PCBs) have been identified as environmental hazards for years. Due to historical issues, a considerable amount of PCBs was released deep underground in Canada. In this research, a nanoscale zero valent iron- (nZVI-) aided dechlorination followed by biosurfactant enhanced soil washing method was developed to remove PCBs from soil. During nZVI-aided dechlorination, the effects of nZVI dosage, initial pH level, and temperature were evaluated, respectively. Five levels of nZVI dosage and two levels of initial pH were experimented to evaluate the PCB dechlorination rate. Additionally, the temperature changes could positively influence the dechlorination process. In soil washing, the presence of nanoiron particles played a key role in PCB removal. The crude biosurfactant was produced using a bacterial strain isolated from the Atlantic Ocean and was applied for soil washing. The study has led to a promising technology for PCB-contaminated soil remediation.

1. Introduction

As family members of chlorinated hydrocarbons, polychlorinated biphenyls (PCBs) are a group of manmade chemicals which were first synthesized in 1881 and commercialized in North American industries from the 1930s to the late 1970s [1–3]. Although never manufactured in Canada, PCBs have been imported and widely used in hundreds of industrial and commercial applications (e.g., electric insulators, plasticizers for adhesives, lubricants, hydraulic fluids, sealants, cutting oils, and flame retardants) due to their nonflammability and electrical insulating properties as well as chemical stability at high temperature and low vapor pressure [4, 5].

These compounds did not exist in nature. After synthesis, they were found in the environment in 1966 [6]. Since then, PCBs were so widely discovered in the global environment where trace concentrations were detected even in remote areas such as the atmosphere of the Arctic and the Antarctic and the hydrosphere and biosphere [3].

Exposure to PCBs can lead to cancer and a variety of serious noncancer health effects on different systems. Hence, Canada restricted the use of PCBs in 1977 and prohibited the

import of PCBs in 1980 [7, 8]. Current legislation allows PCB-containing electrical equipment manufactured before 1980 to remain in use until the end of their service life; however, strict maintenance and handling procedures and regulatory control by governments are required to prevent any release into the environment [2]. As specified in the Federal Contaminated Sites Inventory (FCSI), PCB-contaminated sites are recognized in all the provinces and territories throughout Canada. In fact, most of these sites are contaminated as a consequence of inappropriate handling, storage, and disposal [4].

Federal and provincial governments, as well as associated industries, have been obliged to endeavour research efforts and provide financial support for site identification, remediation, and long term monitoring. Since 1994, the number of PCB-contaminated sites has been reduced under provincial jurisdiction. However, the large amount of remaining untreated sites and the revived problems in the treated sites are still risking the provincial ecosystems and environment. The preliminary assessment process estimates the volume of free products could be 15–20 million litres and the majority of the PCB pollutants are deep underground [9]. Industries have been making efforts to solve individual problems and/or

processes related to site remediation practices during the past years. Among the existing technologies, incineration and landfill were frequently applied. However, the remediation was usually long term and costly, and the exhaust could cause secondary pollution [10]. There is a shortage of effective technologies to treat and remove PCB contaminants from soils and sediments. This situation has hindered the efforts to effectively protect the environments of this region. Therefore, it is desired that innovative technologies that can enhance the efficiencies and effectiveness of remediation of PCB-contaminated sites be developed within Canadian context.

Nanoscale zero valent iron (nZVI) particles have been widely applied in removing chloridized hydrocarbons including PCBs due to their extraordinarily reductive property [11, 12]. Some recent research has revealed that nZVI particles are effective in the transformation of a large variety of environmental contaminants, while they are inexpensive and nontoxic [13]. nZVI may chemically reduce PCBs effectively through reductive dechlorination, allowing the pollutant to be readily biodegradable after treatment. Studies by Mueller and Nowack [14] have shown that nZVI as a reactive barrier is very effective in the reduction of chlorinated methane, chlorinated ethane, chlorinated benzenes, and other polychlorinated hydrocarbons. Varma [15] has successfully applied nZVI in soil columns with a wide range of plant phenols as additives, which allows greater access to the contaminant and creates less hazardous waste in the manufacturing process. The application of nZVI to the contaminated soil could enhance the dechlorination of PCBs; nevertheless, higher chlorinated biphenyls require much longer time than lower ones to be completely dechlorinated. Biphenyls as the final product of PCBs are still environmental and health hazards which need further treatment. A time-saving technology that can completely degrade PCBs in the soils or remove PCBs from the soils is consequently in demand.

Soil washing has been applied to effectively and rapidly remove soil contaminants. This technology provides a closed system that remains unaffected by external conditions [16], and the system permits the control of the conditions (e.g., additive concentration) under which the soil particles are treated [17]. Soil washing is cost-effective and often combined with other remediation technologies. Solvents are critical for soil washing and selected on the basis of their ability to solubilize specific contaminants and on their environmental and health effects [18]. However, although soil washing can provide a high efficiency when extracting contaminants from the soil, there are still some limitations when dealing with PCBs. One of the constraints is that PCBs have low water solubility—0.0027–0.42 ng/L [19]; they are soluble in organic or hydrocarbon solvents, oils, and fats. Moreover, PCBs tend to stay in the soils instead of flushing with solvents or water. Since high-chlorinated biphenyls are less water-soluble than low-chlorinated ones and PCBs often preferentially adhere to the clay or silt fraction of the soils [20], removal of the high-chlorinated biphenyls in clayey or silty soils will become extremely difficult. It is thus very hard to find an appropriate washing solvent for PCB removal from soil.

Biosurfactants are surface-active compounds from biological sources, usually extracellular, produced by bacteria,

yeast, or fungi [21]. Compared with chemical surfactants, biosurfactants have been applied in contaminated soil remediation due to the advantages of low toxicity, high specificity, biodegradability and biocompatibility, and functionality under extreme conditions [22–24]. Applying biosurfactants as the solvents in soil washing systems to treat PCB-contaminated soil has the following benefits: (1) it would effectively enhance solubilization of PCBs in the washing solution, leading to increased removal efficiency; and (2) it could stimulate microbial activity that enhances biodegradation of PCBs which are soil bound [24]. However, although the application of biosurfactants with soil washing can significantly increase the solubility of PCBs that increase the extraction efficiency [23], PCBs that dissolved in the washing solution need to be further treated before being released into the environment. As persistent organic pollutants, PCBs are hard to degrade, leading to costly and complex posttreatment processes before discharge [24]. In addition, larger volumes of washing solution may be needed when additives like biosurfactants are used. A high biosurfactant concentration in the washing solution can cause foaming problems and inhibit the ability to remove PCBs from the soil [25]. Increasing attention has been received on the combination of different technologies in recent years. These technologies can be applied in sequence to enhance the cost effectiveness [26]. Effective dechlorination approaches which can be integrated with soil washing and facilitate PCB biodegradation are thus desired.

This study is essential for the applications to the removal of PCBs from soil. It aims to combine nanotechnology and an existing soil washing system with biosurfactants as the solvent to better clean up the PCB-contaminated sites. Since higher chlorinated biphenyls have lower aqueous solubilities than lower chlorinated ones, biosurfactant-aided soil washing could have higher removal efficiencies on lower chlorinated biphenyls than that on higher ones [27]. Therefore, the sequence of the combined technologies would be better started with nZVI-aided dechlorination and followed by biosurfactant-aided soil washing. Through the experimental study of various factors (one factor at a time) affecting PCB dechlorination (nZVI dosage, pH, and temperature) and soil washing effectiveness (nZVI and concentrations of biosurfactant solution), the research output is expected to generate environmentally friendly and economically/technically feasible solutions for helping solve the challenging site contamination problem in Canada.

2. Materials and Methods

2.1. Materials. The materials were as follows:

- (1) Soil: soil used in this research was fine sands purchased from a local company City Sand & Gravel Ltd., St. John's, NL.
- (2) PCBs: commercial PCB products are no longer manufactured and traded in Canada. The contaminants used in this study were in the form of transformer oil obtained from local industry. The overall PCB

concentration in the transformer oil was measured to be 120 ppm by a commercial lab.

- (3) nZVI particles: nanofer star, one kind of commercialized air-stable nanoiron powders, was purchased from NANO IRON, sro, Czech Republic.
- (4) Biosurfactants: a *Bacillus* sp. bacterial strain isolated from the Atlantic Ocean [28] was cultured to generate biosurfactants in the NRPOP Lab. After culturing and extraction, the crude biosurfactants were separated from the media and characterized through testing the critical micelle concentration (CMC). These crude biosurfactants were then ready for use.
- (5) Other materials and chemicals: anhydrous sodium sulfate (ACS reagent); hexane (CHROMASOLV® Plus, for HPLC, $\geq 95\%$); acetone (CHROMASOLV Plus, for HPLC, $\geq 99.9\%$); Supelclean™ Sulfoxide SPE Tube (PE frit, bed wt. 3 g, volume 6 mL); biphenyl- d_{10} (99 atom% D); EPA 525, 525.1 PCB Mix (500 $\mu\text{g}/\text{mL}$ each component in hexane, analytical standard); barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, ACS reagent, $\geq 99.0\%$); magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, ReagentPlus®, $\geq 99.0\%$); sulfuric acid concentrate (0.1M H_2SO_4 in water (0.2N)); chloroform (CHROMASOLV Plus, for HPLC, $\geq 99.9\%$); methanol (CHROMASOLV, for HPLC, $\geq 99.9\%$); ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, ReagentPlus, $\geq 99.0\%$); sodium chloride (NaCl, BioXtra, $\geq 99.5\%$ (AT)); iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, BioReagent, $\geq 99\%$); monopotassium phosphate (KH_2PO_4 , $\geq 99\%$); dipotassium hydrogenphosphate (K_2HPO_4 , $\geq 99\%$); sucrose (BioXtra, $\geq 99.5\%$); select yeast extract; zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, BioReagent); manganese(II) sulfate tetrahydrate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, BioReagent); Boric acid (H_3BO_3 , BioReagent, $\geq 99.5\%$); Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, BioReagent, $\geq 98\%$); sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ACS reagent, $\geq 99\%$); cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, BioReagent); EDTA (ethylenediaminetetraacetic acid, ACS reagent $\geq 99\%$); nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, BioReagent); and potassium iodide (KI, BioXtra, $\geq 99.0\%$), all of them were purchased from Sigma-Aldrich Canada Co., ON, Canada.

2.2. Methods

2.2.1. nZVI-Aided PCB Dechlorination

(1) *PCB-Contaminated Soil Preparation.* The synthesized soil that contaminated by transformer oil was applied to simulate PCB-contaminated oil spills such as uncontrolled waste disposals or leakage of storage tanks. The soil was dried at room temperature for one week and passed through a 2 mm stainless steel sieve to remove any coarse sand and gravel particles as well as to improve the homogeneity before use. Then soil characterization was conducted. After characterization, PCB-contaminated soil was prepared in two

20 L-stainless steel trays. Each tray was filled with 10 kg of soil and 2 L of transformer oil. The soil and oil were mixed thoroughly until it reached a homogenous phase. The trays were then covered with tin foil and stored for one week. After that, the oil in the tray was drained off until there was no fluid in soil, and the soil was ready for nZVI treatment.

(2) *Air-Stable nZVI Powder Activation.* Before any experiment, the surface character and crystal structure of these commercial nZVI particles were examined by scanning electron microscopy (SEM) and X-ray Diffraction (XRD), respectively, in the Core Research Equipment & Instrument Training Lab (CREAIT) at Memorial University. For the activation, the air-stable nanopowder of nZVI was mixed with deionized water at a ratio of 1 : 4. The mixture was then activated by a Branson Sonifier™ S-450D digital ultrasonic homogenizer for 2 mins at 50% amplitude. The treated mixture was sealed and stored at room temperature for two days before dechlorination experiments.

(3) *Dechlorination.* Activated nZVI slurry was transferred into a 500 mL wide neck amber glass bottle with 200 g PCB-contaminated soil; and 30 mL deionized water was added as well. The solid and liquid phases were thoroughly mixed and each bottle was covered with a solid-top cap. The homogenous mixture was then stored at room temperature and let the reaction between nZVI particles and PCBs last for 75 days. The effects of the nZVI dosage (5, 7.5, 10, 12.5, and 15 g per kg PCB-contaminated soil), initial pH (2, 5), and temperatures (0°C, 35°C, and 100°C) were investigated, respectively.

2.2.2. Biosurfactant-Aided Soil Washing

(1) *Batch-Scale Washing System Design and Setup.* The experimental setup used to perform soil washing experiments consists of a washing fluid reservoir, a soil column, a peristaltic pump, and an effluent collection system (Figure 1). The peristaltic pump contains variable speed drives that can run from 0.4 to 85.0 mL/min. The soil column is made of glass to avoid any interference from phthalate esters when contacting with plastic materials, and with a cylindrical diameter of 19 mm and 15 cm in length. The column was packed with 25 g of nZVI-treated soil and the outlet end of the column was fitted with glass beads and glass wool to prevent soil loss during washing. The system assembly is shown in Figure 1.

(2) *Biosurfactant Production and Washing Fluid Preparation.* The bacteria used to generate biosurfactant were isolated from the Atlantic Ocean recently. Till now, no commercial biosurfactant products associated with this strain were available. Thus, biosurfactants need to be produced before conducting washing experiments. For the media and cultivation conditions, a medium modified from Peng et al. [29] was used, which contains the following composition (g/L): sucrose (10), KH_2PO_4 (3.4), K_2HPO_4 (4.4), $(\text{NH}_4)_2\text{SO}_4$ (10.0), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.8×10^{-4}), NaCl (2.2), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (1.02), yeast extract (0.5), and 0.5 mL of trace element solution including (g/L) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (2.32), $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (1.78),

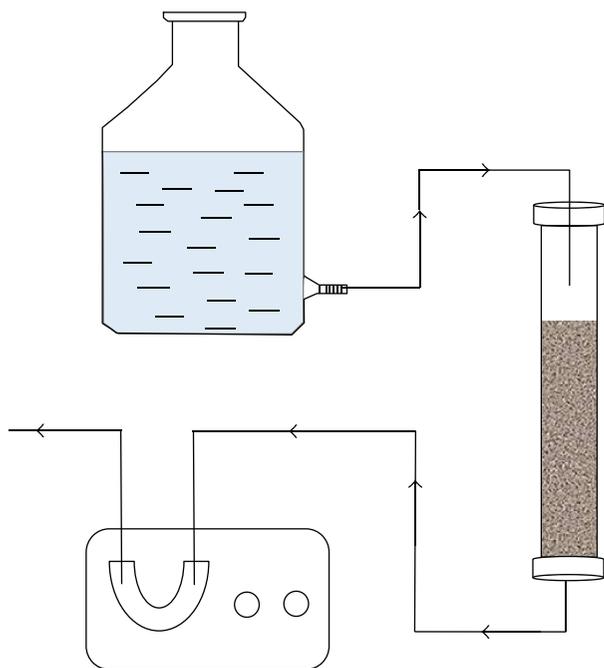


FIGURE 1: Sketch of soil washing system assembly.

H_3BO_3 (0.56), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.0), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.39), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.42), EDTA (1.0), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.004), and KI (0.66). Cultivations were performed in 1L Erlenmeyer flasks containing 750 mL medium at 30°C and stirred in a rotary shaker for 7 days. Enriched culture medium after 7 days was centrifuged at 10,000 rpm for 10 min, and the supernatant layer was extracted using chloroform-methanol (1:2) on a magnetic stirrer for 8 hours. The solvent layer was separated from the aqueous phase and the solvent was removed by rotary evaporation at 40°C and 60 rpm under reduced pressure. The CMC of the resulting crude biosurfactants was determined through measuring the surface tension in accordance with ASTM D1331-14 method. The surface tension of a crude biosurfactant solution was measured by using Du Nouÿ Tensiometer. The CMC value of the crude biosurfactants was estimated by the surface tension curve over a wide concentration range. They were determined by noting the concentrations at which the surface tension reaches the minimum.

(3) *Soil Washing*. Parallel experiments were conducted to investigate the effect of nanoiron particles on soil washing treatment. Both of the PCB-contaminated soil samples treated with 7.5 g/kg and without nZVI particles were loaded into the washing columns, respectively, to test whether the presence of nanoparticles would have any effect on soil washing. Twenty-five grams of the soil was washed with deionized water in a down flow mode for 1.5 hours at a steady flow rate controlled by the peristaltic pump. To investigate the effect of crude biosurfactant, the soil samples were washed with the crude biosurfactant solution (0.25%, 0.5%, and 3% v/v) in a down flow mode for 3 hours at a steady flow rate controlled by the peristaltic pump. The washing effluents

were sampled at 0, 10, 20, 30, 60, 90, 120, and 180 minutes of washing to investigate the change of PCB concentration with time. The change of PCB concentration in soil was determined by measuring the soil sample before and after washing.

2.2.3. *Sample Analysis*. The PCBs in each soil sample were first extracted into the solvent phase according to EPA method 3550B ultrasonic extraction. A modification of the method was conducted to achieve a better testing performance. Two grams of soil sample was transferred to a 30 mL beaker. Two grams of anhydrous sodium sulfate was added to the sample and the solution was well mixed. Two surrogates, 500 μL 10 ppm biphenyl- d_{10} and 200 μL 10 ppm EPA 525, 525.1 PCB Mix, were spiked to the sample. A hexane solvent of 9.3 mL was immediately added to the matrix in order to bring the final volume to 10.0 mL. This was followed by disrupting the sample with a Branson Sonifier ultrasonic probe for 2 minutes at 50% amplitude. After ultrasonic extraction, 1 mL extract was filtered by glass wool and ready for solid phase extraction (SPE) cleanup. Supelclean Sulfoxide SPE cartridges purchased from Sigma-Aldrich were used for transformer oil cleanup. The SPE normal procedure of conditioning, loading, washing, and elution was followed. The conditioning was accomplished by eluting 10 mL of acetone to remove residual moisture from the Supelclean Sulfoxide cartridges. This was followed by adding 20 mL of n-hexane to equilibrate the cartridges. The pretreated 1 mL sample was loaded onto the cartridge and washed with 5.5 mL of n-hexane. Elution was done with 13 mL of n-hexane. The eluate was concentrated to 1 mL by gentle air blow. The cleanup extracts were transferred into GC vials ready for analysis.

The PCB concentration in liquid phase was analyzed using modified Liquid-Liquid Microextraction (LLME) [30] followed by the GC-MS analysis. For modified LLME, 25 μL of 10 ppm biphenyl- d_{10} and 10 μL of 10 ppm EPA 525, 525.1 PCB Mix were spiked as surrogates to each 10 mL water sample (25 ng/L biphenyl- d_{10} and 10 ng/L EPA 525, 525.1 PCB Mix aqueous solution), which was treated by vortex mixing for 10 sec. This was followed by adding 500 μL of hexane and the vortex mixing for 1 min. The water sample was then centrifuged at 4,000 rpm for 5 min. Ten μL of extract was transferred to Microvials for GC analysis. Instrumental analysis was performed using an Agilent 7890A/5975C gas chromatograph–mass spectrometer (GC-MS) equipped with an Agilent 7693 autosampler. GC conditions were set up based on EPA method 8082A. A few adjustments were made to ensure that no PCB congener was retained in the column.

Total ion current (TIC) chromatogram was acquired to examine the changes of PCBs in soil samples. The analysis of each congener and its surrogate was carried out in selected-ion monitoring (SIM) chromatogram. The ratio of sample congener response to standard congener response was defined as the relative concentration, which was used in the results and discussion. All the samples were treated and analyzed in duplicate.

TABLE 1: Soil properties.

Properties	Results
Soil pH	7.53
Bulk density	1.78 g/cm ³
Particle density	2.71 g/cm ³
Pore space	34.3%
Moisture content	0.069%
Cation exchange capacity	95.22 cmol/kg
Hydraulic conductivity	0.024 cm/s

TABLE 2: Soil particle size distribution determined by sieve analysis.

Particle	Diameter (mm)	Size distribution (%)
Gravel	>2.0	4.5
Sand	0.05–2.0	92.5
Silt	0.002–0.05	2.5
Clay	<0.002	0.5

3. Results and Discussion

3.1. nZVI-Aided PCB Dechlorination

3.1.1. Soil Characterization. Before the nZVI-aided PCB dechlorination experiments, basic soil properties including particle size distribution, soil pH, bulk density, particle density, pore space, cation exchange capacity, hydraulic conductivity, and moisture content of the purchased plain soil were measured. The results are shown in Tables 1 and 2. The plain soil used in this research was mainly composed of sand, which was suitable for soil washing. The bulk density, particle density, pore space, hydraulic conductivity, and moisture content are physical properties which can be greatly influenced by soil composition and particle size distribution. The pH of the soil was slight alkalinity, which could result in a higher cation exchange capacity (CEC) value. In an environmental context, CEC stands for the ability of soil to adsorb contaminants. The pH and CEC are two important chemical properties which could affect the soil remediation process and thus need to be examined before remediation.

Metal substances of the plain soil sample were characterized by ICP-MS. Table 3 displays the analytical results. It is noticed that a high concentration of iron was present, which was of 33.6 g per kg soil. The addition of nZVI for PCB dechlorination thus would not much influence the composition of soil.

3.1.2. Analysis of PCB Concentrations in the Original Spiked Soil. The concentrations of PCBs in the spiked soil sample were evaluated before conducting the dechlorination and soil washing experiments. Four PCB congeners were selected as analytes due to their high abundances in the transformer oil, namely Penta-17.8, Penta-18.7, Penta-20.0, and Hexa-20.8. The former parts of the names represent the numbers of chlorine atoms in the congener compounds, while the latter ones are their corresponding retention times (minutes) in the

TABLE 3: Metal substances in the soil sample determined by ICP-MS.

Metals	Concentration in soil (mg/kg)
Arsenic	5.306
Barium	643.918
Cadmium	0.146
Chromium	16.815
Copper	13.727
Iron	33,562.114
Lead	17.681
Mercury	<LDL
Nickel	9.142
Selenium	<LDL
Thallium	0.444
Uranium	1.675
Vanadium	46.084
Zinc	71.958

Note: LDL = lower detection limit.

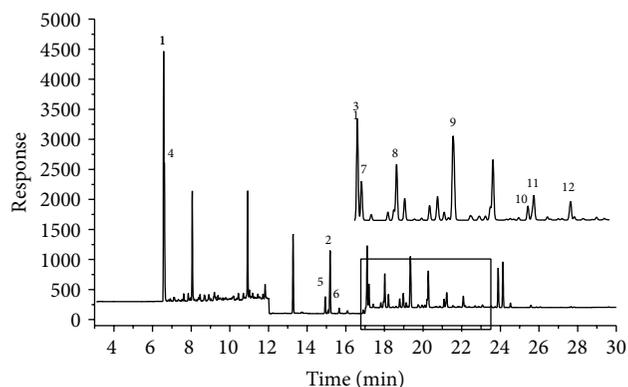


FIGURE 2: GC-MS SIM spectra of PCBs in contaminated soil sample spiked with biphenyl-d₁₀ and EPA 525,525.1 PCBs standard. (1) Biphenyl-d₁₀. (2) 2,2',4,4'-Tetrachlorobiphenyl. (3) 2,2',3',4,6-Pentachlorobiphenyl. (4) Biphenyl. (5) Tetra-15.6. (6) Tetra-16.3. (7) Penta-17.8. (8) Penta-18.7. (9) Penta-20.0. (10) Hexa-20.8. (11) Hexa-21.8. (12) Hexa-22.8.

TABLE 4: The initial relative concentrations of PCBs in the spiked soil.

Analytes	Surrogate	Response ratio
Penta-17.8	2,2',3',4,6-Pentachlorobiphenyl	0.384
Penta-18.7	2,2',3',4,6-Pentachlorobiphenyl	0.551
Penta-20.0	2,2',3',4,6-Pentachlorobiphenyl	0.736
Hexa-20.8	2,2',3',4,6-Pentachlorobiphenyl	0.262

MS spectra (Figure 2). The average response ratios of PCBs to their corresponding surrogates are listed in Table 4.

3.1.3. nZVI Characterization and Activation. The commercial nZVI particles were characterized by SEM and XRD prior to their applications in PCB dechlorination in soil. Figure 3 shows the SEM image of nZVI particles. It can be seen that

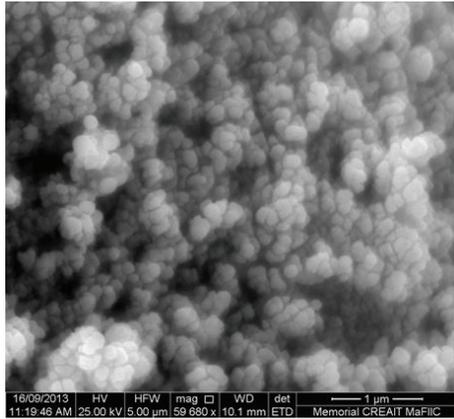


FIGURE 3: SEM Image of the commercial nZVI particles.

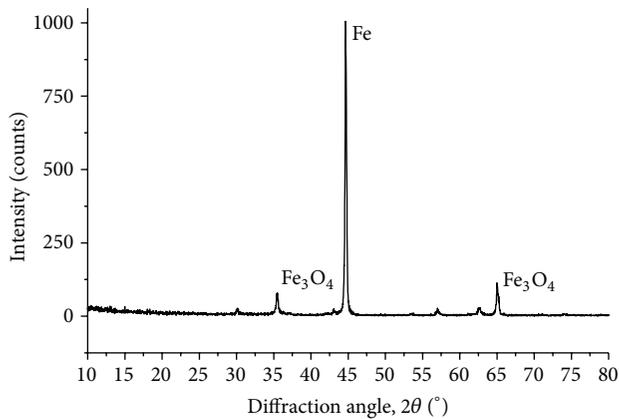


FIGURE 4: XRD of the nZVI particle.

the majority of the particles were nearly spherical in shape and uniform in size. The particle size was in the range of 20–100 nm with an average particle size of 50 nm.

Figure 4 displays the XRD pattern of the nZVI particles and it proved that there were crystal iron particles existed in the commercial product. The 2θ values of the peaks were compared with the standard data for iron and its oxides such as magnetite and α -Fe. Apparent peak at the 2θ of 44.9° indicates the presence of α -Fe, while other apparent peaks show the presence of iron oxides. The redox potential of nZVI slurry was decreased from 360 mV to -300 mV after the activation.

3.1.4. Natural Attenuation of PCBs. The changes of PCB concentrations in the contaminated soil were tracked on the 1st, 15th, and 45th day, respectively, during the natural attenuation process. As depicted in Figure 5, the concentrations of all the four congeners did not change significantly within the 45-day period. It illustrated that the dechlorination rates of PCBs during the natural attenuation process were extremely slow. It also proved that the PCBs were not able to be degraded without any additional treatment.

3.1.5. Effect of nZVI Dosage. The performance of PCB dechlorination using different nZVI dosages is shown in Figure 6.

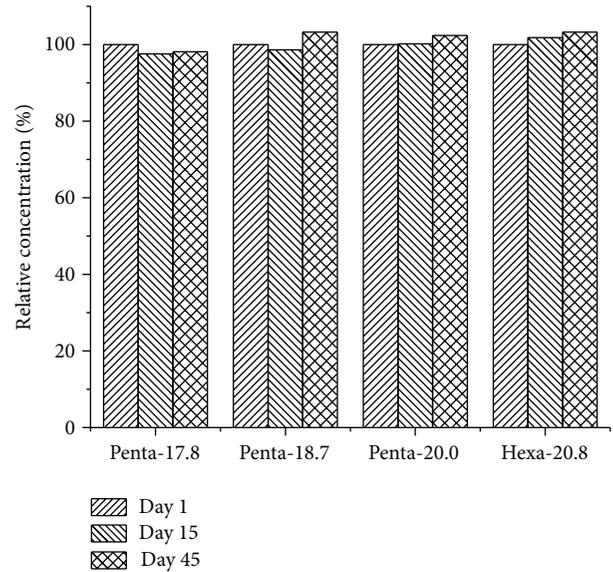


FIGURE 5: Natural attenuation of PCBs in contaminated soil.

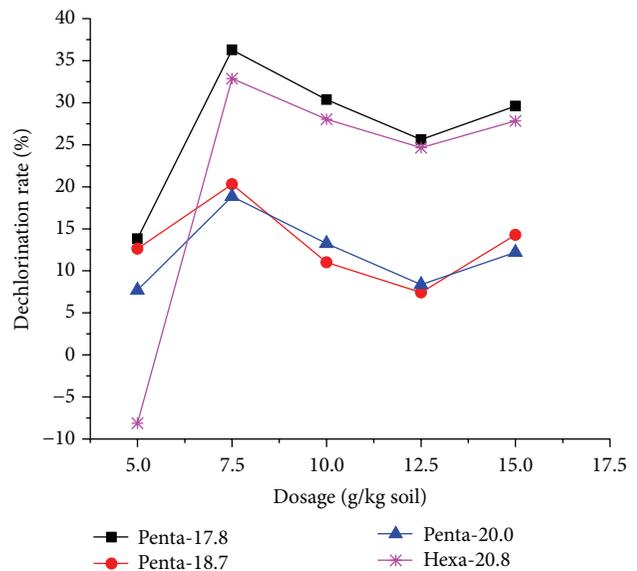


FIGURE 6: Effect of nZVI dosage on PCB dechlorination in the contaminated soil.

The trends of the PCB dechlorination rate versus nZVI dosage were similar based on the results of all the four congeners. The overall PCB dechlorination rate was first increased as nZVI dosage increased from 5 to 7.5 g/kg, indicating that the increase of nZVI dosage can accelerate the dechlorination of PCBs. The overall dechlorination rate of PCBs was then decreased when the nZVI dosage increased higher than 7.5 g/kg. The maximum dechlorination rates of Penta-17.8, Penta-18.7, Penta-20.0, and Hexa-20.8 during 75 days period were 36.3%, 20.3%, 18.9%, and 32.9%, respectively. The results indicated that when choosing 7.5 g/kg as the nZVI dosage, the highest dechlorination rates were achieved in all four congeners. Adding more nZVI particles had shown a negative

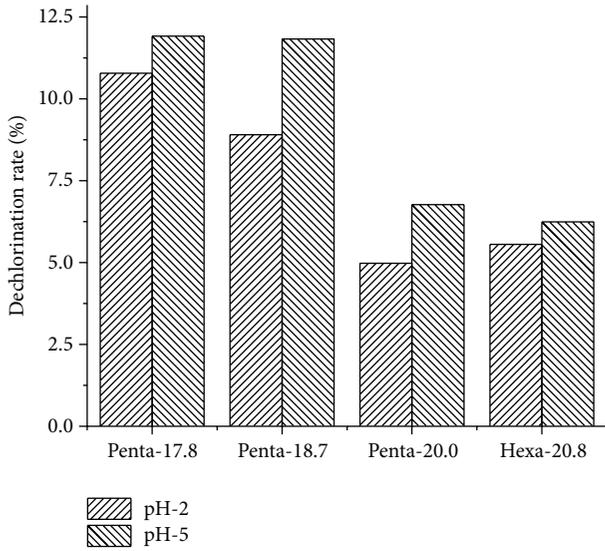


FIGURE 7: Effect of pH on PCB dechlorination in the contaminated soil.

influence on PCB dechlorination. This was possibly due to the particle aggregation formed during mixing [31]. Besides the nZVI aggregation, the biotransformation from higher chlorinated biphenyls to lower ones may also affect the PCB dechlorination rate under multiple nZVI dosages. Based on the experimental results, the nZVI dosage of 7.5 g/kg with the best PCB dechlorination performance was selected for the following treatments.

3.1.6. Effect of pH Level. Two levels of pH were selected to evaluate the effect of pH on PCB dechlorination. The result is shown in Figure 7. After 75 days monitoring, the average dechlorination rates of Penta-17.8, Penta-18.7, Penta-20.0, and Hexa-20.8 at pH of 2 were 10.8%, 8.9%, 5.0%, and 5.6%, respectively; while their average dechlorination rates at pH of 5 were 11.9%, 11.8%, 6.8%, and 6.2%, respectively. The dechlorination rates of each PCB congener were higher at pH of 5 than those at pH of 2. Previous studies have shown that an acid environment with more protons could accelerate the PCB dechlorination [32]. The results of this study led to a different conclusion. It might be because, in this case, the protons were sufficient at pH of 5 so that pH was not a dominating factor on PCB dechlorination anymore. In addition, the addition of H₂SO₄ would have more interference with the mass transfer of PCBs from the soil to the iron (Fe) surface [32]. The pH of 5 was thus selected to be the initial pH condition in the following experiments.

3.1.7. Effect of Temperature. The effect of temperature on PCB dechlorination after 75 days was investigated with results shown in Figure 8. The PCB dechlorination was greatly enhanced when the temperature increased from 0 to 100 °C. As the temperature increased, the PCB dechlorination of Penta-17.8 improved the most, with a rate change from 10.1% to 34.2%. The dechlorination rates of Penta-18.7, Penta-20.0, and Hexa-20.8 were enhanced from 11.3% to 32.2%, from

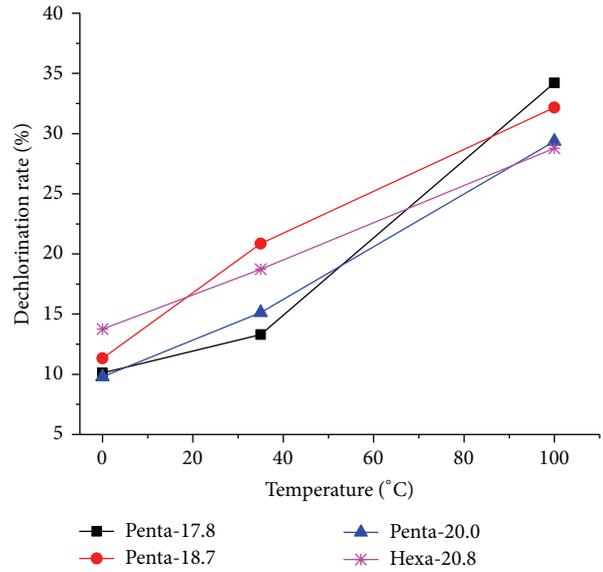


FIGURE 8: Effect of temperature on nZVI-aided PCB dechlorination.

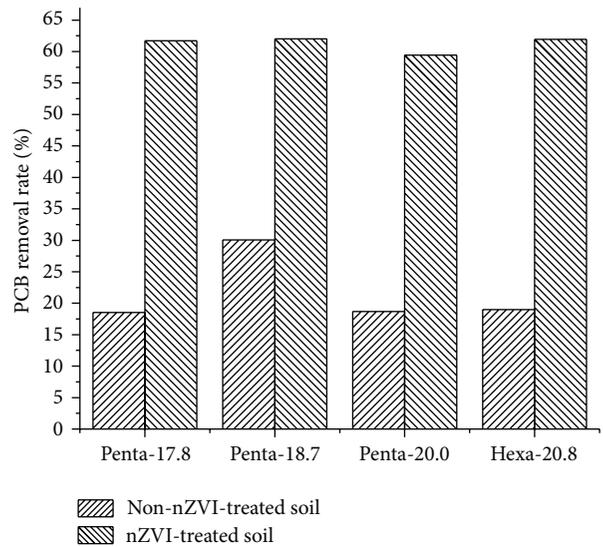


FIGURE 9: Effect of the nZVI particles on PCB removal during soil washing.

9.8% to 29.4%, and from 13.7% to 28.8%, respectively. These results showed that a temperature increase would enhance the mobility of PCBs from the soil to the iron surfaces and thus accelerate the dechlorination reaction [32].

3.2. Biosurfactant-Aided Soil Washing

3.2.1. Effect of nZVI Particles on Soil Washing. The effect of the nZVI particles on PCB removal during the soil washing treatment was investigated. Figure 9 showed the results. Although the insolubility of PCBs makes their distribution negligible in water phase, the PCBs in the transformer oil could be flushed out of the column due to the high flow rate during direct soil washing without using any biosurfactants.

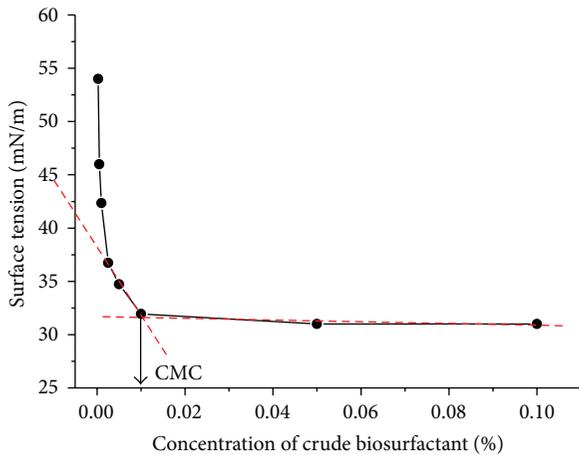


FIGURE 10: CMC of the crude biosurfactant.

As shown in Figure 9, after 1.5 hours of operation, about 18% to 30% of PCBs in the congeners were removed by direct washing of the non-nZVI-treated soil.

After the nZVI-aided dechlorination, a red color was observed in the treated soil, implying the formation of ferric hydroxides or ferric oxides. It indicated that the nZVI particles were transferred to their oxidative forms after the reaction. During washing of the nZVI-treated soil, the PCB concentration of each congener was significantly decreased. In Figure 9, the removal rates of PCBs after washing were between 60% and 62% in the nZVI-treated soil. It was illustrated that the treatment by the nZVI particles greatly enhanced the soil washing efficiency. Besides, the presence of nanoscale ferric oxides in the system plays a key role in PCB removal [33]. The contaminated soil trapped a certain amount of transformer oil, and the oil droplets were blocked by the pore throat of soil due to the high interfacial tension between oil and soil [34]. With the presence of nanoscale ferric oxides, the interfacial tension would be reduced and the mobility of oil droplets would be increased [33]. As a result, more oil droplets were desorbed from the soil, resulting in an increased effectiveness of soil washing. This experiment confirmed that the combination of the nZVI-aided dechlorination and soil washing is reasonable and feasible.

3.2.2. CMC of the Crude Biosurfactant. The surface tension of a series of biosurfactant solutions with different biosurfactant concentrations was tracked. The trend of surface tension versus biosurfactant concentration was shown in Figure 10. The value of surface tension was decreased sharply till the biosurfactant concentration reached 0.01%. When the biosurfactant concentration was higher than 0.01%, the surface tension changes became relatively stable. Therefore, the CMC of the crude biosurfactant was determined to be 0.01%.

3.2.3. Effect of Biosurfactant Concentration on Soil Washing. The nZVI-treated soil sample was washed by crude biosurfactant solutions. The concentration of crude biosurfactant in the washing fluid was set as 3%, 0.5%, and 0.25%. The initial flow rate of the column washing fluid was set within

the range of 18–20 mL/min. The results of relative PCB concentrations (the ratio of sample congener response to standard congener response) in column effluent were shown in Figures 11(a)–11(c). The elution of PCBs started at 10 min. The PCB concentrations in effluents were sharply increased and reached their peaks at 15–45 min. Steep declines were followed by the peaks and the gentle deduction appeared in the final stage.

The overall PCB removal rates after washing of the nZVI-treated soil were examined. As shown in Figure 12, the higher the concentration of the crude biosurfactant solution used, the higher the removal rate achieved. The maximum removal rate was found when using 3% crude biosurfactant and 90% of the total four PCB congeners were removed from the soil. The final removal rates using 0.5% and 0.25% crude biosurfactant solutions were 80% and 75%, respectively. The PCB removal rates using all the three crude biosurfactant solution were higher than 75%, indicating the promising effectiveness of biosurfactant-aided soil washing.

The decreasing of washing flow rates occurred especially with higher biosurfactant doses. When supplying the washing fluid with the 3% crude biosurfactant, a backwashing step was required within 30–60 min washing time. It was observed that the bounce of PCBs at 60 min in Figure 11(a) was because of backwash. The most possible explanation is that the crude biosurfactant contained insoluble particulate matter could block the pathway of washing flow, thus reducing both flow rate and emulsification rate. It could further lead to a longer treatment period. Results indicated that the crude biosurfactant solution with a concentration of 0.5% could remove the majority of the four PCB congeners with the shortest treatment time (within 60 minutes). Therefore, 0.5% was selected as an appropriate biosurfactant concentration for further applications.

The SIM spectrum shows the removal of almost all the PCBs in the soil sample after washing. As shown in Figure 13, the peaks of PCBs had almost disappeared after washing with 0.5% crude biosurfactant solution; only the peaks of surrogates were left. Besides, the contents of the transformer oil that generated the baseline wander were also removed. As a consequence, the crude biosurfactant solution was able to remove almost all the organic components including PCBs in transformer oil unselectively.

4. Conclusions

This research has focused on the development of a two-step treatment consisting of nZVI-aided dechlorination followed by biosurfactant-based soil washing technology to remove PCBs from soil. In nZVI-aided dechlorination, the effects of nZVI dosage, initial pH, and temperature on PCB transformation were evaluated one at a time, respectively. The selected dosage of nZVI was 7.5 g/kg soil. Adding more nZVI particles could have negative influence on PCB dechlorination, since the aggregates could be easily formed as the nZVI dosage increases. An environment with pH lower than 5 did not much influence the removal rates of PCBs, indicating the presence of sufficient protons in the system. The results showed that the lower pH would actually inhibit

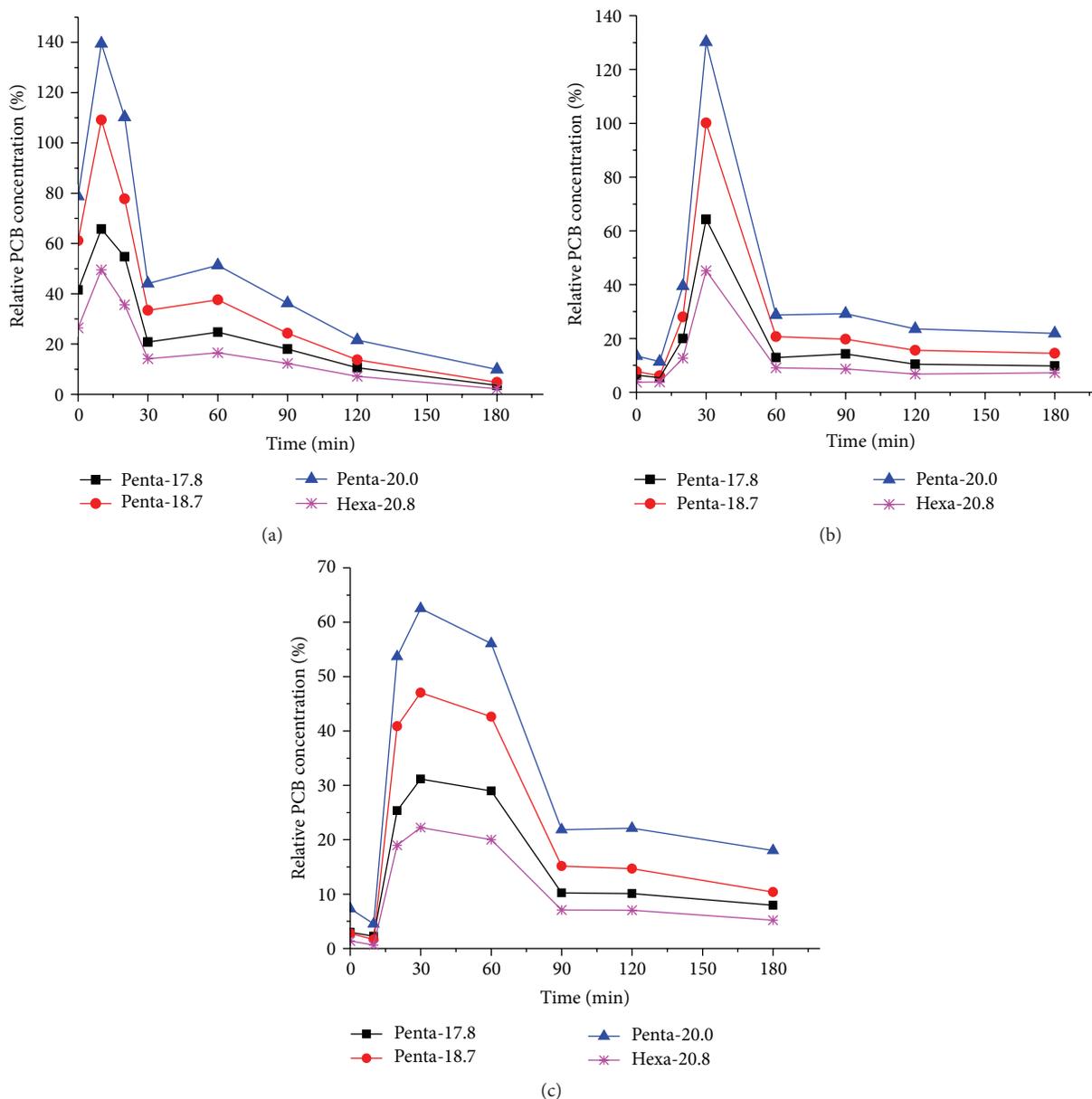


FIGURE 11: Relative concentrations of PCBs in washing effluent with (a) 3%, (b) 0.5%, and (c) 0.25% crude biosurfactant solution.

the dechlorination by the presence of H_2SO_4 , which has an effect on the reduction of mass transfer. An improvement of dechlorination was observed as the temperature increased, since higher temperature would accelerate the dechlorination reaction.

In the soil washing system, the presence of nZVI particles plays a key role in PCB removal. They can greatly enhance the soil washing efficiency because the interfacial tension between the oil phase and the soil phase would be reduced and the mobility of oil droplets would be increased. Soil washing of nZVI remediated soil can be enhanced by biosurfactant. Higher biosurfactant concentration could increase the solubilization of PCBs from soil phase to liquid phase. The overall PCB removal rates using all the three crude biosurfactant concentrations (3%, 0.5%, and 0.25%) were 90%, 80%,

and 75%, respectively, indicating the promising effectiveness of this biosurfactant. Compared with the 3% biosurfactant solution, the crude biosurfactant concentrations of 0.5% and 0.25% were more cost-effective. The 0.5% crude biosurfactant solution could remove the majority of PCBs within a shorter time than the solution with a concentration of 0.25%. Therefore, 0.5% was recommended as an appropriate biosurfactant concentration for future application. This study shows a great potential in developing a promising treatment technology for PCB-contaminated soil remediation. Pilot-scale applications will be carried out to demonstrate the technology transfer.

Competing Interests

The authors declare that they have no competing interests.

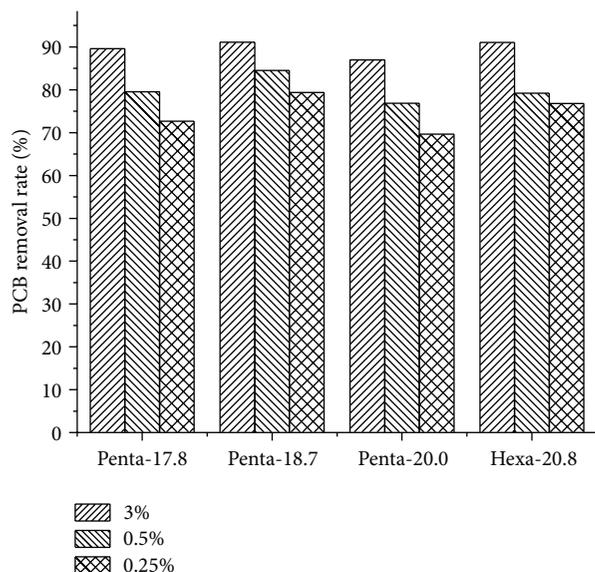


FIGURE 12: The washing efficiencies of PCBs in the nZVI-treated contaminated soil by different concentrations of crude biosurfactant solution.

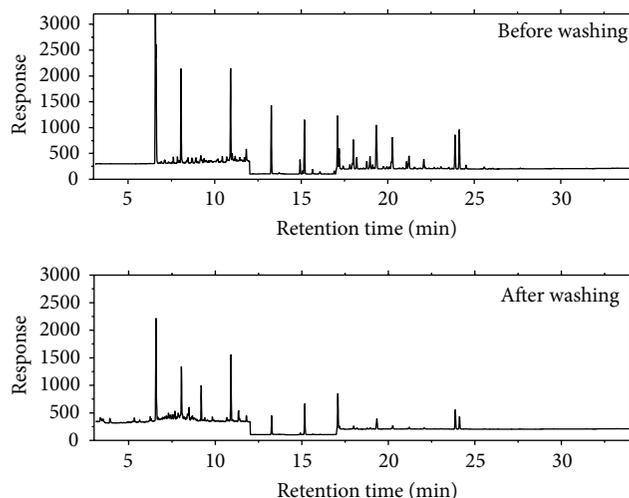


FIGURE 13: GC-MS SIM spectra of PCBs in the contaminated soil before and after washing by 0.5% crude biosurfactant solution.

Acknowledgments

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References

[1] D. Pal, J. B. Weber, and M. R. Overcash, "Fate of polychlorinated biphenyls (PCBs) in soil-plant systems," in *Residue Reviews*, pp. 45–98, Springer, New York, NY, USA, 1980.

[2] Canadian Council of Resource and Environment Ministers (CCREM), *The PCB Story*, (CCREM), Toronto, Canada, 1986.

[3] S. Tanabe, "PCB problems in the future: foresight from current knowledge," *Environmental Pollution*, vol. 50, no. 1, pp. 5–28, 1988.

[4] Canadian Council of Ministers of the Environment (CCME), "Canadian soil quality guidelines for the protection of environmental and human health: polychlorinated biphenyls (total)," in *Canadian Environmental Quality Guidelines*, Canadian Council of Ministers of the Environment, Winnipeg, Canada, 1999.

[5] US Environmental Protection Agency, PCBs in the United States industrial use and environmental distribution, p. 24, 1976, <http://nepis.epa.gov/Exe/ZyPDF.cgi/20001275.PDF?Dockey=20001275.PDF>.

[6] S. Jensen, "Report of a new chemical hazard," *New Scientist*, vol. 32, no. 612, p. 445, 1966.

[7] W. M. J. Strachan, "Polychlorinated biphenyls (PCBs): fate and effects in the Canadian environment," EPS Report 4/HA/2, Environment Canada, 1988.

[8] L. A. Barrie, D. Gregor, B. Hargrave et al., "Arctic contaminants: sources, occurrence and pathways," *Science of The Total Environment*, vol. 122, no. 1-2, pp. 1–74, 1992.

[9] AMEC Earth and Environmental Ltd, *Commission 88.1 Environmental Site Investigation B371 CHPP Tanks*, Prepared for Defence Construction Canada, Goose Bay, Canada, 2008.

[10] Federal Contaminated Sites Portal, Federal Contaminated Sites Action Plan (FCSAP), February 2014, <http://www.federal-contaminatedsites.gc.ca/default.asp?lang=en>.

[11] A. Mikszewski, *Emerging Technologies for the in Situ Remediation of PCB-contaminated Soils and Sediments: Bioremediation and Nanoscale Zerovalent Iron*, US Environmental Protection Agency, 2004.

[12] S. M. Cook, *Assessing the Use and Application of Zero-Valent Iron Nanoparticle Technology for Remediation at Contaminated Sites*, Jackson State University, 2009.

[13] W.-X. Zhang, "Nanoscale iron particles for environmental remediation: an overview," *Journal of Nanoparticle Research*, vol. 5, no. 3-4, pp. 323–332, 2003.

[14] N. C. Mueller and B. Nowack, "Nanoparticles for remediation: solving big problems with little particles," *Elements*, vol. 6, no. 6, pp. 395–400, 2010.

[15] R. Varma, "Greener synthesis of noble metal nanostructures and nanocomposites," in *Presented at the U.S. EPA Science Forum: Innovative Technologies—Key to Environmental and Economic Progress*, Washington, DC, USA, 2008.

[16] W. Chu and K. H. Chan, "The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics," *Science of The Total Environment*, vol. 307, no. 1–3, pp. 83–92, 2003.

[17] K. Urum, T. Pekdemir, and M. Gopur, "Optimum conditions for washing of crude oil-contaminated soil with biosurfactant solutions," *Process Safety and Environmental Protection*, vol. 81, no. 3, pp. 203–209, 2003.

[18] D. Feng, L. Lorenzen, C. Aldrich, and P. W. Maré, "Ex situ diesel contaminated soil washing with mechanical methods," *Minerals Engineering*, vol. 14, no. 9, pp. 1093–1100, 2001.

[19] H. I. Gomes, C. Dias-Ferreira, L. M. Ottosen, and A. B. Ribeiro, "Electrodialytic remediation of polychlorinated biphenyls contaminated soil with iron nanoparticles and two different surfactants," *Journal of Colloid and Interface Science*, vol. 433, pp. 189–195, 2014.

[20] T. Lyons, D. W. Grosse, and R. A. Parker, EPA engineering issue: technology alternatives for the remediation of PCB

- contaminated soils and sediments (No. EPA/600/S-13/079), Washington, DC, USA, 2013.
- [21] B. Zhang, G. H. Huang, and B. Chen, "Enhanced bioremediation of petroleum contaminated soils through cold-adapted bacteria," *Petroleum Science and Technology*, vol. 26, no. 7-8, pp. 955-971, 2008.
- [22] X. Qin, B. Chen, G. Huang, and B. Zhang, "A relation-analysis-based approach for assessing risks of petroleum-contaminated sites in Western Canada," *New Developments in Sustainable Petroleum Engineering*, vol. 1, no. 2, pp. 183-200, 2009.
- [23] P. F. Amaral, M. A. Z. Coelho, I. M. Marrucho, and J. A. Coutinho, "Biosurfactants from yeasts: characteristics, production and application," in *Biosurfactants*, pp. 236-249, Springer, New York, NY, USA, 2010.
- [24] H. Xia and Z. Yan, "Effects of biosurfactant on the remediation of contaminated soils," in *Proceedings of the 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE '10)*, pp. 1-4, IEEE, Chengdu, China, June 2010.
- [25] Unified Facilities Guide Specifications (USGS), Soil Washing through Separation/Solubilization, UFGS-02 54 23, 2010, <https://www.wbdg.org/ccb/DOD/UFGS/UFGS%2002%2054%2023.pdf>.
- [26] H. I. Gomes, C. Dias-Ferreira, and A. B. Ribeiro, "Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application," *Science of the Total Environment*, vol. 445-446, pp. 237-260, 2013.
- [27] W. Y. Shiu and D. Mackay, "A critical review of aqueous solubilities, vapor pressures, Henry's law constants, and octanol-water partition coefficients of the polychlorinated biphenyls," *Journal of Physical and Chemical Reference Data*, vol. 15, no. 2, pp. 911-929, 1986.
- [28] Q. Cai, B. Zhang, B. Chen, Z. Zhu, W. Lin, and T. Cao, "Screening of biosurfactant producers from petroleum hydrocarbon contaminated sources in cold marine environments," *Marine Pollution Bulletin*, vol. 86, no. 1-2, pp. 402-410, 2014.
- [29] F. Peng, Z. Liu, L. Wang, and Z. Shao, "An oil-degrading bacterium: *Rhodococcus erythropolis* strain 3C-9 and its biosurfactants," *Journal of Applied Microbiology*, vol. 102, no. 6, pp. 1603-1611, 2007.
- [30] J. S. Zheng, B. Liu, J. Ping, B. Chen, H. J. Wu, and B. Y. Zhang, "Vortex- and shaker-assisted liquid-liquid microextraction (VSA-LLME) coupled with gas chromatography and mass spectrometry (GC-MS) for analysis of 16 polycyclic aromatic hydrocarbons (PAHs) in offshore produced water," *Water, Air, and Soil Pollution*, vol. 226, no. 9, pp. 318-331, 2015.
- [31] N. C. Müller and B. Nowack, "Nano zero valent iron—the solution for water and soil remediation," Report of the Observatory NANO, 2010.
- [32] P. Varanasi, A. Fullana, and S. Sidhu, "Remediation of PCB contaminated soils using iron nano-particles," *Chemosphere*, vol. 66, no. 6, pp. 1031-1038, 2007.
- [33] L. Hendraningrat and O. Torsæter, "Metal oxide-based nanoparticles: revealing their potential to enhance oil recovery in different wettability systems," *Applied Nanoscience*, vol. 5, no. 2, pp. 181-199, 2015.
- [34] A. Roustaei, S. Saffarzadeh, and M. Mohammadi, "An evaluation of modified silica nanoparticles' efficiency in enhancing oil recovery of light and intermediate oil reservoirs," *Egyptian Journal of Petroleum*, vol. 22, no. 3, pp. 427-433, 2013.

Research Article

Phytoremediation of Gold Mine Tailings Amended with Iron-Coated and Uncoated Rice Husk Ash by Vetiver Grass (*Vetiveria zizanioides* (Linn.) Nash)

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This study was undertaken to determine the effects of rice husk ash (RHA) and iron-coated rice husk ash (Fe-RHA) on phytoavailability of As, Cd, Cr, Cu, Mn, Pb, and Zn to vetiver grass grown in gold mine tailings amended with either RHA or Fe-RHA at 0%, 5%, 10%, and 20% (w/w). The results showed that the RHA amended tailings recorded higher concentration of As in the shoot and the root and higher concentration of Cr and Mn in the root compared to the untreated tailings which was used as a control. The biological accumulation coefficient (BAC) and bioconcentration factor (BCF) values of the vetiver grass for As and Zn increased with RHA application rate but the biological transfer coefficient (BTC) values of As and Zn were decreased. In Fe-RHA amended samples, As concentration in the shoot and root concentrations of Cd and Zn were significantly higher compared to the control. The Fe-RHA treated samples had lower BAC and BTC values for As and Zn than the control. However, the BCF values for those elements were higher than the control. The concentration of Pb was not detected in any of the samples.

1. Introduction

Tailings are the components of the primary mineral-bearing rock left after the extraction of minerals like gold, copper, and silver [1]. Mine tailings are regarded as a major source of environmental pollution due to the presence of high concentration of trace elements in the tailings, which may cause various health effects. The heavy metals in mine tailings are quickly discharged and distributed into the ground water causing serious environmental and health issues in the vicinity of the mine area [2]. Hence, gold mine tailings require proper management to reduce the release of heavy metals into the environment.

There are several methods of cleaning up the harmful effects of heavy metal on contaminated sites which include, among others, physical removal (excavation), *in situ* stabilization of these metals, and utilization of plants to extract the metals from the polluted site. Each of these approaches

nevertheless has its advantages and disadvantages and its success depends on the nature and size of the contaminated site. However, using green plants to contain, degrade, or eliminate metals, for the purpose of removing them is efficient and cost-effective and involves nonenvironmental disruptive compared to operations that require excavation of soil. Different plants have different phytoextraction potentials depending upon the environments and their genetic variability. The ability of plants to take up heavy metals and transfer them from the shoots to the roots is very important in phytoremediation [3]. Phytoremediation can be considerably advantageous when the metals are in the soil solution rather than held by soil constituents and this can be achieved by using different techniques such as adding soil acidifiers, organic and inorganic compounds, and chelates [4]. Organic amendments can be used to either mobilize or immobilize toxic metals in contaminated soils [5, 6]. In the mobilization technique, the metal(loid)s are released into the soil and are

subsequently removed through the native plant species. Plant growth on metal-contaminated soil may be enhanced as a result of organic amendments [7]. Chemical portioning and distribution are also affected by organic amendments [8], which may influence the phytoavailability of metals. A field study was conducted by Singh and Agrawal [9] to assess the suitability of sewage sludge amendment in soil for rice (*Oryza sativa* L.) by evaluating the heavy metal accumulation and growth of plants in soil amended with sewage sludge at either 0, 3, 4.5, 6, 9, or 12 kg m⁻². They found that sewage sludge amendment modified the physicochemical properties of soil, thus increasing the availability of heavy metals in soil and consequently resulting in higher accumulation in plant parts.

The use of waste-based materials for environmental conservation has been stressed under Malaysia's Green Strategies of the National Policy on the Environment [10]. Solid waste disposal is becoming a major issue in Malaysia; for example, milling processes generate approximately 300 000 mt (metric ton) of rice husk annually. Consequently, burning is estimated to produce more than 63 000 mt of ash a year [11]. Rice husk is regarded as agricultural waste, comprising around 20% of the paddy weight, and its annual gross production is 545 million metric tons worldwide [12]. Rice husk ash is a by-product produced from the burning of rice husk. The rice husk and its ash may be used as a natural, low cost adsorbent to remove toxic metals. The ash also contains compounds such as silica, cellulose, lignin, and hemicellulose with binding sites capable of taking up metals [13, 14]. Also, the ash derived from rice husk has good adsorptive ability and it has been used previously by researchers to remove metal ions [15], dye [16], and filtration of arsenic from water [17]. In addition, Nakbanpote et al. [18] tested the ability of RHA to adsorb gold-thiourea complex and the results have shown that the RHA absorb more gold than conventionally activated carbon. There are a number of studies that proved that RHA has a good ability to remove heavy metals such as Cd, Pb, Zn, Cu, Mn, and Hg from aquatic solution [12, 16, 19]. However, there is no information available in the literature for the simultaneous phytoremediation of heavy metals by RHA. Thus, the main objectives of the present study were to determine the effects of rice husk ash (RHA) and Fe-coated RHA on the ability of vetiver grass to phytoremediate mine tailings contaminated with As, Cd, Cr, Cu, Mn, Pb, and Zn.

2. Materials and Methods

2.1. Chemicals and Reagents. All the chemical reagents were of analytical grade, and the solutions were prepared using a Milli-Q system (Direct-Q® 3 UV) ultrapure water (electrical resistivity 18.2 MΩ cm⁻¹). Analytical grade sodium arsenate, cadmium nitrate tetrahydrate, chromium(III) nitrate nonahydrate, copper(II) chloride, manganese(II) sulfate monohydrate, lead(II) nitrate, zinc chloride, and iron(III) chloride were purchased from Sigma-Aldrich.

2.2. Tailings Preparation and Analyses. The tailings were collected from a gold mine located in the state of Pahang, Peninsular Malaysia. Composite samples were taken using

a stainless steel scoop from the upper 30 cm of the tailings. The samples were taken from this layer because they were fresh samples and not waterlogged. The samples were brought to the laboratory and immediately air-dried, homogenized, and grounded to pass through a 2 mm sieve. The samples were stored in plastic bags prior to analysis. The particle size distribution of the tailing was measured using a pipette method [20]. Samples of tailings/water ratio of 1:2.5 were equilibrated for 24 hours and then the pH and EC were measured by using Metrohm 827 pH meter and Eutech Instruments CON 700 EC meter, respectively. Exchangeable bases and CEC were determined using 1 M NH₄OAc buffered at pH 7 [21]. The extracted NH₄⁺ was measured using Lachat QuikChem 8000 Series FIA+ autoanalyzer. The carbons, nitrogen, and sulfur, components of tailings sample, were determined by using a CNS elemental analyzer (model: LECO TruMac CNS Analyzer). One gram of tailing sample was digested with a mixture of three concentrated acids (4 mL HCl, 2 mL HNO₃, and 2 mL HF and filtered through Whatman 44 ashless diameter 125 mm filter papers for total P, Ca, Mg, K, and Na determination) [22]. The concentrations of P, Ca, Mg, K, and Na elements in the digests were determined with Perkin Elmer AAnalyst 400 atomic absorption spectrophotometers and P was measured using an autoanalyzer (Lachat Instruments QuikChem 8000 Series FIA+ System). The acid neutralizing capacity (ANC) was determined using the method described by Shu et al. [23], while the amount of CaCO₃ was determined by acid neutralization method [24]. The total amount of heavy metals in the tailings was determined using a method modified from Güven and Akinci [25]. Details of the digestion programs are presented in Table 1. The digests were then filtered through a 0.45 μm membrane filter, diluted to 50 mL, and stored prior to analysis. The metal concentrations were analyzed by Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

2.3. Rice Husk Ash Characterization. Rice husk ash (RHA) was obtained from a factory located at Sungai Besar, in the state of Selangor, Peninsular Malaysia. The ash was passed through 1 mm sieve and analyzed for its chemical and physical properties. The pH was measured in a 0.5:100 (w/v) RHA:H₂O suspension and the electrical conductivity (EC) was measured by shaking 1g sample in 20 mL water for two hours [26]. The pH and EC were measured using the instruments described previously. The ash content was determined by using a dry combustion method [27]. The cation exchange capacity (CEC) was measured using the method described by Song and Guo [28].

The surface area of the RHA was measured by N₂ adsorption at 77.3 K, using a Quantachrome version 2.01 (Quantachrome ASIWin™) surface area analyzer. The RHA sample was degassed at 100°C for 9 h prior to N₂ adsorption. The multipoint Brunauer-Emmett-Teller (BET) method was employed to calculate the total surface area. The Scanning Electron Microscope-Electron Dispersive Spectroscopy (SEM-EDS) was used to study the RHA morphology, and Fourier Transformed Infrared Spectroscopy (Perkin Elmer

TABLE 1: The operating conditions for the microwave digestion system.

Samples	Reagents (mL)	Steps program	Power (watt)	Time (min)	Temperature (°C)
Tailings					
0.5 g	65% HNO ₃ (6 mL) 37% HCl (2 mL) 40% HF (2 mL)	1	200	8	150
		2	400	7	180
		3	600	1	200
		4	0	10	200
Vetiver grass					
0.25 g	65% HNO ₃ (6 mL) 30% H ₂ O ₂ (2 mL)	1	250	5	100
		2	500	10	150
		3	750	5	200
		4	0	15	200

FTIR-2000 spectrometer) was used to determine the RHA surface functional groups.

2.4. Preparation of Iron-Coated Rice Husk Ash (Fe-RHA). Surface modification of the RHA was done by coating it with Fe(III) as described by Samsuri et al. [29]. The RHA was weighed and washed several times with deionized water and then dried for 48 h in an oven at 50°C. Then, the sample was soaked in a solution containing 2000 mg L⁻¹ of Fe(III) prepared using FeCl₃ salt. The solution pH was adjusted to 6 using either 0.1 M HCl or 0.1 M NaOH. The mixture of RHA and Fe(III) solution was stirred several times per day for four days manually and then filtered on Whatman no. 42 filter paper and the rice husk was washed with deionized water several times to remove the free Fe until no more Fe was detected in the filtrate.

2.5. Greenhouse Study. Untreated tailings (control) and tailings treated with three rates (5, 10, or 20% w/w) of either RHA or Fe-RHA were used for this experiment. Amended tailings were thoroughly homogenized in large plastic containers, and water was added to field capacity and then transferred to plastic bags and kept in a climate-controlled dark room for four weeks. From each bag, approximately 20 g sample was taken to determine the pH and EC at the end of incubation. Pot experiments were conducted in a glass house using square plastic tube pots measuring 5.4 × 5.4 cm at the top and 1.5 × 1.5 cm at the bottom and 29 cm in height with 50 g of acid washed sand placed at the base of the pots. Then, 500 g of tailing mixture was poured into each pot and a one-month age vetiver grass seedling was transplanted into the pot. The experimental units were arranged using a randomized complete block design. The seedlings were watered daily and were allowed to grow for 75 days. At the end of the experiment, the plants were harvested, and the shoots and roots were separated. The plant parts were washed with deionized water several times to remove the tailings and then dried at 60°C for 72 h and weighed for dry biomass determination. The heavy metals (As, Cd, Cr, Cu, Mn, Pb, and Zn) contents in the plant parts were analyzed by ICP-OES after grinding and approximately 0.25 g of sample digested with 6 mL of HNO₃ 65% and 2 mL of H₂O₂ 30% in microwave digestion system; according to the digestion program presented in Table 1, the resulting solutions were cooled and diluted to 50 mL

with ultrapure water. The biological accumulation coefficient (BAC) is defined as the concentration of metals in plant shoots divided by the metal concentration in soil [30] and is given in

$$\text{BAC} = \frac{[\text{Metal}] \text{ shoot}}{[\text{Metal}] \text{ soil}} \quad (1)$$

The biological transfer coefficient (BTC) is defined as the ratio of metal concentration in shoot to the root of the plant [30] and is given in

$$\text{BTC} = \frac{[\text{Metal}] \text{ shoot}}{[\text{Metal}] \text{ root}} \quad (2)$$

The bioconcentration factor (BCF) was calculated as the ratio of the concentration of metal in plant root to the soil [31] as given in

$$\text{BCF} = \frac{[\text{Metal}] \text{ root}}{[\text{Metal}] \text{ soil}} \quad (3)$$

2.6. Statistical Analysis. All data were checked for normality and homogeneity of variances prior to statistical analysis. The precision of the data was calculated and expressed as a standard deviation (SD). Later the data were subjected to statistical analysis of variance (ANOVA) using MINITAB version 16 at the 5% significance level and Tukey's test was employed for mean separation.

3. Results and Discussion

3.1. Physicochemical Properties of the Gold Mine Tailings and RHA and Fe-RHA. The selected physicochemical properties of the gold mine tailings are shown in Table 2. The tailings texture was silty loam (14.23% clay; 36.02% sand; 49.68% silt) and the pH was slightly alkaline at 7.90 due to the use of lime to treat the waste water which was pumped back to the retaining pond. The tailings had high acid neutralization capacity and calcium carbonate content which were 63.9 H₂SO₄ t⁻¹ and 56 g kg⁻¹, respectively. The high concentrations of total heavy metals As (1625.251 mg kg⁻¹), Cd (57 mg kg⁻¹), Cr (31.44 mg kg⁻¹), Cu (75.6 mg kg⁻¹), Mn (790.03 mg kg⁻¹), Pb (81.8 mg kg⁻¹), and Zn (174.8 mg kg⁻¹)

TABLE 2: The selected physicochemical properties of the gold mine tailings.

Parameters	Value
Clay (%)	14.23 ± 0.61
Silt (%)	49.68 ± 0.89
Sand (%)	36.02 ± 1.43
Texture (USDA)	Silty loam
Moisture content % at 33 kpa	25.90 ± 0.36
Moisture content % at 1500 kpa	4.04 ± 0.81
pH	7.90 ± 0.02
EC (dS m ⁻¹)	1.48 ± 0.01
CEC (cmol ₍₊₎ kg ⁻¹)	10.75 ± 0.83
Total carbon (%)	1.56 ± 0.01
ANC (kg H ₂ SO ₄ t ⁻¹)	63.90 ± 2.01
Total N (%)	0.036 ± 0.004
Total P (%)	0.076 ± 0.002
Total K (%)	0.196 ± 0.005
Total S (%)	0.140 ± 0.011
Total Ca (mg kg ⁻¹)	8600 ± 30.51
Total Mg (mg kg ⁻¹)	10750 ± 152
Total Na (mg kg ⁻¹)	1480 ± 21
Total As (mg kg ⁻¹)	1625.25 ± 12
Total Cd (mg kg ⁻¹)	57.00 ± 1.41
Total Cr (mg kg ⁻¹)	31.44 ± 0.61
Total Cu (mg kg ⁻¹)	75.60 ± 0.65
Total Mn (mg kg ⁻¹)	790.03 ± 9.98
Total Pb (mg kg ⁻¹)	81.80 ± 1.75
Total Zn (mg kg ⁻¹)	174.80 ± 1.18
Total Fe (mg kg ⁻¹)	16420 ± 402

Mean of three replicates ± SD.

indicated that the tailings were highly contaminated with these elements. On the other hand the tailings had low CEC (10.75 cmol₍₊₎ kg⁻¹), N (0.036%), P (0.076%), and K (0.196%) contents. In addition to that, the selected physicochemical properties of the RHA and Fe-RHA are shown in Table 3. The pH, EC, CEC, total C, DOC, total P, total K, total Ca²⁺, and ash content values of the RHA were higher than the Fe-RHA. On the other hand, total N and total Na were higher in the Fe-RHA than RHA. The Fe-RHA also had a larger total surface area, pore surface area, pore volume, and pore radius. However, there was no significant difference in the surface functional groups between RHA and Fe-RHA as indicated by the FTIR spectra (Figure 1). The bands at 615.73 and 619.50 cm⁻¹ are associated with the C=C-H (aromatic) functional group. The bands at 784.61 and 781.83 cm⁻¹ are associated with the =C-H out of plane bending and finally the bands at 1057.41 and 1055.05 cm⁻¹ are associated with the C-O stretch. The surface morphology, shape, and pores of RHA and Fe-RHA are shown in Figure 2. It can be seen that the meso- and macropores were more abundant than the micropores. Both intact and deformed cellulose and lignin strands are visible in the scanning electron micrograph images (Figure 2).

TABLE 3: The selected physicochemical properties of the RHA and Fe-RHA.

Parameters	RHA	Fe-RHA
pH	10.33 ± 0.33	7.24 ± 0.06
EC (dS m ⁻¹)	0.56 ± 0.04	208.33 ± 0.01
CEC (cmol ₍₊₎ kg ⁻¹)	13.36 ± 0.37	11.32 ± 0.05
Total C (%)	6.44 ± 0.09	5.45 ± 0.07
DOC mg kg ⁻¹	818.77 ± 2.43	800.8 ± 1.41
Total N (%)	0.047 ± 0.001	0.11 ± 0.01
Total S (%)	ND	ND
Total P (%)	0.23 ± 0.02	0.15 ± 0.01
Total K (%)	0.098 ± 0.003	0.03 ± 0.001
Ash content (%)	8.4 ± 0.23	6.8 ± 0.03
Total Mg (mg kg ⁻¹)	7800 ± 17.61	2600 ± 17.62
Total Ca (mg kg ⁻¹)	585 ± 6.03	ND
Total Na (mg kg ⁻¹)	740 ± 4.58	8100 ± 25.63
Total surface area (m ² g ⁻¹)	24.252	44.686
Pore surface area (m ² g ⁻¹)	4.417	5.648
Pore volume (cm ³ g ⁻¹)	0.016	0.017
Pore radius (Å)	17.165	19.201

Mean of three replicates ± SD; ND: not detected.

3.2. Chemical Properties of the Mine Tailings and Dissolved Organic Carbon (DOC) Content after Burning Rice Husk Application. The application of RHA significantly increased the pH of the tailings in all treatments while Fe-RHA amendment lowered the pH of the tailings compared with the control (Table 4). The highest pH value for RHA amended tailings was 9.05 at the highest application rate (20%). It is also observed that there was no effect of RHA application on the EC of the mine tailings except at the highest rate (20%). The results also revealed that both RHA and Fe-RHA application had no impact on the CEC of the mine tailings. The application of high rates of RHA and Fe-RHA significantly increased DOC of the mine tailings. The DOC of the tailings amended with 10% and 20% RHA and 20% Fe-RHA were higher compared with the control (Table 4). The highest DOC value for RHA amended tailings was 919.80 mg kg⁻¹ at the 20% (w/w) application rate.

The increases in the pH, EC, and DOC of the tailings with RHA application were possibly due to the high ash content, DOC, elemental concentrations, and the presence and dissolution of hydroxides and carbonates in the RHA (Table 3). Even though the CEC of the RHA was higher than the CEC of the tailings, the addition of RHA did not increase the CEC of the tailings significantly. This might be attributed to the short time span between samples incubation and the time of CEC measurement. Karmakar et al. [32] and Masulili et al. [33] found that the application of RHA to soil increased soil pH, organic carbon, and nutrient availability. Therefore, it can be concluded that the effects of RHA application on the pH, EC, and DOC of the tailings depend on both the properties of the RHA and the tailings.

3.3. Concentrations of Heavy Metals in Shoot, Root, and Total Heavy Metal Uptake of the Vetiver Grass. Figures 3(a) and

TABLE 4: The pH (1: 2.5 w_{soil}/v_{water}), EC ($\mu S\ cm^{-1}$), and CEC ($cmol_{(+)}\ kg^{-1}$) of the mine tailings amended with the ashes (mean $n = 3, \pm SD$). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$) in the same column.

Type	Rates (%)	pH	SD	EC ($dS\ m^{-1}$)	SD	CEC ($cmol + kg^{-1}$)	SD	DOC (mg/kg)	SD
Control	0	7.90 ^d	0.02	1.48 ^b	0.012	11.75 ^a	0.83	823.03 ^b	5.28
RHA	5	8.45 ^c	0.01	1.48 ^b	0.015	10.05 ^a	1.47	844.86 ^b	7.84
RHA	10	8.55 ^b	0.00	1.49 ^b	0.015	11.75 ^a	0.63	904.43 ^a	6.59
RHA	20	9.05 ^a	0.02	1.58 ^a	0.045	12.46 ^a	1.46	919.80 ^a	10.30
Control	0	7.90 ^a	0.02	1.48 ^b	0.012	11.75 ^a	0.83	823.03 ^a	5.28
Fe-RHA	5	7.73 ^b	0.03	1.48 ^b	0.034	14.12 ^a	0.12	772.43 ^b	12.41
Fe-RHA	10	7.70 ^b	0.04	1.51 ^b	0.012	12.48 ^a	2.56	815.17 ^a	8.57
Fe-RHA	20	7.66 ^b	0.06	1.64 ^a	0.008	12.25 ^a	0.23	835.63 ^a	5.54

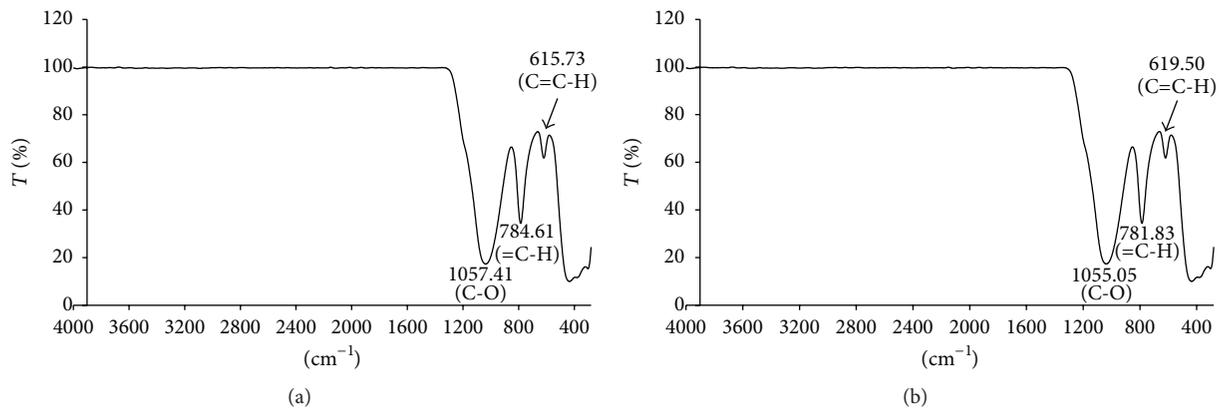


FIGURE 1: The FTIR spectra of RHA (a) and Fe-RHA (b).

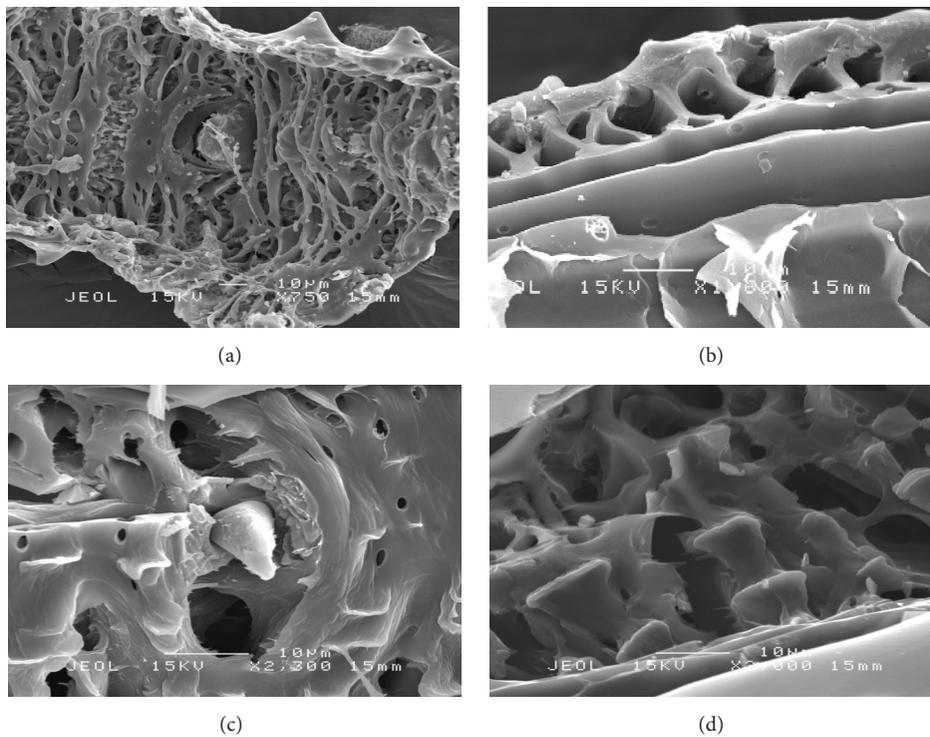


FIGURE 2: The scanning electron microscope images of the RHA magnified at 750 (a), 1600 (b), 2300 (c), and 3000 times (d). The accelerating voltage of the instrument was maintained at 15 kV.

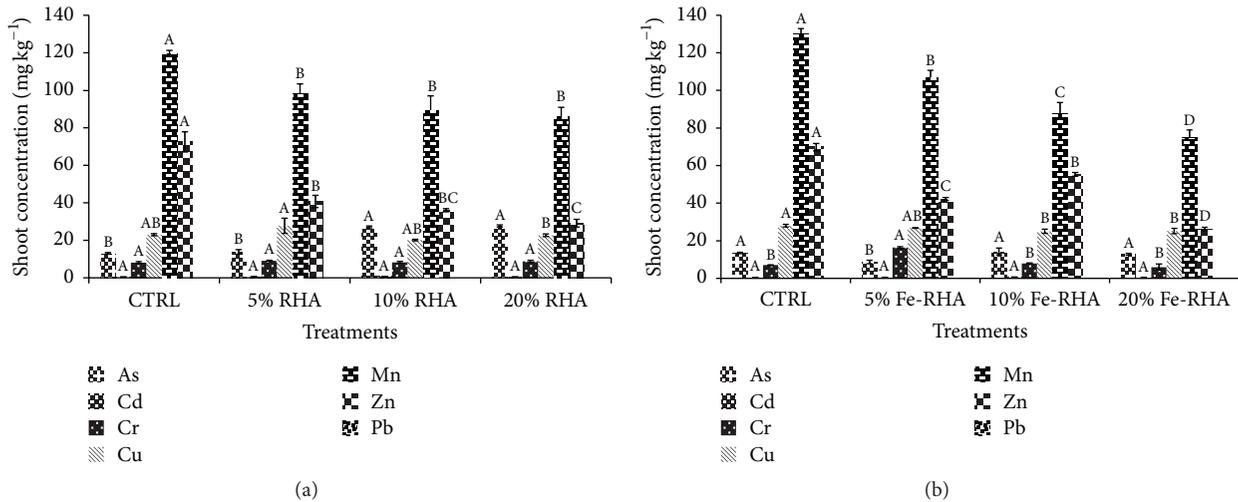


FIGURE 3: Concentration (mg kg^{-1}) of As, Cd, Cr, Cu, Mn, Zn, and Pb in shoot of vetiver grass grown in gold mine amended with (a) RHA and (b) Fe-RHA (mean $n = 3$, \pm SD). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$). Pb was not detected.

3(b) show the concentration of metals in the shoot of the vetiver grass. The As concentration in all RHA amended samples, except at 5% application rate, was higher than the control (Figure 3(a)). The As concentration in all Fe-RHA treatments, except at 5% application rate, was not significantly different from the control, while it was significantly decreased in 5% Fe-RHA application rate (Figure 3(b)). The highest shoot concentration of As ($27.733 \text{ mg kg}^{-1}$) was recorded at 20% RHA. The concentrations of Mn in the shoot of vetiver grass grown in all RHA treated samples were significantly lower than the control. The lowest shoot concentration of Mn ($86.133 \text{ mg kg}^{-1}$) was recorded at 20% RHA (Figure 3(a)). The shoot concentrations of Cr and Cu in all RHA treated samples were not significantly different compared with the control (Figure 3(a)). However, the concentrations of Cr, Cu, and Mn in the shoot of vetiver grass grown in all Fe-RHA treated samples were significantly lower than the control except at 5% application rate for Cr and Cu in which the shoot Cr concentration was higher than control and the shoot concentration of Cu was not significant compared to the control. The lowest shoot concentrations of Cr (6.000 mg kg^{-1}), Cu ($25.000 \text{ mg kg}^{-1}$), and Mn ($74.867 \text{ mg kg}^{-1}$) were recorded in tailings amended with 20%, 10%, and 20% Fe-RHA, respectively (Figure 3(b)). The shoot concentrations of Cd in all RHA and Fe-RHA treated samples were not significantly different compared with the control. However, the shoot concentrations of Zn in all RHA and Fe-RHA treated samples were lower than the control. The lowest shoot Zn concentration ($26.267 \text{ mg kg}^{-1}$) was recorded at 20% Fe-RHA.

The two-way analysis of variance (ANOVA) procedure shows the significant ($P < 0.05$) effects of rice husk type and the interaction term of type * rate on the concentration of As, Cr, Cu, and Zn in the shoot systems of the vetiver grass. However, the effects of rice husk type and the interaction term of rate and type were not significant ($P > 0.05$) on Cd and Mn shoot concentration of the vetiver grass. However,

the application rate of both RHA and Fe-RHA had a significant effect on the concentrations of all elements in the shoot of the vetiver grass.

The concentrations of As, Cd, Cr, Cu, Mn, and Zn in the roots of the vetiver grass are shown in Figures 4(a) and 4(b). The root concentrations of As in Fe-RHA and RHA amended samples were higher than the control (Figures 4(a) and 4(b)). The highest root As concentration ($267.400 \text{ mg kg}^{-1}$) was recorded at 20% RHA treated sample (Figure 4(a)). In contrast, the application of both Fe-RHA and RHA at all rates decreased the concentration of Cu in the root of vetiver grass compared with the control (Figures 4(a) and 4(b)). The lowest root Cu concentration (9.133 mg kg^{-1}) was recorded in 5% RHA treated sample.

In RHA treated samples, the Cd concentration in the roots decreased with the application rate. However, in Fe-RHA samples only the 5% Fe-RHA treated sample had a lower Cd concentration in the root compared with the control. In contrast, the roots Cr concentration in all RHA treated samples, except at 5% treated sample, increased compared with the control. The root Cr concentrations in Fe-RHA treated samples, except at 20%, were not significantly different from the control. The highest root Cr concentration (3.733 mg kg^{-1}) was recorded at 20% RHA treated sample. The application of Fe-RHA at all rates decreased the concentration of Mn in the root of vetiver grass compared with the control. However, RHA rates had different effects on Mn concentration in root. For instance, root Mn concentration at 5% RHA treated sample was lower than the control. However, the highest root Mn concentration ($69.067 \text{ mg kg}^{-1}$) was recorded in 10% RHA sample. The application of RHA at all rates increased the concentration of Zn in the roots of vetiver grass compared with the control. However, in Fe-RHA samples only the 5% Fe-RHA had a higher Zn root concentration than the control. The two-way ANOVA analysis for As, Cd, Cr, Cu, Mn, and Zn concentration in

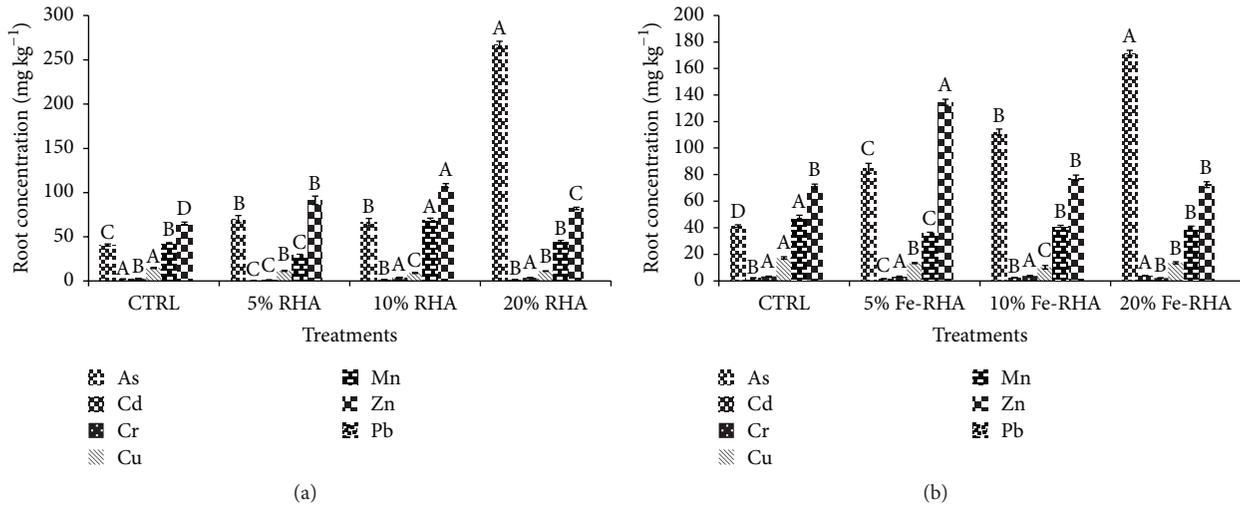


FIGURE 4: Concentration (mg kg⁻¹) of As, Cd, Cr, Cu, Mn, Zn, and Pb in root of vetiver grass grown in gold mine amended with Fe-RHA and RHA (mean n = 3, ±SD). Different letters correspond to significant differences between rates of the same ash (P < 0.05). Pb was not detected.

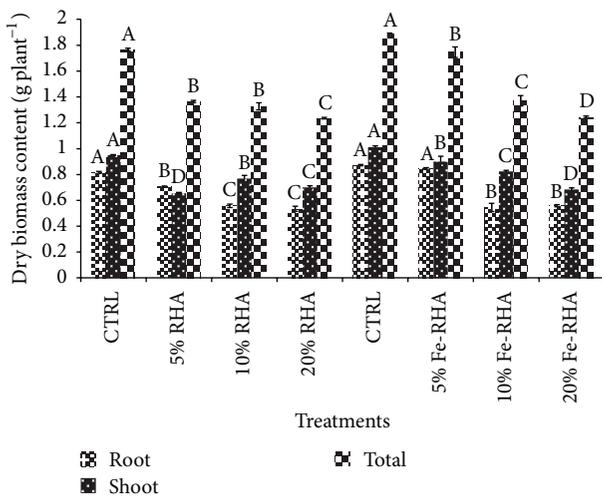


FIGURE 5: Shoot, root, and total dry biomass of vetiver grass grown in gold mine amended with Fe-RHA and RHA (mean n = 3, ±SD). Different letters correspond to significant differences between rates of the same ash (P < 0.05).

the root system of the vetiver grass is shown. Rice husk ash type had significant (P < 0.05) effect on As, Cd, Cu, and Mn concentrations in the roots of the vetiver grass, but not for Cr and Zn. The two-way ANOVA results also revealed that both rates and the interaction term (type * rates) had a significant effect on the concentrations of all elements in the roots of the vetiver grass, except for Cu.

Figure 5 shows the root, shoot, and total plant dry biomass production of the vetiver grass. Vetiver grass grown in all Fe-RHA and RHA amended tailings had lower root, shoot, and total biomass production compared with the vetiver grass grown in the controls. The lowest dry root, shoot, and total biomass of the vetiver (0.535, 0.657, and 1.236 g plant⁻¹) were observed in 20%, 5%, and 20%

RHA amended samples, respectively (Figure 5). The ANOVA results show that type, rate, and interaction term (type * rate) of Fe-RHA and RHA had a significant effect (P < 0.05) on root, shoot, and total plant dry biomass production.

Figures 6(a) and 6(b) show the results of metal uptake in the shoot of vetiver grass grown in mine tailings amended with Fe-RHA and RHA. Amending the tailings with RHA at all rates, except at 5%, increased the shoot uptake of As in the vetiver grass compared with the controls. The highest As uptake (15.225 μg plant⁻¹) was recorded at 10% RHA (Figure 6(a)). In contrast, application of Fe-RHA at all rates decreased As uptake in the shoot of vetiver grass (Figure 6(b)). In addition, the high rate (10% and 20%) of RHA and Fe-RHA Application reduced Cr, Cu, Mn, and Zn uptake in the shoot compared with the control. The lowest Cr (3.346), Cu (11.770), Mn (41.809), and Zn (14.697 μg plant⁻¹) uptakes were observed in the samples amended with the 20% Fe-RHA, 10% RHA, 20% Fe-RHA, and 20% Fe-RHA, respectively. However, application of RHA and Fe-RHA at all rates had no significant effect on Cd uptake in the shoot compared with the control. The type of RHA had significant (P < 0.05) effect on shoot uptake of As, Cr, Cu, Mn, and Zn by the vetiver grass but not for Cd. However, both application rates and the interaction term (type * rate) had significant (P < 0.05) effect on the shoot uptake of all elements by the vetiver grass, except interaction for Cu.

Figures 7(a) and 7(b) also show metal uptake in the roots of vetiver grass grown in mine tailings amended with Fe-RHA and RHA. The root uptakes of As in RHA and Fe-RHA amended samples at all rates were higher than the control. The highest root As uptake (187.504 μg plant⁻¹) was recorded in 20% RHA treated sample (Figure 7(a)) while the lowest root As uptake (38.723 μg plant⁻¹) was recorded in the control. In contrast, the root uptakes of Cu in RHA and Fe-RHA amended samples at all rates were lower than the control. The lowest root Cu uptake (7.031 μg plant⁻¹) was recorded at 10% RHA treated sample. The Cd and Cr uptake in the

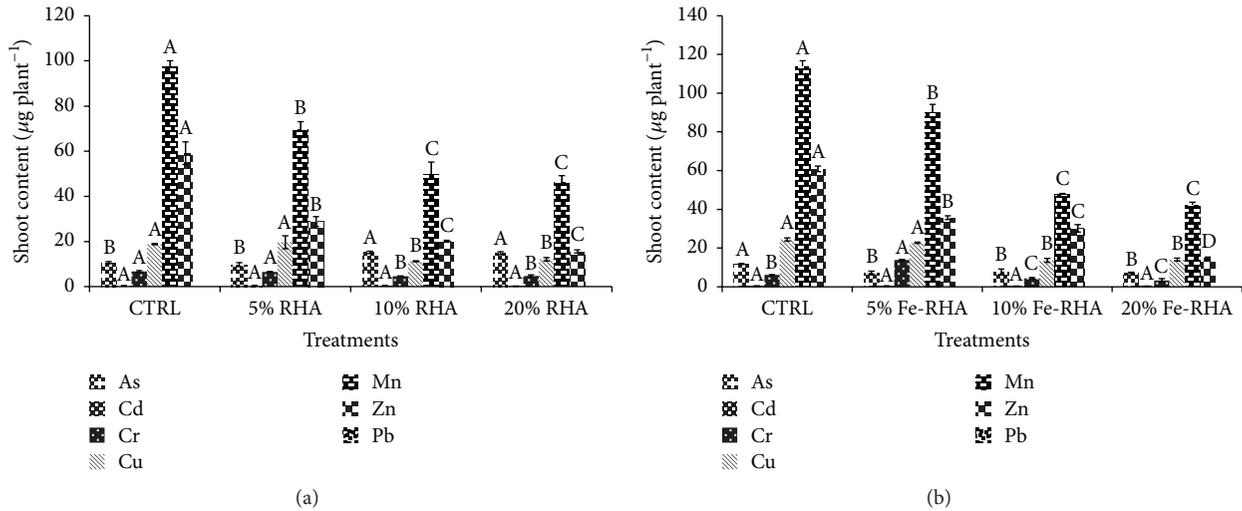


FIGURE 6: The uptake of As, Cd, Cr, Cu, Mn, Zn, and Pb ($\mu\text{g plant}^{-1}$) in shoot of vetiver grass grown in gold mine amended with Fe-RHA and RHA (mean $n = 3$, \pm SD). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$). Pb was not detected.

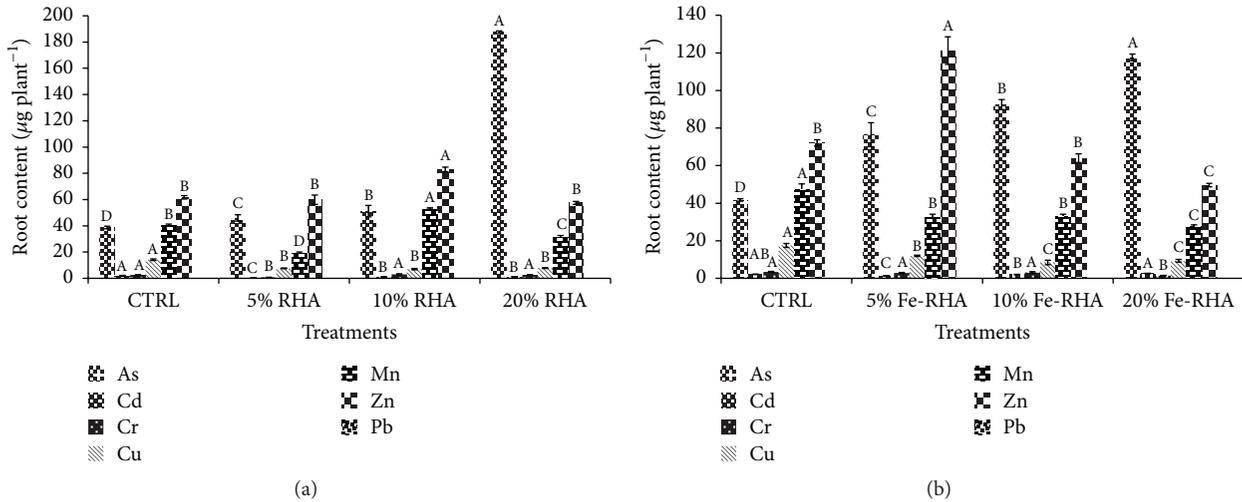


FIGURE 7: The uptake of As, Cd, Cr, Cu, Mn, Zn, and Pb ($\mu\text{g plant}^{-1}$) in root of vetiver grass grown in gold mine amended with Fe-RHA and RHA (mean $n = 3$, \pm SD). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$). Pb was not detected.

root decreased with increasing RHA rates compared to the control. However, application of Fe-RHA at all rates had no significant effect on Cd and Cr uptake in the root, except 5% Fe-RHA for Cd and 20% Fe-RHA for Cr when they had a lower uptake in the root compared with the control (Figure 7(b)). Similarly, the application of either Fe-RHA or RHA at all rates, except the 10% RHA, decreased the root uptake of Mn of vetiver grass compared with the control. The two-way analysis of variance (ANOVA) procedure shows the significant ($P < 0.05$) effects of rice husk type on the uptake of Cd, Cr, Cu, and Zn in the root systems of the vetiver grass but not for As and Mn. However, both application rates and the interaction term (type * rate) had significant ($P < 0.05$) effect on the root uptake of all elements by the vetiver grass.

The total plant metals uptakes of vetiver grass grown in mine tailings amended with Fe-RHA and RHA are presented

in Figures 8(a) and 8(b). The amount of heavy metals uptake by vetiver grass was altered among the treatments. The total As uptake in vetiver grass grown in both Fe-RHA and RHA treated samples at all rates was higher compared with the control. The highest As uptake ($202.342 \mu\text{g plant}^{-1}$) was recorded in 20% RHA treated sample (Figure 8(a)). But, the application of RHA and Fe-RHA at all rates decreased the total plant uptake of Cu and Mn compared with the control and the lowest Cu (18.307) and Mn ($69.465 \mu\text{g plant}^{-1}$) uptakes were recorded at 10% RHA and 20% Fe-RHA, respectively. In addition, the application of RHA at all rates reduced the total vetiver grass uptake of Cd, Cr, and Zn compared with the control. The lowest Cd (0.643), Cr (7.304), and Zn ($73.103 \mu\text{g plant}^{-1}$) uptakes were recorded by plants grown in 5%, 5%, and 20% RHA, respectively. However, in Fe-RHA samples, only plants grown in the 5% Fe-RHA had lower Cd

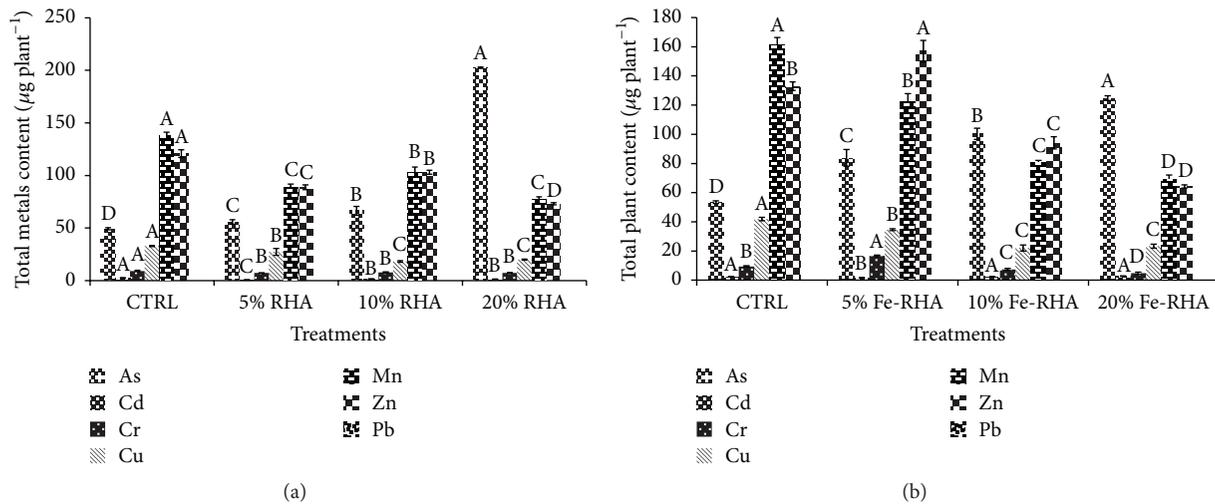


FIGURE 8: Total As, Cd, Cr, Cu, Mn, Zn, and Pb uptake ($\mu\text{g plant}^{-1}$) by vetiver grass grown in gold mine amended with Fe-RHA and RHA (mean $n = 3$, $\pm\text{SD}$). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$). Pb was not detected.

uptake compared with the control. In contrast, the Cr and Zn uptakes by plants at 5% Fe-RHA treated samples were higher compared with control (Figure 8(b)). However, the total uptake of Cr and Zn by the vetiver grass decreased in 10% and 20% Fe-RHA treated samples. The application of type, rate, and the interaction term (type * rate) of RHA had significant ($P < 0.05$) effect on the total plant uptake of all elements by the vetiver grass.

Reduction in root, shoot, and total dry biomass of vetiver grass grown in samples treated with RHA and Fe-RHA might be due to the increase in As uptake and other metals since the elements are toxic and could inhibit plant growth when present at high concentrations. Arsenic has direct toxic effect on the biochemical and physiological processes in the plant. When it is translocated to the shoot, As resulted in a decrease of plant growth and biomass accumulation by severely inhibiting plant growth and slowing or arresting expansion [34, 35]. Eissa et al. [36] studied the phytoextraction of Ni, Pb, and Cd from contaminated soils using different field crops and EDTA treatment and they found that the root and shoot dry weights decreased by more than 25% due to the increase in metal plant uptake as a result of EDTA treatment.

Higher heavy metal uptake by the application of RHA on the gold mine tailings might be due to the presence of dissolved organic carbon (DOC). Previous studies found the positive correlations between mobility and availability of As and Cu with DOC [37]. The DOC affects the mobility of metals and metalloids through either the formation of soluble organic complexes or competition between the DOC and the metals for binding sites on the soil surface [38].

3.4. The Biological Accumulation Coefficient (BAC), Biological Transfer Coefficient (BTC), and Bioconcentration Factor (BCF) of the Vetiver Grass Grown in Mine Tailings Amended with RHA and Fe-RHA. The BACs values of As, Cd, Cr, Cu, Mn, and Zn for vetiver grass grown in RHA and Fe-RHA amended tailings are shown in Table 5. The RHA treated samples at all

rates showed a higher BAC for As compared with the control. The highest BAC for As (0.025) was recorded at 20% RHA amended sample. The application of RHA at all rates did not significantly affect BACs value for Cd, Cr, and Mn compared with the control but the BAC value for the Zn was reduced with the application RHA at all rates. The lowest BAC value for Zn (0.393) was recorded at 20% of the RHA amended sample. In Fe-RHA amended samples, only the 5% treatment had lower BAC value for As compared with the control while there is no significant effect at all rates on BACs value for Cd and Cu. On the other hand, the BAC values of Mn and Zn were reduced by the application of Fe-RHA at all rates compared with the control. The lowest BAC values for Mn (0.118) and Zn (0.356) were both recorded in 20% Fe-RHA samples (Table 5).

The RHA mended samples showed higher BTC values for Cu at all rates compared with the control. The highest BTC for Cu (2.389) was recorded at 5% RHA treated sample, respectively. In contrast, the BTC values for As, Mn, and Zn were lower than the control except for 10% RHA for As and 5% RHA for Mn amended samples. The lowest BTC values for As (0.104), Mn (1.283), and Zn (0.334) were observed at 20%, 10%, and 10% RHA, respectively. The BTC values for Cr were lower than the control except for 5% RHA amended samples. It is also observed that there was no significant effect of RHA application on the BTC values of vetiver grass for Cd.

Meanwhile, in Fe-RHA amended samples, the BTC values for As, Mn, and Zn were lower than the control except at 5% Fe-RHA for Mn. The lowest BTC values for As (0.075), Mn (1.857), and Zn (0.363) were all observed in 20% Fe-RHA amended samples. In addition, there is no effect of Fe-RHA application at all rates on BTC value of Cd, Cr, and Cu except at 5% Fe-RHA for Cd and Cr and 10% Fe-RHA for Cu.

Table 5 also shows the BCF value for the elements in vetiver grass grown in tailings amended with RHA and Fe-RHA. The BCF values for As and Zn in RHA and Fe-RHA amended samples at all rates were higher than the control.

TABLE 5: Biological accumulation coefficient (BAC), biological transfer coefficient (BTC), and bioconcentration factor (BCF) of heavy metals by vetiver grass grown in the gold mine tailings amended with Fe-RHA and RHA (mean $n = 3$). Different letters correspond to significant differences between rates of the same ash ($P < 0.05$) in the same column.

	Type	Rate (%)	As	Cd	Cr	Cu	Mn	Zn
BAC	Control	0	0.009 ^c	0.011 ^a	0.315 ^a	0.493 ^b	0.174 ^a	0.858 ^a
	RHA	5	0.010 ^c	0.015 ^a	0.375 ^a	0.640 ^a	0.148 ^a	0.533 ^b
	RHA	10	0.020 ^b	0.017 ^a	0.343 ^a	0.422 ^b	0.129 ^a	0.436 ^c
	RHA	20	0.025 ^a	0.016 ^a	0.369 ^a	0.542 ^{ab}	0.137 ^a	0.393 ^c
	Control	0	0.009 ^a	0.009 ^a	0.257 ^b	0.619 ^a	0.200 ^a	0.816 ^a
	Fe-RHA	5	0.006 ^b	0.011 ^a	0.643 ^a	0.603 ^a	0.166 ^b	0.567 ^b
	Fe-RHA	10	0.011 ^a	0.015 ^a	0.314 ^b	0.564 ^a	0.134 ^c	0.739 ^c
	Fe-RHA	20	0.011 ^a	0.011 ^a	0.256 ^b	0.610 ^a	0.118 ^c	0.365 ^d
BTC	Control	0	0.321 ^b	0.211 ^b	3.089 ^b	1.554 ^b	2.802 ^a	1.119 ^a
	RHA	5	0.198 ^c	2.000 ^a	7.821 ^a	2.389 ^a	3.355 ^a	0.449 ^b
	RHA	10	0.411 ^a	0.532 ^b	2.054 ^b	2.215 ^a	1.283 ^c	0.334 ^b
	RHA	20	0.104 ^d	0.351 ^b	2.394 ^b	2.031 ^a	1.925 ^b	0.356 ^b
	Control	0	0.329 ^a	0.201 ^{ab}	2.153 ^b	1.631 ^b	2.782 ^a	0.981 ^a
	Fe-RHA	5	0.104 ^b	0.357 ^a	5.350 ^a	2.031 ^{ab}	2.957 ^a	0.314 ^d
	Fe-RHA	10	0.127 ^b	0.273 ^{ab}	2.183 ^b	2.497 ^a	2.193 ^b	0.715 ^b
	Fe-RHA	20	0.075 ^c	0.112 ^b	2.927 ^b	1.867 ^b	1.857 ^c	0.363 ^c
BCF	Control	0	0.027 ^c	0.051 ^a	0.102 ^b	0.318 ^a	0.062 ^c	0.770 ^c
	RHA	5	0.051 ^b	0.008 ^c	0.049 ^c	0.267 ^a	0.044 ^d	1.192 ^{ab}
	RHA	10	0.050 ^b	0.032 ^b	0.167 ^a	0.191 ^b	0.100 ^a	1.307 ^a
	RHA	20	0.243 ^a	0.044 ^{ab}	0.155 ^a	0.267 ^a	0.071 ^b	1.108 ^b
	Control	0	0.027 ^d	0.045 ^b	0.119 ^{ab}	0.380 ^a	0.072 ^a	0.832 ^c
	Fe-RHA	5	0.062 ^c	0.032 ^c	0.120 ^{ab}	0.296 ^{ab}	0.056 ^{ab}	1.806 ^a
	Fe-RHA	10	0.084 ^b	0.056 ^b	0.145 ^a	0.229 ^b	0.061 ^b	1.035 ^b
	Fe-RHA	20	0.145 ^a	0.101 ^a	0.088 ^b	0.327 ^a	0.064 ^{ab}	1.005 ^b

The highest BCF values of As (0.243) and Zn (1.806) were recorded by 20% RHA and 5% Fe-RHA samples, respectively. The application of RHA at all rates except at 20% reduced BCF value for Cd compared with the control and the lowest BCF value for Cd (0.008) was recorded at 5% RHA. The application of 10% and 20% RHA increased the BCF values for Cr, while at 5% RHA the values decreased compared to the control. However, for Cu only the 10% RHA amended sample had lower BCF value compared with the control. Samples treated with Fe-RHA at lower rates had lower BCF values for Cd than the control but, at 20% Fe-RHA, the BCF value was higher than the control. The application of Fe-RHA did not significantly affect the BCF values of Cr, Cu, and Mn at all rates, except at 10% Fe-RHA for Cu and Mn.

A plant is a hyperaccumulator when the heavy metal concentration in its stem and leaf is 10–500 times higher than in plants grown in nonpolluted area and enrichment coefficient is greater than 1 [39]. In general, it can be concluded that the success of a heavy metal-phytoextraction process depends on the ability of the plant to move the metals quickly from the root to the aerial parts of the plant [40]. Though the concentrations of metals were high in the shoot system of the vetiver grass, the BAC values for all heavy metals were less than 1 (Table 5), and this may be attributed

to the very high concentration of contamination in gold mine tailings because the BAC value is the ratio of concentration from the tailings to the shoots.

The mobility of heavy metals from the roots to the shoots is reflected by the BTC values. The results show that the BTC values for Cd, Cr, Cu, Mn, and Zn were greater than 1, while the BTC values for As were less than 1. The BTC values suggest higher concentrations of Cd, Cr, Cu, Mn, and Zn in the shoots than the roots system of the vetiver grass, while for As, the opposite was true. Also, BTC and BAC results indicated the ability of vetiver grass to absorb Cd, Cr, Cu, Mn, and Zn and they were rapidly transferred to shoot. In contrast, the results of As clearly showed the affinity of roots to accumulate a good amount of metals from the tailings but low transfer to the aerial parts. The BCF indicates root metal concentration divided by the tailings concentration. The value was used to explain the uptake of vetiver in roots. The BCF values for all metals except Zn were less than 1 (Table 5) which considered normal because the values demonstrated the ability of vetiver to accumulate a good amount of metals in the root. This might be due to variation in heavy metal concentration and plant species. The BCF values reflected the negative effect of adding RHA to uptake of heavy metals by the vetiver. The overall results indicate that the vetiver

grass can grow in the gold mine tailing containing high concentrations of As, Cd, Cr, Cu, Mn, Pb, and Zn and can accumulate the elements in its roots and shoots.

4. Conclusions

It can be concluded from this study that the vetiver grass was tolerant to high concentrations of As, Cd, Cr, Cu, Mn, and Zn in the tailings. Application of RHA and Fe-RHA reduced the phytoavailability of Cd, Cr, Cu, Mn, and Zn. This may be important during the early part of a phytoremediation project whereby establishment of plant species on tailings containing very high concentrations of heavy metals is difficult. On the other hand, both amendments especially the RHA can also be used to increase the phytoavailability of As. Therefore, the RHA and Fe-RHA can be used in a phytoremediation project to either reduce the phytoavailability of cationic elements like Cd, Cr, Cu, Mn, and Zn or increase the phytoavailability of anionic elements like As. We recommend that field experiments should be carried out to confirm the results obtained in this glass house study.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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References

- [1] S. Taberima, B. Mulyanto, R. J. Gilkes, and Y. Husin, "Fertility status of soils developed on an inactive mine tailings deposition area in Papua," in *Proceedings of the 19th World Congress of Soil Science, Soil Solutions for a Changing World*, pp. 21–26, Brisbane, Australia, August 2010.
- [2] M. C. Navarro, C. Pérez-Sirvent, M. J. Martínez-Sánchez, J. Vidal, P. J. Tovar, and J. Bech, "Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone," *Journal of Geochemical Exploration*, vol. 96, no. 2-3, pp. 183–193, 2008.
- [3] W. H. O. Ernst, "Bioavailability of heavy metals and decontamination of soils by plants," *Applied Geochemistry*, vol. 11, no. 1-2, pp. 163–167, 1996.
- [4] A. Akcil, C. Erust, S. Ozdemiroglu, V. Fonti, and F. Beolchini, "A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes," *Journal of Cleaner Production*, vol. 86, pp. 24–26, 2015.
- [5] S. Khan, M. Waqas, F. Ding, I. Shamsad, H. P. H. Arp, and G. Li, "The influence of various biochars on the bioaccessibility and bioaccumulation of PAHs and potentially toxic elements to turnips (*Brassica rapa* L.)," *Journal of Hazardous Materials*, vol. 300, pp. 243–253, 2015.
- [6] M. Ahmad, S. S. Lee, J. E. Yang, H.-M. Ro, Y. Han Lee, and Y. Sik Ok, "Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil," *Ecotoxicology and Environmental Safety*, vol. 79, pp. 225–231, 2012.
- [7] A. S. Chamon, M. H. Gerzabek, M. N. Mondol, S. M. Ullah, M. Rahman, and W. E. H. Blum, "Influence of soil amendments on heavy metal accumulation in crops on polluted soils of Bangladesh," *Communications in Soil Science and Plant Analysis*, vol. 36, no. 7-8, pp. 907–924, 2005.
- [8] R. P. Narwal and B. R. Singh, "Effect of organic materials on partitioning, extractability and plant uptake of metals in an alum shale soil," *Water, Air, and Soil Pollution*, vol. 103, no. 1–4, pp. 405–421, 1998.
- [9] R. P. Singh and M. Agrawal, "Variations in heavy metal accumulation, growth and yield of rice plants grown at different sewage sludge amendment rates," *Ecotoxicology and Environmental Safety*, vol. 73, no. 4, pp. 632–641, 2010.
- [10] Ministry of Science, Technology, and the Environment of Malaysia, *National Policy on the Environment*, 2002.
- [11] A. B. Hashim, H. Aminuddin, and K. B. Siva, "Nutrient content in rice husk ash of some Malaysian rice varieties," *Pertanika Journal of Tropical Agricultural Science*, vol. 19, no. 1, pp. 77–80, 1996.
- [12] Q. Feng, Q. Lin, F. Gong, S. Sugita, and M. Shoya, "Adsorption of lead and mercury by rice husk ash," *Journal of Colloid and Interface Science*, vol. 278, no. 1, pp. 1–8, 2004.
- [13] C. R. T. Tarley and M. A. Z. Arruda, "Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents," *Chemosphere*, vol. 54, no. 7, pp. 987–995, 2004.
- [14] V. C. Srivastava, I. D. Mall, and I. M. Mishra, "Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 312, no. 2-3, pp. 172–184, 2008.
- [15] V. C. Srivastava, I. D. Mall, and I. M. Mishra, "Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA," *Journal of Hazardous Materials*, vol. 134, no. 1-3, pp. 257–267, 2006.
- [16] V. S. Mane, I. D. Mall, and V. C. Srivastava, "Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash," *Journal of Environmental Management*, vol. 84, no. 4, pp. 390–400, 2007.
- [17] J. C. Saha, K. Dikshit, and M. Bandyopadhyay, "Comparative studies for selection of technologies for arsenic removal from drinking water," in *Proceedings of the BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water*, pp. 76–84, Dhaka, Bangladesh, 2001.
- [18] W. Nakbanpote, P. Thiravetyan, and C. Kalambaheti, "Preconcentration of gold by rice husk ash," *Minerals Engineering*, vol. 13, no. 4, pp. 391–400, 2000.
- [19] C.-Y. Yin, H. B. Mahmud, and M. G. Shaaban, "Stabilization/solidification of lead-contaminated soil using cement and rice husk ash," *Journal of Hazardous Materials*, vol. 137, no. 3, pp. 1758–1764, 2006.
- [20] P. R. Day, "Particle fractionation and particle-size analysis," in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, C. A. Black, D. D. Evans, J. L. White, L. E. Ensminger,

- and F. E. Clak, Eds., pp. 1367–1378, American Society of Agronomy, Madison, Wis, USA, 1965.
- [21] H. D. Chapman, “Cation exchange capacity,” in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, G. A. Black, D. D. Evans, J. L. White, L. E. Ensminger, and F. E. Clark, Eds., pp. 891–901, American Society of Agronomy, Madison, Wis, USA, 1965.
- [22] V. Cappuyens and R. Swennen, “Release of vanadium from oxidized sediments: insights from different extraction and leaching procedures,” *Environmental Science and Pollution Research*, vol. 21, no. 3, pp. 2272–2282, 2014.
- [23] W. S. Shu, Z. H. Ye, C. Y. Lan, Z. Q. Zhang, and M. H. Wong, “Acidification of lead/zinc mine tailings and its effect on heavy metal mobility,” *Environment International*, vol. 26, no. 5–6, pp. 389–394, 2001.
- [24] L. E. Allison and C. D. Moodie, “Carbonate,” in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, G. A. Black, D. D. Evans, J. L. White, L. E. Ensminger, and F. E. Clak, Eds., pp. 1379–1396, American Society of Agronomy, Madison, Wis, USA, 1965.
- [25] D. E. Güven and G. Akinci, “Comparison of acid digestion techniques to determine heavy metals in sediment and soil samples,” *Gazi University Journal of Science*, vol. 24, no. 1, pp. 29–34, 2011.
- [26] Ü. Uras, M. Carrier, A. G. Hardie, and J. H. Knoetze, “Physico-chemical characterization of biochars from vacuum pyrolysis of South African agricultural wastes for application as soil amendments,” *Journal of Analytical and Applied Pyrolysis*, vol. 98, pp. 207–213, 2012.
- [27] M. Ahmedna, W. E. Marshall, and R. M. Rao, “Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties,” *Bioresource Technology*, vol. 71, no. 2, pp. 113–123, 2000.
- [28] W. Song and M. Guo, “Quality variations of poultry litter biochar generated at different pyrolysis temperatures,” *Journal of Analytical and Applied Pyrolysis*, vol. 94, pp. 138–145, 2012.
- [29] A. W. Samsuri, F. Sadegh-Zadeh, and B. J. Seh-Bardan, “Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk,” *Journal of Environmental Chemical Engineering*, vol. 1, no. 4, pp. 981–988, 2013.
- [30] Z. Yanqun, L. Yuan, C. Jianjun, C. Haiyan, Q. Li, and C. Schwartz, “Hyperaccumulation of Pb, Zn and Cd in herbaceous grown on lead-zinc mining area in Yunnan, China,” *Environment International*, vol. 31, no. 5, pp. 755–762, 2005.
- [31] J. Yoon, X. Cao, Q. Zhou, and L. Q. Ma, “Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site,” *Science of the Total Environment*, vol. 368, no. 2–3, pp. 456–464, 2006.
- [32] S. Karmakar, B. N. Mitra, and B. C. Ghosh, “Influence of industrial solid wastes on soil-plant interactions in rice under acid lateritic soil,” in *Proceedings of the World of Coal Ash Conference*, pp. 4–7, Lexington, Ky, USA, May 2009.
- [33] A. Masulili, W. H. Utomo, and M. S. Syechfani, “Rice husk biochar for rice based cropping system in acid soil 1. the characteristics of rice husk biochar and its influence on the properties of acid sulfate soils and rice growth in West Kalimantan, Indonesia,” *Journal of Agricultural Science*, vol. 2, no. 1, pp. 39–47, 2010.
- [34] N. Garg and P. Singla, “Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms,” *Environmental Chemistry Letters*, vol. 9, no. 3, pp. 303–321, 2011.
- [35] A. C. Barrachina, F. B. Carbonell, and J. M. Beneyto, “Arsenic uptake, distribution, and accumulation in tomato plants: effect of arsenite on plant growth and yield,” *Journal of Plant Nutrition*, vol. 18, no. 6, pp. 1237–1250, 1995.
- [36] M. A. Eissa, M. F. Ghoneim, G. A. El-Gharably, and M. A. El-Razek, “Phytoextraction of nickel, lead and cadmium from metals contaminated soils using different field crops and EDTA,” *World Applied Sciences Journal*, vol. 32, no. 6, pp. 1045–1052, 2014.
- [37] M. P. Bernal, R. Clemente, and D. J. Walker, “Interactions of heavy metals with soil organic matter in relation to phytoremediation,” in *Phytoremediation: The Green Salvation of the World*, J. P. Navarro-Aviño, Ed., pp. 109–129, Research Signpost, Kerala, India, 2009.
- [38] R. Clemente, N. M. Dickinson, and N. W. Lepp, “Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity,” *Environmental Pollution*, vol. 155, no. 2, pp. 254–261, 2008.
- [39] Z. G. Shen and Y. L. Liu, “Progress in the study on the plants that hyperaccumulate heavy metal,” *Plant Physiology Communications*, vol. 34, pp. 133–139, 1998.
- [40] M. J. Khan, M. T. Jan, N. U. Farhatullah et al., “The effect of using waste water for tomato,” *Pakistan Journal of Botany*, vol. 43, no. 2, pp. 1033–1044, 2011.

Research Article

Dissolution of Metals from Biosolid-Treated Soils by Organic Acid Mixtures

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Results for the solubilization of metals from biosolid- (BSL-) treated soils by simulated organic acid-based synthetic root exudates (OA mixtures) of differing composition and concentrations are presented. This study used two BSL-treated Romona soils and a BSL-free Romona soil control that were collected from experimental plots of a long-term BSL land application experiment. Results indicate that the solubility of metals in a BSL-treated soil with 0.01 and 0.1 M OA mixtures was significantly higher than that of 0.001 M concentrations. Differences in composition of OAs caused by BSL treatment and the length of growing periods did not affect the solubility of metals. There were no significant differences in organic composition and metals extracted for plants grown at 2, 4, 8, 12, and 16 weeks. The amount of metals extracted tended to decrease with the increase of the pH. Results of metal dissolution kinetics indicate two-stage metal dissolution. A rapid dissolution of metals occurred in the first 15 minutes. For Cd, Cu, Ni, and Zn, approximately 60–70% of the metals were released in the first 15 minutes while the initial releases for Cr and Pb were approximately 30% of the total. It was then followed by a slow but steady release of additional metals over 48 hours.

1. Introduction

Organic acids (OAs) provide attractive options for extracting agents not only because they are biodegradable [1, 2], but also because they are able to extract metal contaminants from soils at mildly acidic conditions (pH 3–5). OAs found in root exudates, such as citric, oxalic, tartaric, and acetic acids, are capable of forming complexes with Cu, Zn, Pb, and Co ions in solutions [3–8] and enhancing their mobilization and uptake by plants [9–12]. Römheld and Awad [13] showed that plants grown on low Fe nutrient mediums in contaminated soil had a higher uptake of Fe, Zn, Ni, and Cd (up to 200%) than control plants in adequate Fe nutrient mediums [14]. Various OAs and/or their salts were tested against two metal chelating agents (EDTA and DTPA) for their potential effects in the remediation of loam and sandy clay loam polluted by heavy metals [15, 16]. Experimental evidence shows that OAs added to humic macromolecules induced the release of adsorbed metal ions [17, 18]. In near neutral and neutral

aqueous solutions, OAs are readily dissociated. The negatively charged OA ligands are capable of forming complexes with metals (e.g., Mn, Fe, and Zn) in solutions, increasing their availability to plants [11, 19, 20].

The extent of complexation depends on the characteristics of the OAs involved (number and proximity of carboxylic groups), their concentrations, types of metal, and the pH of the soil [21]. Organic acids with only one carboxyl group, such as acetic, formic, and lactic acids, have less metal complexing ability than malic and oxalic acids, which are frequently found OAs in soils that have a high affinity for complexing metals [14, 22, 23]. The ability of OAs to complex metals is also dependent on pH [24]. For instance, the complexation of Fe by malic and oxalic acids is highly dependent on soil pH, with little or no complexation at pH > 7.0 [25]. In addition, malic and oxalic acids have the tendency to precipitate in the presence of Ca²⁺, thus reducing their potential to complex with other metals [26]. When compared with rainwater alone, OAs are able to double or even quadruple mineral dissolution

rates. The extent of the chemical reactions, however, is dependent on mineral type, pH, and OA type [22]. Jones and Kochian [23] reported that the presence of OAs increases the dissolution of Fe and Al oxyhydroxides.

OAs may be adsorbed onto the hydroxyaluminum-montmorillonite (HyA-Mt) complex. Cambier and Sposito [27] concluded that the HyA-Mt complex is stable at $4 < \text{pH} < 5.5$, and only external HyA polycations could react with citrate. Janssen et al. [28] noted that citrate did not appear to be adsorbed on the Al-OH groups of the HyA-Mt complex; instead it is adsorbed at the edge of the clay [29]. Sakurai and Huang [30] studied the effect of oxalate on the adsorption of Cd by montmorillonite (Mt) and HyA-Mt complex at pH 5. The reaction was very rapid and virtually completed within 10 minutes. The presence of oxalate markedly interfered with Cd adsorption on clays, especially on the montmorillonite. Taniguchi et al. [31] investigated the adsorption phenomena of Cd on hydroxyaluminosilicate- (HAS-) montmorillonite (Mt) and HyA-Mt complexes as influenced by oxalate and citrate. They concluded that the optimal concentrations of oxalate and citrate for Cd adsorption depended on the form of Cd ions in the solution.

Early research by Eaton [32] showed that plant roots absorbed P and Fe from “water insoluble” P and Fe containing minerals present in the growth medium. Jenny and Overstreet [33] proposed that reactions between root and solid phase minerals that were in direct contact or in close proximity would facilitate plant absorption of sparingly soluble mineral nutrients in soils. Recent studies have demonstrated that root exudates, which contain OAs, play a significant role in the solubilization of metals in soil [5, 11, 34]. In BSL, metals are present almost entirely in solid phases. Upon land application, BSL-borne metals remain largely in their original solid phases in BSL-treated soils [35]. Mobilization of metals by OAs in root exudates would be the most significant pathway through which plant absorption of metals from BSL-treated soils occurs [36]. The total amount of bioavailable metals in BSL-treated soils can be estimated by extracting the soils using OAs found in the rhizosphere of plants grown on BSL-treated medium. It follows that the rate of metal availability for plants would be in proportion to the rate of metal dissolution in the OA mixture [37].

The pH of the rhizosphere is also important in determining metal and nutrient mobilization and uptake. It also affects microbial activity in the vicinity of the root. Root induced pH change in the rhizosphere is a known phenomenon [38, 39] and has an effect on the availability or solubility of nutrients such as P, Fe, Mn, Zn, Cu, and Al [40]. Rhizosphere pH may differ from the bulk soil pH by more than 2 units [41]. Buffer capacities of soil and root activity are the main factors influencing pH at the soil-root interface [42]. Several hypotheses have been postulated to explain the different abilities of plant species in affecting rhizosphere pH: these include differences in root exudation and respiration patterns and differences in cation/anion uptake rates [43]. Since plant roots acquire most mineral nutrients and metals as ions, imbalances between the absorption of cations and anions result in roots’ excretion of compensating H^+ or OH^- ions into the soil in rhizosphere, to prevent changes

TABLE 1: Chemical properties of the soil used for the experiment.

Biosolid treatment [†]	pH [‡]	Total concentration (mg kg ⁻¹)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	7.7	0.5	37	105	24	25	95
135 Mg ha ⁻¹	6.9	11	243	188	88	120	559
1,080 Mg ha ⁻¹	6.1	26	596	478	215	396	1466

[†]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡]1:1 w/v ratio.

in the electroneutrality of the root tissues [44]. Gollany and Schumacher [45] conducted a growth chamber study to characterize patterns of pH change within the rhizosphere of plants and the pH at different root zones was measured by a microelectrode at 1, 2, 3, and 4 mm distances from the root surface. They reported that the pH decreased to 4.82 and 4.95 in the rhizosphere around elongation and meristematic zones, respectively, compared to the control (pH = 7.6) without plants.

The objectives of this study were the following:

- (1) To use an OA mixture as a substitute for actual OAs in root exudates to solubilize metals in BSL-treated soils.
- (2) To test the solubilization of metals in BSL-treated soils by the different concentrations of the OA mixture of corn (*Zea mays* L.).

In order to meet these objectives, the researchers needed to assess OA mixture-specific metal solubility and dissolution rate constants of BSL-treated soils.

2. Materials and Methods

2.1. Chemical Properties of the Soils. Two BSL-treated Romona soils and the BSL-free Romona soil control from the field plots of a long-term BSL land application experiment were used [46]. These experiment plots were established in 1976 on a Romona sandy loam soil (fine-loamy, mixed, thermic Typic Haploxeralf) located in the Moreno Field Station of the University of California, Riverside. The Nu-earth BSL used throughout the experiment contained an average of 40, 600, 475, 250, and 3,547 mg kg⁻¹ of Cd, Cr, Cu, Ni, and Zn, respectively. From 1976 through 1981, composted BSL were applied at a rate of 0 (control), 22.5, 45, 90, and 180 Mg ha⁻¹ yr⁻¹ dry weight. The entire experimental fields were cultivated for 10 years (1982–1991) following the termination of BSL application. Soil collected in 1991 from the control, 22.5, and 180 Mg ha⁻¹ yr⁻¹ treatments was used. Soil samples were air-dried and ground to pass through a 2 mm sieve, homogenized, and stored for subsequent analysis. The chemical properties of the selected soils used in the study are presented in Table 1. For metal determination, aliquots of soil samples were digested in Teflon Parr bombs by a HNO_3 microwave digestion procedure (0.3 g soil with a mixture of 1.0 mL H_2O + 4.5 mL concentrated HNO_3 + 1.5 mL concentrated HCl, in a 120 mL Teflon digestion vessel for 20 minutes and with maximum pressure of 484 kPa) [47].

2.2. Release and Analysis of the Metals. One gram of the soils was mixed with 10 mL of OA mixtures in 50 mL Teflon test tubes. The contents were shaken and allowed to equilibrate at 298°K using a rotary mixer, SA-12 Motor Speed Control (B & B Motor and Control Corp., Long Island City, NY), which rotated the capped test tubes head to tail at approximately 1 rpm for 48 hours. The speed of rotation was maintained constant in all treatments. One mL of chloroform was added to each test tube to control microbial activity and prevent decomposition of OA mixtures during equilibration. The pH and EC of the system in the beginning and at the end of the reaction period were monitored and attempts were made to keep the pH constant. Three OA mixture concentrations 0.001, 0.01, and 0.1 M in 13.5 mM $\text{Ca}(\text{NO}_3)_2$ along with a 13.5 mM $\text{Ca}(\text{NO}_3)_2$ blank were tested. Each treatment combination was replicated two times. After equilibration, the soil suspensions were centrifuged for 20 minutes at 8,000 rpm to separate the solution and solid phases. The solution phase was passed through a 0.45 μm filter paper into 25 mL volumetric flasks. The filtrates were acidified with 0.25 mL of concentrated HNO_3 . The metal contents of the supernatants were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectrophotometry (AAS) [47]. The ICP-OES system was OPTIMA 3000 V (Perkin-Elmer, Norwalk, CT, USA) with AS-91 Autosampler and WinLab™ software for the optima family of ICP-OES. Another instrument utilized was the Perkin-Elmer Analyst 800 Atomic Absorption Spectrometer (Perkin-Elmer, Bodenseewerk, Germany) with AS-800 Autosampler. The same experimental setup was used for the batch metal dissolution kinetics. The metal concentrations at 0, 0.25, 0.5, 1, 2, 4, 8, 24, and 48 hours were determined for the kinetic studies.

2.3. Statistical Analysis. All experiments were repeated. Between-group differences were determined by one-way analysis of variance (ANOVA), followed by Student-Newman-Keuls test using a probability level of $P < 0.05$ in all cases. Tests were performed with SigmaStat 4.01 Software.

3. Results and Discussion

3.1. Formulation of Organic Acid Mixtures. Organic acids in rhizosphere are difficult to collect because the volume produced is limited and the components of the root exudates are readily biodegradable. To evaluate the OAs' ability in the rhizosphere to solubilize metals in the soils, a large amount of root exudates must be collected. Because of the difficulty in collecting and preserving root exudates, it is imperative that an OA-based synthetic root exudate (OA mixture) be formulated.

The OA mixture should contain the primary chemical components responsible for metal complex formation and should be in the concentration and pH ranges commonly observed in the rhizosphere. In addition, the OA mixtures should also be prepared under the same background chemical matrix of the soil solution. In this manner, the OA mixture would exhibit comparable ability of reacting with metals as the actual root exudates.

TABLE 2: Amounts of Cd extracted by organic acid (OA) mixtures of various compositions and concentrations[†].

OA concentration	OA composition [‡]	Cd concentration (mg kg^{-1})	
		Biosolid	Standard
0.1 M	2nd	2.11 ^{Ba}	1.86 ^{Ba}
	4th	2.36 ^{Aa}	2.58 ^{Aa}
	8th	1.98 ^{Ba}	1.63 ^{Ba}
	12th	1.79 ^{Ba}	1.60 ^{Ba}
	16th	1.71 ^{Ba}	1.62 ^{Ba}
0.01 M	2nd	0.39 ^{Aa}	0.31 ^{Aa}
	4th	0.41 ^{Aa}	0.43 ^{Aa}
	8th	0.44 ^{Aa}	0.35 ^{Aa}
	12th	0.47 ^{Aa}	0.37 ^{Aa}
	16th	0.51 ^{Aa}	0.43 ^{Aa}
0.001 M	2nd	0.29 ^{Aa}	0.20 ^{Aa}
	4th	0.32 ^{Aa}	0.24 ^{Aa}
	8th	0.36 ^{Aa}	0.32 ^{Aa}
	12th	0.29 ^{Aa}	0.23 ^{Aa}
	16th	0.30 ^{Aa}	0.29 ^{Aa}
13.5 mM $\text{Ca}(\text{NO}_3)_2$	Not applicable	0.10	

[†]Values represent means of four replicates. The differences of Cd concentrations among the OA compositions of growth periods were tested by one-way ANOVA. In each column of each organic concentration, values followed by the same uppercase letter were not significantly different at $P < 0.05$. The differences of the Cd concentrations between standard (STD) and biosolid (BSL) treatments were tested by Student-Newman-Keuls test. Each pair of Cd concentrations followed by the same lowercase letter was not significantly different at $P < 0.05$.

[‡]Compositions corresponding to OAs recovered from STD and BSL-treated medium of corn at 2nd, 4th, 8th, 12th, and 16th weeks of growth.

To simulate OAs in root exudates, an OA mixture of similar composition to the root exudate composition was formulated. A series of experiments were conducted to test the effect of OA compositions, the total concentration of metals, and the concentration of OAs in the dissolution of metals in the BSL-treated soils. The amount of metals extracted by the OA mixtures, representing compositions of OAs recovered from the rhizosphere of corn grown on BSL-treated medium and the standard (STD) sand medium [34], was illustrated by the Cd extractions summarized in Table 2. The differences of metals extracted due to the compositions representing OAs at 2, 4, 8, 12, and 16 weeks of plant growth were not significant at $P < 0.05$ and the differences due to OAs of STD and BSL-treated medium were not significant at $P < 0.05$. The trends were similar for other metals extracted. The data were then pooled to test the differences in metal extractions due to the concentrations of OA mixtures. They were significant at $P < 0.05$. Based on the results, the OA mixture was formulated.

3.1.1. Composition and Concentration of OAs. Although the OA compositions of the root exudates recovered from plants were grown for various lengths of time from different plant species, they did not vary significantly under our system

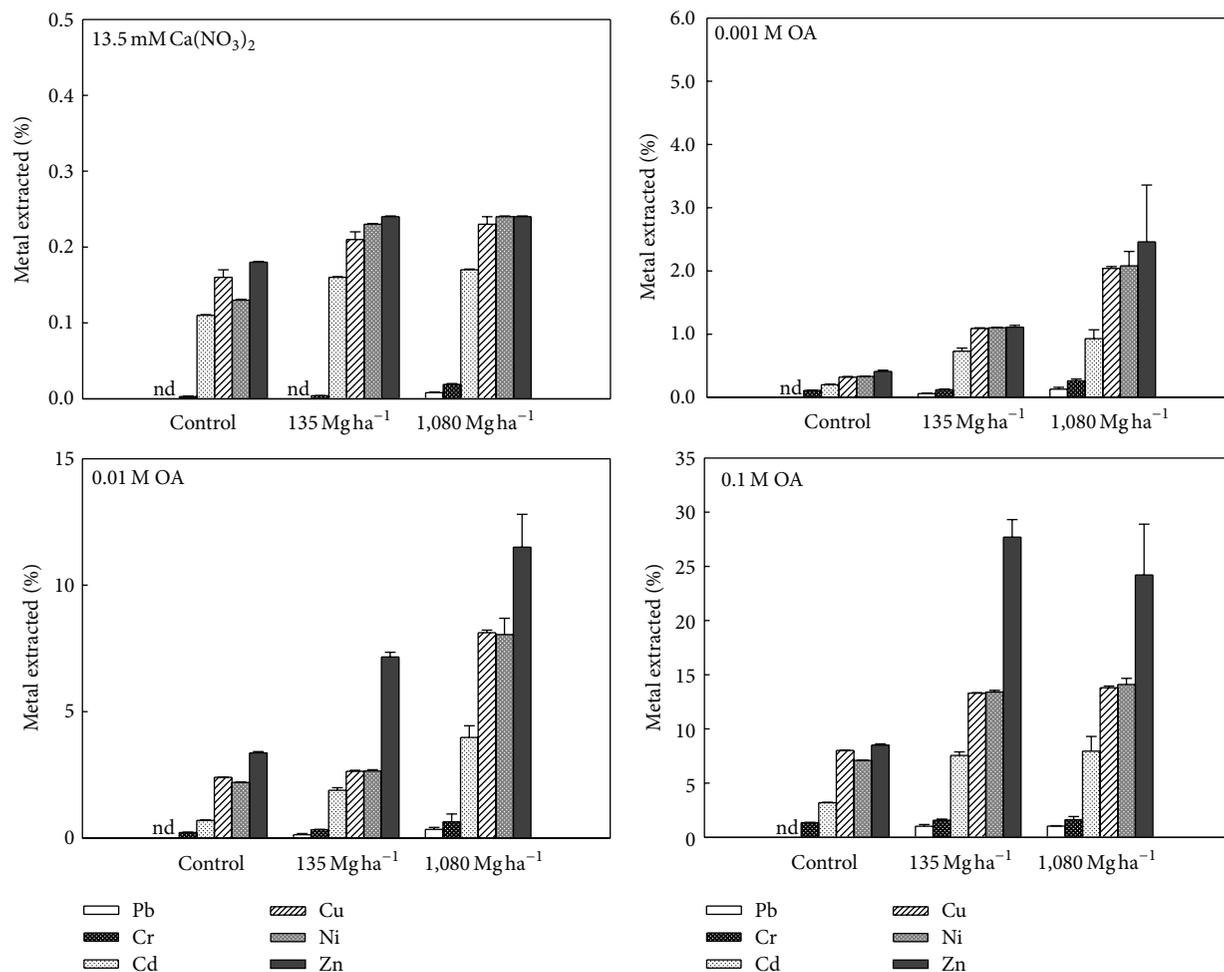


FIGURE 1: Percentages of metal extracted (means \pm SD where $n = 4$) from control and biosolid-treated Romona soil by the organic acid mixtures. Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively. Some of the observations were below detection limits (nd) of the AAS for Pb = 0.001 mg kg⁻¹.

[34]. The OA mixture composition was taken as the average composition of OAs recovered from the rhizosphere of corn grown on BSL-treated medium for 16 weeks and summarized in Table 3.

Figure 1 summarizes the amounts of metals extracted by OA mixtures at concentrations of 0.001, 0.01, and 0.1 M. The experimental results indicate that the concentrations of the OA mixtures significantly affect the amount of metals extracted. The amount of metals extracted by the OA mixtures was considerably greater than that of the neutral electrolyte solution, 13.5 mM of Ca(NO₃)₂, which was used to represent the background chemical matrix of the soil solution. Based on the moisture content of the rhizosphere and the amount of OAs recovered from the rhizosphere [34], the concentrations of OAs in the rhizosphere were estimated to be from 0.001 to 0.013 M (Table 4). As the OAs are closely associated with root exudates, their concentrations are expected to be considerably higher near the root and soil interface and could approach 0.1 M.

TABLE 3: Mole fraction of organic acids collected in root exudates of corn.

Organic acid	Molecular weight	Mole fraction ratio
Acetic	60.05	0.287
Butyric	88.11	0.209
Glutaric	132.12	0.004
Lactic	90.08	0.366
Maleic	116.07	0.042
Oxalic	90.04	0.043
Propionic	74.08	0.010
Pyruvic	88.06	0.0004
Succinic	118.09	0.006
Tartaric	150.09	0.032
Valeric	102.13	0.001

Quantitative measurements of root exudates from plant roots indicate that OA concentrations as high as 50 mM

TABLE 4: Estimated solution concentrations (16-week average) of organic acid mixtures in root exudates of corn[†].

Treatment	Estimated concentration (mM)			
	Standard (control)		Biosolid-treated	
	Mean	SD	Mean	SD
Blank	2.05	0.63	3.41	0.87
Planted	5.23	1.21	12.9	2.04

[†]All experiments performed in four replicates for each 2, 4, 8, 12, and 16 weeks. Values represent means and standard deviation of 20 replicates.

were found within 1 mm from the root surface [53], with typical concentrations in roots at 10–20 mM. For example, in corn, organic solutes present in root cells existed primarily as amino acids (10–20 mM) and sugars (90 mM) [54]. Generally, higher concentrations of OAs are expected in the rhizosphere soil compared to those in the bulk soil [34, 55]. Soil microorganisms do not utilize the carboxylic acids, which play a significant role in complexing metal ions in soils as rapidly as the carbohydrates [3].

3.1.2. pH of the Rhizosphere Soils. The rhizosphere typically extends 1–5 mm outward from the interface of the root and soil but the pH measurement is complicated. Instead of directly measuring the pH of the rhizosphere, it was deduced and estimated from data found in literature. Studies of the rhizosphere changes in pH along roots of crops and pH changes at different distances from roots are listed in Table 5.

Zhang and Pang [50] demonstrated that while pH was essentially uniform in unvegetated soil, pH was lower near the root tips than at other locations around the root in vegetated soil. The pH varied from 6.2 near the surface (0.5 cm depth) to 4.99 at 6 cm below the soil surface.

It is apparent that pH at or near the root of living plants was altered by root exudation. It varied from pH = 4–5 at the soil-root interface and gradually varied to the level comparable to the pH of bulk soils over approximately 5 mm of distance. The pH = 4.8 was chosen as the pH for the synthetic root exudates based on the results of effects of pH on the dissolution of metals in the BSL-treated soils.

3.2. Effects of pH on the Dissolution of Metals in the Biosolid-Treated Soils. The pH of the rhizosphere may vary from 4.0 to 8.0 (Table 5) and may affect the solubility of metals in the soil. The effects of pH on the dissolution of metals in BSL-treated soils by the OA mixture were determined. Based on the outcome of this experiment, the pH of the OA mixture was set at 4.8. A BSL-treated Romona soil (135 Mg ha⁻¹) was extracted by the 0.01 M OA mixture and 13.5 mM Ca(NO₃)₂ that were adjusted to pH = 4.5, 5.5, 6.5, and 7.5.

The amounts of metals extracted tended to decrease with the increase of the pH and, at the same pH level, the OA mixture typically extracted more metals than the 13.5 mM Ca(NO₃)₂ electrolyte solution (Figure 2). The extent of pH-induced changes in metal solubility was not substantial. Cadmium and zinc experienced by far the biggest decrease, from 0.04 to 0.02 and 2.3 to 1.1 mg kg⁻¹, respectively, when pH of the extracting OA mixture increased from 4.5 to 7.5. The

change in extractable Cd and Zn was larger from pH = 4.5 to 5.5 than from 6.5 to 7.5. Under the same circumstance, the Cr extracted decreased from approximately 0.1 to 0.08 mg kg⁻¹. Statistical tests indicated that metals extracted at pH = 4.5 were not significantly different from the corresponding metals extracted at pH = 5.5 (Figure 2).

In general, the holding capacity of soils for metals increases with increasing pH. Exceptions are Cr and Mo, which are commonly more mobile under alkaline conditions. Accordingly, a decrease in plant uptake of Cu, Mn, and Zn was observed when soil pH was increased [56, 57]. The pH can be issued as the main driving factor of all the factors because it can affect the surface charge of layer silicate clays, OM, and oxides of Fe and Al. In addition to the effect on the sorption of cations, which increases with increasing pH, Fernández-Ramos et al. [58] reported that the adsorption of certain trace metals onto hydrous ferric oxide depends on pH. The results correspond to our findings.

3.3. Metal Solubility by Organic Acid Mixtures. Metals in the soils were not readily extractable by the neutral electrolyte solution blank that contained 13.5 mM Ca(NO₃)₂ and, in general, less than 0.25% of any metals were solubilized (Figure 1).

For Pb, the concentrations in the extracts of blank were below limits of quantification of AAS (<0.001 mg kg⁻¹). For the control soil, the total metal concentrations and percent of metals extracted were considerably lower than those in BSL-treated soils.

In BSL-treated soils, the amount of metals extracted was proportional to the amount present in soils and the percentage of the total metals extracted from BSL-treated soils increased with the concentration of OA mixtures; however, the percentage of extraction did not appear to change significantly with the BSL loading when soils were extracted by the 0.1 M OA mixture. In general, Cd, Cu, Ni, and Zn were more readily extractable by the OA mixtures (Figure 1) than Cr and Pb. The least extractable Pb and Cr from the BSL-treated soils follow the general trend reported in the previous paper [34] because of their strong complexation with OM compounds [56] and more specifically the effective role of OM of BSL to serve as electron donors for the reduction of Cr(VI) to Cr(III) [59]. Metals extracted from BSL-treated soils were almost all from BSL. For instance, the amount of Cd extracted from control Romona soil by 13.5 mM Ca(NO₃)₂ was 0.0008 mg kg⁻¹ (Figure 1) and the amount of Cd extracted from BSL-treated soil with the same electrolyte solution blank was 0.023 mg kg⁻¹. We calculated that the amount of Cd extracted from BSL-treated soils is about 97% of the total extracted Cd.

3.4. Metal Dissolution Kinetics of Biosolid-Treated Soils by Organic Acid Mixtures. The batch equilibrium method was used to study the kinetics of metal dissolution in BSL-treated soils. The experimental procedures were similar to those previously described in the metal solubility study, with the exception that samples were equilibrated for time periods ranging from 15 minutes to 48 hours. When the BSL-treated soils (1,080 Mg ha⁻¹) were equilibrated with 0.1 M OA

TABLE 5: Reported pH ranges of rhizosphere.

Plant	Genotype	pH range	Reference
Barley	Bowman	6.2–7.6	Gollany and Schumacher [45]
	Primus II	6.0–7.8	
	Dorirumugi	4.8–7.1	Youssef and Chino [42]
Corn	Pioneer-3737	5.2–7.6	Gollany and Schumacher [45]
	Pioneer-3732	5.2–7.6	
	CM-37	6.0–7.6	
	—	4.8–6.7	Fischer et al. [48]
Clover	Trikkala	6.2–7.1	Hinsinger and Gilkes [49]
Daisy fleabane	—	5.1–6.3	Zhang and Pang [50]
Nectarine tree	Maxim	5.3–8.2	Tagliavini et al. [36]
Oat	Hyttest	6.0–7.6	Gollany and Schumacher [45]
	SD 84104	6.2–7.6	
Rape	—	5.7–6.4	Ruiz and Arvieu [25]
Rye	Standard	5.6–7.1	Hinsinger and Gilkes [49]
Sordan	S-757	6.0–7.6	Gollany and Schumacher [45]
	S-333	6.1–7.6	
Sorghum	SC-33-8-9EY	6.3–7.6	Gollany and Schumacher [45]
	SC-118-15E	6.6–7.6	
Soybean	—	5.5–7.1	Römheld and Marschner [51]
	Hawkeye	4.8–7.6	Gollany and Schumacher [45]
	PI-54169	5.8–7.6	Gollany and Schumacher [45]
	Toyosuzu	5.1–7.0	Youssef and Chino [42]
	—	4.7–7.1	Riley and Barber [52]

mixture, the amount of BSL-borne metals solubilized in the OA mixtures increased from 1.67 to 2.48, 1.46 to 5.04, 20.3 to 33.4, 16.1 to 24.1, 0.77 to 2.33, and 205 to 282 mg kg⁻¹ for Cd, Cr, Cu, Ni, Pb, and Zn, respectively, when equilibration time increased from 15 minutes to 48 hours (Tables 6–8).

The percentages of total BSL-borne metals extracted were 13.8, 1.63, 7.95, 14.1, 1.03, and 24.2% for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. If OAs are responsible for converting metals in solid phases into plant available forms, the amount and rate of the metals' solubilization would be indicative of the metals' availability to plants.

The metal dissolution kinetics data was plotted as a fraction of the total dissolved metals (C_t/C_{48} , based on 48 hours' equilibration, C_{48}) that was found at time t (C_t) (Figure 3). The patterns for dissolution in the OA mixtures were essentially the same for all metals. When the BSL-treated soils were equilibrated with the 0.1 M OA mixture, there appeared to be an immediate and rapid release of metals from the soil. The amount of Cd, Cu, Ni, and Zn solubilized in the first 15 minutes ($C_{0.25}$) accounted for approximately 60–75% of the total dissolved metals. For Cr and Pb, approximately 8 hours was needed to dissolve 60–70% of the total soluble metals. After 15 minutes, the dissolution of metals slowly reached the steady state over a period of 48 hours. When the concentrations of the OA mixtures were 0.001 M and 0.01 M, the dissolution behavior of metals in BSL-treated soils

exhibited the same pattern as those of 0.1 M OA mixture. The amount of metals extracted by 0.001 M and 0.01 M OA mixtures was considerably less than the amount extracted by the 0.1 M OA mixture. The percentages of the total soluble metals that entered into the solution phase in the first 15 minutes, however, were essentially identical for 0.001, 0.01, and 0.1 M OA mixtures (Table 9).

A variety of chemical reactions occur in soils and reactions often take place simultaneously. Reaction time may vary from millisecond scale for ion exchange reactions to days (or months or years) for sorption/desorption reactions to reach equilibrium [60]. Metals present in BSL-treated soils may be present in different forms and therefore dissolve at different rates [61]. In the rhizosphere, the biosolids-borne metals are mainly present in solid forms and are not readily available to the growing plants. The dissolution by the root exudates is a significant pathway through which the plant absorbs metals from biosolid-treated soils. We hypothesized that the phytoavailable metals in biosolid-treated soils can be determined by amount of metals dissolved by root exudate derived organic acids in the rhizosphere. The metal uptake by plants is determined by the kinetics of metal released into solution by organic acids. In this manner, the phytoavailability of biosolid-borne metals may be defined in terms of capacity factor (i.e., organic acids extractable metals in soils), which describes the plant available metal concentration in

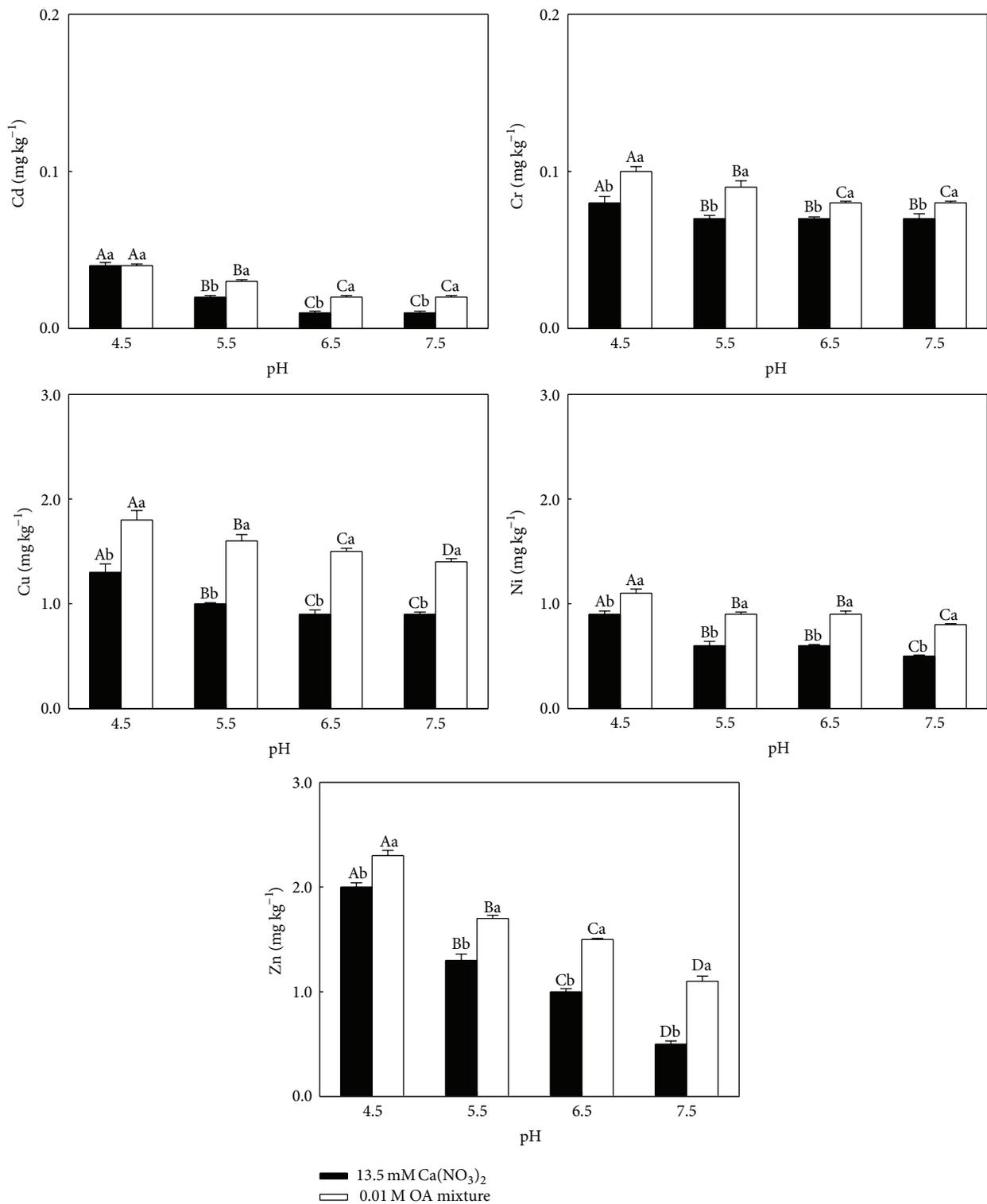


FIGURE 2: Effects of pH on the extraction of metals (four replicates) in biosolid-treated Romona soil (135 Mg ha⁻¹) by 13.5 mM Ca(NO₃)₂ electrolyte solution and 0.01 M organic acid mixtures. The differences of metal concentrations among the pH values were tested by one-way ANOVA. Values followed by the same uppercase letter were not significantly different at $P < 0.05$. The differences of the metal concentrations between 13.5 mM Ca(NO₃)₂ and 0.01 M OA mixture were tested by Student-Newman-Keuls test. Values followed by the same lowercase letter were not significantly different at $P < 0.05$.

TABLE 6: Metals release kinetics of biosolid-treated Romona soil (1,080 Mg ha⁻¹) in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.31	0.32	0.33	0.35	0.37	0.40	0.46	0.47
	0.01 M	1.16	1.21	1.24	1.28	1.35	1.49	1.73	1.75
	0.1 M	1.67	1.70	1.75	1.82	1.90	2.03	2.40	2.48
Cr	0.001 M	0.34	0.40	0.44	0.49	0.57	0.73	1.09	1.12
	0.01 M	0.85	0.95	1.03	1.16	1.39	1.67	2.49	2.57
	0.1 M	1.46	1.78	1.91	2.17	2.53	3.17	4.79	5.04
Cu	0.001 M	2.41	2.48	2.63	2.78	2.88	3.14	3.81	3.89
	0.01 M	10.7	11.1	11.7	12.1	12.8	13.8	16.8	17.5
	0.1 M	20.3	21.2	22.5	23.7	25.2	26.4	32.1	33.4
Ni	0.001 M	2.53	2.64	2.83	2.94	3.13	3.28	3.72	3.79
	0.01 M	9.80	10.2	10.9	11.4	12.1	12.5	14.5	14.8
	0.1 M	16.1	16.8	18.0	18.8	19.5	20.8	23.3	24.1
Pb	0.001 M	0.13	0.14	0.15	0.18	0.22	0.29	0.42	0.46
	0.01 M	0.34	0.36	0.38	0.45	0.54	0.67	0.99	1.03
	0.1 M	0.77	0.82	0.87	1.02	1.09	1.89	2.01	2.33
Zn	0.001 M	25	26	28	29	31	32	36	38
	0.01 M	104	108	111	115	123	129	145	148
	0.1 M	205	211	220	227	235	245	275	282

TABLE 7: Metals release kinetics of biosolid-treated Romona soil (135 Mg ha⁻¹) in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.055	0.059	0.063	0.066	0.068	0.073	0.089	0.091
	0.01 M	0.18	0.19	0.20	0.21	0.23	0.25	0.29	0.30
	0.1 M	0.79	0.83	0.88	0.92	1.01	1.10	1.26	1.29
Cr	0.001 M	0.07	0.08	0.09	0.10	0.13	0.16	0.22	0.23
	0.01 M	0.23	0.27	0.30	0.34	0.38	0.46	0.69	0.71
	0.1 M	0.91	1.07	1.13	1.23	1.47	1.80	2.63	2.68
Cu	0.001 M	0.86	0.88	0.92	0.97	1.05	1.15	1.38	1.42
	0.01 M	2.21	2.35	2.49	2.63	2.80	2.93	3.59	3.66
	0.1 M	7.6	7.8	8.3	8.9	9.4	10.1	12.6	12.7
Ni	0.001 M	0.53	0.55	0.59	0.62	0.66	0.68	0.79	0.81
	0.01 M	1.57	1.67	1.80	1.93	2.01	2.13	2.52	2.57
	0.1 M	6.8	7.3	7.8	8.4	8.9	9.5	11.0	11.3
Pb	0.001 M	0.021	0.023	0.025	0.030	0.035	0.044	0.063	0.065
	0.01 M	0.06	0.07	0.08	0.09	0.11	0.13	0.19	0.20
	0.1 M	0.32	0.34	0.38	0.45	0.53	0.62	0.90	0.94
Zn	0.001 M	3.96	4.19	4.35	4.48	4.69	4.91	5.60	5.66
	0.01 M	21.4	22.6	23.3	24.8	25.7	27.1	30.7	31.0
	0.1 M	100	103	108	114	117	121	134	137

biosolid-treated soil and intensity factor (i.e., the rate at which metals may be dissolved by organic acids), which indicates the rate at which metals will be absorbed by plants. The data presented in Tables 6–8 and Figure 3 may fit the two-site bicontinuum model. Under this conception, there appeared to be two dissolution reactions, a fast reaction, which quickly solubilized this component of the metals, followed by a slow reaction of the remaining components that may continue for

a long period of time. These two reactions may occur in series or in parallel. Location and chemical bonding of metals in soil and solution versus metal ratio might be the effects for two pools of metal [62]. The rapid release of metals in the first 15 minutes was fitted into a zero-order kinetics model that

$$C_t = k_0 \times t \quad \text{for } t = 0 \text{ to } t = 0.25, \quad (1)$$

TABLE 8: Metals release kinetics of control Romona soil in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.0013	0.0014	0.0015	0.0015	0.0016	0.0017	0.002	0.002
	0.01 M	0.0084	0.0088	0.0091	0.0097	0.0102	0.0115	0.0137	0.014
	0.1 M	0.020	0.021	0.022	0.023	0.025	0.027	0.031	0.032
Cr	0.001 M	0.010	0.012	0.013	0.016	0.019	0.023	0.034	0.035
	0.01 M	0.015	0.018	0.020	0.023	0.028	0.035	0.052	0.053
	0.1 M	0.11	0.13	0.14	0.16	0.20	0.23	0.35	0.36
Cu	0.001 M	0.1071	0.1139	0.1207	0.1275	0.1343	0.1433	0.170	0.177
	0.01 M	0.35	0.36	0.39	0.41	0.44	0.47	0.56	0.58
	0.1 M	1.97	2.03	2.12	2.21	2.34	2.51	3.11	3.17
Ni	0.001 M	0.0603	0.063	0.0675	0.0702	0.0737	0.0773	0.0891	0.090
	0.01 M	0.39	0.42	0.47	0.48	0.51	0.53	0.63	0.64
	0.1 M	1.07	1.12	1.18	1.24	1.33	1.42	1.64	1.67
Pb	0.001 M	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]
	0.01 M	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]
	0.1 M	0.014	0.016	0.017	0.019	0.024	0.030	0.042	0.044
Zn	0.001 M	0.30	0.32	0.34	0.35	0.37	0.38	0.44	0.45
	0.01 M	1.95	2.06	2.17	2.26	2.34	2.44	2.77	2.79
	0.1 M	5.3	5.6	6.0	6.2	6.5	6.8	7.8	7.9

[†] Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

where C_t (mg kg⁻¹) is the metal concentration at time t (hour) and k_0 (mg kg⁻¹ hr⁻¹) is the zero-order kinetics constant. The remainder portion of the metal dissolution reaction follows a first-order kinetics model that

$$C_t = (0.25 \times k_0) + \{C_s \times [1 - e^{-k_1 \times (t-0.25)}]\}; \quad \text{for } t > 0.25, \quad (2)$$

where C_s represents the ultimate metal release due to the first-order dissolution reaction (mg kg⁻¹) and k_1 is the first-order kinetics constant (hr⁻¹). The kinetics models depicting the metal dissolution reactions are summarized in Table 10. The concentrations of OA mixtures and the amount of BSL-borne metals in the soils determined the metals' dissolution and their availability to plants. For the first-order slow metal release, the rate constants for a metal (k_1) did not vary significantly. k_1 ranged from 0.07 to 0.13, 0.08 to 0.09, 0.07 to 0.09, 0.12 to 0.14, 0.08 to 0.09, and 0.1 to 0.13 for Cd, Cr, Cu, Ni, Pb, and Zn, respectively.

For the zero-order rapid metal release, the metal dissolution of the soil increased with the concentration of OA mixtures and the amount of metals dissolved by the OA mixture of a given concentration increased with the amount of BSL-borne metals in the soils. When the concentrations of OA mixtures varied from 0.001 to 0.1 M, k_0 for a given soil generally increased by 5 to 10 times. At the same OA mixture concentration, k_0 of metals varied by 20–100, 15–60, and 10–60 times for control, soil receiving 135 Mg ha⁻¹, and soil receiving 1,080 Mg ha⁻¹ of BSL, respectively.

The total metals that were extractable by the OA mixtures were calculated as the sum of metal rapidly released by the zero-order reaction ($0.25 \times k_0$) and the metal slowly released through the subsequent first-order reaction (C_s). The total

OA extractable metals would indicate the amount of metals possibly available to plants. The amount of metals that were extractable from BSL-treated soil (1,080 Mg ha⁻¹) by 0.1 M OA mixture is presented in Table 11.

Under this metal release model, plants grown on BSL-treated soils would be expected to absorb metals from the rapid release pool first. As the metal release followed a zero-order reaction, one would expect the plant uptake, and therefore tissue concentration, of metals to remain essentially the same until metals in this pool are exhausted, at which time the plant uptake of metals, and therefore the tissue concentration, is expected to decrease as metals in the slow release pool would be available to plants at a much slower rate.

The data presented in Tables 6–8 and Figure 3 also may fit the first-order kinetics model. Under this conception, the slope of the curve approached 0 as the time increased (Table 12). The trend on the cumulative metal extracted with respect to time was fitted into a first-order kinetics model and can be expressed as

$$C_t = C_0 \times (1 - e^{-k_1 \times t}), \quad (3)$$

where C_t (mg kg⁻¹) is the metal concentration at time t (hour) and k_1 (hr⁻¹) is the first-order kinetics constant and C_0 represents the ultimate metal release due to the first-order dissolution reaction (mg kg⁻¹). The concentrations of OA mixtures and the amount of BSL-borne metals in the soils determined the metals' dissolution and their availability to plants. For the first-order metal release, the rate constants for a metal (k_1) ranged from 3.88 to 6.25, 0.30 to 0.51, 3.81 to 4.88, 3.79 to 5.53, 0.24 to 0.50, and 4.85 to 6.80 for Cd, Cr, Cu, Ni,

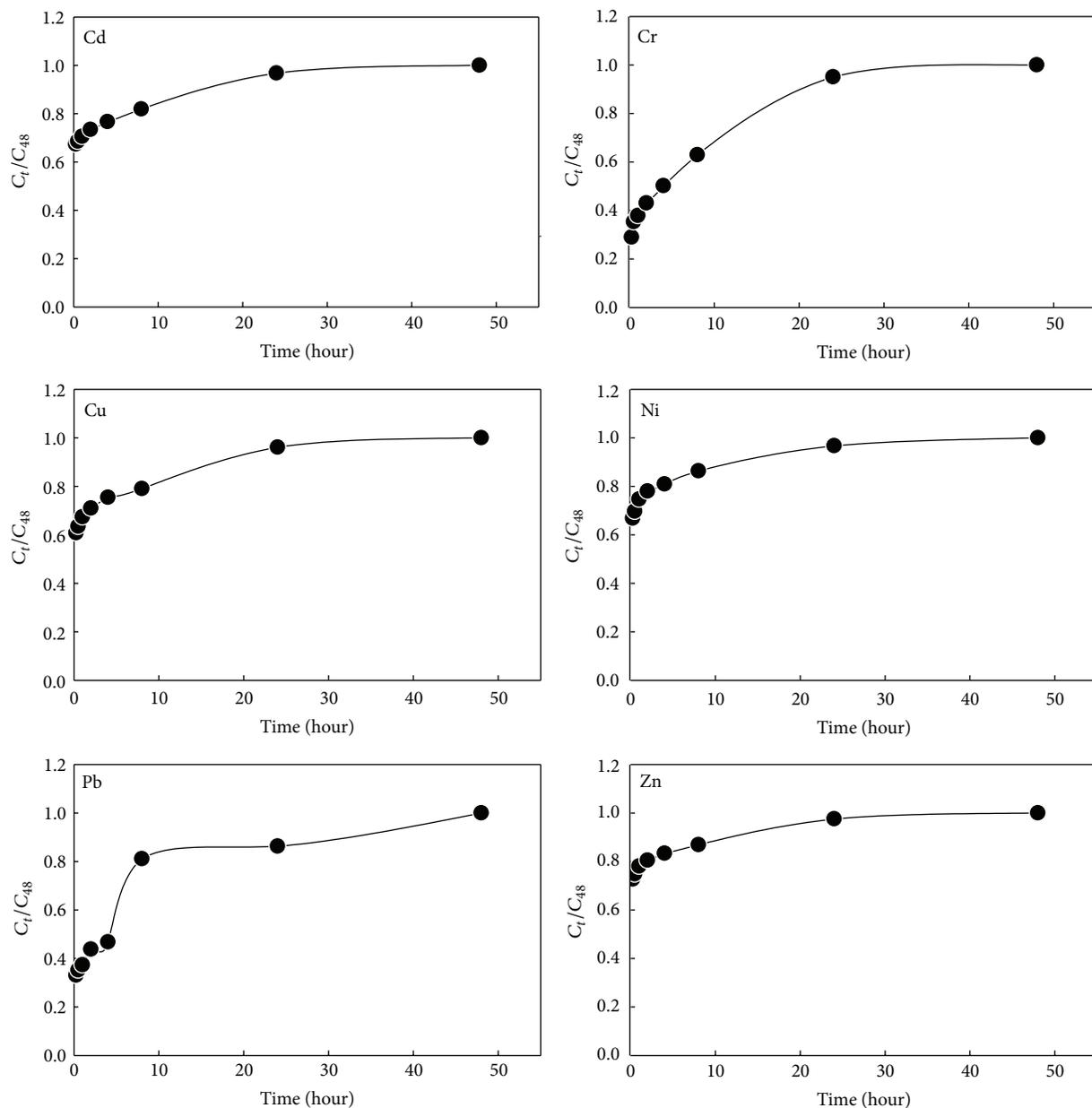


FIGURE 3: Time-dependent Cd, Cr, Cu, Ni, Pb, and Zn dissolutions of the biosolid-treated Romona soil ($1,080 \text{ Mg ha}^{-1}$) in 0.1 M organic acid mixtures (C_t denotes concentration at time t and C_{48} denotes concentration at 48 hours).

Pb, and Zn, respectively (Table 13). The total metals (C_0) that were extractable by the OA mixtures were the same as the total released amounts in Table 11. The total OA extractable metals would indicate the amount of metals possibly available to plants.

4. Conclusion

- (1) Metals present in BSL-treated soils are more extractable by an OA mixture than indigenous metals of the soil. In BSL-treated soil, more than 90% of metals extracted may be attributed to BSL-borne metals.
- (2) In general, the amount of metals extracted decreased with the increase of the pH, and at the same (4.8) pH level, the OA mixture extracted more metals than the 13.5 mM $\text{Ca}(\text{NO}_3)_2$ electrolyte solution.
- (3) In general, Cd, Cu, Ni, and Zn were more readily extractable by the OA mixtures and readily absorbed by plants grown on BSL-treated soils than Cr and Pb.
- (4) The amount of metals extracted was a function of concentration of OA mixtures. Higher concentrations of OA mixture resulted in greater extraction of metals from the BSL-treated soils.

TABLE 9: Metals of control and biosolid-treated soils solubilized by organic acid (OA) mixtures in the first 15 minutes of equilibration.

Biosolid treatment [†]	Concentration of OA mixtures	Metals dissolved in 15 minutes (% of total dissolved)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	0.001 M	63	29	61	67	n.d. [‡]	67
	0.01 M	60	28	60	61	n.d. [‡]	70
	0.1 M	63	31	62	64	32	67
135 Mg ha ⁻¹	0.001 M	60	30	61	66	32	70
	0.01 M	60	32	60	61	30	69
	0.1 M	62	34	60	60	34	73
1,080 Mg ha ⁻¹	0.001 M	66	30	62	67	28	66
	0.01 M	66	33	61	66	33	70
	0.1 M	67	29	61	67	33	73

[†]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡]Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

TABLE 10: Kinetics constant for metal dissolution reaction extracted by organic acid (OA) mixtures according to (1) and (2)[†].

Biosolid treatment [†] (Mg ha ⁻¹)	Metal extracted by OAs	Zero- and first-order kinetics constant											
		Cd		Cr		Cu		Ni		Pb		Zn	
		k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁
Control	0.001 M	0.01	0.11 ^a	0.04	0.09	0.43	0.09	0.24	0.12	n.d. [§]	n.d. [§]	1.2	0.12
	0.01 M	0.03	0.10 ^a	0.06	0.09	1.40	0.09	1.56	0.14	n.d. [§]	n.d. [§]	7.8	0.13
	0.1 M	0.08	0.12 ^a	0.44	0.08	7.88	0.07	4.28	0.12	0.06	0.09	21.2	0.13
135	0.001 M	0.22	0.09 ^a	0.28	0.09	3.44	0.09	2.12	0.12	0.84	0.09	15.8	0.11
	0.01 M	0.72	0.12 ^a	0.92	0.08	8.84	0.09	6.28	0.12	0.24	0.09	85.6	0.13
	0.1 M	3.16	0.13 ^a	3.64	0.09	30.4	0.08	26.8	0.14	1.28	0.08	400	0.13
1,080	0.001 M	1.24	0.10 ^a	1.36	0.09	9.64	0.08	10.1	0.14	0.52	0.08	100	0.12
	0.01 M	4.64	0.10 ^a	3.40	0.08	42.8	0.07	39.2	0.12	1.36	0.08	416	0.12
	0.1 M	6.68	0.07 ^a	5.84	0.08	81.2	0.08	64.4	0.12	3.08	0.08	820	0.10

[†]Values represent means of two replicates. The differences of first-order kinetics constant for Cd among the treatments were tested by one-way ANOVA. In each column, values followed by the same lowercase letter were not significantly different at $P < 0.05$.

[‡]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[§]Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

TABLE 11: Amounts of metals that were extractable from the biosolid-treated Romona soil (1,080 Mg ha⁻¹) by 0.1 M organic acid mixture.

Element	Rapid release (mg kg ⁻¹)	Slow release (mg kg ⁻¹)	Total release (mg kg ⁻¹)
Cd	1.67	0.86	2.53
Cr	1.46	3.74	5.20
Cu	20.3	13.7	34.0
Ni	16.1	8.60	24.7
Pb	0.77	1.73	2.50
Zn	205	80.0	285

TABLE 12: The slope[†] of metal extracted from the biosolid-treated Romona soil (1,080 Mg ha⁻¹) by 0.1 M organic acid mixtures according to (3).

Element	k ₁	k ₂	k ₃	k ₄	k ₅	k ₆	k ₇	k ₈
Cd	6.68	3.40	1.75	0.91	0.48	0.25	0.10	0.05
Cr	5.84	3.56	1.91	1.09	0.63	0.40	0.20	0.11
Cu	81.2	42.4	22.5	11.9	6.30	3.30	1.34	0.70
Ni	64.4	33.6	18.0	9.40	4.88	2.60	0.97	0.50
Pb	3.08	1.64	0.87	0.51	0.27	0.24	0.08	0.05
Zn	820	422	220	113	58.8	30.6	11.5	5.88

[†]Values of k₁, k₂, k₃, k₄, k₅, k₆, k₇ or k₈ indicate the slopes of metal extracted at 15 min., 30 min., 1 hr, 2 hrs., 4 hrs., 8 hrs., 24 hrs., and 48 hrs.

(5) The percentages of total BSL-borne metals extracted were 13.8, 1.63, 7.95, 14.1, 1.03, and 24.2% for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. If OAs were responsible for converting metals in solid phases

into plant available forms, the amount and rate of metals' solubilization would be indicative of metals' availability to plants.

TABLE 13: First-order kinetics constant for metal dissolution reaction extracted by organic acid (OA) mixtures according to (3).

Biosolid treatment [†]	Metal extracted by OAs	First-order kinetics constant (k_1)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	0.001 M	4.71	0.34	4.11	4.87	n.d. [‡]	5.00
	0.01 M	3.99	0.30	3.90	3.93	n.d. [‡]	5.42
	0.1 M	4.30	0.37	4.49	4.46	0.36	4.92
135 Mg ha ⁻¹	0.001 M	4.13	0.38	4.05	4.65	0.38	5.63
	0.01 M	3.88	0.51	4.03	3.95	0.40	5.33
	0.1 M	3.96	0.48	3.81	3.79	0.50	6.06
1,080 Mg ha ⁻¹	0.001 M	4.93	0.32	4.30	4.81	0.24	4.85
	0.01 M	5.16	0.40	4.41	4.81	0.32	5.75
	0.1 M	6.25	0.37	4.88	5.53	0.43	6.80

[†] Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981 composted BSL were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡] Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

- (6) A rapid dissolution of metals occurred in the first 15 minutes of mixture. For Cd, Cu, Ni, and Zn, approximately 60–70% of the metals were released. For Cr and Pb, the initial releases were approximately 30% of the total.
- (7) The data of the metal dissolution kinetics in BSL-treated soils may fit either the two-site bicontinuum model in which significant amounts of the soluble metals were dissolved rapidly, following a zero-order dissolution kinetics and the remaining soluble metals released slowly over a long period of time, following a first-order dissolution kinetics, or first-order dissolution kinetics alone.

Competing Interests

The authors declare that they have no competing interests.

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References

- [1] A. H. M. Veeken and H. V. M. Hamelers, "Removal of heavy metals from sewage sludge by extraction with organic acids," *Water Science and Technology*, vol. 40, no. 1, pp. 129–136, 1999.
- [2] D. del Mundo Dacera and S. Babel, "Use of citric acid for heavy metals extraction from contaminated sewage sludge for land application," *Water Science and Technology*, vol. 54, no. 9, pp. 129–135, 2006.
- [3] W. P. Inskeep and S. D. Comfort, "Thermodynamic predictions for the effects of root exudates on metal speciation in the rhizosphere," *Journal of Plant Nutrition*, vol. 9, no. 3–7, pp. 567–586, 1986.
- [4] M. Mench, J. L. Morel, A. Guckert, and B. Guillet, "Metal binding with root exudates of low molecular weight," *Journal of Soil Science*, vol. 39, no. 4, pp. 521–527, 1988.
- [5] G. S. R. Krishnamurti, G. Cieslinski, P. M. Huang, and K. C. J. Van Rees, "Kinetics of cadmium release from soils as influenced by organic acids: implication in cadmium availability," *Journal of Environmental Quality*, vol. 26, no. 1, pp. 271–277, 1997.
- [6] J. Kumpiene, A. Lagerkvist, and C. Maurice, "Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review," *Waste Management*, vol. 28, no. 1, pp. 215–225, 2008.
- [7] M. C. Hernandez-Soriano and J. C. Jimenez-Lopez, "Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals," *Science of the Total Environment*, vol. 423, pp. 55–61, 2012.
- [8] A. C. Chang, A. L. Page, and B.-J. Koo, "Biogeochemistry of phosphorus, iron, and trace elements in soils as influenced by soil-plant microbial interactions," *Developments in Soil Science*, vol. 28, no. 2, pp. 43–57, 2002.
- [9] M. Treeby, H. Marschner, and V. Römheld, "Mobilization of iron and other micronutrient cations from a calcareous soil by plant-borne, microbial, and synthetic metal chelators," *Plant and Soil*, vol. 114, no. 2, pp. 217–226, 1989.
- [10] F. Awad and V. Römheld, "Mobilization of heavy metals from a contaminated calcareous soil by plant borne and synthetic chelators and their uptake by wheat plants," *Journal of Plant Nutrition*, vol. 23, no. 11–12, pp. 1847–1855, 2000.
- [11] B.-J. Koo, A. C. Chang, A. L. Page, D. E. Crowley, and A. Taylor, "Availability and plant uptake of biosolid-borne metals," *Applied and Environmental Soil Science*, vol. 2013, Article ID 892036, 10 pages, 2013.
- [12] T. Mimmo, M. Ghizzi, C. Marzadori, and C. E. Gessa, "Organic acid extraction from rhizosphere soil: effect of field-moist, dried and frozen samples," *Plant and Soil*, vol. 312, no. 1–2, pp. 175–184, 2008.
- [13] V. Römheld and F. Awad, "Significance of root exudates in acquisition of heavy metals from a contaminated calcareous soil by graminaceous species," *Journal of Plant Nutrition*, vol. 23, no. 11–12, pp. 1857–1866, 2000.
- [14] L. Ström, A. G. Owen, D. L. Godbold, and D. L. Jones, "Organic acid behaviour in a calcareous soil implications for rhizosphere nutrient cycling," *Soil Biology and Biochemistry*, vol. 37, no. 11, pp. 2046–2054, 2005.

- [15] S. A. Wasay, S. F. Barrington, and S. Tokunaga, "Remediation of soils polluted by heavy metals using salts of organic acids and chelating agents," *Environmental Technology*, vol. 19, no. 4, pp. 369–379, 1998.
- [16] L. Di Palma and R. Mecozzi, "Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents," *Journal of Hazardous Materials*, vol. 147, no. 3, pp. 768–775, 2007.
- [17] A. Piccolo, S. Nardi, and G. Concheri, "Structural characteristics of humic substances as related to nitrate uptake and growth regulation in plant systems," *Soil Biology and Biochemistry*, vol. 24, no. 4, pp. 373–380, 1992.
- [18] S. Nardi, F. Reniero, and G. Concheri, "Soil organic matter mobilization by root exudates of three maize hybrids," *Chemosphere*, vol. 35, no. 10, pp. 2237–2244, 1997.
- [19] B. Dinkelaker, V. Römheld, and H. Marschner, "Citric acid excretion and precipitation of calcium citrate in the rhizosphere of white lupin (*Lupinus albus* L.)," *Plant, Cell and Environment*, vol. 12, no. 3, pp. 285–292, 1989.
- [20] Z. Rengel and V. Römheld, "Root exudation and Fe uptake and transport in wheat genotypes differing in tolerance to Zn deficiency," *Plant and Soil*, vol. 222, no. 1-2, pp. 25–34, 2000.
- [21] H. Niefeld and J. Prenzel, "Modeling the reactive ion dynamics in the rhizosphere of tree roots growing in acid soils. I. Rhizospheric distribution patterns and root uptake of M_b cations as affected by root-induced pH and Al dynamics," *Ecological Modelling*, vol. 307, pp. 48–65, 2015.
- [22] A. A. Pohlman and J. G. McColl, "Kinetics of metal dissolution from forest soils by soluble organic acids," *Journal of Environmental Quality*, vol. 15, no. 1, pp. 86–92, 1986.
- [23] D. L. Jones and L. V. Kochian, "Aluminium-organic acid interactions in acid soils: I. Effect of root-derived organic acids on the kinetics of Al dissolution," *Plant and Soil*, vol. 182, no. 2, pp. 221–228, 1996.
- [24] M. Mench and E. Martin, "Mobilization of cadmium and other metals from two soils by root exudates of *Zea mays* L., *Nicotiana tabacum* L. and *Nicotiana rustica* L.," *Plant and Soil*, vol. 132, no. 2, pp. 187–196, 1991.
- [25] L. Ruiz and J. C. Arvieu, "Measurement of pH gradients in the rhizosphere," *Symbiosis*, vol. 9, no. 1-3, pp. 71–75, 1990.
- [26] K. Fujii, C. Hayakawa, P. A. W. Van Hees, S. Funakawa, and T. Kosaki, "Biodegradation of low molecular weight organic compounds and their contribution to heterotrophic soil respiration in three Japanese forest soils," *Plant and Soil*, vol. 334, no. 1, pp. 475–489, 2010.
- [27] P. Cambier and G. Sposito, "Interactions of citric acid and synthetic hydroxy-aluminum montmorillonite," *Clays and Clay Minerals*, vol. 39, no. 2, pp. 158–166, 1991.
- [28] R. P. T. Janssen, M. G. M. Bruggenwert, and W. H. Van Riemsdijk, "Interactions between citrate and montmorillonite-Al hydroxide polymer systems," *European Journal of Soil Science*, vol. 48, no. 3, pp. 463–472, 1997.
- [29] J. L. Schroder, H. Zhang, D. Zhou et al., "The effect of long-term annual application of biosolids on soil properties, phosphorus, and metals," *Soil Science Society of America Journal*, vol. 72, no. 1, pp. 73–82, 2008.
- [30] K. Sakurai and P. M. Huang, "Cadmium adsorption on the hydroxyaluminum-montmorillonite complex as influenced by oxalate," in *Environmental Impact of Soil Component Interactions: Vol. II, Metals, Other Inorganics, and Microbial Activities*, P. M. Huang, J. Berthelin, J.-M. Bollag, W. B. McGill, and A. L. Page, Eds., pp. 39–46, Lewis Publisher, Boca Raton, Fla, USA, 1995.
- [31] S. Taniguchi, N. Yamagata, and K. Sakurai, "Cadmium adsorption on hydroxyl-aluminosilicate-montmorillonite complex as influenced by oxalate and citrate," *Soil Science and Plant Nutrition*, vol. 46, no. 2, pp. 315–324, 2000.
- [32] F. M. Eaton, "Automatically operated sand-culture equipment," *Journal of Agricultural Research*, vol. 53, pp. 433–444, 1936.
- [33] H. Jenny and R. Overstreet, "Contact effects between plant roots and soil colloids," *Proceedings of the National Academy of Sciences of the United State of America*, vol. 24, no. 9, pp. 384–392, 1938.
- [34] B.-J. Koo, A. C. Chang, D. E. Crowley, and A. L. Page, "Characterization of organic acids recovered from rhizosphere of corn grown on biosolids-treated medium," *Communications in Soil Science and Plant Analysis*, vol. 37, no. 5-6, pp. 871–887, 2006.
- [35] L. M. Candalaria, *Interactions of citric acid and synthetic hydroxy-aluminum montmorillonite [Ph.D. dissertation]*, University of California, Riverside, Calif, USA, 1995.
- [36] M. Tagliavini, A. Masia, and M. Quartieri, "Bulk soil pH and rhizosphere pH of peach trees in calcareous and alkaline soils as affected by the form of nitrogen fertilizers," *Plant and Soil*, vol. 176, no. 2, pp. 263–271, 1995.
- [37] W. D. C. Schenkeveld and S. M. Kraemer, "Equilibrium and kinetic modelling of the dynamic rhizosphere," *Plant and Soil*, vol. 386, no. 1, pp. 395–397, 2015.
- [38] P. H. Nye, "Changes of pH across the rhizosphere induced by roots," *Plant and Soil*, vol. 61, no. 1-2, pp. 7–26, 1981.
- [39] H. Marschner, V. Romheld, and M. Kissel, "Different strategies in higher plants in mobilization and uptake of iron," *Journal of Plant Nutrition*, vol. 9, no. 3, pp. 695–713, 1986.
- [40] T. S. Gahoonia, "Influence of root-induced pH on the solubility of soil aluminium in the rhizosphere," *Plant and Soil*, vol. 149, no. 2, pp. 289–291, 1993.
- [41] H. Marschner, V. Römheld, and I. Cakmak, "Root-induced changes of nutrient availability in the rhizosphere," *Journal of Plant Nutrition*, vol. 10, no. 9, pp. 1175–1184, 1987.
- [42] R. A. Youssef and M. Chino, "Root-induced changes in the rhizosphere of plants: I. pH changes in relation to the bulk soil," *Soil Science and Plant Nutrition*, vol. 35, no. 3, pp. 461–468, 1989.
- [43] H. Marschner and V. Römheld, "In vivo measurement of root-induced pH changes at the soil-root interface: effect of plant species and nitrogen source," *Zeitschrift für Pflanzenphysiologie*, vol. 111, no. 3, pp. 241–251, 1983.
- [44] P. R. Darrah, "The rhizosphere and plant nutrition: a quantitative approach," *Plant and Soil*, vol. 155-156, no. 1, pp. 1–20, 1993.
- [45] H. T. Gollany and T. E. Schumacher, "Combined use of colorimetric and microelectrode methods for evaluating rhizosphere pH," *Plant and Soil*, vol. 154, no. 2, pp. 151–159, 1993.
- [46] H.-N. Hyun, A. C. Chang, D. R. Parker, and A. L. Page, "Cadmium solubility and phytoavailability in sludge-treated soil: effects of soil organic carbon," *Journal of Environmental Quality*, vol. 27, no. 2, pp. 329–334, 1998.
- [47] C. G. Millward and P. D. Kluckner, "Microwave digestion technique for the extraction of minerals from environmental marine sediments for analysis by inductively coupled plasma atomic emission spectrometry and atomic absorption spectrometry," *Journal of Analytical Atomic Spectrometry*, vol. 4, no. 8, pp. 709–713, 1989.
- [48] W. R. Fischer, H. Flessa, and G. Schaller, "pH values and redox potentials in microsites of the rhizosphere," *Zeitschrift für*

- Pflanzenernährung und Bodenkunde*, vol. 152, no. 2, pp. 191–195, 1989.
- [49] P. Hinsinger and R. J. Gilkes, “Mobilization of phosphate from phosphate rock and alumina-sorbed phosphate by the roots of ryegrass and clover as related to rhizosphere pH,” *European Journal of Soil Science*, vol. 47, no. 4, pp. 533–544, 1996.
- [50] T. C. Zhang and H. Pang, “Applications of microelectrode techniques to measure pH and oxidation—reduction potential in rhizosphere soil,” *Environmental Science and Technology*, vol. 33, no. 8, pp. 1293–1299, 1999.
- [51] V. Römheld and H. Marschner, “Plant-induced pH changes in the rhizosphere of ‘Fe-efficient’ and ‘Fe-inefficient’ soybean and corn cultivars,” *Journal of Plant Nutrition*, vol. 7, no. 1–5, pp. 623–630, 2008.
- [52] D. Riley and S. A. Barber, “Effect of ammonium and nitrate fertilization on phosphorus uptake as related to root-induced pH changes at the root-soil interface,” *Soil Science Society of America Journal*, vol. 35, no. 2, pp. 301–306, 1971.
- [53] D. A. Barber and K. B. Gunn, “The effect of mechanical forces on the exudation of organic substances by the roots of cereal plants grown under sterile conditions,” *New Phytologist*, vol. 73, no. 1, pp. 39–45, 1974.
- [54] D. L. Jones and P. R. Darrah, “Re-sorption of organic compounds by roots of *Zea mays* L. and its consequences in the rhizosphere. III. Characteristics of sugar influx and efflux,” *Plant and Soil*, vol. 178, no. 1, pp. 153–160, 1996.
- [55] B.-J. Koo, D. C. Adriano, N. S. Bolan, and C. D. Barton, “Root exudates and microorganisms,” in *Encyclopedia of Soils in the Environment*, D. Hillel, Ed., vol. 3, pp. 421–428, Elsevier, Oxford, UK, 2005.
- [56] D. C. Adriano, *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*, Springer, New York, NY, USA, 2nd edition, 2001.
- [57] B.-J. Koo, W. Chen, A. C. Chang, A. L. Page, T. C. Granato, and R. H. Dowdy, “A root exudates based approach to assess the long-term phytoavailability of metals in biosolids-amended soils,” *Environmental Pollution*, vol. 158, no. 8, pp. 2582–2588, 2010.
- [58] C. Fernández-Ramos, O. Ballesteros, A. Zafra-Gómez et al., “Sorption and desorption of alcohol sulfate surfactants in an agricultural soil,” *Environmental Toxicology and Chemistry*, vol. 33, no. 3, pp. 508–515, 2014.
- [59] N. S. Bolan, D. C. Adriano, R. Natesan, and B.-J. Koo, “Effects of organic amendments on the reduction and phytoavailability of chromate in mineral soil,” *Journal of Environmental Quality*, vol. 32, no. 1, pp. 120–128, 2003.
- [60] S. P. Mishra, “Adsorption-desorption of heavy metal ions,” *Current Science*, vol. 107, no. 4, pp. 601–612, 2014.
- [61] S. A. Wasay, S. Barrington, S. Tokunagal, and S. Prasher, “Kinetics of heavy metal desorption from three soils using citric acid, tartaric acid, and EDTA,” *Journal of Environmental Engineering and Science*, vol. 6, no. 6, pp. 611–622, 2007.
- [62] J. Liu, J. Dai, R. Wang, F. Li, X. Du, and W. Wang, “Adsorption/desorption and fate of mercury (II) by typical black soil and red soil in China,” *Soil and Sediment Contamination*, vol. 19, no. 5, pp. 587–601, 2010.

Review Article

Oil and Gas Production Wastewater: Soil Contamination and Pollution Prevention

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During oil and natural gas production, so-called “produced water” comprises the largest byproduct stream. In addition, many oil and gas operations are augmented via injection of hydraulic fracturing (HF) fluids into the formation. Both produced water and HF fluids may contain hundreds of individual chemicals, some known to be detrimental to public health and the environment. Oil and gas production wastewater may serve a range of beneficial purposes, particularly in arid regions, if managed correctly. Numerous treatment technologies have been developed that allow for injection, discharge to the land surface, or beneficial reuse. Although many papers have addressed the effects of oil and gas production wastewater (OGPW) on groundwater and surface water quality, significantly less information is available on the effects of these fluids on the soil resource. This review paper compiles fundamental information on numerous chemicals used and produced during oil and gas development and their effects on the soil environment. Additionally, pollution prevention technologies relating to OGPW are presented. An understanding of the effects of OGPW on soil chemical, physical, and biological properties can provide a foundation for effective remediation of OGPW-affected soils; additionally, sustainable reuse of oil and gas water for irrigation and industrial purposes may be enhanced.

1. Introduction

Production of conventional oil and gas and coal bed methane is often accompanied by production of large volumes of produced water. The United States generates an estimated 21 billion barrels of produced water every year [1].

In certain geologic strata substantial volumes of oil and natural gas are present, yet they experience poor recovery rates due to low permeability of local strata. This is especially true for shales, tight sands, oil sands, and coal beds [2]. In hydraulic fracturing (HF) (“fracking”), a specially tailored mixture of fluids is pumped into recovery wells under high pressure to fracture low permeability formations and enhance gas and oil production [3–5]. Extraction of hydrocarbon resources using HF is commonly referred to as “unconventional production.” Unconventional wells include those drilled horizontally, allowing the borehole to bend 90 degrees and penetrate the target formation laterally up to thousands of meters [6]. Within the past two decades the combination of HF with horizontal drilling has opened immense new oil and gas reserves worldwide which were previously considered

inaccessible or unprofitable [7, 8] and brought large-scale drilling to new regions [3, 9].

Hydraulic fracturing is performed at depths between 5,000 and 10,000 feet and requires 2,500,000–4,200,000 gallons of water per well [10]. Fracturing operations inject highly pressurized fluids, that is, between 2,000 and 12,000 psi, at an average flow rate of 2000 gpm (47 bbl/min) [11]. The water is mixed with 0.5–2.0% (by volume) of selected chemical additives to increase water flow and improve deposition efficiency. Approximately 1,000 chemicals are known to be used in the HF process [7, 11].

Following initial injection into the well to generate fractures, a portion of the injected water returns to the surface immediately and is termed “flowback” [3]. The remaining fluids either permeate into the formation or return to the surface over the life of the producing well and are termed “produced water.” Both types of wastewater may contain HF fluids, naturally occurring salts, radioactive materials, heavy metals, and other compounds from the formation such as polycyclic aromatic hydrocarbons, alkenes, alkanes, and other volatile and semivolatile organics [12–18]. In this

paper, oil and gas flowback water, produced water, and hydraulic fracturing fluids will collectively be termed oil and gas production wastewater (OGPW).

As HF operations are expanding, the volumes of wastewater being generated are increasing exponentially [19]. Wastewater from drilling activities is typically managed via disposal in injection wells or evaporation ponds, application to fields, spreading on roads, and/or treatment and reuse for future oil and gas operations [8, 13, 20, 21].

Hydraulic fracturing components may pose a threat to public health and the environment as some are known to be acutely toxic, some are carcinogenic, and others are believed to be endocrine-disruptors [12, 22–24]. Other chemicals remain proprietary information [25] whose effects on public health and the environment are unavailable. Recent work found that 67%, 37%, and 18% of assessed wells were fractured with ≥ 1 , 5, or 10 proprietary chemicals, respectively [12, 26].

Contamination of soil can occur through spills of fluids during drilling and fracturing processes and during transport by truck or through wastewater pipelines and failure of well casings and equipment failures and corrosion of pipes and tanks. In some regions OGPW is transferred to wastewater treatment plants [20]; however, facilities may be unable to remove several anthropogenic or naturally occurring compounds [27–29]. This can result in their discharge, following treatment, to surface water and ultimately to soil [30, 31].

Between 2009 and 2013 a total of 1933 spills were documented in Colorado [32]. In 2013, spills were reported at 1% of Colorado wells (550 of 51,000 active wells). An analysis of permitted Pennsylvania wells shows a spill rate of 2% (103 of 5,580 active wells) [26]. A total of 24 states with active shale reservoirs currently report spills; however, reporting limits and information required vary markedly. Only five states require maintenance of public records for spills and violations [12, 26, 33]. In light of the limited mandatory reporting, it is possible that the degree of oil and gas operations on water quality is underestimated [26, 33]. For example, an analysis in Pennsylvania found that only 59% of documented spills were reported [12, 26]. Elevated concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) have been detected in groundwater near surface spills [34, 35]; soils have been affected by excess salinity and sodicity [36, 37].

A great number of papers have described the effects of OGPW on groundwater [14, 38–40] and surface water [40–42]; however, studies of the effects of OGPW on the soil resource are scant, and reclamation of OGPW-affected soils has received minimal attention in the scientific literature. In order to understand the potential effects of OGPW on soil chemical, physical, and biological properties as well as potential effects on plant growth, it is necessary to identify the chemicals used in HF and those produced from active wells, as well as their behavior in soil. The objectives of this paper are to cite common chemicals that are used for, and produced during, oil and gas development and compile essential information on their effects on the soil environment. Additionally, both remediation of OGPW-affected soils and pollution prevention technologies will be presented.

2. Hydraulic Fracturing Fluids

Oil and gas production chemicals can be pure compounds or mixtures containing active ingredients dissolved in a solvent or cosolvent and used to serve numerous processes (Table 1) [53].

In response to concerns about the potential public health and environmental impacts associated with HF, key reagents have, in recent years, been compiled and made publicly available. Regulatory agencies in many states have established reporting requirements for unconventional production; however, not all such requirements are mandatory [54, 55]. Many oil and gas producers choose to publish lists of HF chemicals on company websites or in the FracFocus Chemical Disclosure Registry [56].

The broad categories of HF fluids in routine use consist of [57] (1) viscosified water-based fluids; (2) nonviscosified water-based fluids; (3) gelled oil-based fluids; (4) acid-based fluids; and (5) foam fluids. For many hydrocarbon reservoirs, water-based fluids are most suitable due to the historic ease with which large volumes of mix water can be acquired.

Hydraulic fracturing fluids contain approximately 98 to 99.5% water plus a specially prepared mixture that helps optimize the fracturing process [3, 56]. Typical additives include proppants (propping agents), gelling and foaming components, friction reducers, cross-linkers, breakers, pH adjusters, biocides, corrosion inhibitors, scale inhibitors, iron controlling compounds, clay stabilizers, and surfactants (Table 1) [46, 58]. Not all these additives are used in every fracturing project, and sometimes one class of additives can serve multiple purposes; that is, a surfactant can be used as a cross-linker and gelling agent in certain situations [46]. Chemicals are added throughout the entire production process including drilling and fracturing and through closure to serve numerous functions [7, 13]. Some common HF additives are listed in Table 2.

A comprehensive study of the properties of HF chemicals was carried out by Stringfellow et al. [46] and includes commonly used compounds for each class of agents as well as data for toxicity and biodegradability.

2.1. Proppants. Propping agents are employed to “prop open” the fracture once pumps are turned off and fractures begin to close. The ideal propping agent is resistant to crushing and to corrosion, of low density, and is readily available and inexpensive [59]. Common propping agents are silica sand, resin-coated sand (RCS), and ceramic proppants (e.g., sintered bauxite, intermediate-strength proppant [ISP], and lightweight proppant [LWP]) [60]. Generally, sand is used to prop open fractures in shallow formations. RCS is stronger than sand and is used where more compressive strength is required to minimize proppant crushing. Ceramic proppants are used to stimulate deep (>8,000 ft) wells where significant in situ stresses impart large forces on the propping agent [61].

2.2. Gelling Agents. Gellants increase the viscosity of HF fluids. Greater viscosities increase fracture width so higher concentrations of proppant can be injected, fluid loss is

TABLE 1: Common classes of hydraulic fracturing compounds and their uses.

Chemical category	Application in hydraulic fracturing	Example compounds
Proppants	Hold fissures open and allow gas to flow out of the formation	Sand, sintered bauxite, zirconium oxide, ceramic beads, and graphite
Gellants	Increase viscosity and suspend sand during proppant transport	Propylene glycol, guar gum, ethylene glycol, and petroleum distillate
Foamers	Increase carrying capacity while transporting proppants and decrease overall volume of fluid needed	2-Butoxyethanol, diethylene glycol
Cross-linkers	Thicken fluids to increase viscosity and proppant transport into fractures	Potassium hydroxide, ethylene glycol, borate salts, and petroleum distillates
Breakers	Reduce the viscosity of the fluid so proppant will flow into fractures; added near the end of hydraulic fracturing to enhance flowback	Ammonium persulfate, magnesium peroxide
Acids	Clean up cement and drilling mud before fracturing fluid is injected and clear the path through the formation. Used later to dissolve minerals and clays to reduce clogging, allowing gas to flow to the surface	Hydrochloric acid
pH control	Maintains pH at various stages to ensure maximum effectiveness of various additives	Sodium hydroxide, acetic acid
Biocides	Kill bacteria that produce gases (particularly H ₂ S) which could contaminate methane gas, corrode pipes and fittings, and break down gellants	Glutaraldehyde, 2-bromo-2-nitro-1,2-propanediol
Corrosion inhibitors	Reduce damage to steel from acidic HF fluids	Ethoxylated octylphenol and nonylphenol, isopropanol
Scale inhibitors	Prevent buildup of mineral scale that can block fluid and gas passage through the pipes. Prevent steel materials from being damaged by acidic fracking fluids	Acrylamide, sodium polycarboxylate, methanol, and ammonium bisulfate
Iron control	Prevents carbonate and sulfate compounds from precipitating to form plugs in shale formation	Ammonium chloride, ethylene glycol, and polyacrylate
Clay stabilizers	Block clays from swelling to block the open channels created in the mining operation	Tetramethyl ammonium chloride, sodium chloride
Defoamers	Reduce foaming after it is no longer needed; lowers surface tension; and allows trapped gas to escape	2-Ethylhexanol, oleic acid, and oxalic acid
Friction reducers	To make water slick and minimize the friction created under high pressure and to increase the rate and efficiency of moving the HF fluid	Acrylamide, ethylene glycol, petroleum distillate, methanol, sodium acrylate-acrylamide copolymer, polyacrylamide (PAM), and petroleum distillates
Surfactants	Reduce surface tension and improve fluid passage through pipes in either direction	Methanol, ethanol, isopropanol, naphthalene, 1,2,4-trimethylbenzene, and 2-butoxyethanol

[3, 12, 43–45].

reduced, proppant transport is improved, and friction pressure is reduced [62].

Gelling agents primarily consist of guar and derivatives (e.g., hydroxypropyl guar, carboxymethyl guar, and carboxymethyl hydroxypropyl guar), celluloses, acids, and alcohols [62, 63]. Gellants can be linear or cross-linked to increase fluid viscosity. Agents are selected based on site-specific conditions in the well including temperature and salinity [5, 46].

Diesel fuel is sometimes used to form a viscous HF gel when combined with guar concentrate. The US Environmental Protection Agency (US EPA) has attempted to regulate the use of diesel fuel in HF; however, it is still used in place of water as it can carry more guar concentrate per unit volume [43].

2.3. Friction Reducers. Friction reducers are sometimes used as an alternative to gelling agents. The most commonly used friction reducer is 2-propenamide (polyacrylamide,

[C₃H₅NO]_n) [46]. Friction reducers are water-soluble, non-volatile, and nontoxic.

2.4. Cross-linkers. Cross-linkers bind gel molecules and thereby increase viscosity and proppant transport. Cross-linkers frequently used in HF include borate salts; titanium, zirconium, and aluminum compounds; monoethanolamine; and monoethylamine [5, 47, 56]. Ammonium chloride, ethylene glycol, and potassium hydroxide are also used. Concentrations of cross-linkers in HF fluid are relatively low and range from 0.5 to 250 mg/L [47, 64–67]. Borate ions are the most commonly used cross-linking agents for guar polymer applications [68]. Borax (sodium tetraborate decahydrate) and boric acid plus caustic soda and cross-linking agents (0.024–0.09% w/w) have been used as sources of borate ions to cross-link guar [68].

2.5. Breakers. The viscous HF fluid, whether cross-linked or linear, must be degraded in order to achieve high conductivity

TABLE 2: Chemicals and chemical mixtures identified as being commonly used in hydraulic fracturing based on available sources.

Chemical name	CAS number	Formula
Acetaldehyde	75-07-0	C ₂ H ₄ O
Acetic acid	64-19-7	C ₂ H ₄ O ₂
Acetone	67-64-1	C ₃ H ₆ O
Adipic acid	124-04-9	C ₆ H ₁₀ O ₄
Alkyl benzyl dimethyl ammonium chloride	68424-85-1	Various
Ammonium chloride	12125-02-9	ClH ₄ N
Ammonium persulfate	7727-54-0	(NH ₄) ₂ S ₂ O ₈
Ammonium sulfate	7783-20-2	(NH ₄) ₂ SO ₄
Borate salts	Various	Various
Boric acid sodium salt	1333-73-9	Na ₃ BO ₃
Calcium chloride	10043-52-4	CaCl ₂
Calcium peroxide	1305-79-9	CaO ₂
Carbon dioxide	124-38-9	CO ₂
Carboxymethyl guar	39346-76-4	Various
Carboxymethyl hydroxyethyl cellulose	9004-30-2	Various
Carboxymethyl hydroxypropyl guar	68130-15-4	Various
Choline chloride	67-48-1	C ₅ H ₁₄ ClNO
Citric acid	77-92-9	C ₆ H ₈ O ₇
Copolymer of acrylamide and sodium acrylate	25987-30-8	Various
Copper compounds	Various	Various
Didecyl dimethyl ammonium chloride	7173-51-5	C ₂₂ H ₄₈ ClN
Diesel fuel	Various	Various
Diethanolamine	111-42-2	C ₄ H ₁₁ NO ₂
Dimethyl dihydrogenated tallow ammonium chloride	Various	Various
Ester salt	Various	Various
Ethanol	64-17-5	C ₂ H ₆ O
Ethyl methyl derivatives	Various	Various
Ethylene glycol	107-21-1	C ₂ H ₆ O ₂
Formic acid	64-18-6	CH ₂ O ₂
Fumaric acid	110-17-8	C ₄ H ₄ O ₄
Glutaraldehyde	111-30-8	C ₅ H ₈ O
Glycol ethers	Various	Various
Guar gum	9000-30-0	Various
Isopropanol	67-63-0	C ₃ H ₈ O
Magnesium oxide	1309-48-4	MgO
Magnesium peroxide	14452-57-4	MgO ₂
Methanol	67-56-1	CH ₄ O
Monoethanolamine	141-43-5	C ₂ H ₇ NO
Monoethylamine	75-04-7	C ₂ H ₇ N
<i>N,N</i> -Dimethyl formamide	68-12-2	C ₃ H ₇ NO
Naphthalene	91-20-3	C ₁₀ H ₈
Nitrogen	7727-37-9	N ₂
Petroleum distillate	64741-85-1	Various
Phosphonic acid salt	Various	Various
Polyacrylamide	9003-05-8	(C ₃ H ₅ NO) _n
Polyglycol ether	Various	Various
Potassium carbonate	584-08-7	K ₂ CO ₃

TABLE 2: Continued.

Chemical name	CAS number	Formula
Potassium chloride	7447-40-7	KCl
Potassium hydroxide	1310-58-3	KOH
Potassium metaborate	13709-94-9	BKO ₂
Potassium persulfate	7727-21-1	K ₂ O ₈ S ₂
Propargyl alcohol	107-19-7	C ₃ H ₄ O
Pyridinium	16969-45-2	C ₅ H ₆ N
Quaternary ammonium chloride	61789-71-1	Various
Sodium carbonate	497-19-8	Na ₂ CO ₃
Sodium chloride	7647-14-5	NaCl
Sodium erythorbate	6381-77-7	C ₆ H ₇ NaO ₆
Sodium hydroxide	1310-73-2	NaOH
Sodium lauryl sulfate	151-21-3	C ₁₂ H ₂₅ NaO ₄ S
Sodium persulfate	7775-27-1	Na ₂ O ₈ S ₂
Sodium polycarboxylate	Various	Various
Sodium tetraborate decahydrate	1303-96-4	B ₄ O ₇ ·2Na·10H ₂ O
Tetrakis hydroxymethyl phosphonium sulfate	55566-30-8	(C ₄ H ₁₂ O ₄ P) ₂ O ₄ S
Tetramethyl ammonium chloride	75-57-0	C ₄ H ₁₂ ClN
Thioglycolic acid	68-11-1	C ₂ H ₄ O ₂ S
Thiourea	62-56-6	CH ₄ N ₂ S
Tributyl tetradecyl phosphonium chloride	81741-28-8	C ₂₆ H ₅₆ PCl
Triethanolamine zirconate	101033-44-7	C ₂₄ H ₅₆ N ₄ O ₁₂ Zr
Zirconium hydroxy lactate sodium complex	113184-20-6	C ₁₂ H ₁₉ NaO ₁₆ Zr
Zirconium nitrate	13746-89-9	Zr(NO ₃) ₄
Zirconium sulfate	14644-61-2	Zr(SO ₄) ₂
1-Bromo-3-chloro-5,5-dimethylhydantoin	16079-88-2	C ₅ H ₆ BrClN ₂ O ₂
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	C ₃ H ₂ Br ₂ N ₂ O
2-Bromo-3-nitrilopropionamide	1113-55-9	C ₃ H ₃ BrN ₂ O
2-Butoxyethanol	111-76-2	C ₆ H ₁₄ O ₂

[5, 44, 46–48].

in the proppant pack. Likewise, the filter cake formed on the face of the rock, which may restrict the flow of oil and gas and reduce well productivity, must be degraded. Breakers reverse cross-linking and cleave polymers into low molecular weight fragments thus reducing viscosity of gelled fluids [46, 69–71].

The general types of breakers are oxidizers, acids, and enzymes [62]. Oxidizers are the most commonly used class of breakers, in particular ammonium, potassium, and sodium salts of peroxydisulfate (persulfate) [68]. Enzymes may be used depending on fracturing conditions, particularly pH and temperature.

2.6. Acids and Bases. Acids and bases are added to HF fluids to adjust pH, which improves the effectiveness of almost all HF compounds, particularly cross-linked polymers. The use of acids also clears debris in the wellbore and provides an open channel for other HF fluids by dissolving carbonate minerals [56]. Lastly, pH adjustment prevents unwanted microbial activity in the wellbore.

Typical pH adjusters include inorganic acids such as hydrochloric and sulfuric acids, as well as organics such as acetic acid and fumaric acid. Common bases include potassium hydroxide, sodium hydroxide, sodium carbonate, and potassium carbonate [46].

2.7. Biocides. Biocides are used to control microbial growth in the boreholes and well areas, as such growths degrade HF chemicals and accelerate corrosion of well tubing, casings, and equipment [47, 70]. Biocides used for HF include quaternary ammonium compounds (QACs), glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (THPS), tributyl tetradecyl phosphonium chloride (TTPC), and brominated compounds including 2,2-dibromo-3-nitrilopropionamide (DBNPA) [47, 56, 71]. QACs are extensively used as bioactive agents; the most commonly used ones are dialkyl ammonium and benzalkonium chlorides. Ammonium chloride is also used [46, 72].

2.8. Corrosion Inhibitors. Corrosion inhibitors form a protective layer on metal well components, thus preventing corrosion by acids, salts, and corrosive gases [73–75]. Common corrosion inhibitors include acetaldehyde, acetone, ethyl methyl derivatives, formic acid, and isopropanol [46, 76].

2.9. Scale Inhibitors. Scale inhibitors protect piping in the wells and prevent formation plugging. These inhibitors consist of polycarboxylates and acrylate polymers [46].

2.10. Iron Control Substances. Precipitates of ferric iron (Fe^{3+}) block paths within pipes and rock formations, which impact productivity [77, 78]. Ferric iron also inadvertently acts as a cross-linker in HF fluids containing gelling agents, thereby altering fluid viscosity [77]. Iron precipitation is prevented using citric acid, acetic acid, thioglycolic acid, and sodium erythorbate [79]. Iron controlling agents act as chelating agents, forming complexes with ferrous iron (Fe^{2+}) to prevent oxidation and subsequent precipitation as Fe^{3+} [70, 80].

2.11. Clay Stabilizers. In order to prevent clay swelling around shale formations, clay stabilizers are injected with HF fluids. These work via ion exchange, replacing cations such as Na^+ in the clay with other, often divalent cations that undergo less hydration and have a lesser tendency to swell the clay [81]. Commonly used clay stabilizers are choline chloride, potassium chloride, and tetramethyl ammonium chloride [46]. There has been some shift towards choline chloride use, which is nontoxic and readily biodegradable.

2.12. Surfactants. Surfactants are used to achieve optimal viscosity of HF fluids, reduce surface tension, and assist in fluid recovery after fracturing [5, 46, 70]. Surfactants can be used in place of cross-linkers and gelling agents in high temperature or high pressure formations. Surfactant formulations used in HF vary greatly, but common compounds include sodium lauryl sulfate and dimethyl dehydrogenated tallow ammonium chloride [46, 76].

The large quantity and diversity of compounds used in HF additives underscore the complexity of understanding their fates in the event of release, whether accidental or managed, to soil. Furthermore, the compounds described for each agent are only the known compounds; hazards relating to proprietary compounds remain unknown.

3. Flowback and Produced Water

As oil and gas production proceed, formation water eventually reaches the production well, and water begins to appear alongside the hydrocarbons. This produced water is a mixture of injected water, formation water, HF chemicals, and hydrocarbons [82–85].

Produced water has a complex composition but its constituents can be broadly classified into organic and inorganic compounds. These include dissolved and dispersed oil components, grease, heavy metals, radionuclides, HF chemicals, dissolved formation minerals, salts, dissolved gases (including CO_2 and H_2S), scale products, waxes, microorganisms, and dissolved oxygen [49, 50, 53, 83, 86, 87]. The composition will vary widely as a function of geologic formation, lifetime of the reservoir, and type of hydrocarbon produced [83].

A generalized chemical composition of produced water appears in Table 3.

3.1. Production Chemicals. Production chemicals, that is, HF fluids, enter produced water in traces and sometimes significant quantities [88] and vary from platform to platform. Active ingredients partition themselves into all phases present depending on their relative solubilities in oil, gas, or water.

3.2. Dissolved Minerals. Flowback water tends to have extremely high concentrations of total dissolved solids (TDS); this is due to dissolution of constituents from the formation following injection of HF fluids [89, 90]. High salinity may also originate from release of in situ brines (formation water) [90–93]. Levels of TDS can be 5–10 times the concentration in seawater [90]. Na^+ and Cl^- are responsible for salinity and range from a few mg/L to 300,000 mg/L [94]. For comparison, seawater and salt lakes are defined as having an upper limit of 50,000 mg/L [95]. Ions such as Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^{2-} , Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Mg^{2+} , Fe^{2+} , and Sr^{2+} affect conductivity and scale-forming potential. High levels of organic carbon also occur in substantial levels in flowback fluids and produced water [89, 96].

Fluid chemical composition is dependent, in part, upon its interaction time with the shale play. It has been found that TDS levels in produced water and late flowback can increase four-fold over that of early flowback. Similarly, total suspended solids (TSS) concentrations increase over 100-fold between early and late flowback. Concentrations of inorganic ions in produced water from Marcellus shale (PA) wells increased over the course of oil production [89, 96–98], rising significantly during the initial days after fracturing and then increasing more slowly as the well aged [76, 89, 96].

TABLE 3: Composition of oilfield produced water.

Parameter	Range	Metal	Range (mg/L)
Density (kg/m ³)	1014–1140	Ca	13–29,222
Conductivity (μS/cm)	4200–58,600	Na	132–97,000
Surface tension (dyn/cm)	43–78	K	24–4,300
Turbidity (NTU)	182	Mg	8–6,000
pH	4.3–10	Fe	<0.1–100
TOC (mg/L)	0–1,500	Al	310–410
TDS	267,588	B	5–95
TSS (mg/L)	1.2–10,623	Ba	1.3–650
Dissolved oxygen (mg/L)	8.2	Cd	<0.005
Total oil (mg/L)	2–565	Cu	<0.02–1.5
Volatiles (BTEX; mg/L)	0.39–35	Cr	0.02–1.1
TPH (mg/L)	>20	Li	3–50
Chloride (mg/L)	80–200,000	Mn	<0.004–175
Bicarbonate (mg/L)	77–3,990	Pb	0.002–8.8
Sulfate (mg/L)	<2–1,650	Sr	0.02–2,204
Sulfite (mg/L)	10	Ti	
NH ₃ -N (mg/L)	10–300	Zn	<0.01–0.7
Phenol (mg/L)		As	0.01–35
Volatile fatty acids (mg/L)	0.009–23 2–4,900	Hg	<0.005–0.3
		Ag	<0.005–0.3
		Be	<0.001–0.15
		Ni	<0.001–0.004 <0.001–1.7

[49–51].

3.3. Metals. Oilfield produced water contains heavy metals such as mercury and lead, as well as metalloids such as arsenic, in varied concentrations depending on formation geology and age of the well [49, 99]. Metal concentrations in produced water are usually higher than those found in sea water [83, 94]. The most commonly studied metals are Ba, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn (Table 3) [50]. Produced water contains other trace metals including Al, B, Fe, Li, Mn, Se, and Sr. Certain metals are of particular environmental concern as they may bioaccumulate and/or be toxic [50].

3.4. Dissolved and Dispersed Oil Components. Dispersed and dissolved oil components are derived from the source rock and chemical additives in HF fluids, and their concentrations may be very high at some oilfields [86, 88, 100, 101]. BTEX, phenols, aliphatic hydrocarbons, carboxylic acid, and low molecular weight aromatics are classified as dissolved oil, while the more hydrophobic PAHs and heavy alkyl phenols are present in produced water as dispersed oil [100].

Produced water from the Marcellus (PA) and Barnett (TX) plays contains predominantly C₆–C₁₆ hydrocarbons, while Eagle Ford (TX) produced water shows the highest concentration in the C₁₇–C₃₀ range [102]. The structures of saturated hydrocarbons identified generally follow the trend of linear > branched > cyclic. Heterocyclic compounds, fatty alcohols, esters, and ethers have also been identified. The presence of various fatty acid phthalate esters in the Barnett and Marcellus produced water may be related to their use in

HF fluids [102]. No polyaromatic hydrocarbons (PAHs) were observed in these shale plays [102].

3.5. Produced Solids. Produced solids include clays, precipitated solids, waxes, microbial biomass, carbonates, sand and silt, corrosion and scale products, proppant, formation solids, and other suspended solids [49]. Their concentrations vary from one oilfield to another.

4. OGPW in the Terrestrial Environment: Releases, Effects, and Remediation

4.1. Releases. The management of OGPW is largely monitored and controlled; however, accidental releases are inevitable. In addition, application of HF fluids to soil is considered an acceptable form of disposal in many states [103]. Inadvertent releases and intentional land application could potentially expose soil to hundreds of heterogeneous chemicals. The US EPA has studied potential scenarios that could lead to environmental contamination by HF fluids [104].

4.1.1. Pipe Overflows, Leaks, and Blowouts. In a 2009 study it was revealed that 630 out of 4,000 legally permitted wells in Pennsylvania had drilling site leaks [105]. In 2011 a mechanical problem at a Pennsylvania natural gas well caused thousands of gallons of briny water and HF fluid to erupt from the well, overwhelm containment facilities, and flow into surrounding fields. Local families were ordered to evacuate their homes. After six days workers sealed the leak, replaced the wellhead, and got the well “under control” [3].

In 2014 a North Dakota oil well leaked HF fluid and oil, releasing between 2,100 and 2,940 gallons per day of OGPW and 8,400 gallons per day of oil [106]. In a 2015 North Dakota well blowout, 4,620 gallons of OGPW and 23,100 gallons of oil were released. Most of the spill was contained at the well site, but some escaped and contaminated nearby terrain [107]. From January 2006 to October 2014 more than 18 million gallons of OGPW and oil was spilled in North Dakota alone. Most individual spills were contained to the immediate drilling area, but many larger spills affected surrounding farms and waterways [36].

4.1.2. Deliberate Improper Disposal. A petroleum subsidiary had permission to discharge drilling mud and boring waste to an oilfield sump near almond orchards in Shafter, California. State investigators, however, found that the fluid contained excess salinity, boron, benzene, and gasoline and diesel hydrocarbons believed to have been used in HF [19, 108].

4.1.3. Holding Ponds. Gas and oil producers are increasingly reusing spent HF fluids. However, reuse involves storage in holding ponds and eventually diluting the OGPW with fresh water [109]. In 2009 a wastewater pit overflowed at a Pennsylvania gas well and an unknown quantity of OGPW entered a “high quality watershed.” The company failed to report the spill and in 2010 a fine of \$97,350 was levied against the company [3].

4.1.4. *Natural Events.* Natural disasters such as floods add to the potential for soil contamination by OGPW. During the late 2013 floods in Colorado, floodwaters in Weld County (where 20,000 oil and gas wells are located) surged into drilling centers and damaged pipes, overflowed wells, and shifted oil tanks from their foundations [110]. Approximately 35,000 gallons of oil and condensate were released. HF fluids from evaporation pits may have contaminated local soils and possibly been carried farther by the floodwaters [19].

4.2. *Effects on the Soil Resource.* Potential soil quality and plant impacts from OGPW include the following [100]:

- (i) Excess sodicity can cause clays to deflocculate, thereby lowering the permeability of soil to air and water.
- (ii) Excess soluble salts will cause plants to desiccate and die. Where levels of natural precipitation are low, salts may accumulate to excessive concentrations in soil.
- (iii) Existing plant species may become displaced by new species as a result of chemical changes in soils resulting from contact with OGPW.
- (iv) Salt-tolerant plants may increase in distribution.

In a greenhouse study Swiss chard (*Beta vulgaris* L.) and ryegrass (*Lolium perenne* L.) were grown in soils containing synthetic HF fluids [111]. The HF fluids increased soil pH, EC, and concentrations of total and extractable Zn, Cu, Cd, Pb, and As. Chard and ryegrass yields may have been reduced by high soil Zn and EC levels. The HF fluids may have resulted in lower levels of trace elements in plant tissue due to increased soil pH. In a greenhouse study Miller et al. [112] studied the effects of OGPW components on plant growth and found that diesel oil, KCl, NaOH, Cr, starches, and other compounds reduced yields of sweet corn (*Zea mays* L. var. *saccharata*) and/or green beans (*Phaseolus vulgaris* L.).

Six drilling fluids reduced yields of green beans and sweet corn when added to soils at differing ratios [113]. High levels of soluble salts or high percentage exchangeable Na^+ was considered to be the major cause of reduced plant growth. Adams [103] reported severe acute and chronic toxicity of mixed hardwood trees (*Quercus* spp., *Acer rubrum* L., and *Liriodendron tulipifera*), mixed shrub subcanopy (*Fagus grandifolia* Ehrh.), *A. rubrum*, and *Sassafras albidum* (Nutt.), and ground vegetation (*Vaccinium* L., *Smilax rotundifolia* L., and *Kalmia latifolia* L.) that resulted in 56% vegetation mortality after two years of land application of HF fluid. Soil Na^+ and Cl^- concentrations increased by approximately 50-fold as a result of land application of the fluids.

OGPW components in soil may substantially impact each other's fate and transport; for instance, the presence of biocides may decrease the potential for biodegradation, while viscosity-enhancing compounds may hinder the mobility of other compounds. Factors that affect the behavior of OGPW constituents in soil and therefore their potential impact on terrestrial life include the following [100]:

- (i) Dilution of the OGPW in the receiving environment.

- (ii) Immediate and long-term precipitation of metals and other contaminants.
- (iii) Volatilization of low molecular weight hydrocarbons.
- (iv) Physical-chemical reactions with other chemical species present in soil.
- (v) Adsorption to particulate matter.
- (vi) Biodegradation of organic constituents.

Some specific HF components and their possible fates are described below.

4.2.1. *Gelling Agents.* Gellants such as guar and cellulose occur naturally and are nontoxic and readily biodegradable. The same is true for the common acids and alcohols used as gelling agents [46]. It is likely that these compounds, when in contact with soil, will enhance microbiological growth.

Ethylene glycol is highly soluble in water; it adsorbs poorly to soil colloids and is thus highly mobile in the soil profile [114]. Volatilization of ethylene glycol from soil is not expected.

4.2.2. *Friction Reducers.* Polyacrylamide is readily biodegradable. McLaughlin [115] studied transformation kinetics of PAM and polyethylene glycol (PEG) in the presence of cocontaminants. Over time higher rates of disappearance occurred in raw, that is, biologically active, soil compared with sterilized soil, indicating that PEG disappearance is due to both sorption and biodegradation. In a study by Wen et al. [116], two PAM-degrading bacterial strains were isolated from soil in an oilfield contaminated by PAM; these were identified as *Bacillus cereus* and *Bacillus flexus*. No acrylamide, which is a known human carcinogen, mutagen, and teratogen, was produced during aerobic biodegradation of polyacrylamide [116, 117]; however, it has been suggested that acrylamide may be formed via heating or exposure of polyacrylamide to ultraviolet radiation [116, 118].

4.2.3. *Cross-Linkers.* Human exposure to boron and amines used in cross-linkers is of concern as they have known toxic effects and can be mobile in soil and groundwater; however, the amines are not known to persist in the environment [46].

4.2.4. *Breakers.* The use of enzymes as breakers for fracturing fluids is preferred over the use of oxidizers because enzymes are environmentally benign [68]. Their mobility, however, remains largely unknown [76].

4.2.5. *Acids and Bases.* Organic acids are potentially biodegradable depending on concentration. Strong acids or bases are known to cause adverse effects on soil. For example, strong acidity will result in leaching of bases such as Ca^{2+} and Mg^{2+} [119]; extremes of acidity will cause dissolution of soil solids [120]. The hydrated Na^+ ion in sodium hydroxide disperses soil aggregates and destroys soil structure. Extremes in pH may drastically alter microbial composition [121].

4.2.6. *Biocides*. Some common HF biocides are known to be volatile or sorb to soils and can persist in the environment, although their fates are largely unknown [76].

QACs have distinct physical/chemical properties which are conferred by their substituents, primarily alkyl chain length. The mechanism of QAC sorption to solids is complex, but both hydrophobic and ionic interactions probably occur [122]. The $\log K_{OC}$ values of several mono-, di-, and benzalkonium chlorides range between 0.28 and 2.97 [123, 124]. QACs are therefore expected to sorb to soil colloids and not leach to groundwater. Sorption of QACs on organic surfaces such as humic compounds and sediment increases as the alkyl chain length increases [122]. In the benzalkonium chlorides the benzyl group enhances adsorption.

QACs have been identified in sediments near wastewater discharge sites, suggesting that at least some are environmentally persistent [125, 126]. The degree of biodegradability is variable; biodegradation decreases with increasing length of the alkyl chain, and QACs that contain a benzyl group experience lower biodegradation rates [127]. QACs were found to be recalcitrant under methanogenic conditions [122]. Under nitrate reducing and fermentative conditions, benzalkonium chlorides (BACs) were transformed to alkyldimethyl amines via abiotic reactions [122]. Microorganisms have been isolated that are resistant to QACs and capable of QAC degradation [128–132]. In a study by Tezel [122] the bacterial community involved in aerobic degradation of BACs was mainly composed of species belonging to the genus *Pseudomonas*.

Generally, QAC sorption exceeds biodegradation in aerobic biological systems [46, 125, 129].

Glutaraldehyde (GA) and the phosphonium-based biocides are sometimes considered “green” alternatives to conventional biocides as they are less persistent in the environment. GA is readily biodegradable under both aerobic and anaerobic conditions [133, 134]. In aerobic batch experiments McLaughlin [115] studied decomposition of GA and didecyl dimethyl ammonium chloride (DDAC) to determine transformation kinetics in the presence of cocontaminants. DDAC underwent almost immediate sorption to soil. GA slowed the initial rate of PEG and PAM biodegradation. After one week, GA was completely eliminated from the aqueous phase due to sorption.

DDAC-degrading bacteria were isolated via enrichment culture with DDAC as the sole carbon source [130]. One isolate, *Pseudomonas fluorescens* TN4, degraded DDAC to produce decyldimethylamine and subsequently dimethylamine as intermediates. The TN4 strain also assimilated other QACs, alkyltrimethyl- and alkyl benzyl dimethyl ammonium salts, but not alkylpyridinium salts. TN4 was highly resistant to these QACs and degraded them by an N-dealkylation process [130].

Tetrakis hydroxymethyl phosphonium sulfate (THPS) has low K_{OW} (140) [135], K_{OC} , and K_H values, which suggests it will not sorb to soil but will leach to groundwater. Under abiotic conditions THPS is readily biodegradable [46]. THPS decomposes under natural conditions via hydrolysis, oxidation, and photodegradation [104]; it initially degrades to trihydroxymethyl phosphine (THP), releasing formaldehyde

and sulfuric acid [136]. Carbon dioxide, water, and inorganic phosphate are among the final products [137]. At pH 5–7 the half-lives of THPS exceed 30 days; at pH > 8 THPS degrades within 7 days. THPS is expected to volatilize from dry soil surfaces [138].

DBNPA has low $\log K_{OW}$ and K_{OC} , suggesting it will not sorb to soil and may leach to groundwater. Disappearance of DBNPA in soil may be due to hydrolysis, adsorption, chemical degradation, and/or microbial degradation. Sunlight also degrades DBNPA [139]. Hydrolysis reactions convert DBNPA into dibromoacetoneitrile, followed by dibromoacetamide, dibromoacetic acid, glyoxylic acid, and oxalic acid. The most stable product of these products is dibromoacetic acid.

4.2.7. *Corrosion Inhibitors*. In general, corrosion inhibitors are highly soluble and biodegradable. Their low $\log K_{OW}$ and K_{OC} values indicate that these chemicals are not likely to sorb to soils, and there is potential for leaching to groundwater. This group contains compounds that are toxic and/or carcinogenic [46, 76].

Propargyl alcohol and thiourea are GHS Category 2 chemicals, making them among the most toxic chemicals used in HF fluids. Propargyl alcohol is considered readily biodegradable; it is also highly mobile in soil [140]. Volatilization of propargyl alcohol from moist soil surfaces is expected to be substantial, given an estimated Henry's Law constant of 1.1×10^{-6} atm-cu m/mole [140]. Volatilization from dry soils is also expected to occur. The half-life of propargyl alcohol in an alkaline silt loam soil (pH 7.8, 3.25% organic carbon) was 12.6 days and 13 days in an acidic sandy loam (pH 4.8, 0.94% organic carbon) [140, 141]. Thiourea is considered biodegradable and highly mobile in soil. Sorption of thiourea to organic matter of three different soil orders was characterized as low (spodosol) to moderate (entisol/alfisol) [142].

4.2.8. *Iron Control Agents*. Acetic acid, citric acid, sodium erythorbate, and mercaptoacetic acid (thioglycolic acid) are highly soluble in water. The low K_{OC} values of citric acid and thioglycolic acid indicate that they will not sorb markedly to soils but will be mobile in the profile. The pK_a of thioglycolic acid is 3.55, suggesting that it will exist almost entirely in the anionic form in soil and will therefore not sorb to clay and organic matter [46]. With the exception of acetic acid, these compounds are not expected to volatilize from OGPW based on their Henry's Law constants [46].

All iron control agents, in particular acetic acid, citric acid, and thioglycolic acid, tend to be readily degraded and are not persistent [143, 144]; however, some are known to be toxic [76]. Acetic acid, citric acid, and sodium erythorbate are of low toxicity to humans. Of the iron control agents, thioglycolic acid appears to be the greatest concern as a soil contaminant as it poses a toxicity risk based on an oral LD_{50} value of 114 mg kg^{-1} [145].

4.2.9. *Surfactants*. Most surfactants are highly soluble in water and readily biodegradable. Sodium lauryl sulfate has a moderately high K_{OC} value and is expected to have moderate to low mobility in soil [46, 76, 146, 147]. Sodium lauryl sulfate

occurs in household products and is not anticipated to be a health risk due to its LD₅₀ value.

4.2.10. Excess Salinity. Soil salinity imposes ion toxicity, nutrient (N, Ca, K, P, Fe, and Zn) deficiencies, nutritional imbalances, osmotic stress, and oxidative stress on plants [148, 149]. Soil salinity significantly reduces plant phosphorus (P) uptake because phosphate ions precipitate with Ca ions [150]. Some elements, such as Na, Cl, and B, impart specific toxic effects on plants. Excessive accumulation of Na in cell walls can lead to osmotic stress and cell death [151]. All these factors cause adverse effects on plant growth and development at physiological and biochemical levels [152] and at the molecular level [153]. Salinity hinders seed germination; seedling growth; enzyme activity; DNA, RNA, and protein synthesis; and mitosis [154, 155].

4.2.11. Hydrocarbons. The primary hydrocarbons which contribute to acute toxicity of OGPW are the aromatic and phenol fractions of dissolved hydrocarbons [156].

4.3. Soil Remediation. In situ remediation of HF-affected soil involves (1) removal of salts in the soil solution via leaching with irrigation or natural precipitation; (2) replacement of exchangeable Na⁺ with Ca²⁺; (3) removal or destruction of hydrocarbons; and (4) removal or immobilization of metals. Remediation practices on OGPW-contaminated soils often tend to be straightforward.

4.3.1. Treatment of Salinity and Sodicity. Simple soil dilution may relieve salinity problems following release of OGPW. In the study by Wolf et al. [157], OGPW occurred primarily at the soil surface. Mixing of the less-contaminated deeper soil with the surface soil resulted in dilution of contaminants. Ahmad et al. [158] and Lloyd [159] concluded that the salt concentration of drilling waste was the primary factor in determining the waste loading rate in soil systems.

Addition of inexpensive amendments is often successful in treating soil salinity and sodicity problems. Both inorganic amendments (e.g., CaSO₄ [160]) and organic materials (animal manures) have proven to be successful. The most commonly used dry amendments are gypsum (CaSO₄·2H₂O) and calcium nitrate (Ca(NO₃)₂), although calcium chloride (CaCl₂) may be used if adequate drainage control is provided and leachate is managed [37]. Use of calcium amendments may require subsequent irrigation and leachate collection to move the calcium amendment into the affected soil layers for replacement of Na and to leach salts beyond the root zone. Sulfur may be applied, either as elemental S or as aluminum sulfate, to decrease pH.

Livestock manure can be successfully used as a soil amendment. Organic material creates macropores thus allowing for soil drainage; it furthermore greatly augments soil biological activity. Only well-decomposed or composted manure should be used in order to limit inputs of salts and to prevent proliferation of weeds. Addition of significant organic amendments such as chicken or some feedlot manures can increase soil salinity over several applications. Testing manure and compost for salinity is recommended [37, 161].

Organic amendments must be thoroughly mixed into soil upon application. Low-N organic matter such as cereal straw requires additional N for decomposition; therefore, a high-N fertilizer such as ammonium nitrate, ammonium sulfate, or calcium nitrate should be included [37].

Additional amendments may prove to be beneficial in treating OGPW-affected soil. For example, use of synthetic polymers (e.g., polyacrylamides) to stabilize aggregates has proved to be successful in improving the physical properties of Na-enriched soil [37, 162]. Given that soil biological activity may be drastically reduced in OGPW-contaminated soil, it is recommended that mycorrhizal fungi be applied [163].

Electrokinetic remediation has been suggested for treatment of saline soils [160]. This technology involves application of low density direct current between electrodes placed in the soil to mobilize contaminants which occur as charged species. This allows for separation and removal of Na⁺, Cl⁻, and other highly soluble ions. Electrodes can be installed horizontally or vertically in deep, directionally drilled tunnels or in trenches around sites contaminated by OGPW [164].

When the average EC of the uppermost soil is > 35,000 uS/cm, soil removal and replacement may be more economical than treatment [160]. It may be costly, however, to haul and dispose contaminated soil at a special waste landfill. There is also potential long-term liability of impacted soil placed in a landfill [165].

4.3.2. Treatment of Hydrocarbon Contamination. Hydrocarbon contamination of OGPW-affected soils is typically not expected to be significant, given the relatively low concentrations occurring in OGPW. However, in cases of a catastrophic release, microbial decomposition of oily wastes is encouraged. So-called bioremediation processes, if conducted properly, should result in few residuals and minimal alteration of the local environment [164].

In situ bioremediation systems introduce aerated, nutrient-enriched water into the contaminated zone through an array of injection wells, sprinklers, or trenches. Sufficient time is allowed for the reaction of indigenous microbial communities with the contaminants, and the treated water is eventually recovered downgradient. The recovered water may be further treated (e.g., passage over granular activated carbon) and reintroduced to the affected soil. Otherwise it may be discharged to a municipal wastewater treatment plant or to surface water [164, 166].

The affected soil should receive adequate nutrients (in particular, N and P) to promote microbial growth and activity. Also, it is essential that adequate oxygen be available, which may be provided by aeration of the flushing solution. Soil pH must be maintained near neutral in order to promote microbial proliferation [164].

In slurry biodegradation, contaminated soil is transferred from the affected area to a lined lagoon and mixed with water. The slurry is continuously stirred and aerated in the lagoon. Decomposition of organic contaminants takes place via aerobic microbial processes. Slurry biodegradation can treat a range of hydrocarbons including crude and refined petroleum products [167–169]. The presence of heavy metals

and other potential toxins in OGPW (e.g., biocides) may inhibit microbial metabolism and require pretreatment.

A significant benefit in the use of slurry biodegradation is the enhanced rate of contaminant degradation, a direct result of improved contact between the microorganisms and hydrocarbons. The agitation of contaminants in the liquid phase provides for a high degree of solubilization of compounds and significant homogeneity [167].

Land treatment techniques for bioremediation, for example, landfarming, are commonly used for treatment of hydrocarbon-contaminated soil [170]. Contaminants treated include fuel, lubricating oil, and pesticides. Landfarming can be regarded as a combination of biodegradation and soil venting; microbial oxidation reactions occur in combination with volatilization.

A common field installation calls for the affected soil to be excavated and transferred to a prepared location (a land treatment unit or cell) which is designed for controlling the process. Treatment involves installation of layers (“lifts”) of contaminated soil to the cell. The cell is usually graded at the base to provide for drainage and lined with clay and/or plastic to contain all runoff within the unit. It may also be provided with sprinklers or irrigation and drainage. Because of the high water application rates, LTUs are often bordered by berms [164].

A major benefit of the land treatment technique is that it allows for very close monitoring of process variables that control the decomposition of hydrocarbons [164, 170].

4.3.3. Treatment of Metals Contamination. Metals at OGPW-contaminated sites may occur in complex forms.

Metals may be extracted from soil via elutriation for eventual recovery, treatment, and disposal. Also known as soil flushing, contaminants are solubilized or similarly desorbed from solid forms and recovered [171]. Metal removal efficiencies during soil flushing depend not only on soil characteristics but also on metal concentration, chemistry of the metal(s), extractant chemistry, and overall processing conditions [171].

In situ extraction processes are applicable for either the vadose zone or the saturated zone. The flushing solution is applied to the affected site via sprinklers or irrigation, or by subsurface injection. A sufficient period is allowed for the applied reagents to percolate downward and react with contaminant metals. The contaminants are subsequently mobilized by solubilization. The elutriate is collected in strategically placed wells [164]. Metals which are minimally soluble in water often require acids, chelating agents, or other solvents for successful washing [172].

One drawback to soil flushing technology is the possible production of residuals. These include excess chelating agents, some of which may be toxic to biota. In addition, leaching of soil with dilute acids may destroy the biological portion of the soil, alter its chemical and physical properties, and create a relatively inert material [164].

Phytoremediation is a cost-effective, low-technology process defined as the engineered use of green plants to extract, accumulate, and/or detoxify environmental contaminants. Phytoremediation employs common plants including trees,

vegetable crops, grasses, and even annual weeds to treat heavy metals in soil [173–175].

A simple and common application of phytoremediation is *phytoextraction*, which involves the use of hyperaccumulating plants to take up metals from the soil and concentrate them into roots and aboveground shoots. In certain cases contaminants can be concentrated thousands of times higher in the plant than in the soil. Following harvest of the extracting crop, the metal-rich plant biomass can be ashed to reduce its volume, and the residue can be processed as an “ore” to recover the contaminant metals. If recycling the metal is not economically feasible, the small amount of ash (compared to the original plant biomass or the large volume of contaminated soil) can be disposed [164, 173–176].

Phytoremediation is useful for soils contaminated with metals to shallow depths. This technology can work well in low permeability soils, where many technologies have a low success rate. It can also be used in combination with conventional cleanup technologies (e.g., “pump and treat” of groundwater). Phytoremediation can be an alternative to harsher remediation technologies such as soil flushing [164].

5. Pollution Prevention for OGPW

Once OGPW has been brought to the surface it is either disposed or reused. Given that OGPW is enriched in TDS, TSS, metals, dispersed oil, dissolved and volatile organic compounds, HF additives, and other contaminants to varying degrees (Table 3), significant management challenges face operators. OGPW must be managed in ways that both reduce the operational costs as well as are protective of the environment. OGPW management practices vary widely across the United States and in some instances across a single oil and gas field [177].

OGPW management falls under two broad categories: underground injection and surface management. Selection of a management option for OGPW at a site varies based on the following [178]:

- (i) Chemical and physical properties of the OGPW.
- (ii) Volumes, duration, and flow rate generated.
- (iii) Desired end-use of the wastewater.
- (iv) Treatment and disposal options allowed by state and federal regulations.
- (v) Technical and economic feasibility of a particular option, including transportation.
- (vi) Availability of suitable infrastructure for management.
- (vii) Willingness of companies to employ a particular technology or management option, including concerns about potential liability.

Some common options available to oil and gas operators for managing OGPW are addressed below.

5.1. Limit Production of Water at the Surface. Technologies are available for managing water within the wellbore. These

technologies do not reduce the volume of water entering the well but minimize the quantity of OGPW that rises to the surface.

5.1.1. Downhole Oil/Water Separation and Injection. Downhole oil/water separators (DHOWS) separate water from oil within the wellbore so that oil or gas with little water is brought to the surface. Significant quantities of water are disposed in nonproducing formations above or below the oil- or gas-producing formation using injection tools within the well [100]. The downhole separator assembly comprises several compact elements installed within the wellbore including (1) a separation tool, which separates OGPW from incoming hydrocarbons from the formation; (2) a pump that pressurizes water from the separator and injects the OGPW into the disposal zone; (3) a heavy-duty motor to perform the pumping; and (4) miscellaneous equipment such as downhole monitoring equipment and cables [177].

5.1.2. Downhole Gas/Water Separators. Devices similar to DHOWS are available for gas wells. A study by the Gas Research Institute identified 53 commercial field tests of downhole gas/water separators involving 34 operators in the USA and Canada [179]. Gas production rates increased in 57% of the tests; 47% of the field tests were considered successful [100].

5.1.3. Dual Completion Wells. Oil production may decline in a well as water generates a “cone” around the production perforations, limiting the volume of oil that can be recovered. This phenomenon may be reversed and managed by completing the well with two separate tubing strings and pumps. The primary completion is made at a depth corresponding to strong oil production, and a secondary completion is made lower in the strata at a depth experiencing significant water production. The two completions are separated by a packer. The oil collected above the packer is brought to the surface, and the water collected below the packer is injected into a lower formation [100, 180, 181]. Swisher [182] reports on the results of using a dual completion well compared to three wells with conventional completions in a Louisiana oilfield. The dual completion well costs about twice as much to install but took the same number of months to reach payout as the other wells. However, at payout, it was producing 55 bpd of oil compared to about 16 bpd from the other three wells. Wojtanowicz [183] provides additional examples of using dual completion wells from differing geological settings.

5.2. Injection of OGPW. Injection involves the emplacement of OGPW into porous geologic strata by pumping, via an injection well, into a formation capable of receiving and storing water. Injection wells are regulated by the Federal Underground Injection Control (UIC) program which was initiated under the Safe Drinking Water Act to prevent contamination of underground sources of drinking water (USDW).

Approximately 90% of OGPW from land-based oil and gas recovery operations in the United States is reinjected into underground formations. Hundreds of thousands of

injection wells operate daily to manage produced water and flowback [178, 184]. OGPW may be injected back to its formation or into other suitable formations [185]. Injection is dependent upon several variables including the availability of receiving formation(s); the quality of OGPW being injected; the quality of water in the receiving formation; and the ultimate storage capacity of the receiving formation(s). These factors will influence what type of injection well can be used for managing OGPW.

Many papers have described the process of underground injection of wastewater. Only a brief review is provided here.

The US EPA classifies five different injection well categories (Table 4); three may be applicable for management of produced water. In general, OGPW is considered an exempt waste and therefore can be injected in Class II or Class V injection wells. Class II wells may be used to hold fluids associated with oil and natural gas production [52] and are classified either as disposal wells (IID) or as enhanced recovery wells (IIR). Wastewater resulting from OGPW treatment must be disposed in Class I injection wells. EPA defines Class I wells as technologically sophisticated wells that inject hazardous and nonhazardous wastes below the lowermost USDW. Injection occurs into deep, isolated rock formations that are separated from the lowermost USDW by layers of impermeable clay and rock [52]. Class V wells (i.e., shallow injection, subsurface drip irrigation) are injection wells not included in the other four classes. Their simple construction provides little protection against possible soil and groundwater contamination.

Underground injection of OGPW often requires transport, along with treatment to reduce fouling and bacterial growth. Storage over the long-term may be required.

5.3. Beneficial Use: Discharge OGPW to the Surface. Some important emerging opportunities for management of OGPW are (1) treatment and reuse as a water supply for public consumption, agriculture, and industry and (2) secondary industrial processes such as extraction of minerals [178]. The presence of certain constituents, however, may limit produced water use in selected areas [178]. Produced water may be discharged to the land as long as it meets both onshore and offshore discharge regulations [83].

OGPW may be discharged to the land surface to surface impoundments, for land application for crop use and industrial uses (i.e., oil and gas completion activities, truck wash station, dust suppression, and cooling tower water) [177]. A surface impoundment is defined as an excavation or diked area used for treatment, storage, or disposal of liquids [186]. Impoundments are usually constructed in low permeability soils. These vary in size from < 1 acres to several hundred acres. Based on an EPA national survey that characterized 180,000 impoundments, the oil and gas industry uses impoundments for storage (29%), disposal (67%), and treatment (4%) [186].

Impoundments are used for OGPW management including evaporation and/or infiltration; storage prior to injection or irrigation; or beneficial use such as livestock and wildlife watering ponds, constructed wetlands, fishponds, or a recreational pond.

TABLE 4: US EPA injection well classification system.

Well class	Injection well description	Approximate inventory
Class I	Inject hazardous wastes beneath the lowermost USDW	500
	Inject industrial nonhazardous liquid beneath the lowermost USDW	
	Inject municipal wastewater beneath the lowermost USDW	
Class II	Dispose of fluids associated with the production of oil and natural gas	147,000
	Inject fluids for enhanced oil recovery	
	Inject liquid hydrocarbons for storage	
Class III	Inject fluids for the extraction of minerals	17,000
Class IV	Inject hazardous or radioactive waste into or above USDW, 40 sites	
	This activity is banned. These wells can only inject as part of an authorized cleanup	
Class V	Wells not included in the other classes. Inject nonhazardous liquid into or above a USDW	500,000 to >685,000

[52].

5.3.1. Evaporation Ponds. An evaporation pond is a large body of water that is designed to evaporate water by solar energy [187]. Such ponds are constructed to prevent subsurface infiltration [188]. Ponds are a favorable technology in regions where annual rainfall is relatively low and evaporation rates are high. If the pond is constructed solely for evaporative loss, it is typically designed as a broad shallow pool that takes advantage of the large surface area. Areas with high winds and few natural windbreaks provide additional evaporative potential and may be considered in siting a pond. Ponds are usually covered with netting to prevent problems to migratory waterfowl caused by contaminants in OGPW [189].

As pure water evaporates from the pond, TDS increase in the remaining water. Over time the remaining water may become concentrated brine [177].

Over 80 million gallons of OGPW are managed daily by EPA under the Clean Water Act's National Pollutant Discharge Elimination System (NPDES) for beneficial reuses such as agricultural irrigation [100, 184]. The following is a summary of beneficial OGPW use practices in the USA.

5.3.2. Irrigation and Land Application. In the United States crop irrigation is the largest single use of freshwater, comprising 40% of all freshwater withdrawn, or 137 million gallons per day [190].

The determination of whether OGPW water can be used for agricultural purposes (i.e., irrigation, land application, and stock watering) depends both on the quality of the produced water and on characteristics of the recipient site. Relevant water and site variables include quantity of water required; length of time the water has been stored in impoundments prior to use; soil mineralogy, texture, and structure; and sensitivity of plant species [188].

The three most critical parameters regarding crop irrigation water quality requirements are salinity, sodicity, and elemental toxicity [100, 188]. As salinity rises above a species-specific salinity threshold, crop yields decrease. Irrigation water high in TDS diminishes the ability of roots to incorporate water, and reduces crop yield. The tolerance of various

crops to salinity has been documented [191]. EC levels > 3,000 $\mu\text{S}/\text{cm}$ are considered saline.

Excess sodium can damage soil physical properties. Irrigation water with SAR > 12 is considered sodic [100, 188]. Higher SAR values lead to soil dispersion and loss of structure and infiltration capability [119].

Under the Clean Water Act's Subpart E of 40 CFR Part 435, the NPDES permit system allows for the specialized reuse of wastewater from oil and gas facilities west of the 98th meridian. To qualify, the wastewater must contain < 35 mg/L of oil and grease and be used either for agriculture or for livestock watering [100]. The combination of the NPDES permitting allowance, the substantial requirement of water needed to perform HF, and the frequent geographical overlap between extraction sites and agricultural land has led to reuse of OGPW for irrigation in some states [100].

Raw water either is discharged directly to the land surface or is pretreated with amendments prior to application. Amendments are site-specific depending on soil properties, water chemistry, and plant species grown. Amendments could also be added to soil prior to, or following, application. Wolf et al. [157] found that addition of inorganic fertilizer, broiler litter, and Milorganite® to OGPW-treated soil markedly improved growth of Bermuda grass [*Cynodon dactylon* (L.) Pers.].

A program was created at Texas A&M University to develop a portable produced water treatment system that can be transported to oilfields to convert OGPW into irrigation or potable water. The goal was to produce water to levels of < 500 mg/L TDS and < 0.05 mg/L hydrocarbons [100, 192, 193]. Chevron Texaco developed a system to treat OGPW in Southern California [194]; 21 million gallons of oilfield water is recycled daily and sold to farmers who use it on about 45,000 acres of crops, about 10% of Kern County's farmland. The treated water is used for irrigation of fruit trees and other crops and for recharging shallow aquifers. An additional 360,000 bpd of water is further purified and used to make steam at a cogeneration facility. State and local officials praise the two-decade-old program as a national model for coping with the region's water shortages [195].

Thousands of acres in the Powder River Basin (WY) have been transformed to productive agricultural land using produced water [1, 196]. Livestock forage was irrigated using either OGPW on research plots or a blend of surface water and OGPW. Both treatments resulted in adequate crop production; however, the OGPW had to be applied at higher rates as plants did not utilize it as efficiently as the surface water blend [197]. Between watering intervals CaSO_4 and other supplements were applied to offset high SAR. After two years the rangeland was converted into highly productive grassland yielding livestock and wildlife benefits [100, 198].

The use of subsurface drip irrigation of OGPW is gaining popularity [199]. BeneTerra LLC has developed subsurface drip irrigation technology to provide produced water for crops [200]. Produced water is filtered, treated, and pumped through polyethylene tubing which spreads it uniformly through soil. The tubing is installed with a chisel plow to depths ranging from 18 to 48 inches. Haying operations can continue while the field is being irrigated. The drip irrigation systems are designed to utilize the native Ca and Mg present in the soil to offset the effects of Na. The salts percolate to a lower depth [1].

In some cases produced water may be treated for domestic supplies and drinking water. However, produced water from coal seams > 200-foot depth often has water that exceeds salinity levels appropriate for domestic use (i.e., about 3,000 mg/L). Also, water with high metal concentrations stains faucets and sinks. Water used by municipalities with treatment systems may be capable of removing certain harmful constituents or reducing their concentrations via existing processes [100, 188].

5.3.3. Aquaculture and Hydroponic Vegetable Culture. Greenhouse experiments were conducted to raise vegetables and fish using either produced water or potable water [201]. In a system using a combination of hydroponic plant cultivation and aquaculture, tomatoes grown with OGPW were smaller than those grown in potable water. The produced water tank grew a larger weight of tilapia (*Oreochromis niloticus/aureus*); however, some fish died, while none in the potable water tank died [100].

5.3.4. Constructed Wetlands. Constructed wetlands were developed approximately 50 years ago to exploit the ability of plants to treat contaminants in aqueous ecosystems [202]. Advantages of these systems include low construction and operation costs [188, 202] and public acceptance. Wetlands provide significant environmental benefits—they can be used by wetland birds and animals as well as by aquatic life. Wetlands can also be utilized for livestock and wildlife watering purposes [1, 203].

An artificial sedge wetland system was constructed to treat produced water [14]. After one year of operation the wetland effectively treated Fe and, to a lesser extent, Ba [188, 204]; however, SAR increased from 12.1 to 14.1. This was attributed to calcite precipitation without associated dissolution of Ca and Mg [204]. It was concluded that “clean water is needed to supplement sodicity and salinity treatment by vegetation and soil” [205].

5.3.5. Livestock Watering/Confined Animal Feeding Operations (CAFO). The water needs of CAFOs include animal consumption, irrigation of forage crops, and waste management. Livestock watering is one of the most common and proven beneficial uses of produced water [177].

The quality of OGPW presents the greatest constraint for use of livestock watering. Livestock are known to tolerate a range of contaminants in their drinking water. ALL [188] provides data showing acceptable TDS levels for livestock watering. In general, animals may tolerate higher TDS if they are gradually acclimated to the elevated levels. Water with TDS < 1,000 mg/L is considered excellent source water. Water with TDS from 1,000 to 7,000 mg/L can be used for livestock but may cause digestive problems [188]. Water with TDS of 10,000 is considered unsatisfactory for animal consumption.

5.3.6. Wildlife. Some Rocky Mountain area gas projects have created impoundments measuring at least several acres that collect and retain large volumes of produced water. These impoundments provide a source of drinking water for wildlife and offer habitat for fish and waterfowl and can provide additional recreational opportunities [100]. In some areas, watering ponds provide wintering areas for migrating waterfowl, neotropical birds, or other transient species. In severe drought conditions, watering ponds are used to provide water for large mammals and other wildlife. At Custer Lake, Wyoming, approximately 30,000 barrels of water per day are discharged to what would normally be a seasonal playa lake. Waterfowl and big game are reported to flourish there [177].

The quality of OGPW may limit the use of this management practice, as contaminants may adversely affect fish and wildlife. Research conducted by the USGS has demonstrated acute and chronic sodium bicarbonate toxicity to aquatic species [206]. Coal bed methane-produced water discharges containing Se in concentrations > 2 $\mu\text{g/L}$ may cause bioaccumulation in sensitive species [1, 206]. Water with TDS > 10,000 mg/L is not of sufficient quality for wildlife consumption.

5.3.7. Reuse in Oil and Gas Operations. Water is required for a range of day-to-day operations in the oil and gas industries. Activities such as well completions and truck washing may not require water to be of high quality. Therefore, OGPW can be used with little concern for water quality. Minimally treated produced water may be reused by petroleum operators for drilling operations.

Lebas et al. [51] found that produced water with TDS levels as high as 285,000 mg/L (28.5% salinity) could generate proper cross-linked rheology for hydraulic fracturing consistent with wells that were fracturing with just 20,000 mg/L. A mixture of common drilling chemicals including carboxymethyl hydroxypropyl guar gum, a Zr-based cross-linker, sodium chlorite breakers, and nonemulsified surfactants was blended with 100% treated OGPW to generate HF fluid that performed as well as that expected from a fluid based on fresh water. The fluids were used to complete seven wells in New Mexico's Delaware basin. The study showed that OGPW possesses all the characteristics required for effective HF, that is, easy preparation, rapid hydration, low

fluid loss, good proppant transport capacity, low pipe friction, and effective recovery from the reservoir. Lebas et al. [51] state that, in addition to preserving fresh water for agricultural and commercial use, employing produced water for HF can help reduce approximately 1400 truck-loads from the roads and all but eliminate the use of disposal wells.

Erskine et al. [207] report on the use of produced water for drilling projects in New Mexico's San Juan Basin. The authors state that a combination of advection and dilution reduced Cl concentrations of 10,000 mg/L to <1 mg/L in one year. In the Powder River Basin of Wyoming a water truck load-out facility utilizes produced water for oil and gas well operations, thus taking some pressure off the local water supply to meet this demand. In the Barnett Shale play (Texas) as much as 2 million gallons of make-up water is required for a fracture job. This water is subsequently produced back to the surface in the early stages of development. To reduce the cost of fracturing wells, the produced water is reclaimed and recycled by using it to fracture the next well. In the Battle Creek play (Montana), a zero-discharge system was developed to manage produced water through enhanced evaporation ponds coupled with recycling the produced water for well completion and dust prevention [177].

The main constraint to using produced water for oil and gas operations is the fact that the volume of water used may be modest when compared to the total volume of OGPW produced; therefore, it may be uneconomical to put practices in place solely for recycling produced water for operational uses. This can be overcome by formulating a set of water management practices, where the water is readily available for operations, but for additional purposes as needed [177].

5.3.8. Other Uses/Fire Control. In the Western USA, only limited surface and ground water resources may be available for firefighting. Application of large volumes of saline produced water may adversely impact soil quality to some degree; however, this impact is less devastating than that from a large fire. ALL [188] reports that firefighters near Durango, Colorado, used produced water impoundments as sources of water for firefighting.

5.4. Technologies for Treatment of OGPW. Where reuse of OGPW is practical, authorized by regulatory agencies, and cost-effective, it constitutes a beneficial use of what would otherwise be considered a waste [178]. Beneficial use of produced water may require significant treatment [83]. The primary objectives for treating produced water include desalinization; removal of dispersed oil and grease, suspended particles and sand, soluble organic compounds, dissolved gases, and naturally occurring radioactive material; disinfection; and softening (i.e., to remove excess water hardness) [83, 208].

The optimal wastewater treatment technologies available are not able to strip all toxic chemicals from OGPW and are often selectively implemented due to cost [100, 184]. A range of dedicated and combined physical, biological, and chemical treatment processes have been developed to treat OGPW. Some popular technologies are reviewed here.

5.4.1. Membrane Processes for Removal of TDS

(1) Membrane Filtration. Membrane separation processes available for treating OGPW include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [209]. Membranes are microporous films with specific pore sizes which selectively separate components from a fluid. MF uses the largest pore size (0.1–3 mm) and is typically employed for removal of suspended solids and turbidity reduction. UF pore sizes are between 0.01 and 0.1 mm; this technology is employed for removal of color, odor, viruses, and colloidal organic matter [189, 210, 211]. UF is the most effective method for oil removal from produced water as compared with conventional separation methods [212]. UF is more efficient than MF for removal of hydrocarbons, suspended solids, and dissolved constituents from oilfield produced water [213].

NF is a successful technology for water softening and metals removal and is designed to remove contaminants as small as 0.001 mm [189]. NF is selective for multivalent ions such as Ca^{2+} and Mg^{2+} [214]. It is applicable for treating water containing TDS in the range of 500–25,000 mg/L. NF membranes have been employed for produced water treatment on both bench and pilot scales [209, 215]. Mondal and Wickramasinghe [216] studied the effectiveness of NF membranes for treatment of oilfield produced water. Effectiveness of treatment of brackish feed water was similar between NF and RO techniques [83].

(2) Ceramic Membranes. Ceramic UF/MF membranes have been used in a full-scale facility for treatment of produced water [189]. Treated product water was reported to be free of suspended solids and nearly all nondissolved organic carbon [217–223]. Ceramic UF/MF membranes have a lifespan of about 10 years. Chemicals are not required for this technology except during cleaning of membranes [83].

(3) Reverse Osmosis. RO is a pressure-driven membrane processes. Osmotic pressure of the feed solution is suppressed by applying hydraulic pressure whose forces permeate (i.e., clean water) to diffuse through a dense, nonporous membrane [224]. The major disadvantage of the technology is membrane fouling and scaling [189, 225]. Nicolaisen and Lien [226] reported successful RO treatment of oilfield OGPW in Bakersfield, California. The pilot system was operated for over 6 months and produced 20 gpm of clean water. A process for converting oilfield produced water into irrigation/drinking quality water consisted of air flotation, clarification, softening, filtration, RO, and water reconditioning [227]. A pilot plant handled water with approximately 7,000 mg/L TDS, 250 mg/L silica, and 170 mg/L soluble oil, ranging in pH from 7 to 11. The major source of fouling of RO membranes was from organics in the feed water, including organic sulfur compounds. A portion of these entered the RO system as TSS and some precipitated. The quality of treated water met the stringent California Title 22 Drinking Water Maximum Contaminant Levels [227].

RO membrane technology should be appropriate for treating oilfield produced water with appropriate

pretreatment technology [200]. RO membrane systems generally have a life expectancy of 3–7 years [189].

(4) *Electrodialysis/Electrodialysis Reversal*. Electrodialysis (ED) and ED reversal (EDR) are well-established desalination technologies. These electrochemically driven processes separate dissolved ions from water through ion exchange membranes. A series of membranes containing electrically charged functional sites are arranged in an alternating mode between an anode and a cathode to remove charged substances from feed water [189]. EDR and ED technologies have been tested at the laboratory-scale for treatment of produced water. Sirivedhin et al. [87] reported that ED is an excellent produced water treatment technology; however, it works optimally for treating relatively low-saline produced water.

The ED/EDR membrane lifetime is between 4 and 5 years. Major limitations of this technology are regular membrane fouling and high treatment cost [189].

(5) *Biological Aerated Filters*. Biological aerated filtration (BAF) consists of permeable media under aerobic conditions to facilitate biochemical oxidation and removal of organic constituents in wastewater. Media do not exceed 10 cm in diameter to prevent clogging of pore spaces when sloughing occurs [228]. BAF can remove oil, ammonia, suspended solids, nitrogen, BOD, COD, heavy metals, Fe, soluble organics, trace organics, and H₂S from produced water [189, 229]. Removal efficiencies of up to 70% N, 80% oil, 60% COD, 95% BOD, and 85% TSS have been achieved with BAF treatment [229]. Water recovery is nearly 100% since waste generated is removed in solid form [230]. The method is most effective for produced water with Cl levels < 6600 mg/L [189].

BAF systems usually have a long lifespan; they do not require any chemicals or cleaning during normal operations. Accumulated sludges are captured in sedimentation basins. Solid waste disposal can account for up to 40% of the total cost of this technology [228].

(6) *Vibrating Membrane Process*. The vibrating membrane process VSEP® (*Vibratory Shear Enhanced Process*) limits membrane fouling, removing the main contaminants from wastewater without the addition of antiscalant chemical substances. The design greatly reduces the fouling common to all membrane processes [231]. The pressure vessel moves in a vigorous vibratory motion, tangential to membrane surface, thus creating shear waves which prevent membrane fouling [232, 233]. RO may be implemented as tertiary treatment.

5.5. Thermal Technologies for Removing Oil and Grease Content

5.5.1. *Multistage Flash (MSF)*. MSF distillation involves evaporation of water by reducing atmospheric pressure instead of raising temperature. Feed water is preheated and flows into a chamber with reduced air pressure where it immediately flashes into steam [234]. Water recovery from MSF treatment is approx. 20%; it often requires posttreatment because it typically contains 2–10 mg/L TDS [189]. A setback

in operating MSF is scale formation on heat transfer surfaces which often requires the use of scale inhibitors and acids. MSF is a relatively cost-effective treatment method with plant life expectancy of more than 20 years [235].

5.5.2. *Multieffect Distillation*. The MED process involves application of energy that converts saline water into steam, which is condensed and recovered as pure water. Multiple effects are employed in order to improve the efficiency and minimize energy consumption. A major advantage of this system is the energy efficiency gained through the combination of several evaporator systems.

MED is suitable for treatment of high TDS produced water [189, 236]. Product water recovery from MED systems ranges from 20 to 67% depending on design [234]. Despite the high water recovery, MED has not been extensively used for water production like MSF because of scaling problems associated with early designs. Recently, falling film evaporators have been introduced to improve heat transfer rates and reduce the rate of scale formation [236]. Scale inhibitors and acids may be required to prevent scaling, and pH control is essential to prevent corrosion. MED has a lifespan of 20 years and can be applied to a wide range of feed water qualities, similar to MSF.

5.5.3. *Vapor Compression Distillation*. The VCD process is an established desalination technology for treating seawater and RO concentrate [189]. Vapor generated in the evaporation chamber is compressed thermally or mechanically, which raises the temperature and pressure of the vapor. The heat of condensation is returned to the evaporator and is used as a heat source. VCD can operate at temperatures below 70°C, which reduces scale formation problems [237]. Energy consumption of a VCD plant is significantly lower than that of MED and MSF. Although this technology is mainly associated with sea water desalination, various enhanced vapor compression technologies have been employed for produced water treatment [189].

5.5.4. *Multieffect Distillation-Vapor Compression Hybrid*. Multistage flash (MSF) distillation, vapor compression distillation (VCD) and multieffect distillation (MED) are extensively used thermal desalination technologies [234]; however, hybrid thermal desalination plants, that is, MED-VCD, have achieved higher efficiencies [236]. Increased production and enhanced energy efficiency are major advantages of this system [189]. GE has developed produced water evaporators which use mechanical vapor compression. These evaporators exhibit a number of advantages over conventional produced water treatment methods including reduction in chemical use, overall cost, fouling severity, and handling [238].

Membrane technologies are often preferred over thermal technologies; however, recent innovations in thermal process engineering have made the latter more competitive in treating highly contaminated water [83, 189, 235].

Gradient Corporation (Woburn, MA) is attempting to make HF a “water-neutral process” by reusing water for the HF process. The technology, carrier gas extraction (CGE), is a humidification and dehumidification technique;

it heats produced water into vapor and condenses it back to contaminant-free water. This process yields freshwater and saturated brine [239].

5.5.5. Freeze Thaw Evaporation. The FTEw process employs freezing, thawing, and conventional evaporation for produced water management. When produced water is cooled below 32°F but above its freezing point, relatively pure ice crystals and an unfrozen solution form. The solution contains high concentrations of dissolved constituents and is drained from the ice. The ice is collected and melted to produce clean water.

FTEw can remove >90% of TDS, TSS, volatile and semivolatile organics, total recoverable petroleum hydrocarbons, and heavy metals in produced water [220, 240]. FTE requires no chemical additives, infrastructure, or supplies that might restrict its use. It is easy to operate and monitor and has a life expectancy of approximately 20 years [189]. However, the technology can only work in a climate that has a substantial number of days with temperatures below freezing and requires significant land area. FTE technology generates a significant amount of concentrated brine and oil; therefore, waste management and disposal must be addressed.

5.5.6. Dewvaporation: AltelaRainSM Process. The principle of operation of Dewvaporation is based on counter current heat exchange to produce distilled water [241]. Feed water is evaporated in one chamber and condenses in the opposite chamber of a heat transfer wall as distilled water. Approximately 100 bbl/day of produced water with salt concentrations > 60,000 mg/L TDS can be processed [165]. High removal rates of organics, heavy metals, and radionuclides from produced water have been reported for this technology. In one plant, Cl⁻ concentration was reduced from 25,300 to 59 mg/L, TDS was reduced from 41,700 to 106 mg/L, and benzene concentration was reduced from 450 mg/L to nondetectable after treatment with AlterRainSM Dewvaporation technology [242].

5.6. Physical Separation Technologies

5.6.1. Hydrocyclones. Hydrocyclones physically separate solids from liquids; hydrocyclones can remove particles in the 5–15 mm range and have been widely used for treatment of OGPW [189, 243].

Hydrocyclones are used in combination with other technologies as a pretreatment process. They have a long lifespan and do not require chemical use or pretreatment of feed water. A major disadvantage of this technology is generation of substantial slurry of concentrated solid waste.

5.6.2. Gas Flotation. Flotation technology is extensively used for treatment of conventional oilfield produced water.

Flotation technology uses fine gas bubbles to separate suspended particles that are not easily separated by sedimentation. When gas is injected into produced water, suspended particulates and oil droplets become attached to air bubbles as they rise. This results in the formation of foam on the water surface which is skimmed off [244]. Flotation can be

used to remove grease and oil, natural organic matter, volatile organics, and small particles from produced water [50, 189, 243, 245].

Two types of gas flotation technology are in use, that is, dissolved gas flotation and induced gas flotation, based on the method of gas bubble generation and resultant bubble sizes. Gas flotation can remove particles as small as 25 mm but cannot remove soluble oil constituents from water [189]. Flotation is most effective when gas bubble size is smaller than oil droplet size. It is expected to work best at low temperature since the process involves dissolving gas into a water stream. The technology does not require chemical use, except for coagulation chemicals that are added to enhance removal of target contaminants. Solids disposal is necessary for the sludge generated from this process.

5.6.3. Media Filtration. Filtration technology is used for removal of oil and grease and total organic carbon (TOC) from produced water [189]. Filtration is carried out using various media such as sand, gravel, anthracite, and walnut shells. This process is not affected by salinity levels and may be applied to any type of produced water. Media filtration technology is highly efficient for removal of oil and grease; efficiency of >90% has been reported [189]. Efficiency can be further enhanced if coagulants are added to the feed water prior to filtration. Media regeneration and solid waste disposal are drawbacks to this technology.

5.6.4. Adsorption. Adsorption is generally used as a polishing step in the OGPW treatment process rather than as a stand-alone technology, since adsorbents can be overloaded with organics. Adsorption is used to remove Mn, Fe, TOC, BTEX, oil, and more than 80% of heavy metals present in produced water [189]. A wide range of adsorbents is available including activated carbon, organoclays, activated alumina, and zeolites [246]. Adsorption processes are successfully applied to water treatment regardless of salinity. Replacement or regeneration of the sorption media may be required depending on feed water quality and media type [189, 246]. Chemicals are used to regenerate media when all active sites are blocked.

5.6.5. Ion Exchange Technology. Ion exchange technology is in demand for numerous industrial operations including treatment of OGPW. It is especially useful in the removal of monovalent and divalent ions and metals from produced water [247]. Ion exchange technology has a lifespan of about 8 years and requires pretreatment for solids removal. It also requires chemicals for resin regeneration and disinfection [181].

5.6.6. Macroporous Polymer Extraction Technology. Macroporous polymer extraction (MPPE) is a liquid-liquid extraction technology where the extraction liquid is immobilized within polymer particles impregnated with macropores. The particles have pore sizes of 0.1–10 mm and a porosity of 60–70%. The polymers were initially designed for absorbing oil from water but later applied to produced water treatment [248]. In the MPPE unit, produced water is passed through a column packed with MPPE particles containing a specific

extraction liquid. The immobilized extraction liquid removes hydrocarbons from the produced water [71].

In a commercial unit, MPPE was used for removal of dissolved and dispersed hydrocarbons and achieved 99% removal of BTEX, PAHs, and aliphatic hydrocarbons at 300–800 mg/L influent concentration. It had a removal efficiency of 95–99% for aliphatics below C₂₀ and it was reported that total aliphatic removal efficiency of 91–95% was feasible [249].

The hydrocarbons recovered from the MPPE process can be disposed or recycled. Stripped hydrocarbons can be condensed and separated from feed water by gravity, and product water is either discharged or reused. This technology can withstand produced water high in salinity and containing methanol, glycols, corrosion inhibitors, scale inhibitors, H₂S scavengers, demulsifiers, defoamers, and dissolved heavy metals [83].

6. Conclusions

This review paper has described the composition of oil and gas produced water including common HF additives and documented several key effects on soil properties. Beneficial use of OGPW must take into consideration its chemical make-up, the properties of the recipient soil, and long-term land use objectives. For example, it has been shown that untreated OGPW may be directly applied to the land surface with limited adverse effects. In others, where the water is to be used for domestic or industrial purposes, extensive treatment is required. There is a significant need for further field studies, in particular the study of complex mixtures and how interactions between individual OGPW chemicals influence their environmental fate.

Future OGPW management technologies are likely to focus on (1) capturing secondary value from repurposed water; (2) minimizing transportation; (3) minimizing energy inputs; and (4) reduced air emissions (including CO₂) all the while with a vision to reduce overall management costs.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

References

- [1] Aqwaterc, *Produced Water Beneficial Use Case Studies*, Produced Water Treatment and Beneficial Use Information Center, 2015, http://aqwaterc.mines.edu/produced_water/assessbu/case/.
- [2] Unconventional Oil and Gas Report (UOGR), *Unconventional Resources*, 2015, <http://www.ogj.com/unconventional-resources.html>.
- [3] Earthworks, "Hydraulic Fracturing 101. Hydraulic fracturing—What it is," 2015, https://www.earthworksaction.org/issues/detail/hydraulic_fracturing_101#.Vi4kGSv6G0I.
- [4] L. Britt, "Fracture stimulation fundamentals," *Journal of Natural Gas Science and Engineering*, vol. 8, pp. 34–51, 2012.
- [5] M. J. Economides and K. G. Nolte, *Reservoir Stimulation*, John Wiley & Sons, Chichester, UK, 3rd edition, 2000.
- [6] R. A. Kerr, "Natural gas from shale bursts onto the scene," *Science*, vol. 328, no. 5986, pp. 1624–1626, 2010.
- [7] H. A. Waxman, E. J. Markey, and D. DeGette, *United States House of Representatives. Committee on Energy and Commerce. Chemicals Used In Hydraulic Fracturing*, Government Printing Office, Washington, DC, USA, 2011.
- [8] H. J. Wiseman, "Untested waters: the rise of hydraulic fracturing in oil and gas production and the need to revisit regulation," *Fordham Environmental Law Review*, vol. 20, pp. 115–169, 2008.
- [9] M. Ratner and M. Tiemann, *An Overview of Unconventional Oil and Natural Gas: Resources and Federal Actions*, Congressional Research Service, Washington, DC, USA, 2015.
- [10] E. Gruber, *Recycling Produced & Flowback Wastewater for Fracking*, 2013, <http://blog.ecologixsystems.com/wp-content/uploads/2013/04/Recycling-Produced-and-Flowback-Water-for-Fracking.pdf>.
- [11] U.S. Environmental Protection Agency, "Assessment of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources," EPA/600/R-15/047a, 2015, <http://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=244651>.
- [12] C. D. Kassotis, D. E. Tillitt, C.-H. Lin, J. A. McElroy, and S. C. Nagel, "Endocrine-disrupting chemicals and oil and natural gas operations: potential environmental contamination and recommendations to assess complex environmental mixtures," *Environmental Health Perspectives*, 2015.
- [13] J. Deutch, S. Holditch, F. Krupp et al., "The Secretary of the Energy Board Shale Gas Production Subcommittee Ninety-Day Report," 2001, https://www.edf.org/sites/default/files/11903_Embargoed_Final_90_day_Report%20.pdf.
- [14] B. E. Fontenot, L. R. Hunt, Z. L. Hildenbrand et al., "An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett shale formation," *Environmental Science & Technology*, vol. 47, no. 17, pp. 10032–10040, 2013.
- [15] J. S. Harkness, G. S. Dwyer, N. R. Warner, K. M. Parker, W. A. Mitch, and A. Vengosh, "Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: environmental implications," *Environmental Science & Technology*, vol. 49, no. 3, pp. 1955–1963, 2015.
- [16] T. G. Harvey, T. W. Matheson, and K. C. Pratt, "Chemical class separation of organics in shale oil by thin-layer chromatography," *Analytical Chemistry*, vol. 56, no. 8, pp. 1277–1281, 1984.
- [17] A. L. Maule, C. M. Makey, E. B. Benson, I. J. Burrows, and M. K. Scammell, "Disclosure of hydraulic fracturing fluid chemical additives: analysis of regulations," *New Solutions*, vol. 23, no. 1, pp. 167–187, 2013.
- [18] N. R. Warner, R. B. Jackson, T. H. Darrah et al., "Geochemical evidence for possible natural migration of Marcellus formation brine to shallow aquifers in Pennsylvania," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 109, no. 30, pp. 11961–11966, 2012.
- [19] B. Ong, "The potential impacts of hydraulic fracturing on agriculture," *European Journal of Sustainable Development*, vol. 3, no. 3, pp. 63–72, 2014.
- [20] K. R. Gilmore, R. L. Hupp, and J. Glathar, "Transport of hydraulic fracturing water and wastes in the susquehanna river basin, Pennsylvania," *Journal of Environmental Engineering*, vol. 140, no. 5, pp. 10–21, 2014.
- [21] D. S. Lee, J. D. Herman, D. Elsworth, H. T. Kim, and H. S. Lee, "A critical evaluation of unconventional gas recovery from the marcellus shale, northeastern United States," *KSCE Journal of Civil Engineering*, vol. 15, no. 4, pp. 679–687, 2011.

- [22] A. Bergman, J. J. Heindel, S. Jobling, K. A. Kidd, and R. T. Zoeller, "State of the science of endocrine disrupting chemicals 2012," World Health Organization, 2013, <http://www.who.int/ceh/publications/endocrine/en/>.
- [23] E. Diamanti-Kandarakis, J.-P. Bourguignon, L. C. Giudice et al., "Endocrine-disrupting chemicals: an endocrine society scientific statement," *Endocrine Reviews*, vol. 30, no. 4, pp. 293–342, 2009.
- [24] R. Zoeller, Å. Bergman, G. Becher et al., "A path forward in the debate over health impacts of endocrine disrupting chemicals," *Environmental Health*, vol. 13, article 118, 2014.
- [25] S. B. C. Shonkoff, J. Hays, and M. L. Finkel, "Environmental public health dimensions of shale and tight gas development," *Environmental Health Perspectives*, vol. 122, no. 8, pp. 787–795, 2014.
- [26] S. Souther, M. W. Tingley, V. D. Popescu et al., "Biotic impacts of energy development from shale: research priorities and knowledge gaps," *Frontiers in Ecology and the Environment*, vol. 12, no. 6, pp. 330–338, 2014.
- [27] O. Braga, G. A. Smythe, A. I. Schafer, and A. J. Feitz, "Steroid estrogens in primary and tertiary wastewater treatment plants," *Water Science and Technology*, vol. 52, no. 8, pp. 273–278, 2005.
- [28] C. G. Campbell, S. E. Borglin, F. B. Green, A. Grayson, E. Wozei, and W. T. Stringfellow, "Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review," *Chemosphere*, vol. 65, no. 8, pp. 1265–1280, 2006.
- [29] P. Westerhoff, Y. Yoon, S. Snyder, and E. Wert, "Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes," *Environmental Science & Technology*, vol. 39, no. 17, pp. 6649–6663, 2005.
- [30] K. J. Ferrar, D. R. Michanowicz, C. L. Christen, N. Mulcahy, S. L. Malone, and R. K. Sharma, "Assessment of effluent contaminants from three facilities discharging marcellus shale wastewater to surface waters in Pennsylvania," *Environmental Science & Technology*, vol. 47, no. 7, pp. 3472–3481, 2013.
- [31] N. R. Warner, C. A. Christie, R. B. Jackson, and A. Vengosh, "Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania," *Environmental Science and Technology*, vol. 47, no. 20, pp. 11849–11857, 2013.
- [32] Natural Resources Defense Council (NRDC), *Fracking's Most Wanted: Lifting the Veil on Oil and Gas Company Spills and Violations*, IP:15-01-A, 2015, <http://www.nrdc.org/land/drilling/files/fracking-company-violations-IP.pdf>.
- [33] M. Soraghan, *Oil and Gas: Spills up 17 Percent in U.S. in 2013*, Environment & Energy Publishing, 2014, <http://www.eenews.net/stories/1059999364>.
- [34] S. A. Gross, H. J. Avens, A. M. Banducci, J. Sahlmeier, J. M. Panko, and B. E. Tvermoes, "Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations," *Journal of the Air & Waste Management Association*, vol. 63, no. 4, pp. 424–432, 2013.
- [35] P. F. Ziemkiewicz, J. D. Quaranta, A. Darnell, and R. Wise, "Exposure pathways related to shale gas development and procedures for reducing environmental and public risk," *Journal of Natural Gas Science and Engineering*, vol. 16, pp. 77–84, 2014.
- [36] D. Sontag and R. Gebeloff, "The downside of the boom," *The New York Times*, 2014, <http://www.nytimes.com/images/2014/11/23/nytfpage/scan.pdf>.
- [37] Alberta Environment, "Salt Contamination Assessment & Remediation Guidelines," Environmental Sciences Division, Environmental Service, 2001, <http://environment.gov.ab.ca/info/library/6144.pdf>.
- [38] R. B. Jackson, A. Vengosh, T. H. Darrah et al., "Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 110, no. 28, pp. 11250–11255, 2013.
- [39] S. G. Osborn, A. Vengosh, N. R. Warner, and R. B. Jackson, "Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 108, no. 20, pp. 8172–8176, 2011.
- [40] A. Vengosh, R. B. Jackson, N. Warner, T. H. Darrah, and A. Kondash, "A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States," *Environmental Science & Technology*, vol. 48, no. 15, pp. 8334–8348, 2014.
- [41] S. L. Brantley, D. Yoxheimer, S. Arjmand et al., "Water resource impacts during unconventional shale gas development: the Pennsylvania experience," *The International Journal of Coal Geology*, vol. 126, pp. 140–156, 2014.
- [42] G. A. Burton Jr., N. Basu, B. R. Ellis, K. E. Kapo, S. Entekin, and K. Nadelhoffer, "Hydraulic 'fracking': are surface water impacts an ecological concern?" *Environmental Toxicology and Chemistry*, vol. 33, no. 8, pp. 1679–1689, 2014.
- [43] Environmental and Energy Study Institute (EESI), *Shale Gas and Oil Terminology Explained: Technology, Inputs & Operations*, EESI, Washington, DC, USA, 2011.
- [44] Ostroff Law, "Dangerous fracking chemicals," 2015, <http://frackinginjurylaw.com/dangerous-fracking-chemicals/>.
- [45] FracFocus.org, "Chemical Use in Hydraulic Fracturing," 2015, <http://fracfocus.org/>, <http://www.fiercewater.com/story/business-booming-fracking-wastewater/2015-07-28>.
- [46] W. T. Stringfellow, J. K. Domen, M. K. Camarillo, W. L. Sandelin, and S. Borglin, "Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing," *Journal of Hazardous Materials*, vol. 275, pp. 37–54, 2014.
- [47] US Environmental Protection Agency, "Hydraulic fracturing fluids," in *Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs*, EPA 816-R-04-003, US Environmental Protection Agency, Washington, DC, USA, 2004.
- [48] Halliburton Energy Services, *GBW-30 Breaker MSDS*, Halliburton Energy Services, Duncan, Okla, USA, 2009.
- [49] A. Fakhru'l-Razi, A. Pendashteh, L. C. Abdullah, D. R. A. Biak, S. S. Madaeni, and Z. Z. Abidin, "Review of technologies for oil and gas produced water treatment," *Journal of Hazardous Materials*, vol. 170, no. 2-3, pp. 530–551, 2009.
- [50] J. P. Ray and F. Rainer Engelhardt, *Produced Water: Technological/Environmental Issues and Solutions*, vol. 46 of *Environmental Science Research*, Springer, New York, NY, USA, 1992.
- [51] R. A. Lebas, T. W. Shahan, P. Lord, and D. Luna, "Development and use of high-TDS recycled produced water for crosslinked-gel-based hydraulic fracturing," in *Proceedings of the SPE Hydraulic Fracturing Technology Conference*, SPE-163824-MS, Society of Petroleum Engineers, The Woodlands, Tex, USA, February 2013, <http://www.ftwatersolutions.com/pdfs/ProducedWaterPaper.pdf>.
- [52] U.S. Environmental Protection Agency, "Underground Injection Control Well Classes," 2002, <http://water.epa.gov/type/groundwater/uic/wells.cfm>.

- [53] B. R. Hansen and S. R. H. Davies, "Review of potential technologies for the removal of dissolved components from produced water," *Chemical Engineering Research and Design*, vol. 72, pp. 176–188, 1994.
- [54] D. Rahm, "Regulating hydraulic fracturing in shale gas plays: the case of Texas," *Energy Policy*, vol. 39, no. 5, pp. 2974–2981, 2011.
- [55] B. G. Rahm, J. T. Bates, L. R. Bertoia, A. E. Galford, D. A. Yoxheimer, and S. J. Riha, "Wastewater management and Marcellus Shale gas development: trends, drivers, and planning implications," *Journal of Environmental Management*, vol. 120, pp. 105–113, 2013.
- [56] FracFocus, "Hydraulic fracturing—the process," 2015, <https://fracfocus.org/hydraulic-fracturing-how-it-works/hydraulic-fracturing-process>.
- [57] PetroWiki, "Fracturing fluids and additives," 2015, http://petrowiki.org/Fracturing_fluids_and_additives.
- [58] R. D. Vidic, S. L. Brantley, J. M. Vandenbossche, D. Yoxheimer, and J. D. Abad, "Impact of shale gas development on regional water quality," *Science*, vol. 340, no. 6134, 2013.
- [59] S. A. Holditch, *Criteria for Propping Agent Selection*, Norton Company, Dallas, Tex, USA, 1979.
- [60] Saint-Gobain, Products, 2015, <http://www.proppants.saint-gobain.com/products>.
- [61] PetroWiki, "Propping agents and fracture conductivity," 2015, http://petrowiki.org/Propping_agents_and_fracture_conductivity.
- [62] C. Montgomery, "Fracturing fluid components," in *Effective and Sustainable Hydraulic Fracturing*, A. P. Bungler, J. McLennan, and R. Jeffrey, Eds., chapter 2, InTech, Vienna, Austria, 2013.
- [63] R. Hodge, "Crosslinked and Linear Gel Composition—Chemical and Analytical Methods," EPA's Study of Hydraulic Fracturing and Its Potential Impact on Drinking Water Resources, 2015, <http://www2.epa.gov/hfstudy/crosslinked-and-linear-gel-composition-chemical-and-analytical-methods>.
- [64] New York State Department of Environmental Conservation (NYS DEC), *Revised Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program, Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing in the Marcellus Shale and Other Low-Permeability Gas Reservoirs*, New York State Department of Environmental Conservation, Albany, NY, USA, 2011, <http://www.dec.ny.gov/energy/75370.html>.
- [65] ALL Consulting, *Ground Water Protection Council, Modern Shale Gas Development in the United States: A Primer*, U.S. Department of Energy, Office of Fossil Energy, Washington, DC, USA, 2009.
- [66] G. E. King, "Hydraulic fracturing 101: what every representative, environmentalist, regulator, reporter, investor, university researcher, neighbor and engineer should know about estimating frac risk and improving frac performance in unconventional gas and oil wells," in *Proceedings of the SPE Hydraulic Fracturing Technology Conference*, Society of Petroleum Engineers, The Woodlands, Tex, USA, February 2012.
- [67] URS Corporation, "Water-related issues associated with gas production in the Marcellus Shale: additives use, flowback quality and quantities, regulations, on-site treatment, green technologies, alternate water sources, water well-testing," Contract PO 10666, URS Corporation, Fort Washington, Pa, USA, 2011.
- [68] R. Barati and J.-T. Liang, "A review of fracturing fluid systems used for hydraulic fracturing of oil and gas wells," *Journal of Applied Polymer Science*, vol. 131, no. 16, Article ID 40735, 2014.
- [69] G. Zimmermann, G. Blöcher, A. Reinicke, and W. Brandt, "Rock specific hydraulic fracturing and matrix acidizing to enhance a geothermal system—concepts and field results," *Tectonophysics*, vol. 503, no. 1-2, pp. 146–154, 2011.
- [70] R. McCurdy, "High rate hydraulic fracturing additives in non-marcellus unconventional shale," in *Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods*, U.S. Environmental Protection Agency, Arlington, Va, USA, February 2011.
- [71] Akzo Nobel MPP Systems, *Macro-Porous Polymer Extraction for Offshore Produced Water Removes Dissolved and Dispersed Hydrocarbons*, Business Briefing: Exploration & Production: The Oil & Gas Review, Pasadena, Calif, USA, 2004.
- [72] A. Aminto and M. S. Olson, "Four-compartment partition model of hazardous components in hydraulic fracturing fluid additives," *Journal of Natural Gas Science and Engineering*, vol. 7, pp. 16–21, 2012.
- [73] A. A. Al-Zahrani, "Innovative method to mix corrosion inhibitor in emulsified acids," in *Proceedings of the 6th International Petroleum Technology Conference*, Beijing, China, March 2013.
- [74] A. Rostami and H. A. Nasr-El-Din, "Review and evaluation of corrosion inhibitors used in well stimulation," in *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Society of Petroleum Engineers, April 2009.
- [75] J. Yang, V. Jovancevic, S. Mancuso, and J. Mitchell, "High performance batch treating corrosion inhibitor," in *Proceedings of the Corrosion Conference & Expo*, NACE International, Nashville, Tenn, USA, March 2007.
- [76] M. McHugh, *The natural degradation of hydraulic fracturing fluids in the shallow subsurface [Ph.D. thesis]*, The Ohio State University, Columbus, Ohio, USA, 2015.
- [77] M. M. Brezinski, T. R. Gardner, W. M. Harms, J. L. Lane, and K. L. King, "Controlling iron in aqueous well fracturing fluids," US Patent, vol. 5, pp. 674, 817, Halliburton Energy Services, 1997.
- [78] K. C. Taylor, H. A. Nasr-El-Din, M. J. Al-Alawi, and S. Aramco, "Systematic study of iron control chemicals used during well stimulation," *Society of Petroleum Engineers Journal*, vol. 4, pp. 19–24, 1999.
- [79] International Energy Agency (IEA), *Water Management Associated with Hydraulic Fracturing, AP Guidance Document HF2*, International Energy Agency (IEA), Washington, DC, USA, 2010.
- [80] W. R. Dill and G. Fredette, "Iron control in the Appalachian basin," in *Proceedings of the SPE Eastern Regional Meeting*, Society of Petroleum Engineers, Pittsburgh, Pa, USA, November 1983.
- [81] Z. Zhou and D. H. S. Law, *Swelling Clays in Hydrocarbon Reservoirs: The Bad, the Less Bad, and the Useful*, Alberta Research Council, Alberta, Canada, 1998.
- [82] T. Strömngren, S. E. Sørström, L. Schou et al., "Acute toxic effects of produced water in relation to chemical composition and dispersion," *Marine Environmental Research*, vol. 40, no. 2, pp. 147–169, 1995.
- [83] E. T. Igunnu and G. Z. Chen, "Produced water treatment technologies," *International Journal of Low-Carbon Technologies*, vol. 9, no. 3, pp. 157–177, 2014.

- [84] R. R. Reynolds, "Produced water and associated issues: a manual for the independent operator," *Oklahoma Geological Survey Open-File Report*, vol. 6, pp. 1–56, 2003.
- [85] L.-H. Chan, A. Starinsky, and A. Katz, "The behavior of lithium and its isotopes in oilfield brines: evidence from the Heletz-Kokhav field, Israel," *Geochimica et Cosmochimica Acta*, vol. 66, no. 4, pp. 615–623, 2002.
- [86] T. Hayes and D. Arthur, "Overview of emerging produced water treatment technologies," in *Proceedings of the 11th Annual International Petroleum Environmental Conference*, Albuquerque, NM, USA, 2004.
- [87] T. Sirivedhin, J. McCue, and L. Dallbauman, "Reclaiming produced water for beneficial use: salt removal by electrodialysis," *Journal of Membrane Science*, vol. 243, no. 1-2, pp. 335–343, 2004.
- [88] C. M. Hudgins Jr., "Chemical use in North Sea oil and gas E&P," *Journal of Petroleum Technology*, vol. 46, no. 1, pp. 67–74, 1994.
- [89] M. E. Blauch, R. R. Myers, T. R. Moore, and B. A. Lipinski, "Marcellus Shale postfrac flowback waters—where is all the salt coming from and what are the implications?" in *Proceedings of the Society of Petroleum Engineers Eastern Regional Meeting*, SPE 125740, pp. 1–20, Charleston, SC, USA, 2009.
- [90] L. O. Haluszczak, A. W. Rose, and L. R. Kump, "Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA," *Applied Geochemistry*, vol. 28, pp. 55–61, 2013.
- [91] C. W. Poth, *Occurrence of Brine in Western Pennsylvania*, Pennsylvania Geological Survey, Report 47, 4th series, Mineral Resource, 1962.
- [92] P. E. Dresel, *The geochemistry of oilfield brines from western pennsylvania [M.S. thesis]*, Pennsylvania State University, 1985.
- [93] P. E. Dresel and A. W. Rose, "Chemistry and origin of oil and gas well brines in Western Pennsylvania," Pennsylvania Geological Survey, 4th Series, Open-File Report OFOG 10-01.0, 2010.
- [94] R. W. Roach, R. S. Carr, and C. L. Howard, *An Assessment of Produced Water Impacts at Two Sites in the Galveston Bay System*, United States Fish and Wildlife Service, Clear Lake Field Office, Houston, Tex, USA, 1993.
- [95] K. S. E. Al-Malahy and T. Hodgkiess, "Comparative studies of the seawater corrosion behaviour of a range of materials," *Desalination*, vol. 158, no. 1–3, pp. 35–42, 2003.
- [96] E. C. Chapman, R. C. Capo, B. W. Stewart et al., "Geochemical and strontium isotope characterization of produced waters from Marcellus shale natural gas extraction," *Environmental Science & Technology*, vol. 46, no. 6, pp. 3545–3553, 2012.
- [97] M. A. Cluff, *Microbial aspects of shale flowback fluids and response to hydraulic fracturing fluids [M.S. thesis]*, The Ohio State University, Columbus, Ohio, USA, 2013.
- [98] T. Hayes, "Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas," 2009, <http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCcommission-Report.pdf>.
- [99] T. I. R. Utvik, "Composition, characteristics of produced water in the North Sea," in *Proceedings of the Produced Water Workshop*, Aberdeen, UK, March 2003.
- [100] J. A. Veil, M. G. Puder, D. Elcock et al., *A White Paper Describing Produced Water from Production of Crude oil, Natural Gas, and Coal Bed Methane*, US. D.O.E, Argonne National Laboratory, 2004.
- [101] Nature Technology Group (NTG), *Introduction to Produced Water Treatment*, Nature Technology Solutions, 2005.
- [102] S. J. Maguire-Boyle and A. R. Barron, "Organic compounds in produced waters from shale gas wells," *Environmental Sciences: Processes and Impacts*, vol. 16, no. 10, pp. 2237–2248, 2014.
- [103] M. B. Adams, "Land application of hydrofracturing fluids damages a deciduous forest stand in West Virginia," *Journal of Environmental Quality*, vol. 40, no. 4, pp. 1340–1344, 2011.
- [104] U.S. Environmental Protection Agency, "Presidential green chemistry challenge award recipients 1996–2012," Tech. Rep. 744F12001, EPA, Washington, DC, USA, 2012.
- [105] D. J. Rozell and S. J. Reaven, "Water pollution risk associated with natural gas extraction from the Marcellus Shale," *Risk Analysis*, vol. 32, no. 8, pp. 1382–1393, 2012.
- [106] Reuters, "Update 2-Oil well in North Dakota out of control, leaking," 2014, <http://www.reuters.com/article/2014/02/14/energy-crude-blowout-idUSL2N0LJ15820140214>.
- [107] A. Dalrymple, "ND well blowout leaks 23,000 gallons of oil, but company says minimal damage," InForum, 2015, <http://www.eeia.myindustrytracker.com/en/article/73089/nd-well-blowout-leaks-23-000-gallons-of-oil-but-company-says-minimal-damage>.
- [108] M. Grossi, "Fracking probe extends in Central Valley," Fresno Bee, November 2013.
- [109] K. Bullis, "One Way to Solve Fracking's Dirty Problem," MIT Technology Review, 2013.
- [110] J. Healy, "After the floods in Colorado, a deluge of worry about leaking oil," *The New York Times*, 2013.
- [111] D. W. Nelson, S. L. Liu, and L. E. Somers, "Extractability and plant uptake of trace elements from drilling fluids," *Journal of Environmental Quality*, vol. 13, no. 4, pp. 562–566, 1983.
- [112] R. W. Miller, S. Honarvar, and B. Hunsaker, "Effects of drilling fluids on soils and plants. I. Individual fluid components," *Journal of Environmental Quality*, vol. 9, no. 4, pp. 547–552, 1980.
- [113] R. W. Miller and P. Pesaran, "Effects of drilling fluids on soils and plants: II. Complete drilling fluid mixtures," *Journal of Environmental Quality*, vol. 9, no. 4, pp. 552–556, 1980.
- [114] Toxnet, "Ethylene glycol," National Library of Medicine, Toxicology Data Network, 2015, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+5012>.
- [115] M. McLaughlin, "Fate of hydraulic fracturing chemicals in agricultural topsoil," in *Proceedings of the American Chemical Society National Meeting*, Denver, Colo, USA, March 2015, <http://presentations.acs.org/common/presentation-detail.aspx/Spring2015/ENVR/ENVR021a/2139634>.
- [116] Q. Wen, Z. Chen, Y. Zhao, H. Zhang, and Y. Feng, "Biodegradation of polyacrylamide by bacteria isolated from activated sludge and oil-contaminated soil," *Journal of Hazardous Materials*, vol. 175, no. 1–3, pp. 955–959, 2010.
- [117] L. L. Liu, Z. P. Wang, K. F. Lin, and W. M. Cai, "Microbial degradation of polyacrylamide by aerobic granules," *Environmental Technology*, vol. 33, no. 9, pp. 1049–1054, 2012.
- [118] M. T. Bao, Q. G. Chen, Y. M. Li, and G. C. Jiang, "Biodegradation of partially hydrolyzed polyacrylamide by bacteria isolated from production water after polymer flooding in an oil field," *Journal of Hazardous Materials*, vol. 184, no. 1–3, pp. 105–110, 2010.
- [119] N. C. Brady and R. R. Weil, *The Nature and Properties of Soils*, Prentice-Hall, New York, NY, USA, 14th edition, 2007.
- [120] M. C. Steele and J. Pichtel, "Ex-situ remediation of a metal-contaminated Superfund soil using selective extractants," *Journal of Environmental Engineering*, vol. 124, no. 7, pp. 639–645, 1998.

- [121] A. J. Francis, "Effects of acidic precipitation and acidity on soil microbial processes," *Water, Air, and Soil Pollution*, vol. 18, no. 1–3, pp. 375–394, 1982.
- [122] U. Tezel, *Fate and effect of quaternary ammonium compounds in biological systems [Ph.D. thesis]*, Georgia Institute of Technology, Atlanta, Ga, USA, 2009.
- [123] G.-G. Ying, "Fate, behavior and effects of surfactants and their degradation products in the environment," *Environment International*, vol. 32, no. 3, pp. 417–431, 2006.
- [124] C. Hansch, A. Leo, and D. H. Hoekman, *Exploring QSAR*, American Chemical Society (ACS), Washington, DC, USA, 1995.
- [125] N. Kreuzinger, M. Fuerhacker, S. Scharf, M. Uhl, O. Gans, and B. Grillitsch, "Methodological approach towards the environmental significance of uncharacterized substances—quaternary ammonium compounds as an example," *Desalination*, vol. 215, no. 1–3, pp. 209–222, 2007.
- [126] C. A. M. Bondi, "Applying the precautionary principle to consumer household cleaning product development," *Journal of Cleaner Production*, vol. 19, no. 5, pp. 429–437, 2011.
- [127] M. T. García, I. Ribosa, T. Guindulain, J. Sánchez-Leal, and J. Vives-Rego, "Fate and effect of monoalkyl quaternary ammonium surfactants in the aquatic environment," *Environmental Pollution*, vol. 111, no. 1, pp. 169–175, 2001.
- [128] C. G. van Ginkel, J. B. van Dijk, and A. G. M. Kroon, "Metabolism of hexadecyltrimethylammonium chloride in *Pseudomonas* Strain-B1," *Applied and Environmental Microbiology*, vol. 58, no. 9, pp. 3083–3087, 1992.
- [129] R. S. Boethling, "Environmental aspects of cationic surfactants," in *Cationic Surfactants: Analytical and Biological Evaluation*, J. Cross and E. J. Singer, Eds., vol. 53, Marcel Dekker, New York, NY, USA, 1994.
- [130] T. Nishihara, T. Okamoto, and N. Nishiyama, "Biodegradation of didecyltrimethylammonium chloride by *Pseudomonas fluorescens* TN4 isolated from activated sludge," *Journal of Applied Microbiology*, vol. 88, no. 4, pp. 641–647, 2000.
- [131] M. A. Patrauchan and P. J. Oriol, "Degradation of benzyl-dimethylalkylammonium chloride by *Aeromonas hydrophila* sp," *Applied Microbiology*, vol. 94, pp. 266–272, 2003.
- [132] S. Takenaka, T. Tonoki, K. Taira, S. Murakami, and K. Aoki, "Adaptation of *Pseudomonas* sp. strain 7-6 to quaternary ammonium compounds and their degradation via dual pathways," *Applied and Environmental Microbiology*, vol. 73, no. 6, pp. 1799–1802, 2007.
- [133] D. McIlwaine, "Challenging traditional biodegradation tests: the biodegradation of glutaraldehyde," 2002, <http://ipec.utulsa.edu/Conf2002/mcilwaine.136.pdf>.
- [134] L. Laopaiboon, N. Phuoketphim, K. Vichitphan, and P. Laopaiboon, "Biodegradation of an aldehyde biocide in rotating biological contactors," *World Journal of Microbiology and Biotechnology*, vol. 24, no. 9, pp. 1633–1641, 2008.
- [135] Toxnet, "Tetrakis(hydroxymethyl) phosphonium sulfate," National Library of Medicine, Toxicology Data Network, 2015, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+4215>.
- [136] A. N. Shamim, *Scoping Document: Product Chemistry/Environmental Fate/Ecotoxicity of: Tetrakis (Hydroxymethyl) Phosphonium Sulfate*, U.S. Environmental Protection Agency (U.S. EPA), Washington, DC, USA, 2011.
- [137] S. Groome, "Tetrakis (hydroxymethyl) phosphonium sulfate THPS," Chemistry Document EPA-HQ-OPP-2011-0067, U.S. Environmental Protection Agency, Washington, DC, USA, 2011.
- [138] W. J. Lyman, *Environmental Exposure from Chemicals*, vol. 1, Edited by W. B. Neely and G. E. Blau, CRC Press, Boca Raton, Fla, USA, 1985.
- [139] J. H. Exner, G. A. Burk, and D. Kyriacou, "Rates and products of decomposition of 2,2-dibromo-3-nitropropionamide," *Journal of Agricultural and Food Chemistry*, vol. 21, no. 5, pp. 838–846, 1973.
- [140] Wisner, "Propargyl Alcohol," 2015, <http://webwisner.nlm.nih.gov/WebWISER/pda/getSubstanceData.do?jsessionid=E0B34CF5-6185EB60A4EA84DB4E4A255A?substanceId=146&menuItemID=76&identifier=Propargyl+Alcohol&identifierType=Name>.
- [141] United States Environmental Protection Agency, "Environmental Impact and Benefit Assessment for the Final Effluent Limitation Guidelines and Standards for the Airport Deicing Category," 2006, <http://water.epa.gov/scitech/wastetech/guide/airport/upload/Environmental-Impact-and-Benefit-Assessment-for-the-Final-Effluent-Limitation-Guidelines-and-Standards-for-the-Airport-Deicing-Category.pdf>.
- [142] World Health Organization (WHO), "Thiourea," Concise International Chemical Assessment Document 49, 2003, <http://www.who.int/ipcs/publications/cicad/en/cicad49.pdf>.
- [143] Chemicals Inspection Testing Institute (CITI), *Biodegradation and Bioaccumulation Data of Existing Chemicals based on the CSCL Japan*, Japan Chemical Industry Ecology—Toxicology and Information Center, Saitama, Japan, 1992.
- [144] Toxnet, "Mercaptoacetic acid," National Library of Medicine, Toxicology Data Network, 2015, <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+2702>.
- [145] R. J. Lewis Sr., Ed., *Sax's Dangerous Properties of Industrial Materials*, Wiley-Interscience, John Wiley & Sons, Hoboken, NJ, USA, 11th edition, 2004.
- [146] Toxnet, "Hazardous Substance Data Bank (HSDB)," National Library of Medicine, Toxicology Data Network, 2015, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.
- [147] European Chemicals Agency (ECHA) and International Uniform Chemical Information Database (IUCLID), *CD-ROM Year 2000 Edition*, European Chemicals Agency (ECHA), Helsinki, Finland, 2000.
- [148] P. Shrivastava and R. Kumar, "Soil salinity: a serious environmental issue and plant growth promoting bacteria as one of the tools for its alleviation," *Saudi Journal of Biological Sciences*, vol. 22, no. 2, pp. 123–131, 2015.
- [149] M. Ashraf, "Some important physiological selection criteria for salt tolerance in plants," *Flora*, vol. 199, no. 5, pp. 361–376, 2004.
- [150] A. Bano and M. Fatima, "Salt tolerance in *Zea mays* (L). following inoculation with *Rhizobium* and *Pseudomonas*," *Biology and Fertility of Soils*, vol. 45, no. 4, pp. 405–413, 2009.
- [151] R. Munns, "Comparative physiology of salt and water stress," *Plant, Cell and Environment*, vol. 25, no. 2, pp. 239–250, 2002.
- [152] R. Munns and R. A. James, "Screening methods for salinity tolerance: a case study with tetraploid wheat," *Plant and Soil*, vol. 253, no. 1, pp. 201–218, 2003.
- [153] M. Tester and R. Davenport, "Na⁺ tolerance and Na⁺ transport in higher plants," *Annals of Botany*, vol. 91, no. 5, pp. 503–527, 2003.
- [154] S. Tabur and K. Demir, "Role of some growth regulators on cytogenetic activity of barley under salt stress," *Plant Growth Regulation*, vol. 60, no. 2, pp. 99–104, 2010.
- [155] M. G. Javid, A. Sorooshzadeh, F. Moradi, S. A. M. M. Sanavy, and I. Allahdadi, "The role of phytohormones in alleviating salt stress in crop plants," *Australian Journal of Crop Science*, vol. 5, no. 6, pp. 726–734, 2011.

- [156] T. K. Frost, S. Johnsen, and T. I. Utvik, *Environmental Effects of Produced Water Discharges to the Marine Environment*, OLF, Norway, 1998, <http://www.olf.no/static/en/rapporter/producedwater/summary.html>.
- [157] D. C. Wolf, K. R. Brye, and E. E. Gbur, "Using soil amendments to increase Bermuda grass growth in soil contaminated with hydraulic fracturing drilling fluid," *Soil and Sediment Contamination*, vol. 24, no. 8, pp. 846–864, 2015.
- [158] M. Ahmad, S. Soo Lee, J. E. Yang, H.-M. Ro, Y. Han Lee, and Y. Sik Ok, "Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil," *Ecotoxicology and Environmental Safety*, vol. 79, pp. 225–231, 2012.
- [159] D. Lloyd, "Drilling waste disposal in Alberta," in *Proceedings of the National Conference on Disposal of Drilling Wastes, Environmental and Ground Water Institute*, Norman, Okla, USA, May 1985.
- [160] D. Anderson, "Effective saltwater remediation," NDPC Brine Task Force, Oasis Petroleum, 2015, <https://www.ndoil.org/image/cache/AndersonDustin.pdf>.
- [161] E. de Jong, *The Final Report of a Study Conducted on the Reclamation of Brine and Emulsion Spills in the Cultivated Area of Saskatchewan*, Saskatchewan Department of Mineral Resources and the Canadian Petroleum Association, Saskatchewan Division, Saskatchewan, Canada, 1979.
- [162] M. E. Sumner, "Sodic soils: new perspectives," *Australian Journal of Soil Research*, vol. 31, no. 6, pp. 683–750, 1993.
- [163] J. Sharma, A. V. Ogram, and A. Al-Agely, *Mycorrhizae: Implications for Environmental Remediation and Resource Conservation*, IFAS Extension ENH-1086, University of Florida, Gainesville, Fla, USA, 2015, <http://ufdcimages.uflib.ufl.edu/IR/00/00/17/79/00001/EP35100.pdf>.
- [164] J. Pichtel, *Fundamentals of Site Remediation for Metal- and Hydrocarbon-Contaminated Soils*, Government Institutes, Rockville, Md, USA, 2nd edition, 2007.
- [165] Energy & Environmental Research Center (EERC), "Spills Cleanup Primer," BakkenSmart, 2015, <http://www.northdakotaoilcan.com/home-menu/news-info/resources/spills-cleanup-primer/>.
- [166] M. Farhadian, C. Vachelard, D. Duchez, and C. Larroche, "In situ bioremediation of monoaromatic pollutants in groundwater: a review," *Bioresource Technology*, vol. 99, no. 13, pp. 5296–5308, 2008.
- [167] I. V. Robles-González, F. Fava, and H. M. Poggi-Varaldo, "A review on slurry bioreactors for bioremediation of soils and sediments," *Microbial Cell Factories*, vol. 7, article 5, 2008.
- [168] M. E. Fuller, J. Kruczek, R. L. Schuster, P. L. Sheehan, and P. M. Arienti, "Bioslurry treatment for soils contaminated with very high concentrations of 2,4,6-trinitrophenylmethylnitramine (tetryl)," *Journal of Hazardous Materials*, vol. 100, no. 1–3, pp. 245–257, 2003.
- [169] D. Dean-Ross, "Biodegradation of selected PAH from sediment in bioslurry reactors," *Bulletin of Environmental Contamination and Toxicology*, vol. 74, no. 1, pp. 32–39, 2005.
- [170] O. Ward, A. Singh, and J. Van Hamme, "Accelerated biodegradation of petroleum hydrocarbon waste," *Journal of Industrial Microbiology and Biotechnology*, vol. 30, no. 5, pp. 260–270, 2003.
- [171] C. N. Mulligan, R. N. Yong, and B. F. Gibbs, "Remediation technologies for metal-contaminated soils and groundwater: an evaluation," *Engineering Geology*, vol. 60, no. 1–4, pp. 193–207, 2001.
- [172] S. A. Wasay, S. Barrington, and S. Tokunaga, "Organic acids for the in situ remediation of soils polluted by heavy metals: soil flushing in columns," *Water, Air, and Soil Pollution*, vol. 127, no. 1–4, pp. 301–314, 2001.
- [173] M. N. V. Prasad, "Phytoremediation of metals in the environment for sustainable development," *Proceedings of the National Academy of Sciences, India Section B: Biological Sciences*, vol. 70, no. 1, pp. 71–98, 2004.
- [174] I. Alkorta, J. Hernández-Allica, J. M. Becerril, I. Amezaga, I. Albizu, and C. Garbisu, "Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead, and arsenic," *Reviews in Environmental Science and Biotechnology*, vol. 3, no. 1, pp. 71–90, 2004.
- [175] C. Garbisu, J. Hernández-Allica, O. Barrutia, I. Alkorta, and J. M. Becerril, "Phytoremediation: a technology using green plants to remove contaminants from polluted areas," *Reviews on Environmental Health*, vol. 17, no. 3, pp. 173–188, 2002.
- [176] M. N. V. Prasad, "Phytoremediation of metals and radionuclides in the environment: the case for natural hyperaccumulators, metal transporters, soil-amending chelators and transgenic plants," in *Heavy Metal Stress in Plants*, M. N. V. Prasad, Ed., chapter 14, pp. 345–391, Springer, Berlin, Germany, 1999.
- [177] U.S. Department of Energy, *A Guide to Practical Management of Produced Water from Onshore Oil and Gas Operations in the United States*, Interstate Oil and Gas Compact Commission and ALL Consulting, 2006, <http://www.all-llc.com/publicdownloads/ALL-PWGGuide.pdf>.
- [178] National Petroleum Council (NPC), "Management of Produced Water from Oil and Gas Wells, Paper #2–17," NPC North American Resource Development Study, 2011, https://www.npc.org/Prudent_Development-Topic_Papers/2-17_Management_of_Produced_Water_Paper.pdf.
- [179] GRI, "Technology assessment and economic evaluation of downhole gas/water separation and disposal tools," Tech. Rep. GRI-99/0218, Radian Corporation for the Gas Research Institute, Des Plaines, Ill, USA, 1999.
- [180] E. I. Shirman and A. K. Wojtanowicz, "More oil using downhole water-sink technology: a feasibility study," SPE 66532, SPE Production and Facilities, 2002.
- [181] A. K. Wojtanowicz, E. I. Shirman, and H. Kurban, "Downhole Water Sink (DWS) completions enhance oil recovery in reservoirs with water coning problem," in *Proceedings of the SPE Annual Technical Conference and Exhibition*, SPE 56721, Houston, Tex, USA, October 1999.
- [182] M. Swisher, "Summary of DWS application in Northern Louisiana," in *Proceedings of the Downhole Water Separation Technology Workshop*, Baton Rouge, La, USA, March 2000.
- [183] A. K. Wojtanowicz, "Smart dual completions for downhole water control in oil and gas wells," in *Proceedings of the Produced Water Management Workshop*, Houston, Tex, USA, April 2003.
- [184] L. Shariq, "Uncertainties associated with the reuse of treated hydraulic fracturing wastewater for crop irrigation," *Environmental Science and Technology*, vol. 47, no. 6, pp. 2435–2436, 2013.
- [185] J. D. Arthur, B. G. Langhus, and C. Patel, *Technical Summary of Oil & Gas Produced Water Treatment Technologies*, NETL, Tulsa, Okla, USA, 2005.
- [186] U.S. Environmental Protection Agency, "Design, construction, and operation of hazardous and nonhazardous waste surface impoundments," Tech. Rep. EPA/530/SW-91/054a, EPA, Cincinnati, Ohio, USA, 1991.

- [187] V. Velmurugan and K. Srithar, "Prospects and scopes of solar pond: a detailed review," *Renewable & Sustainable Energy Reviews*, vol. 12, no. 8, pp. 2253–2263, 2008.
- [188] ALL Consulting, *Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives*, ALL Consulting, Tulsa, Okla, USA, 2003.
- [189] Colorado School of Mines, "Technical assessment of produced water treatment technologies. An integrated framework for treatment and management of produced water," RPSEA Project 07122-12, Golden, Colo, USA, 2009.
- [190] Agricultural Water Clearing House (AWCH), *FAQ—Water Supply, Sources, & Agricultural Use*, 2015, http://www.agwaterconservation.colostate.edu/FAQs_WaterSupplySourcesAgriculturalUse.aspx#A1.
- [191] A. Horpestad, D. Skaar, and H. Dawson, "Water quality impacts from CBM development in the powder river basin, Wyoming and Montana," Water Quality Technical Report, 2001.
- [192] D. B. Burnett and J. A. Veil, "Decision and risk analysis study of the injection of desalination by-products into oil-and gas-producing zones," in *Proceedings of the SPE International Symposium and Exhibition on Formation Damage Control*, SPE-86526-MS, Lafayette, La, USA, February 2004.
- [193] The Ground Water Protection Council, "Making water produced during oil and gas operations a managed resource for beneficial uses," in *Proceedings of the Ground Water Protection Council Produced Water Conference*, Colorado Springs, Colo, USA, October 2002, <http://www.gwpc.org/sites/default/files/events/Agenda.pdf>.
- [194] International Association of Oil and Gas Producers, "Guidelines for produced water injection," Report 2.80/302, 2002, <http://www.ogp.org.uk/pubs/302.pdf>.
- [195] J. Cart, "Central Valley's growing concern: crops raised with oil field water," *Los Angeles Times*, 2014, <http://www.latimes.com/local/california/la-me-drought-oil-water-20150503-story.html#page=1>.
- [196] Wyoming Department of Environmental Quality, UIC Program, 2015, <http://deq.wyoming.gov/wqd/underground-injection-control/>.
- [197] A. J. DeJoia, "Developing sustainable practices for CBM-produced water irrigation," in *Proceedings of the Ground Water Protection Council Produced Water Conference*, Colorado Springs, Colo, USA, October 2002, <http://www.gwpc.org/sites/default/files/events/Agenda.pdf>.
- [198] R. J. Paetz and S. Maloney, "Demonstrated economics of managed irrigation for CBM produced water," in *Proceedings of the Ground Water Protection Council Produced Water Conference*, Colorado Springs, Colo, USA, October 2002, <http://www.gwpc.org/sites/default/files/events/Agenda.pdf>.
- [199] C. R. Bern, G. N. Breit, R. W. Healy, J. W. Zupancic, and R. Hammack, "Deep subsurface drip irrigation using coal-bed sodic water: part I. Water and solute movement," *Agricultural Water Management*, vol. 118, pp. 122–134, 2013.
- [200] R. Chhabra, *Soil Salinity and Water Quality*, Balkema, Rotterdam, Netherlands, 1996.
- [201] L. Jackson and J. Myers, "Alternative use of produced water in aquaculture and hydroponic systems at naval petroleum reserve no. 3," in *Proceedings of the Ground Water Protection Council Produced Water Conference*, Colorado Springs, Colo, USA, October 2002, <http://www.gwpc.org/sites/default/files/events/Agenda.pdf>.
- [202] P. F. Cooper, G. F. Job, M. B. Green, and R. B. E. Shutes, *Reed Beds and Constructed Wetlands for Wastewater Treatment*, Water Research Centre Publications, Swindon, UK, 1996.
- [203] J. R. Kuipers, "Technology-based effluent limitations for coalbed methane produced wastewater discharges in the Powder River basin of Montana and Wyoming," Draft Report, Northern Plains Resource Council, Billings, Mont, USA, 2004.
- [204] F. Sanders, S. Gustin, and P. Pucel, *Natural Treatment of CBM Produced Water: Field Observations*, CBM Associates, 2001.
- [205] J. Bauder, *The Role and Potential of Use Selected Plants, Plant Communities, Artificial, Constructed, and Natural Wetlands in Mitigation of Impaired Water for Riparian Zone Remediation*, Montana State University, Water Quality & Irrigation Management, Bozeman, Mont, USA, 2002.
- [206] K. E. Lynch, "Agency collection activities: coalbed methane extraction sector survey," Survey Docket ID No. EPA-HQ-OW-2006-0771, Trout Unlimited to EPA Docket Center, 2008.
- [207] D. W. Erskine, P. W. Bergman, and D. L. Wacker, "Use of produced water for oil and gas drilling in the San Juan Basin," in *Proceedings of the 9th Annual Petroleum Environmental Conference*, Albuquerque, NM, USA, October 2002.
- [208] A. J. Daniel, B. G. Langhus, and C. Patel, *Technical Summary of Oil & Gas Produced Water Treatment Technologies*, NETL, 2005.
- [209] P. Xu and J. E. Drewes, "Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use of methane produced water," *Separation and Purification Technology*, vol. 52, no. 1, pp. 67–76, 2006.
- [210] S. S. Madaeni, "The application of membrane technology for water disinfection," *Water Research*, vol. 33, no. 2, pp. 301–308, 1999.
- [211] R. Han, S. Zhang, D. Xing, and X. Jian, "Desalination of dye utilizing copoly(phthalazinone biphenyl ether sulfone) ultrafiltration membrane with low molecular weight cut-off," *Journal of Membrane Science*, vol. 358, no. 1–2, pp. 1–6, 2010.
- [212] Y. He and Z. W. Jiang, "Technology review: treating oilfield wastewater," *Filtration & Separation*, vol. 45, no. 5, pp. 14–16, 2008.
- [213] T. Bilstad and E. Espedal, "Membrane separation of produced water," *Water Science and Technology*, vol. 34, no. 9, pp. 239–246, 1996.
- [214] S. Judd and B. Jefferson, *Membranes for Industrial Wastewater Recovery and Re-Use Oxford*, Elsevier, Philadelphia, Pa, USA, 2013.
- [215] C. Bellona and J. E. Drewes, *Reuse of Produced Water Using Nanofiltration and Ultra-Low Pressure Reverse Osmosis to Meet Future Water Demands*, Ground Water Protection Council, Oklahoma City, Okla, USA, 2015, http://www.gwpc.org/sites/default/files/event-sessions/Jorge_Drewes_PWC2002_0.pdf.
- [216] S. Mondal and S. R. Wickramasinghe, "Produced water treatment by nanofiltration and reverse osmosis membranes," *Journal of Membrane Science*, vol. 322, no. 1, pp. 162–170, 2008.
- [217] R. S. Faibish and Y. Cohen, "Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water emulsions and microemulsions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 191, no. 1–2, pp. 27–40, 2001.
- [218] R. S. Faibish and Y. Cohen, "Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions," *Journal of Membrane Science*, vol. 185, no. 2, pp. 129–143, 2001.

- [219] K. Konieczny, M. Bodzek, and M. Rajca, "A coagulation-MF system for water treatment using ceramic membranes," *Desalination*, vol. 198, no. 1-3, pp. 92-101, 2006.
- [220] J. Boysen, "The freeze-thaw/evaporation (FTE) process for produced water treatment, disposal and beneficial uses," in *Proceedings of the 14th Annual International Petroleum Environmental Conference*, Houston, Tex, USA, 2007.
- [221] M. Ebrahimi, D. Willershausen, K. S. Ashaghi et al., "Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment," K-State Research Exchange, 2015, <http://krex.k-state.edu/dspace/bitstream/handle/2097/3520/EbrahimiDesalination2010.pdf?sequence=1>.
- [222] A. Lobo, Á. Cambiella, J. M. Benito, C. Pazos, and J. Coca, "Ultrafiltration of oil-in-water emulsions with ceramic membranes: influence of pH and crossflow velocity," *Journal of Membrane Science*, vol. 278, no. 1-2, pp. 328-334, 2006.
- [223] G. Gutiérrez, A. Lobo, D. Allende et al., "Influence of coagulant salt addition on the treatment of oil-in-water emulsions by centrifugation, ultrafiltration, and vacuum evaporation," *Separation Science and Technology*, vol. 43, no. 7, pp. 1884-1895, 2008.
- [224] K. S. Spiegler and O. Kedem, "Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes," *Desalination*, vol. 1, no. 4, pp. 311-326, 1966.
- [225] W. Mark, *The Guidebook to Membrane Desalination Technology: Reverse Osmosis, Nanofiltration and Hybrid Systems Process, Design, Applications and Economic*, L'Aquila Desalination Publications, 1st edition, 2007.
- [226] B. Nicolaisen and L. Lien, "Treating oil and gas produced water using membrane filtration technology," in *Proceedings of the Produced Water Workshop*, Aberdeen, UK, 2003.
- [227] F. T. Tao, S. Curtice, R. D. Hobbs et al., "Conversion of oilfield produced water into an irrigation/drinking quality water," in *Proceedings of the SPE/EPA Exploration and Production Environmental Conference*, SPE-26003-MS, San Antonio, Tex, USA, March 1993.
- [228] US Environmental Protection Agency, *Onsite Wastewater Treatment and Disposal Systems Design Manual*, US Environmental Protection Agency, Washington, DC, USA, 1980.
- [229] D. Su, J. Wang, K. Liu, and D. Zhou, "Kinetic performance of oil-field produced water treatment by biological aerated filter," *Chinese Journal of Chemical Engineering*, vol. 15, no. 4, pp. 591-594, 2007.
- [230] H. L. Ball, "Nitrogen reduction in an on-site trickling filter/upflow filters wastewater treatment system," in *Proceedings of the 7th International Symposium on Individual and Small Community Sewage Systems*, American Society of Agricultural Engineers, Atlanta, Ga, USA, December 1994.
- [231] W. Shi and M. M. Benjamin, "Membrane interactions with NOM and an adsorbent in a vibratory shear enhanced filtration process (VSEP) system," *Journal of Membrane Science*, vol. 312, no. 1-2, pp. 23-33, 2008.
- [232] A. I. Zouboulis and M. D. Petala, "Performance of VSEP vibratory membrane filtration system during the treatment of landfill leachates," *Desalination*, vol. 222, no. 1-3, pp. 165-175, 2008.
- [233] V. Piemonte, M. Prisciandaro, L. di Paola, and D. Barba, "Membrane processes for the treatment of produced waters," *Chemical Engineering Transactions*, vol. 43, 2015.
- [234] O. A. Hamed, "Evolutionary developments of thermal desalination plants in the Arab gulf region," in *Proceedings of the Beirut Conference*, Beirut, Lebanon, June 2004, http://www.researchgate.net/publication/228945604_Evolutionary_developments_of_thermal_desalination_plants_in_the_Arab_Gulf_region.
- [235] United States Bureau of Reclamation, *Desalting Handbook for Planners*, Desalination and Water Purification Research and Development Program Report no. 72, United States Department of the Interior, Bureau of Reclamation, Washington, DC, USA, 3rd edition, 2003.
- [236] GWI, IDA Worldwide Desalting Plants Inventory Report no. 19 (Global water intelligence) Gnarrenburg, Germany, 2006.
- [237] A. D. Khawaji, I. K. Kutubkhanah, and J.-M. Wie, "Advances in seawater desalination technologies," *Desalination*, vol. 221, no. 1-3, pp. 47-69, 2008.
- [238] B. Heins, *World's First SAGB Facility Using Evaporators, Drum Boilers, and Zero Discharge Crystallizers to Treat Produced Water*, Efficiency and Innovation Forum for Oil Patch, Calgary, Canada, 2005.
- [239] J. Brandt, *Business is Booming for Fracking Wastewater*, Fierce Water, 2015.
- [240] J. E. Boysen, J. A. Harju, B. Shaw et al., "The current status of commercial deployment of the freeze thaw evaporation treatment of produced water," in *Proceedings of the SPE/EPA Exploration and Production Environmental Conference*, SPE-52700-MS, pp. 1-3, Austin, Tex, USA, March 1999.
- [241] AltelaRain™ System ARS-4000, *New Patented Technology for Cleaning Produced Water On-Site*, Altela Information, 2007.
- [242] N. A. Godshall, "AltelaRainSM produced water treatment technology: making water from waste," in *Proceedings of the International Petroleum Environmental Conference (IPEC '06)*, pp. 1-9, ALTELATM, San Antonio, Tex, USA, October 2006.
- [243] Jain Irrigation Systems, *Sand Separator—Jain Hydro Cyclone Filter*, Jain Irrigation Systems, Jalgaon, India, 2010.
- [244] A. L. Cassidy, "Advances in flotation unit design for produced water treatment," in *Proceedings of the Production Operations Symposium*, SPE-25472-MS, pp. 21-23, Oklahoma City, Okla, USA, March 1993.
- [245] M. Çakmakce, N. Kayaalp, and I. Koyuncu, "Desalination of produced water from oil production fields by membrane processes," *Desalination*, vol. 222, no. 1-3, pp. 176-186, 2008.
- [246] F. R. Spellman, *Handbook of Water and Wastewater Treatment Plant Operations*, CRC Press, Boca Raton, Fla, USA, 2003.
- [247] D. A. Clifford, "Ion exchange and inorganic adsorption," in *Water Quality and Treatment*, R. D. Letterman, Ed., McGraw-Hill, New York, NY, USA, 1999.
- [248] D. T. Meijer and C. Madin, "Removal of dissolved and dispersed hydrocarbons from oil and gas produced water with mppe technology to reduce toxicity and allow water reuse," *APPEA Journal*, pp. 1-11, 2010.
- [249] H. M. Pars and D. T. Meijer, "Removal of dissolved hydrocarbons from production water by macro porous polymer extraction (MPPE)," in *Proceedings of the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production*, SPE-46577-MS, Society of Petroleum Engineers, Caracas, Venezuela, June 1998.

Research Article

A Rationale for Pollutograph Evaluation in Ungauged Areas, Using Daily Rainfall Patterns: Case Studies of the Apulian Region in Southern Italy

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In the context of the implementation of sustainable water treatment technologies for soil pollution prevention, a methodology that try to overcome the lack of runoff quality data in Puglia (Southern Italy) is firstly tackled in this paper. It provides a tool to obtain total suspended solid (TSS) pollutographs in areas without availability of monitoring campaigns. The proposed procedure is based on the relationship between rainfall characteristics and pollutant wash-off. In particular, starting from the evaluation of the observed regional rainfall patterns by using a rainfall generator model, the storm water management model (SWMM) was applied on five case studies located in different climatic subareas. The quantity SWMM parameters were evaluated starting from the drainage network and catchments characteristics, while the quality parameters were obtained from results of a monitoring campaign conducted for quality model calibration and validation with reference to the pollutograph's shape and the peak-time. The research yields a procedure useful to evaluate the first flush phenomenon in ungauged sites and, in particular, it provides interesting information for designing efficient and sustainable drainage systems for first flush treatment and diffuse pollution treatment.

1. Introduction

The concentration of human population near cities has increased markedly in recent years all over the world. The improvements in transportation, the expansion of manufacturing industries, and increased employment opportunities have resulted in increased density of population in cities. Due to this process, known as urbanization, the natural characteristics of the land are changed by various anthropogenic activities common to urban areas. These anthropogenic activities are among the most important pollutant sources [1]. Thus, numerous pollutants are introduced into the urban environment by vehicular traffic, industrial processes, building construction, and commercial activities, which are carried by stormwater. It is not surprising that the characterization of quality of stormwater that washes away impervious surfaces

is assuming growing importance in the last few years [2–4]. The impact of the mentioned above activities on the water environment includes increased risks in terms of floods, erosion and degradation of stream habitats, and deterioration of water quality [5, 6].

Moreover it is worth mentioning that there is a very strong correlation between stormwater quality and soil contamination for both anthropized and natural areas. In natural areas a significant fraction of precipitation infiltrates into the soil, usually covered by forest, woods, or grass. This water infiltrates as it travels underground, allowing the increasing of soil contamination and the alteration of the natural porosity of the soil. In the anthropized area, stormwater runoff increases in both rate and volume due to increases of impervious area and soil compaction; this development dramatically alters the hydrologic cycle by changing

the relative percentage of precipitation that contributes to groundwater recharge, evapotranspiration, and runoff by adding impervious surfaces.

Starting from the seventies, several studies, based on monitoring campaigns, have been carried out in order to evaluate the characterization of the quality of stormwater runoff of urbanized areas and to analyze the buildup/wash-off and transport phenomena of pollutants during wet periods in both separate and combined sewer systems [7–15]. Nowadays, the quality data collected during monitoring campaigns represent an important dataset; nevertheless the featured Apulian urban landscapes, characterized by peculiar socioeconomic, climatic, and geological conditions, require further experimental assessments [16].

Measurements and monitoring campaigns are useful to provide important information necessary to define models and to enhance design procedures for improving the efficiency of systems for water treatment. In this context, it is necessary to ensure high cooperation between measurements and modeling, which significantly affects an overall success of the whole work. Regarding the equipment used for the monitoring campaign, it is important to select measurement devices with a high degree of reliability and also to put emphasis on the interfacing of the adopted equipment (according to the operation and maintenance). Moreover, in order to be able to handle such amount of data, it is necessary to have relevant and capable software tools for data processing. Finally, it is necessary to mention that the efficiency and success of the monitoring activities depend on the planning and the organization of each measurement campaign. On the base of these considerations, monitoring campaigns are very expensive and conspicuous; therefore, a functional database of runoff quality is quite difficult to collect, especially in areas where the monitoring network is characterized by lack of discharge gauged stations and low frequency of precipitation.

In the context of stormwater treatment design, another important topic highlighted in recent literature is the need of deeper understanding of the relationship between pollutant wash-off processes and rainfall characteristics [17, 18]. Past research studies commonly consider rainfall characteristics included in lumped parameters in numerical models used for investigating the role of rainfall characteristics on pollutant wash-off [17, 19–21].

Based on these considerations, in this paper, a methodology that try to overcome the lack of runoff quality data in Puglia (Southern Italy) is tackled. It provides a tailored relationship between rainfall characteristics and pollutant wash-off in the context of the implementation of water treatment procedures for preventing the soil pollution. In particular, we exploited the iterated random pulse (IRP) rainfall generator model proposed by Veneziano and Iacobellis [22], by finding climatic subareas, characterized by different rainfall features. Time series of precipitation generated by the IRP model were used as input data in the quality model, providing information about qualitative characteristics of runoff in urban catchments. The above-mentioned model takes into account also the influence of catchment characteristics such as surface area, land use, percentage of impervious surface, and slope

on pollutant wash-off process. For example, the impervious surface area layout plays an important role in runoff routing, controlling the time of concentration and hence influencing the pollutant wash-off process [23].

In the previous work, Di Modugno et al. [24], a monitoring campaign was carried out within a residential area by collecting and evaluating quantity and quality data. With reference to the buildup/wash-off processes, total suspended solid (TSS) concentrations were used for calibration of storm water management model (SWMM), which was validated on the base of the pollutograph's shape and the peak-time for a urban basin located in Sannicandro di Bari (central Puglia, Italy). The quality parameters identified were used in the present work for evaluating the pollutant wash-off processes in five urban basins of the region, located in Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina, using synthetic rainfall series generated by IRP model with parameters accounting for regional rainfall patterns [25, 26].

Since past researches were focused above all on rural areas [27–35] and less effort has been done about anthropized areas [36], the present work provides an important contribution to this topic, by improving the stormwater treatment design (i.e., first flush capturing devices) in the context of soil pollution prevention in Mediterranean semiarid areas. Moreover it provides a deeper understanding of stormwater quality modeling approaches where commonly, the pollutant wash-off process is reproduced using only the rainfall intensity rather than other rainfall event parameters or using a stochastic approach without considering the characteristics of the rainfall event.

In phase A, reported in Section 2, the SWMM model is briefly described, distinguishing between the calibrated parameters in previous work [24] and those evaluated by considering catchment characteristics. In phase B, reported in Section 3, the rainfall generator model providing the synthetic time series of precipitation (used as input in SWMM model) is described. Moreover, in the same section, the regional pattern of rainfall features is explained. In phase C, as reported in Section 4, the catchment characteristics of Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina municipalities are described and in Section 5 the pollutographs evaluated coupling the IRP and the SWMM models are shown and discussed. The conclusions are presented in Section 6.

2. Phase A: Estimation of SWMM Model Parameters

The main objective of the research presented is to improve the stormwater quality evaluation in areas ungauged. With this aim, the quality model parameters calibrated by Di Modugno et al. [24] for the case study of Sannicandro di Bari, where a monitoring campaign is available, are exported to the catchments located in Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina municipalities (described in phase C). In this way, for each rainfall station, time series of precipitation of suitable length may be generated in order to be implemented in SWMM model to evaluate the subsequent pollutographs.

2.1. The Storm Water Management Model (SWMM). SWMM simulates the hydrograph and the pollutograph [37] for a real storm event (for single and long-term event) on the base of rainfall (hyetograph) and other meteorological inputs and system characteristics (catchment, conveyance, and storage/treatment) for developed urban and undeveloped or rural areas. The runoff component of SWMM operates on a collection of subcatchment areas that receive precipitation and generate runoff and pollutant loads. The routing portion of SWMM transports this runoff overland and underground through a system of pipes, channels, storage and treatment devices, pumps, and regulators. SWMM tracks the quantity and quality of runoff generated within each subcatchment and the flow rate, flow depth, and quality of water in each pipe and channel during a simulation period characterized by multiple time steps [38].

The losses taken into account in the present work are represented by the infiltration process that was modeled evaluating, for each subcatchment, the percentage of pervious and impervious area obtained from the land use map. The infiltration model used in this study is based on Horton's equation, whose parameters values have been chosen according to the typical values reported in literature [39, 40], in relation to soil type, and specifically tested in the Apulian karstic watersheds [41].

SWMM allows evaluating the pollutants buildup process on the basin surface, all processes involving the solid transportation by runoff through the drainage system.

Pollutant buildup within a land use category is described by a mass per unit of subcatchment area; the amount of buildup is a function of the number of dry weather days antecedent to the rainfall event. On the base of the assumptions of Alley and Smith [42], the buildup function follows an exponential growth curve that approaches a maximum limit asymptotically as in

$$M_a(d_{ts}) = \left(\frac{\text{Accu}}{\text{Disp}} \right) \cdot A \cdot P_{\text{imp}} \cdot \left(1 - e^{-(\text{Disp} \cdot d_{ts})} \right), \quad (1)$$

where $M_a(d_{ts})$ is the pollutant buildup during the antecedent dry days [kg/ha]; Disp identifies the disappearance of accumulated solids due to the action of wind or vehicular traffic [1/d]; $A \cdot P_{\text{imp}}$ represents the impervious area percentage; Accu characterizes the solids buildup rate [kg/(ha·d)]; $(\text{Accu}/\text{Disp}) \cdot A \cdot P_{\text{imp}}$ represents the maximum asymptotical limit of the buildup curve.

The pollutant wash-off over different land uses takes place during wet periods and it was described by the Jewell and Adrian [43] exponential function:

$$\frac{dM_a(t)}{dt} = -\text{Arra} \cdot i(t)^{\text{wash}} \cdot M_a(t), \quad (2)$$

where $dM_a(t)/dt$ represents the wash-off load in units of mass per hour; Arra is the wash-off coefficient [mm^{-1}]; $i(t)$ is the runoff rate; wash is the wash-off exponent, a numerical parameter that controls the influence of rainfall intensity on the amount of leached pollutants.

2.2. Estimation of Quantity and Quality Parameters. Several works [44–49] report sensitivity analysis performed to assess the importance of various parameters in SWMM equations that most affect results in terms of runoff and water quality.

In particular, Liong et al. [45] subdivided the calibration parameters of the Runoff block of SWMM into two groups:

- (1) First group is “Traditional” calibration parameters, which include Manning's coefficient for overland flow over the pervious and impervious portion of the subcatchment (N-Perv and N-Imperv), the depth of depression storage on the pervious and impervious portion of the Subcatchment (Dstore-Perv and Dstore-Imperv), and the infiltration parameters.
- (2) Second group is “Nontraditional” calibration parameters, whose values are obtained from the measures and/or the interpretation of the available information. Sources of information, which provide the definition of a specific value associated with the parameter, are, for instance, topographic maps, aerial photographs, and land use maps. Since topographic maps may be plotted at different scales, larger errors can be expected for the subcatchment areas represented by a larger map scale; these areas are in turn used to compute the widths of the overland flow path; errors are also inevitable in assigning values to slopes, from the topographical map. Similarly, errors can be expected in the values assigned to the fraction of imperviousness (% Imperv), the percentage of impervious area with no depression storage (% Zero Imperv), and the roughness coefficients for the channel (Roughness).

In the present work, as well as in [24], values extracted from the literature [41, 50, 51] were assigned to all parameters belonging to the first group. The infiltration losses parameters were estimated, in relation to soil type, by using values tabulated in technical handbooks and verified by [40] for karstic areas. The range of variation and the values chosen for these parameters are shown in Table 1.

In Table 1, among “Traditional” calibration parameters, the percentage of impervious area with no depression storage (% Zero Imperv) was added, because there is not enough information available to evaluate it for the investigated basins. Therefore, as for Sannicandro di Bari, a mean-low value of % Zero Imperv was chosen, corresponding to a quite high runoff generation potential such that it is expected in an urban basin.

Regarding the other “Nontraditional” calibration parameters, area, width, slope, percentage of impervious area, and roughness coefficients for the channel, they were evaluated for the five case studies investigated and are reported in Table 5.

All the parameters mentioned above are referred to the hydraulic-hydrological model. Since the main objective of the proposed research is to extend the stormwater quality evaluation to ungauged areas, in this work the same quality parameter values obtained from the calibration and validation procedure (based on monitoring campaign) in Sannicandro di Bari [24] were considered and they are listed in Table 2.

TABLE 1: “Traditional” calibration parameters of the hydraulic-hydrological model.

Parameters	Description	Range	Value
Dstore-Imperv	Depth of depression storage on the impervious portion of the subcatchment [mm]	1.27–2.54*	1.30
Dstore-Perv	Depth of depression storage on the pervious portion of the subcatchment [mm]	2.54–5.08*	2.60
N-Imperv	Manning’s coefficient for overland flow over the impervious portion of the subcatchment	0.011–0.024**	0.012
N-Perv	Manning’s coefficient for overland flow over the previous portion of the subcatchment	0.15–0.41**	0.15
%Zero Imperv	Percent of the impervious area with no depression storage [%]	—	45
Horton’s equation	Maximum infiltration rate [mm/h]	117–76***	76
	Minimum infiltration rate [mm/h]	17–6***	13
	Decay constant [1/h]	5.34–4.14***	4.14

*Reference [50]; **reference [51]; ***reference [41].

TABLE 2: Calibrated quality parameters exported in ungauged basins.

Parameters	Range	Value
Buildup		
Accu [kg/(ha-d)]	10–25*	13.143
Disp [1/d]	0.08**	0.08
Wash-off		
Arra [1/mm]	0.11–0.19	0.18
Wash	0–3	2.35

*For highly populated residential areas.

**Italian residential basin typical values.

3. Phase B: Identification of Climatic Subareas

In this paper we subdivided the entire Puglia region in different climatic subareas, consistently with the parametrization of the IRP rainfall generator model proposed by Veneziano and Iacobellis [22]. Then, time series of precipitation generated by the IRP model were used as input data of the quality model, providing qualitative characteristics of runoff in urban catchments. These results provide interesting information useful to enhance treatment procedures and to improve the efficiency of systems aimed at first flush treatment. In the following subsections, the structure of the IRP model and the approach for identification of different rainfall features are briefly described.

3.1. IRP Model. The rainfall generator proposed by Veneziano and Iacobellis [22] uses the classical representation of the exterior process of the rainfall as an alternating process with independent mean rainfall intensities for different rainstorms, characterizing the duration and average intensity of rainfall events at the synoptic scale. The interior process exploits the IRP, Veneziano et al. [52], pulse representation with multifractal properties of location and intensity, describing the detailed fluctuations of rainfall intensity at subsynoptic scales. In particular the wet periods of the exterior model are scattered through the “interior” scheme, in which rainfall is represented as the superposition of pulses with a hierarchically nested structure of temporal occurrences;

pulses at different scales have amplitudes with cascade-like dependence.

The exterior process consists of an alternating sequence of dry and wet periods with independent durations, which characterizes the arrival, duration, and average intensity of rainfall events at the synoptic scale; the distribution of the wet periods is assumed to be exponentially distributed instead of that of the dry periods which is assumed to be Weibull distributed; the average rainfall intensities in different wet periods are independent and identically distributed as exponential distribution.

The model consists of six parameters derived from the study of the precipitation process aggregate in the exterior and interior processes mentioned above. The exterior process is characterized by four parameters: the mean duration of the wet periods (m_{wet}), the mean value (m_{dry}), and the exponent k of the Weibull distribution of the dry intervals and the mean value (m_r) of the average of rainfall intensity during the synoptic events, while for the definition of the interior process two other parameters related to its multifractality are introduced: the parameter C_1 that controls the multifractal properties of rainfall at small scales and the multiplicity r which controls the quasifractal behavior of the rainfall support at small scales; the latter assumes a value equal to 2.

3.2. Different Rainfall Patterns in Puglia. Iacobellis et al. [53] evaluated the parameters of the IRP rainfall generator for all the rainfall time series of the monitoring network of the Regional Hydrographic Service reported in the Hydrological Annals. For this purpose they used the method of estimation from coarse data proposed by Iacobellis et al. [54], the daily rainfall records, and the annual maxima hourly precipitation intensities for 124 different sites of Puglia, Basilicata, and Campania in Southern Italy located in the following river basins: Candelaro, Cervaro, Carapelle, Ofanto, Lesina and Varano Lakes, Gargano, Salso-Salpi Lakes, Celentano marshes, Murge, Salento, Lato, and Galeso.

The significant rain gauges considered for this study were those with daily rainfall time series not shorter than twenty years. Moreover, all the values characterized by a particular uncertainty (i.e., the data obtained by interpolation and those accumulated over a given period) have been deleted from

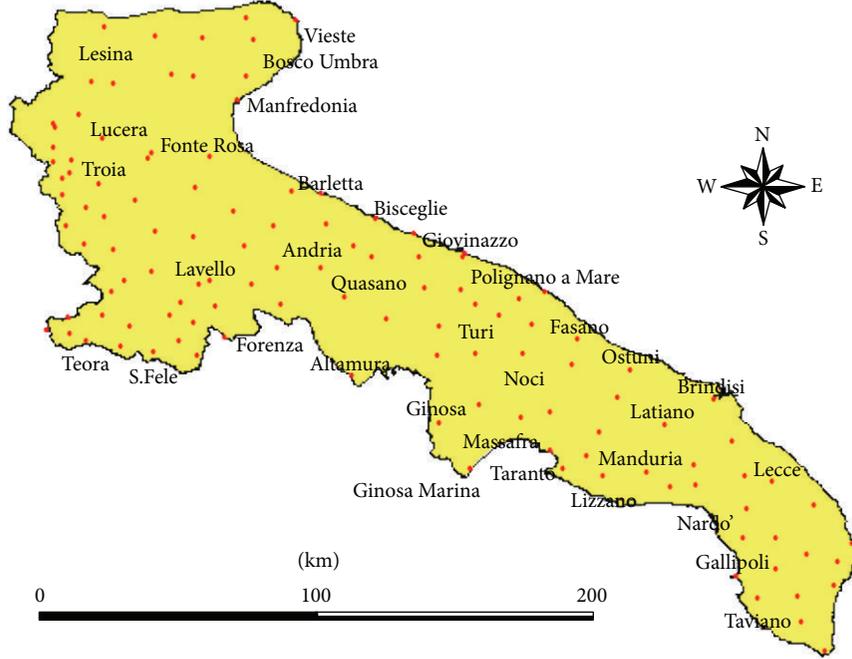


FIGURE 1: Rain gauges stations located in Puglia.

the time series reported in the Hydrological Annals. Figure 1 shows the position of the gauged rainfall stations considered.

The values of daily precipitation, organized as a vector, were processed in Matlab environment, in order to evaluate the four parameters of the exterior model. Starting from this vector, the following processes were studied:

- (i) The distribution of wet periods called “wet distribution”: assuming that the variable “consecutive number of rainy days” (τ_{wet}) or “duration of a storm” is characterized by an exponential distribution, we can consider its mean value ($m_{\tau_{\text{wet}}}$) as a representative value of this distribution. The results are collected in Table 3.
- (ii) The distribution of dry periods called “dry distribution”: in this case the assumption is that the variable “consecutive number of dry days” (τ_{dry}) is characterized by a Weibull distribution; therefore, it can be represented by its mean value ($m_{\tau_{\text{dry}}}$) and its exponent (k). The results are collected in Table 3.
- (iii) The “mean of intensities distribution”: assuming that the variable “average intensity of each storm” is characterized by an exponential distribution, we can consider its mean value (m_I) as a representative value of this distribution. The results are collected in Table 3.

In particular, to assess the average intensity in the distribution of synoptic events, the relationship proposed by Veneziano and Iacobellis [22] was considered:

$$m_I = R \cdot \frac{m_{\tau_{\text{wet}}} + m_{\tau_{\text{dry}}}}{m_{\tau_{\text{wet}}}}, \quad (3)$$

where R is the mean annual hourly rainfall intensity over the entire investigated period: $R = h_{\text{tot}}/(365 \times 24)$ and h_{tot} is the total annual precipitation mean value for each rain gauge station.

Table 3 shows all the parameters of the exterior model, obtained as mentioned above, and the total annual mean value of precipitation (h_{tot}) for each rain gauge station in Puglia.

In this work, we assumed that the parameter, C_1 , related to the multifractality of the interior process of IRP, is equal to 0.1, being the general best fit value reported in the literature (e.g., [22]). The seasonal variation of such parameters, investigated by Portoghese et al. [55], was also not considered in this paper.

After identifying the parameters of the exterior process, the correlation between $m_{\tau_{\text{dry}}}$ and h_{tot} parameters, that characterize respectively dry and wet intervals (Figure 2), was found.

In order to identify the different values of these parameters that represent different rainfall patterns which can be found in Puglia, the area of the plot [$m_{\tau_{\text{dry}}} - h_{\text{tot}}$] was divided into three equiprobable classes on the base of $m_{\tau_{\text{dry}}}$ values and into other three equiprobable classes on the base of h_{tot} . In this case nine classes were obtained, as shown in Figure 2.

Identification of nine climatic classes representing different rainfall patterns in Puglia. The Thiessen polygons of the investigated rainfall stations were used to trace these climatic areas thus obtaining the map in Figure 3.

On the base of the relationship between $m_{\tau_{\text{dry}}}$ and h_{tot} parameters, nine classes having different rainfall features were identified, as shown in the following matrix reported in Figure 4(a), in which each climatic class was symbolized by different colors: red color was used to represent the class with low h_{tot} values, blue color was used to represent the class

TABLE 3: Parameters of the exterior model.

Basin	Number	Name	m_{dry} [h]	k	m_{wet} [h]	m_r [mm/h]	h_{tot} [mm]
Lesina Lake	1	Lesina	91,0516	0,7125	24,3482	0,3159	637,9
	2	Sannicandro Garganico	93,0884	0,7305	27,9399	0,3817	804,8
Varano Lake	3	Cagnano Varano	87,8152	0,7218	27,0604	0,3545	816,0
Various basins	4	Vico del Gargano	86,9864	0,7544	27,0476	0,3593	777,0
	5	Vieste	104,3825	0,7205	24,0248	0,3142	570,1
	6	Bosco Umbra	71,8175	0,7139	34,6593	0,3512	1160,3
	7	Monte S.Angelo	77,6689	0,6978	29,7351	0,2733	774,1
	8	Torremaggiore	90,6646	0,6641	22,8815	0,2723	585,3
	9	S.Severo	91,2114	0,707	22,3729	0,2675	514,9
	10	S.Marco in Lamis	74,9043	0,6723	31,0812	0,3073	905,8
Candelaro	11	Mass. Pidocchiaro	80,8978	0,6377	22,6061	0,2479	527,4
	12	Pietramontecorvino	72,4838	0,6632	27,45	0,3179	872,0
	13	Pietramontecorvino (Eaap)	85,0966	0,6882	22,4847	0,2663	539,9
	14	Volturino	81,9527	0,6728	24,381	0,2626	651,5
	15	Alberona	69,7892	0,6669	31,085	0,2792	849,4
	16	Tertiveri	82,1544	0,6585	25,7195	0,2523	559,0
	17	Orto di Zolfo	57,7321	0,6339	32,8889	0,255	879,7
	18	Lucera	81,526	0,6903	23,1071	0,2484	594,3
	19	Biccari	80,3834	0,7105	29,1397	0,2998	791,0
	20	Faeto (S.Vito)	68,2987	0,6672	33,2925	0,2618	799,0
	21	Troia	89,6227	0,7368	24,79	0,2943	653,3
	22	Foggia oss.	91,1316	0,7185	21,1423	0,2762	467,5
	23	Foggia iac	100,6901	0,7279	20,0741	0,2675	410,6
Salso-Salpi-Celentano	24	S.Giovanni Rotondo	78,8768	0,7029	27,041	0,3245	813,3
	25	Manfredonia	81,9479	0,6444	21,1135	0,2159	448,8
	26	Fonte Rosa	72,3978	0,6472	20,4555	0,2189	448,4
	27	Cerignola	74,9811	0,6687	22,4028	0,2584	560,9
	28	Mass. S.Chiana	87,1738	0,6821	20,9691	0,2537	465,5
Cervaro, Carapelle	29	Savignano di Puglia	70,3321	0,6726	28,9864	0,262	733,3
	30	Monteleone di Puglia	58,7039	0,6668	31,8446	0,2462	819,5
	31	Orsara di Puglia	72,7858	0,6694	29,7488	0,3103	878,0
	32	Bovino	63,9046	0,6573	27,8255	0,2952	819,2
	33	Castelluccio dei Sauri	89,1752	0,7275	22,6852	0,2933	528,5
	34	Bisaccia	59,2551	0,6322	29,0387	0,2539	530,5
	35	S.Agata di Puglia	86,2517	0,6858	22,5079	0,2583	531,4
	36	Ascoli Satriano	77,7202	0,6621	23,5389	0,283	619,6
	37	Ortanova scalo	98,4128	0,708	19,8689	0,2774	446,0
Ofanto	38	Nusco	57,0676	0,579	36,0346	0,2994	820,6
	39	Lioni	26,4681	0,4782	32,4311	0,1738	948,5
	40	S.Angelo dei Lombardi	53,0217	0,5726	32,5761	0,256	952,0
	41	Teora	49,6926	0,5937	36,3906	0,2752	1012,8
	42	Andretta	54,0938	0,6216	32,0935	0,2185	821,4
	43	Pescopagano	66,308	0,6851	35,3984	0,3222	1091,9
	44	Calitri	61,3074	0,6515	29,8333	0,2498	769,8
	45	S.Fele	61,3794	0,6295	37,7991	0,2634	925,0
	46	Castel Lago Pesole	56,2687	0,6242	32,1645	0,2761	905,6
	47	Atella	52,6494	0,587	27,3338	0,1989	661,0
	48	Lacedonia	70,4878	0,7031	28,463	0,2689	780,4
	49	Monticchio Bagni	55,9144	0,6263	31,5205	0,2537	820,3
	50	Rocchetta S.Antonio scalo	80,627	0,6756	23,5446	0,2903	673,4
	51	Ripacandida	73,4722	0,7075	27,0046	0,2611	656,6
	52	Melfi	61,6199	0,652	28,4248	0,2884	843,5
53	Forenza	66,7412	0,6813	29,2743	0,2338	683,4	
54	Venosa	74,0361	0,674	26,8496	0,2788	710,5	
55	Diga sul Rendina	74,6143	0,6763	24,0994	0,2668	585,4	
56	Lavello	80,952	0,6991	22,8191	0,2833	598,2	
57	Loconia	75,1722	0,6582	20,9225	0,2476	506,2	
58	Borgo Libertà	85,8346	0,6979	22,9415	0,2718	563,3	
59	Spinazzola	69,4975	0,6555	25,1559	0,2521	655,4	
60	Montemilone	82,8718	0,6575	23,4572	0,2769	596,5	
61	Minervino Murge	81,175	0,6653	23,7927	0,2792	584,0	
62	Canosa di Puglia	89,0553	0,6814	22,1361	0,2995	542,2	

TABLE 3: Continued.

Basin	Number	Name	m_{dry} [h]	k	m_{wet} [h]	m_r [mm/h]	h_{tot} [mm]	
Murge	63	Barletta	94,0299	0,6835	21,3386	0,2885	522,2	
	64	Andria	82,7299	0,6608	22,6215	0,2715	577,4	
	65	Castel del Monte	59,5571	0,5816	26,2625	0,2022	640,2	
	66	Corato	86,5411	0,6884	21,7316	0,3073	538,5	
	67	Bisceglie	88,0699	0,6865	22,5811	0,2732	578,5	
	68	Ruvo di Puglia	82,6408	0,6514	22,7895	0,2726	599,1	
	69	Giovinazzo	96,5196	0,688	22,713	0,2966	536,8	
	70	Quasano	70,8268	0,6391	21,9957	0,2369	560,1	
	71	Bitonto	80,5965	0,6217	22,2512	0,2827	585,4	
	72	Altamura	63,6599	0,6249	25,0068	0,2056	549,1	
	73	Grumo Appula	72,9712	0,6009	22,5292	0,2677	571,7	
	74	Bari sez. idrografica	86,7493	0,6384	21,6093	0,2921	514,2	
	75	Bari osservatorio	91,2586	0,652	22,2619	0,2829	532,7	
	76	Bari fac. ingegneria	85,9745	0,6054	24,3858	0,2342	520,1	
	77	Mercadante	53,8352	0,5726	27,4403	0,2035	645,2	
	78	Cassano delle Murge	85,0081	0,6569	24,8709	0,2878	658,9	
	79	Adelfia Canneto	88,6833	0,6604	25,1834	0,2765	589,8	
	80	Casamassima	83,569	0,6284	24,3611	0,2539	562,6	
	81	Santeramo in Colle	77,145	0,6174	23,4071	0,2627	636,7	
	82	Gioia del Colle	63,9207	0,5979	24,4868	0,2559	628,1	
	83	Turi	74,1393	0,62	23,8318	0,2553	604,3	
	84	Conversano	79,9444	0,6242	23,9081	0,2839	625,6	
	85	Polignano a Mare	86,8408	0,6304	25,0996	0,2772	583,3	
	86	Castellana Grotte	54,4983	0,5488	26,109	0,2017	657,3	
	87	Noci	59,7421	0,57	24,2529	0,2232	662,6	
	88	Fasano	95,8643	0,6718	24,809	0,3179	593,5	
	89	Locorotondo	58,3498	0,5541	28,2275	0,2188	682,4	
	90	Ceglie Messapico	84,1875	0,6335	25,15	0,285	659,9	
	91	Ostuni	68,4693	0,59	27,9963	0,2737	705,2	
	92	Massafra	101,113	0,7134	22,1631	0,3251	517,3	
	93	Crispiano	96,3672	0,6822	22,4204	0,3056	546,0	
	Salento	94	Latiano	49,8272	0,5118	25,0408	0,1951	632,8
		95	Brindisi	82,4609	0,6109	24,072	0,2739	600,2
96		S.Pancrazio Salentino	59,3335	0,5466	23,8694	0,2427	639,9	
97		S.Pietro Vernotico	65,7885	0,5479	25,9981	0,2352	632,5	
98		Novoli	57,5226	0,542	28,5556	0,2137	643,2	
99		Lecce	65,0108	0,5575	24,9573	0,252	649,4	
100		Melendugno	58,2878	0,4957	25,8149	0,2177	599,9	
101		Maglie	44,9812	0,5099	28,9804	0,2055	762,9	
102		Otranto	58,0359	0,5765	27,4795	0,2512	787,5	
103		Minervino di Lecce	52,1476	0,5234	28,4833	0,2456	826,6	
104		Vignacastrisi	42,8536	0,5003	30,9247	0,2016	783,8	
105		Ruffano	61,7285	0,5466	25,591	0,2786	773,5	
106		S.Maria di Leuca	51,7732	0,4824	25,1729	0,2297	691,1	
107		Presicce	57,1893	0,5352	26,2804	0,2684	794,0	
108		Taviano	68,846	0,5572	24,6328	0,2502	604,7	
109		Collepasso	63,6108	0,5369	25,7089	0,2487	626	
110		Gallipoli	79,4586	0,5756	22,503	0,2782	563,7	
111		Galatina	52,8941	0,5133	28,5291	0,2193	692,2	
112		Nardo'	69,2597	0,5553	25,1713	0,2412	596,2	
113		Copertino	76,4832	0,5776	25,7796	0,2675	629,5	
114	Mass. Monteruga	44,6302	0,5079	25,9965	0,1839	615,6		
115	Avetrana	86,3732	0,6812	23,0938	0,3007	600,6		
116	Manduria	77,4516	0,6252	22,469	0,2852	620,8		
117	Lizzano	98,8352	0,6858	21,0276	0,3244	556,5		
118	Grottaglie	84,3978	0,6246	22,1172	0,2761	529,0		
119	S.Giorgio Jonico	86,2638	0,6117	21,4668	0,2953	561,9		
120	Taranto	106,3039	0,6766	20,4759	0,3378	471,6		
121	Talsano	82,1817	0,6126	20,9189	0,2432	421,3		
Lato and Galeso	122	Castellaneta	90,1218	0,7498	22,7253	0,3095	556,8	
	123	Ginosa	104,3585	0,7044	22,3677	0,3253	597,9	
	124	Ginosa Marina	61,2166	0,569	22,8324	0,2099	545,5	

TABLE 4: Rain gauges belonging to five climatic subareas with their characteristics.

Area	Number																					
1	34	72	124																			
2	5	9	13	22	23	28	33	35	37	58	62	63	64	66	67	69	74	75	76	80	85	92
	93	117	118	119	120	122																
3	14	18	36	51	55	56	59	61	71	81	83	84	95	108	112	113	116					
4	2	3	4																			
5	17	30	32	38	39	40	41	42	43	44	45	46	49	52	53	89	101	102	103	104	105	106
	107	111																				

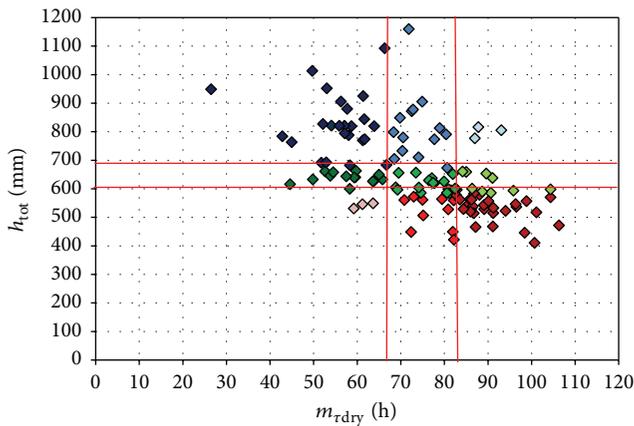


FIGURE 2: Identification of nine climatic classes representing different rainfall patterns in Puglia.

with high h_{tot} values, and green color was used to represent the class with mean values of h_{tot} . Then different shades of these three colors were used in order to better identify the nine classes; for instance, dark red symbolizes the least rainy areas (low values of h_{tot} and high values of $m_{\tau_{dry}}$), while dark blue represents the most rainy areas (high values of h_{tot} and low values of $m_{\tau_{dry}}$).

In order to reach the aim of this work, that is, to extend the stormwater quality to ungauged areas, a smaller number of classes can be considered. Therefore, among these nine classes, four classes that represent the four extreme conditions and one that represents the central condition were taken into account and they are reported in Figure 4(b):

Area 1 (light red): characterized by a low value of total annual precipitation (h_{tot}) and a low value of mean of consecutive number of dry days ($m_{\tau_{dry}}$);

Area 2 (dark red): characterized by precipitation with a low h_{tot} and high $m_{\tau_{dry}}$; this is a typical arid zone;

Area 4 (dark blue): characterized by precipitation with a high h_{tot} and low $m_{\tau_{dry}}$; this is a typical wet zone;

Area 5 (light blue): characterized by precipitation with a high h_{tot} and high $m_{\tau_{dry}}$.

And finally

Area 3 (green) was considered, in order to have a central condition, characterized by mean values of h_{tot} and $m_{\tau_{dry}}$.

All the other classes excluded from the current work represent other average conditions that reveal information which can be located among the results obtained from the classes considered.

In both matrices, the numbers 1, 2, and 3 represent low, medium, and high value of each parameter, respectively.

For each of five classes, we considered only the rain gauge station characterized by the longest time series of precipitation (44 years) and that represents the centroid of the cluster of each climatic subarea, being, in this way, the most representative station of its own class (Figure 3):

- (i) Ginosa Marina for Area 1;
- (ii) Barletta for Area 2;
- (iii) Manduria for Area 3;
- (iv) Presicce for Area 4;
- (v) Cagnano Varano for Area 5.

It is well known that the representative point of a cluster, or cluster center for the k -means algorithm, is the component-wise mean of the points in its cluster, chosen for minimizing the within cluster variances (minimizing within the cluster the squared Euclidean distance).

In Table 4 the rain gauges belonging to each of five classes are reported. They are represented with the same correspondent numbers of Table 3.

Since the main objective of the proposed research is to evaluate stormwater quality including pollutographs and their characteristics in ungauged basins, synthetic scenarios of precipitation were generated in Matlab environment and then input to SWMM model. The characteristics of the rainfall data were reproduced using series with time step of 15 minutes of aggregation (which is the reference time provided by Italian Legislation [56] for first flush analysis) and length of 10 years. In order to provide information about qualitative characteristics of runoff, it was necessary to introduce in the model the characteristics of the catchments and of the drainage network. For this purpose, in the following phase C, the different case studies are presented.

TABLE 5: “Nontraditional” parameters of ungauged basins.

Parameters	Ungauged basins									
	Barletta		Manduria		Cagnano Varano		Presicce		Ginosa Marina	
Area [ha]	30.18		31.5		20.11		30.78		31.45	
Width [m]	Sub. 1		Sub. 1		Sub. 1	531.26			Sub. 1	519.88
	Sub. 2		Sub. 2		Sub. 2	130.18			Sub. 2	522.08
	Sub. 3		Sub. 3		Sub. 3	453.7	Sub. 1	527.1	Sub. 3	38.1
					Sub. 4	550.52	Sub. 2	845.36	Sub. 4	324.78
					Sub. 5	236.48			Sub. 5	232.6
					Sub. 6	550.88			Sub. 6	327.92
Slope [%]	0.16		0.97		0.5		0.08		0.09	
% Imperv [%]	93		81.69		74.95		30.73		48.98	
Roughness [s/m ^{1/3}]	0.013		0.013		0.013		0.013		0.013	

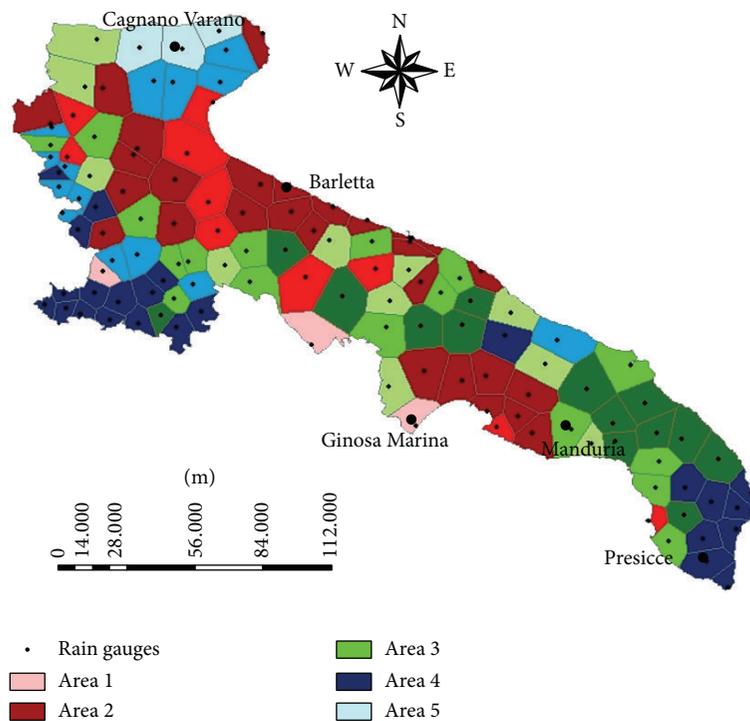


FIGURE 3: Representation of the climatic subareas identified on the base of the correlations between parameters of IRP model: $m_{\tau dry}$ and h_{tot} .

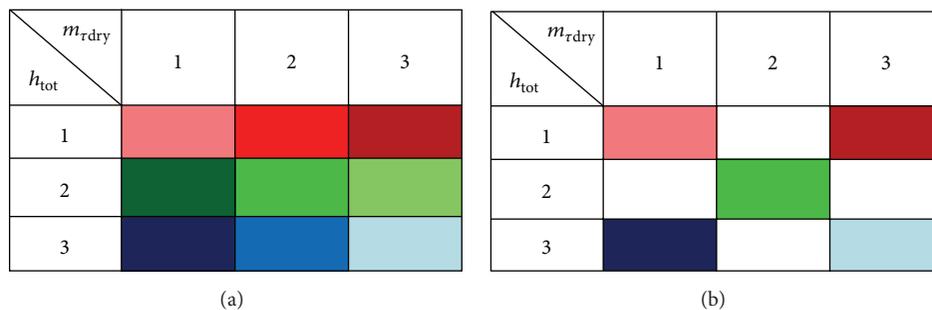


FIGURE 4: (a) Matrix of nine climatic subareas. (b) Matrix of five climatic subareas chosen.

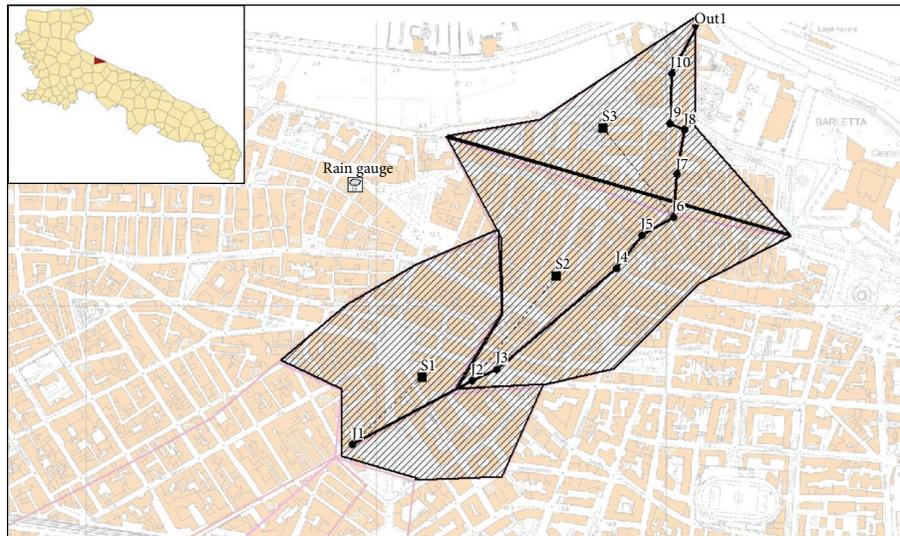


FIGURE 5: Barletta basin and representation of sewer system.

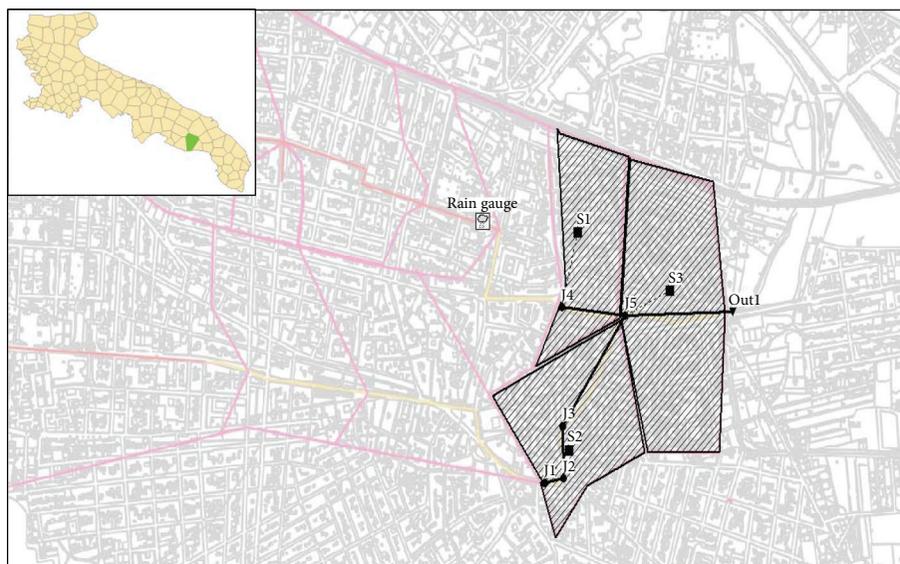


FIGURE 6: Manduria basin and representation of sewer system.

4. Phase C: Exporting Calibration Parameters in Ungauged Basins: The Case Studies of Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina

In Barletta the total area of the drainage basin is equal to 30.18 ha with a percentage of impervious surface equal to 93% (28.17 ha). The average slope of the basin is 0.16%. In particular, the land use thematic map, extracted from the regional geographical information system (SIT Puglia), shows that the entire area is exclusively residential.

The sewage system, used exclusively for the collection of rainwater, has a total length of 1054.85 m.

Figure 5 shows the SWMM scheme of the basin including 3 subcatchments and a drainage network with 10 nodes (black dots) and 10 channels (black solid lines).

The sewer system in Manduria has a total drainage basin of 31.85 ha with a percentage of impervious surface equal to 81.69% (25.73 ha). The average slope of the basin is 0.97%; the land use map shows that the entire area is residential.

In this basin the sewage system, used exclusively for the collection of rainwater, is composed by circular concrete conduits for a total length of 857.48 m.

Figure 6 shows the SWMM scheme of the basin including 3 subcatchments and a drainage network with 5 nodes (black dots) and 5 channels (black solid lines).

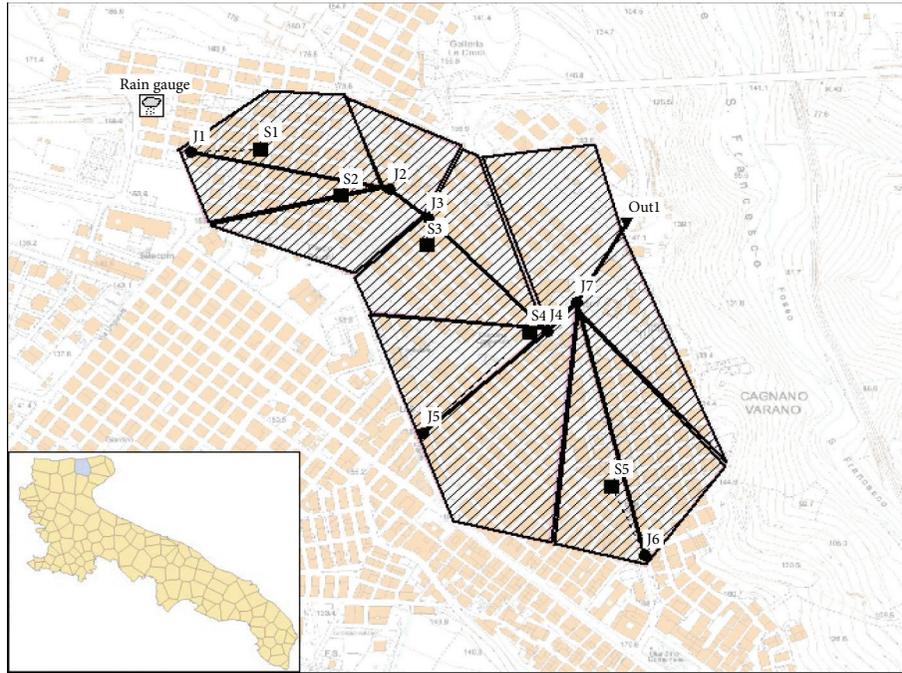


FIGURE 7: SWMM depiction of Cagnano Varano basin with its drainage network.

The total contributing area of Cagnano Varano catchment above the gauging station is 20.11 ha, and 74.95% (15.07 ha) of the total area is residential with impervious surface. The average slope of the basin is 0.5%. A total of 6 subcatchments are delineated within the watershed. All surface flow is collected at the watershed outlet after routing through 7 conduits, whose total length is equal to 1326.51 m.

Figure 7 illustrates the SWMM depiction of the Cagnano Varano watershed.

In Presicce the catchment has a total surface of 30.78 ha with 30.73% (9.45 ha) of impervious area characterized by residential land use like the previous basins. The average slope of the basin is equal to 0.08%. The catchment area is covered by a main sewer which is circular and has a diameter of 2.2 m in the initial section and 2.4 m in the final section. The estimated length of this sewer is 306.23 m up to the downstream point.

Figure 8 illustrates the SWMM depiction of the basin including 2 subcatchments and a drainage network with 3 nodes (black dots) and 3 channels (black solid lines).

The basin located in Ginosa Marina has total contributing area equal to 31.45 ha, of which the 48.98% (15.40 ha) is impervious and destined to residential use. The average slope of the watershed is equal to 0.09%. The discretization of the catchment provides 8 subcatchments. The surface runoff flows through a drainage network of 1695.09 m long.

In Figure 9, the SWMM depiction of the subcatchment is shown.

As already explained in Section 2.2, we considered these five catchments, because they are characterized by values of “Nontraditional” calibration parameters that may be considered similar to those estimated for Sannicandro di Bari in [24]. In Table 5, these parameters catchment are listed.

5. Coupling IRP with SWMM Model for Pollutograph Evaluation and Discussion

In this section a pollutographs evaluation in all the investigated ungauged sites by coupling IRP and SWMM model is reported. In particular, by using the IRP model, time series of precipitation of a given length were generated in order to be implemented in SWMM. The estimated parameters used in SWMM model were

- (i) the “Traditional” and qualitative parameters already evaluated for the case study of Sannicandro di Bari, where a monitoring campaign is available;
- (ii) the “Nontraditional” parameters, calculated for the investigated case studies of Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina, starting from the catchment characteristics.

As already explained in Section 3.1, the IRP model consists of six parameters derived from the study of the precipitation process aggregate in the exterior and interior processes. The exterior process is characterized by four parameters, the average of the intervals of rain ($m_{\tau_{wet}}$), the mean and the exponent of the Weibull distribution for the dry intervals (k and $m_{\tau_{dry}}$), and the average of rainfall intensity (m_I), while for the definition of the interior process two other parameters related to its multifractality are introduced, C_1 and r . For Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina basins, the values of these parameters are listed in bold in Table 3.

Figure 10 shows, for the case study of Barletta, the generated synthetic scenarios of precipitation; a series of 15 minutes of aggregation and length of 10 years was used.

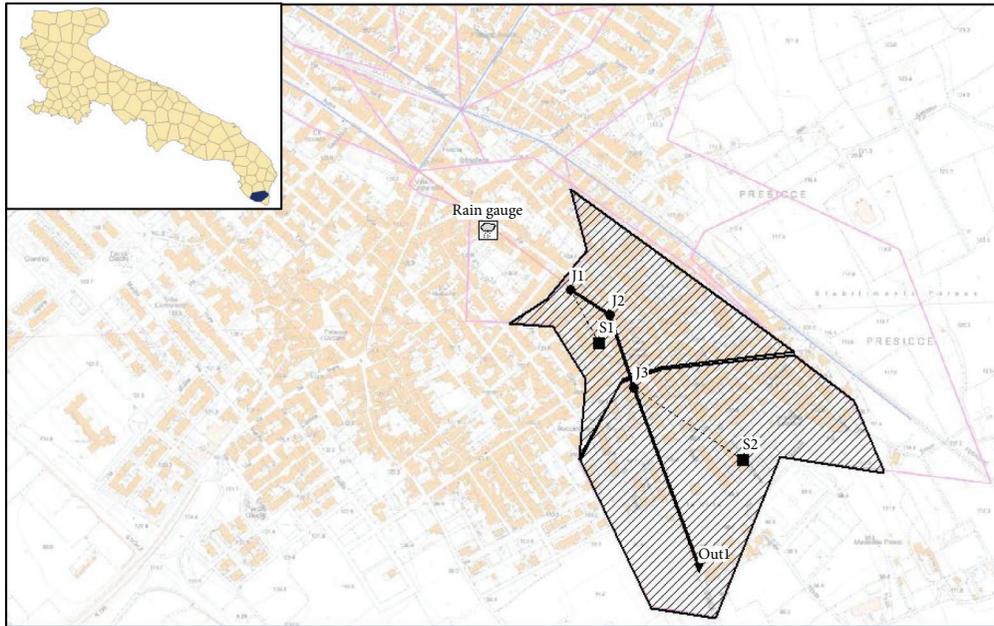


FIGURE 8: SWMM depiction of Presicce basin with its drainage network.

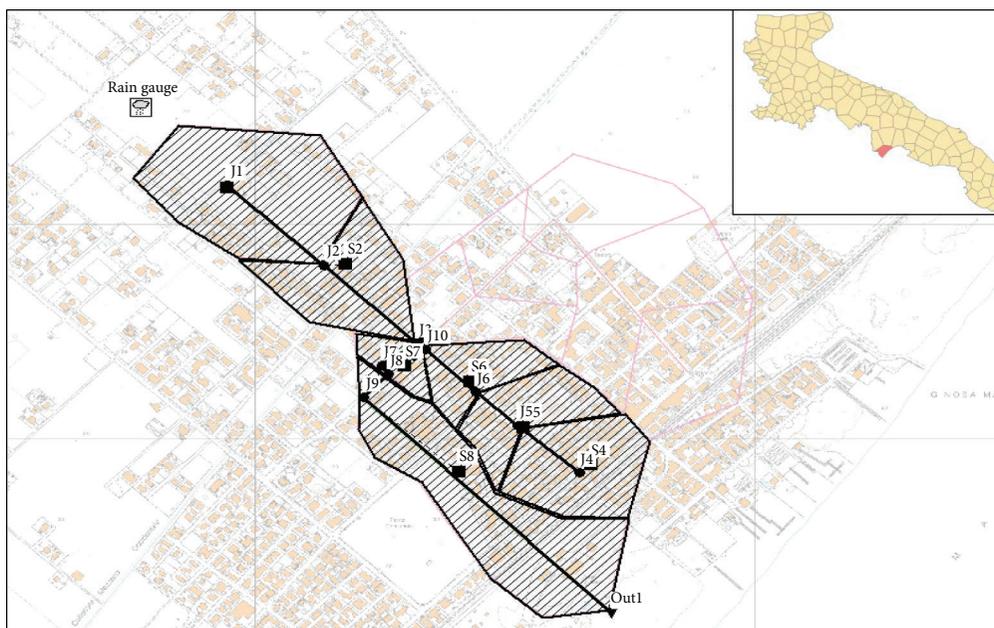


FIGURE 9: SWMM depiction of Ginosa Marina basin with its drainage network.

The hyetographs shown in Figure 10 was implemented in SWMM model for the TSS pollutographs evaluation (Figure 11). Due to the high affinity of many contaminants with solid matter, in the present study only the TSS prediction was taken into account. In fact, several works in literature [57, 58] consider TSS as a synthetic index of the general level of pollution in urban areas. For this reason, TSS are often used in mathematical models that simulate the dynamics of pollutants in urban runoff.

The analysis of the distribution of pollutant mass versus volume in stormwater discharges in dimensionless terms by using the so-called “ $M(V)$ curves” [59] was performed on the five case studies investigated. This representation provides the variation of the cumulative pollutant mass divided by the total pollutant mass in relation to the cumulative volume divided by the total volume. If the concentration remains constant during the storm event, the pollutant mass is proportional to the volume and the $M(V)$ curve is merged with the 1:1 line.

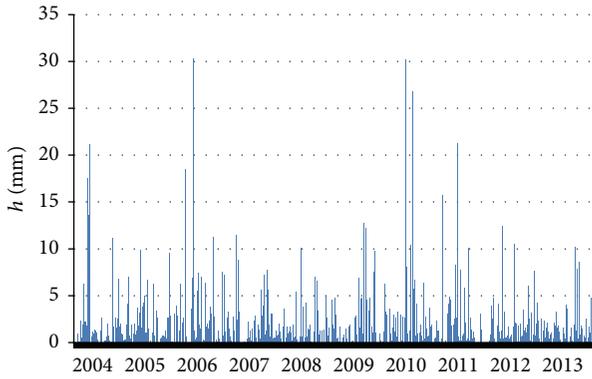


FIGURE 10: Hyetograph generated using IRP model for Barletta basin.

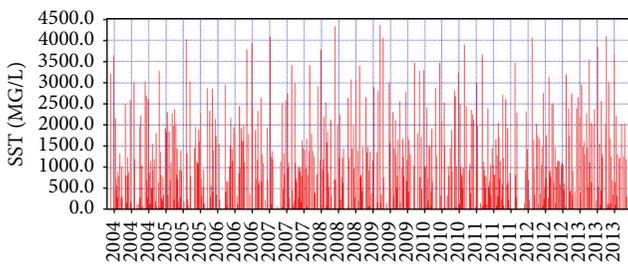


FIGURE 11: Pollutograph generated with SWMM model for Barletta basin.

When the $M(V)$ curve is above the 1:1 line, the first flush is noticed and the extent of the phenomenon increases with the slope of the curve for small values of volume.

The $M(V)$ curves obtained from the predicted TSS data of Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina basins are shown in Figure 12. In particular, for each basin the $M(V)$ curve was obtained from the TSS pollutograph simulated starting from the generated synthetic series of precipitation, obtained by selecting a maximum annual rainfall event of duration equal to 15 minutes, with a return period equal to that associated with the design rainfall event (generally equal to 5 years for stormwater network design in Italy).

The $M(V)$ curves in Figure 12 indicate that the first flush phenomenon is occurring in all five catchments. Various hydrologic and sewer system characteristics are usually investigated to determine their influence on the first flush effect [60]. In a combined storm/sanitary sewer system, the first flush load for total suspended solids was shown to correlate well with the event maximum rainfall intensity, storm duration, and antecedent dry weather period [61]. Similar results were also shown in a study involving separate storm and sewer systems [24, 62]. In the current work, from Figure 12, it is worth noting the site dependence of $M(V)$ curves or, in other words, the influence that catchment characteristics have on this phenomenon. In fact, the first flush effect is the most pronounced for the sites that are characterized by high values of impervious surface and slope, and it is much weaker at lower levels of imperviousness and

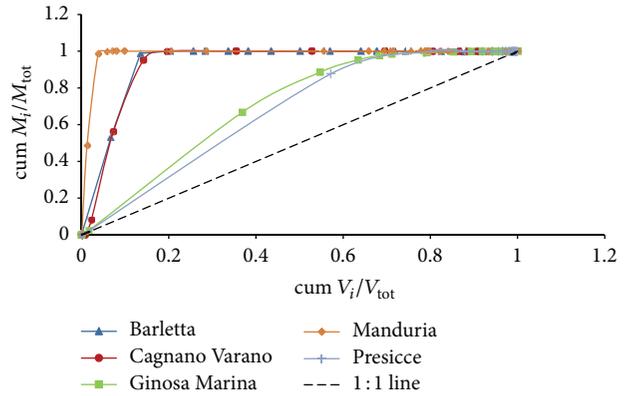


FIGURE 12: $M(V)$ curves for Barletta, Manduria, Cagnano Varano, Presicce, and Ginosa Marina basins.

TABLE 6: Percentage of impervious surface and slope of five catchments.

Basins	% Imp	% slope
Barletta	93.33	0.16
Cagnano Varano	74.95	0.50
Ginosa Marina	48.98	0.09
Manduria	81.69	0.97
Presicce	30.73	0.08

slope too (Table 6). In particular, we can see that the 10% (for Manduria) and 20% (for Barletta and Cagnano Varano) of the volume of washed-off water carry the total quantity of TSS from concrete surfaces, while, on the base of the definition of the 30/80 first flush by Bertrand-Krajewski et al. [59], for Ginosa Marina and Presicce, the two cities characterized by the lowest values of slope and percentage of impervious surface, the first 30% of the volume carries a quantity of TSS, respectively, equal to 50% and 60%.

6. Conclusions

This paper proposes a procedure for evaluating the quality and the quantity characteristics of stormwater runoff in ungauged areas, providing useful information for the design of efficient and sustainable stormwater treatment systems (i.e., first flush capturing devices) and, in general, in the context of the implementation of water treatment procedures for soil pollution management and prevention. In this work a methodology that tries to overcome the lack of runoff quality data in Puglia (Southern Italy), by coupling a rainfall generator model with a storm water management model for evaluating TSS pollutographs, is proposed. The SWMM model uses quantity parameters evaluated using catchments and drainage network characteristics and quality information extracted from observed data obtained by monitoring campaigns.

Five selected ungauged sites, located in the region as the most representative of the evaluated rainfall patterns at regional scale, were used to apply the proposed procedure. In particular, exploiting the IRP rainfall generator model

proposed by Veneziano and Iacobellis [22], different climatic subareas, characterized by different rainfall features, were identified. By using time series of precipitation generated by the IRP model as input data in the quality model, it was possible to obtain, from the latter, information about qualitative characteristics of runoff in urban catchments, exploiting the data collected during a brief monitoring campaign described in a previous work [24].

Finally, the distribution of pollutant mass versus volume in stormwater discharges, using the so-called “ $M(V)$ curves,” was provided for the investigated study cases. These curves show that a significant first flush phenomenon is occurring in all five catchments; in particular the first flush effect is the most pronounced for the sites that are characterized by high values of impervious surface and slope, and it is much weaker at lower levels of imperviousness and slope too. Furthermore, a strict correlation between the first flush phenomenon and basin characteristics was found. The characteristics of the $M(V)$ curves depend on the pollutant, the rainfall event, and the overall operation of the sewer system. The possibility of reproducing in a synthetic way the TSS pollutographs in ungauged river basins represents the originality of this paper, with respect to the recent literature in this field. Further improvements may be conducted by new monitoring campaigns focused on the evaluation of the different pollutants present in the water that washes away impervious surfaces. In this way it is possible to improve the performances of the quality models in the context of evaluation and prediction of pollutants for proper and efficient design of sustainable sewer systems in order to prevent soil pollution.

In the next works, the analysis will be extended, in order to assess the relative importance of different parameters and evaluating the role of climate with respect to other features of the sewer system.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] W. R. L. Masamba and D. Mazvimavi, “Impact on water quality of land uses along Thamalakane-Boteti River: an outlet of the okavango Δ ,” *Physics and Chemistry of the Earth, Parts A/B/C*, vol. 33, no. 8–13, pp. 687–694, 2008.
- [2] C. S. S. Ferreira, A. J. D. Ferreira, R. L. Pato, M. do Carmo Magalhães, C. de Oliveira Coelho, and C. Santos, “Rainfall-runoff-erosion relationships study for different land uses, in a sub-urban area,” *Zeitschrift für Geomorphologie*, vol. 56, no. 3, pp. 5–20, 2012.
- [3] C. S. S. Ferreira, R. P. D. Walsh, T. S. Steenhuis et al., “Spatiotemporal variability of hydrologic soil properties and the implications for overland flow and land management in a peri-urban Mediterranean catchment,” *Journal of Hydrology*, vol. 525, pp. 249–263, 2015.
- [4] P. Raska, J. Klimes, and J. Dubisar, “Using local archive sources to reconstruct historical landslide occurrence in selected urban regions of the Czech Republic: examples from regions with different historical development,” *Land Degradation and Development*, vol. 26, no. 2, pp. 142–157, 2015.
- [5] J. W. Beniston, R. Lal, and K. L. Mercer, “Assessing and managing soil quality for urban agriculture in a degraded vacant lot soil,” *Land Degradation & Development*, 2015.
- [6] T. K. Udeigwe, J. Young, T. Kandakji, D. C. Weindorf, M. A. Mahmoud, and M. H. Stietiya, “Elemental quantification, chemistry, and source apportionment in golf course facilities in a semi-arid urban landscape using a portable X-ray fluorescence spectrometer,” *Solid Earth*, vol. 6, no. 2, pp. 415–424, 2015.
- [7] J. D. Sartor, G. B. Boyd, and F. J. Agardy, “Water pollution aspects of street surface contaminants,” *Journal of the Water Pollution Control Federation*, vol. 46, no. 3, pp. 458–667, 1974.
- [8] J. B. Ellis and D. M. Revitt, “Incidence of heavy metals in street surface sediments: solubility and grain size studies,” *Water, Air, and Soil Pollution*, vol. 17, no. 1, pp. 87–100, 1982.
- [9] A. Saget, G. Chebbo, and J.-L. Bertrand-Krajewski, “The first flush in sewer systems,” *Water Science and Technology*, vol. 33, no. 9, pp. 101–108, 1996.
- [10] J. E. Ball, R. Jenks, and D. Aubourg, “An assessment of the availability of pollutant constituents on road surfaces,” *Science of the Total Environment*, vol. 209, no. 2–3, pp. 243–254, 1998.
- [11] J. J. Sansalone, J. M. Koran, J. A. Smithson, and S. G. Buchberger, “Physical characteristics of urban roadway solids transported during rain events,” *Journal of Environmental Engineering*, vol. 124, no. 5, pp. 427–440, 1998.
- [12] J. J. Sansalone, F. Calomino, V. Singh, and T. Zheng, “In situ storm water eco-treatment and recharge through infiltration: quality and quantity attenuation,” in *Proceedings of the 2nd International Conference on New Trend in Water and Environmental Engineering for Safety and Life: Eco-Compatible Solutions for Aquatic Environments*, Capri, Italy, June 2002.
- [13] J. Vaze and F. H. S. Chiew, “Experimental study of pollutant accumulation on an urban road surface,” *Urban Water*, vol. 4, no. 4, pp. 379–389, 2002.
- [14] C. Van Lienden, L. Shan, S. Rao, E. Ranieri, and T. M. Young, “Metals removal from stormwater by commercial and non-commercial granular activated carbons,” *Water Environment Research*, vol. 82, no. 4, pp. 351–356, 2010.
- [15] M. Kayhanian, B. D. Fruchtman, J. S. Gulliver, C. Montanaro, E. Ranieri, and S. Wuertz, “Review of highway runoff characteristics: comparative analysis and universal implications,” *Water Research*, vol. 46, no. 20, pp. 6609–6624, 2012.
- [16] C. Ciaponi, S. Papiri, and S. Todeschini, “Qualità delle acque meteoriche di dilavamento dei siti sperimentali di Cascina Scala (Pavia) e di Cremona,” in *Atti dei Seminari “La Tutela Idrica e Ambientale dei Territori Urbanizzati”*, Parma e Cosenza, Italy, February 2004 (Italian).
- [17] A. Liu, A. Goonetilleke, and P. Egodawatta, “Taxonomy for rainfall events based on pollutant wash-off potential in urban areas,” *Ecological Engineering*, vol. 47, pp. 110–114, 2012.
- [18] S. Carroll, A. Liu, L. Dawes, M. Hargreaves, and A. Goonetilleke, “Role of land use and seasonal factors in water quality degradations,” *Water Resources Management*, vol. 27, no. 9, pp. 3433–3440, 2013.
- [19] P. Egodawatta, E. Thomas, and A. Goonetilleke, “Mathematical interpretation of pollutant wash-off from urban road surfaces using simulated rainfall,” *Water Research*, vol. 41, no. 13, pp. 3025–3031, 2007.
- [20] L.-H. Kim, S.-O. Ko, S. Jeong, and J. Yoon, “Characteristics of washed-off pollutants and dynamic EMCs in parking lots and

- bridges during a storm," *Science of the Total Environment*, vol. 376, no. 1–3, pp. 178–184, 2007.
- [21] N. Alias, A. Liu, P. Egodawatta, and A. Goonetilleke, "Sectional analysis of the pollutant wash-off process based on runoff hydrograph," *Journal of Environmental Management*, vol. 134, pp. 63–69, 2014.
- [22] D. Veneziano and V. Iacobellis, "Multiscaling pulse representation of temporal rainfall," *Water Resources Research*, vol. 38, no. 8, pp. 131–1313, 2002.
- [23] A. Liu, P. Egodawatta, Y. Guan, and A. Goonetilleke, "Influence of rainfall and catchment characteristics on urban stormwater quality," *Science of the Total Environment*, vol. 444, pp. 255–262, 2013.
- [24] M. Di Modugno, A. Gioia, A. Gorgoglione et al., "Build-up/wash-off monitoring and assessment for sustainable management of first flush in an urban area," *Sustainability*, vol. 7, pp. 5050–5070, 2015.
- [25] V. Iacobellis, P. Claps, and M. Fiorentino, "Climatic control on the variability of flood distribution," *Hydrology and Earth System Sciences*, vol. 6, no. 2, pp. 229–237, 2002.
- [26] M. Fiorentino, S. Manfreda, and V. Iacobellis, "Peak runoff contributing area as hydrological signature of the probability distribution of floods," *Advances in Water Resources*, vol. 30, no. 10, pp. 2123–2134, 2007.
- [27] A. Cerdà and S. H. Doerr, "Soil wettability, runoff and erodibility of major dry-mediterranean land use types on calcareous soils," *Hydrological Processes*, vol. 21, no. 17, pp. 2325–2336, 2007.
- [28] S. D. Keesstra, "Impact of natural reforestation on floodplain sedimentation in the Dragonja basin, SW Slovenia," *Earth Surface Processes and Landforms*, vol. 32, no. 1, pp. 49–65, 2007.
- [29] S. D. Keesstra, L. A. Bruijnzeel, and J. van Huissteden, "Mesoscale catchment sediment budgets: combining field surveys and modeling in the Dragonja catchment, southwest Slovenia," *Earth Surface Processes and Landforms*, vol. 34, no. 11, pp. 1547–1561, 2009.
- [30] S. D. Keesstra, O. van Dam, G. Verstraeten, and J. van Huissteden, "Changing sediment dynamics due to natural reforestation in the Dragonja catchment, SW Slovenia," *CATENA*, vol. 78, no. 1, pp. 60–71, 2009.
- [31] X. H. Li, J. Yang, C. Y. Zhao, and B. Wang, "Runoff and sediment from orchard terraces in southeastern China," *Land Degradation and Development*, vol. 25, no. 2, pp. 184–192, 2014.
- [32] Z. Liu, Z. Yao, H. Huang, S. Wu, and G. Liu, "Land use and climate changes and their impacts on runoff in the Yarlung Zangbo river basin, China," *Land Degradation and Development*, vol. 25, no. 3, pp. 203–215, 2014.
- [33] L. O. Olang, P. M. Kundu, G. Ouma, and J. Fürst, "Impacts of land cover change scenarios on storm runoff generation: a basis for management of the Nyando Basin, Kenya," *Land Degradation and Development*, vol. 25, no. 3, pp. 267–277, 2014.
- [34] T. Bisantino, R. Bingner, W. Chouaib, F. Gentile, and G. T. Liuzzi, "Estimation of runoff, peak discharge and sediment load at the event scale in a medium-size Mediterranean watershed using the annagnps model," *Land Degradation and Development*, vol. 26, no. 4, pp. 340–355, 2015.
- [35] P. Sarah and M. Zonana, "Livestock redistribute runoff and sediments in semi-arid rangeland areas," *Solid Earth*, vol. 6, no. 2, pp. 433–443, 2015.
- [36] P. Pereira, A. Gimeinez-Morera, A. Novara et al., "The impact of road and railway embankments on runoff and soil erosion in eastern Spain," *Hydrology and Earth System Sciences Discussions*, vol. 12, no. 12, pp. 12947–12985, 2015.
- [37] W. C. Huber and R. E. Dickinson, *Storm Water Management Model, Version 4: User's Manual*, Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Athens, Greece, 1992.
- [38] W. James, L. E. Rossman, and W. R. C. James, *User's Guide to SWMM5*, CHI, Guelph, Canada, 13th edition, 2010.
- [39] D. R. Maidment, *Handbook of Hydrology*, McGraw-Hill, New York, NY, USA, 1993.
- [40] R. E. Horton, "An approach toward a physical interpretation of infiltration capacity," *Soil Science Society of America*, vol. 5, pp. 399–417, 1940.
- [41] V. Iacobellis, A. Castorani, A. R. Di Santo, and A. Gioia, "Rationale for flood prediction in karst endorheic areas," *Journal of Arid Environments*, vol. 112, part A, pp. 98–108, 2015.
- [42] W. M. Alley and P. E. Smith, "Estimation of accumulation parameters for urban runoff quality modeling," *Water Resources Research*, vol. 17, no. 6, pp. 1657–1664, 1981.
- [43] T. K. Jewell and D. Adrian, "SWMM stormwater pollutant washoff functions," *Journal of the Environmental Engineering Division*, vol. 104, no. 5, pp. 1036–1040, 1978.
- [44] C. S. Hopkinson Jr. and J. W. Day Jr., "Modeling the relationship between development and storm water and nutrient runoff," *Environmental Management*, vol. 4, no. 4, pp. 315–324, 1980.
- [45] S. Y. Liong, W. T. Chan, and L. H. Lum, "Knowledge-based system for SWMM runoff component calibration," *Journal of Water Resources Planning and Management*, vol. 117, no. 5, pp. 507–524, 1991.
- [46] N. A. Zaghoul and M. A. Abu Kiefa, "Neural network solution of inverse parameters used in the sensitivity-calibration analyses of the SWMM model simulations," *Advances in Engineering Software*, vol. 32, no. 7, pp. 587–595, 2001.
- [47] E. W. Peterson and C. M. Wicks, "Assessing the importance of conduit geometry and physical parameters in karst systems using the Storm Water Management Model (SWMM)," *Journal of Hydrology*, vol. 329, no. 1–2, pp. 294–305, 2006.
- [48] J. Barco, K. M. Wong, and M. K. Stenstrom, "Automatic calibration of the U.S. EPA SWMM model for a large urban catchment," *Journal of Hydraulic Engineering*, vol. 134, no. 4, pp. 466–474, 2008.
- [49] S. B. K. Tan, L. H. C. Chua, E. B. Shuy, E. Y.-M. Lo, and L. M. Lim, "Performances of rainfall-runoff models calibrated over single and continuous storm flow events," *Journal of Hydrologic Engineering*, vol. 13, no. 7, pp. 597–607, 2008.
- [50] ASCE, *Design & Construction of Urban Stormwater Management Systems*, ASCE, New York, NY, USA, 1992.
- [51] R. H. McCuen, P. Johnson, and R. Ragan, *Highway Hydrology: Hydraulic Design Series No. 2; FHWA-SA-96-067*, Federal Highway Administration, Washington, DC, USA, 1996.
- [52] D. Veneziano, P. Furcolo, and V. Iacobellis, "Multifractality of iterated pulse processes with pulse amplitudes generated by a random cascade," *Fractals*, vol. 10, no. 2, pp. 209–222, 2002.
- [53] V. Iacobellis, G. Gioia, and D. Veneziano, "Rappresentazione delle precipitazioni in Puglia mediante un modello di tipo IRP," in *28° Convegno di Idraulica e Costruzioni Idrauliche*, Potenza, Italy, September 2002 (Italian).
- [54] V. Iacobellis, G. Gioia, and D. Veneziano, "Estimation of a multifractal model of temporal rainfall using coarse data, Mediterranean storms," in *Proceedings of the 3rd EGS Plinius Conference*, pp. 293–296, Baja Sardinia, Italy, October 2001.

- [55] I. Portoghese, E. Bruno, N. Guyennon, and V. Iacobellis, "Stochastic bias-correction of daily rainfall scenarios for hydrological applications," *Natural Hazards and Earth System Science*, vol. 11, no. 9, pp. 2497–2509, 2011.
- [56] Regolamento Regionale 9 dicembre 2013, n.26 "Disciplina delle acque meteoriche di dilavamento e di prima pioggia" (attuazione dell'art.113 del D. lgs. n. 152/06 e ss.mm. ed ii.), 2013.
- [57] Y. H. Han, S. L. Lau, M. Kayhanian, and M. K. Stensrtom, "Correlation analysis among highway stormwater pollutants and characteristics," in *Proceedings of the IWA 8th International Conference on Diffuse/Nonpoint Pollution*, Kyoto, Japan, October 2004.
- [58] C. Ciaponi, S. Papiri, and S. Todeschini, "Analisi e interpretazione della correlazione tra alcuni parametri inquinanti nella rete fognaria di Cascina Scala in tempo di pioggia," in *XXX Convegno di Idraulica e Costruzioni Idrauliche (IDRA '06)*, Rome, Italy, September 2006.
- [59] J.-L. Bertrand-Krajewski, G. Chebbo, and A. Saget, "Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon," *Water Research*, vol. 32, no. 8, pp. 2341–2356, 1998.
- [60] J. M. Hathaway, R. S. Tucker, J. M. Spooner, and W. F. Hunt, "A traditional analysis of the first flush effect for nutrients in stormwater runoff from two small urban catchments," *Water, Air, and Soil Pollution*, vol. 223, no. 9, pp. 5903–5915, 2012.
- [61] K. Gupta and A. J. Saul, "Specific relationships for the first flush load in combined sewer flows," *Water Research*, vol. 30, no. 5, pp. 1244–1252, 1996.
- [62] A. Taebi and R. L. Droste, "First flush pollution load of urban stormwater runoff," *Journal of Environmental Engineering and Science*, vol. 3, no. 4, pp. 301–309, 2004.

Research Article

Role of Inorganic and Organic Fractions in Animal Manure Compost in Lead Immobilization and Microbial Activity in Soil

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This study aimed to identify how the ratio of inorganic-to-organic components in animal manure compost (AMC) affected both lead immobilization and microbial activity in lead-contaminated soil. When AMC containing 50% or more inorganic fraction with high phosphorous content was applied to contaminated soil, the amounts of water-soluble lead in it were suppressed by over 88% from the values in the soil without compost. The residual fraction under sequential extraction increased with the inorganic fraction in the AMC; however, in those AMCs, the levels of microbial enzyme activity were the same or less than those in the control soil. The application of AMC containing 25% inorganic fraction could alter the lead phases to be more insoluble while improving microbial enzyme activities; however, no suppression of the level of water-soluble lead existed during the first 30 days. These results indicate that compost containing an inorganic component of 50% or more with high phosphorus content is suitable for immobilizing lead; however, in the case where low precipitation is expected for a month, AMC containing 25% inorganic component could be used to both immobilize lead and restore microbial activity.

1. Introduction

Lead is one of the most common and harmful heavy-metal soil contaminants worldwide, particularly near mines and shooting ranges. Lead contamination in the soil of such sites poses a risk to human and animal health as well as plant growth. Thus, its mobility and bioavailability should be reduced by appropriate treatments. In addition, the rehabilitation of soil ecosystems that have undergone destruction by lead contamination should be accomplished through the remediation of such soil. Since contamination in these sites is extensive and asset values are extremely low, chemical immobilization capable of transforming lead into less soluble phases is a cost-effective remedial approach. Thus, various immobilization materials have been studied and developed [1–7].

Animal manure compost (AMC), which is the most abundantly found organic waste material in Japan, can immobilize heavy metals and improve plant growth and microbial activity [8–16] by supplying nutrients to plant and soil biota. Therefore, in addition to lead immobilization, the application of AMC to lead-contaminated soil can help rehabilitate soil ecosystems, which inorganic immobilization materials cannot [17]. Numerous studies have investigated the effectiveness of AMC for lead immobilization [18, 19]; however, consistent conclusions on the mechanisms behind this process have not been obtained as such immobilization that greatly depends upon the AMC type, that is, AMC's physicochemical properties. In particular, the presence of both inorganic and organic components in AMC makes it complicated to understand lead immobilization.

TABLE 1: Physicochemical properties of contaminated soil used in this study (on the basis of air-dried weight).

Sand (%)	Silt (%)	Clay (%)	pH	TC (g kg ⁻¹)	TN (g kg ⁻¹)	WSOC ^a (mg kg ⁻¹)	WS-Pb ^b (mg kg ⁻¹)	Pb (g kg ⁻¹)	P (g kg ⁻¹)	Total Al (g kg ⁻¹)	Fe (g kg ⁻¹)	Amorphous Fe (g kg ⁻¹)
81.5	9.5	9.0	7.3	6.0	0.0	139	35	4.40	0.40	13.1	33.8	1.3

^aWater-soluble organic carbon.

^bWater-soluble lead.

Lead immobilization by AMC can be separated into indirect and direct mechanisms. The typical indirect mechanisms of lead immobilization are explained by the pH increase owing to the alkalinity of the inorganic component in AMC; this pH increase can promote the precipitation of lead carbonate and hydroxide minerals, resulting in a reduction of lead mobility and bioavailability [1, 20]. The direct mechanisms of lead immobilization by AMC have been considered to be the reaction of the lead with the inorganic and organic components in AMC. Phosphorus, sulfate, and iron in the inorganic component and humic substances in the organic component in AMC seem to be the sources responsible for the reaction with lead [10, 18, 21–23]. Katoh et al. [24] applied a specific method for the fractionation of the inorganic and acid-insoluble organic components from AMC to elucidate their separate contributions to lead immobilization. They indicated that the inorganic component in AMC could immobilize lead more effectively than its organic components [24]. These results imply that the inorganic component in AMC has a crucial role in lead immobilization, and AMC with a higher inorganic content is more suitable. However, to rehabilitate microbial activity, the organic component in AMC is also required since it supplies sufficient nutrients to soil microorganisms [17]. This component, however, may negatively affect lead mobility; water-soluble organic matter in AMC reacts and forms complexes with lead ions, resulting in enhancements in lead mobility. Therefore, a suitable ratio of inorganic and organic components in AMC should be clarified to reduce the mobility and bioavailability of lead and enhance the microbial activities in the soil. AMC has a wide range of the inorganic-to-organic component ratios [25]; however, to our knowledge, the optimal ratio of inorganic-to-organic components in AMC for lead immobilization and the rehabilitation of microbial activity have not been studied.

We investigated the mobility and bioavailability of the lead, lead phases, and microbial activities in soil amended with the AMCs of various inorganic-to-organic component ratios. The inorganic fraction was derived from swine manure compost and the acid-insoluble organic fraction was derived from cattle manure compost. These fractions can immobilize lead more effectively than other AMCs owing to the high content of phosphorus and mature organic matter in the inorganic and acid-insoluble organic fractions, respectively [24]. We aimed to identify how the ratio of inorganic-to-organic components in AMC affected the mobility and bioavailability of lead, lead phase, and microbial activity. On the basis of the obtained results, we discuss the optimal ratio of the inorganic and organic components in AMC to immobilize lead and rehabilitate microbial activity in soil.

TABLE 2: Chemical properties of inorganic and acid-insoluble organic fractions used in this study (on the basis of air-dried weight, mg g⁻¹) [24].

Characteristic	Inorganic fraction	Acid-insoluble organic fraction
Total calcium	152	ND ^{*1}
Total magnesium	44	ND
Total potassium	53	ND
Total iron	7	ND
Total phosphorus	131	ND
Total carbon	ND	452
ADF-C ^{*2}	ND	344
Humic acid carbon	ND	25
Fulvic acid carbon	ND	52

^{*1}Not determined.

^{*2}Acid detergent fiber carbon.

2. Materials and Methods

2.1. Preparation of Soil. The lead-contaminated soil used herein was collected from depths of 5–15 cm at a shooting range located at 35°28'6"N and 137°29'2"E in Gifu, Japan. The soil sample was air-dried, passed through a 2 mm sieve, and was used for chemical analysis and incubation tests. The selected physicochemical properties of the soil used are shown in Table 1. The soil had a sandy loam texture. The total lead content of the soil was 4.40 g kg⁻¹ and the soil pH was 7.3.

2.2. Preparation of Animal Manure Compost. Commercial swine and cattle manure composts were used herein to obtain the inorganic and acid-insoluble organic fractions, respectively. We selected these composts since each fraction of the compost can immobilize lead more effectively than other composts [24]. The fractionation followed the method described by Katoh et al. [24]. In brief, the swine manure compost was combusted at 600°C for 2 h; the residue after combustion was used as the inorganic fraction. The cattle manure compost was subjected to extraction with 1 M HCl for 1 h to remove almost all inorganic components, and the residue after extraction was used as the acid-insoluble organic fraction. The pH of each fraction was adjusted to 7 to match that of the soil. Table 2 shows the selected chemical properties of each fraction [24]. The calcium, magnesium, potassium, iron, and phosphorus contents in the inorganic fraction were 152, 44, 53, 7, and 131 mg g⁻¹, respectively; moreover, the total, acid-detergent fiber, humic acid, and fulvic acid carbon

contents in the acid-insoluble organic fraction were 452, 344, 25, and 52 mg g⁻¹, respectively [24]. After pH adjustment, the fractions were well mixed at the inorganic-to-acid-insoluble organic fraction ratios of 100/0, 75/25, 50/50, 25/75, and 0/100; the mixed samples were used as the AMCs herein (hereafter referred to AMC with inorganic-to-organic ratios of 100/0, 75/25, 50/50, 25/75, and 0/100).

2.3. Soil-Incubation Experiment. The contaminated soil was mixed with each AMC sample at 10 wt% and incubated at room temperature (25°C) for 184 days. Soil without AMC was also prepared as a control. Three replicates were prepared for each treatment. The water content in the soil was maintained at 60% of its maximum water-holding capacity during the incubation period. Soil samples were collected at 0, 7, 30, 90, and 184 days; the samples were freeze-dried and analyzed to determine the levels of water-soluble lead and water-soluble organic carbon. The soil sampled on day 184 was analyzed to assess lead phases by sequential extraction and microbial enzyme activities. Herein, the level of water-soluble lead was employed as an indicator of lead mobility and bioavailability in the soil, because its water-soluble form is easily mobile and utilized by plant and soil biota.

Another soil-incubation experiment was conducted to evaluate CO₂ emission from the soil with the AMCs with inorganic-to-organic ratios of 100/0, 50/50, and 0/100. A 100 mL polypropylene bottle including the soil with and without the AMC, and two glass beakers—one having 0.5 M NaOH and the other having 0.5 M H₂SO₄—were placed into a 5 L glass bottle and incubated at room temperature (25°C). A 5 L bottle without soil was also prepared. Three replicates were prepared for each treatment. At days 7, 14, 30, 60, 120, and 194, the glass beaker containing 0.5 M NaOH was replaced with a fresh 0.5 M NaOH-containing beaker. The collected NaOH was titrated with 0.2 M HCl and the CO₂ emission was calculated from the following equation:

$$C_s = \frac{V \times F - C_b}{S}, \quad (1)$$

where C_s is the amount of CO₂ emission (mol g-soil⁻¹), V is the amount of 0.2 M HCl titrated (mL), F is the factor of 0.2 M HCl (mol-CO₂ mL⁻¹), C_b is the amount of CO₂ emission in the blank (mol), and S is the amount of soil (10.0 g). The CO₂ emission derived from AMC was calculated by subtracting the emission by the AMC-treated soil samples from that by the control soil sample.

2.4. Analytical Methods. The soil's pH value was measured in ultra-pure water using a pH meter (MM-60M, DKK-TOA Co., Japan). Soil texture was determined using the hydrometer method [26]. The total carbon and nitrogen contents in the soil were determined using a carbon, hydrogen, and nitrogen elemental analyzer (MT-6; Yanaco New Science Inc., Japan).

The water-soluble lead and organic carbon in soil were extracted using ultra-pure water (1:10 soil:solution ratio) and analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES; ULTIMA2; HORIBA Ltd., Japan) and a total organic carbon analyzer (TOC-V_{WS};

Shimadzu Co., Japan). The amorphous iron was extracted using Shuman's method [27]. The total lead, phosphorus, aluminum, and iron contents in the soil were determined by acid digestion with HNO₃ and HCl using a microwave. A sequential extraction procedure was performed on the soil samples in accordance with the procedure described by Tessier et al. [28]. In brief, each fraction was extracted with a 1 M MgCl₂ solution (exchangeable fraction), 1 M sodium acetate solution at pH 5 (carbonate fraction), 0.04 M NH₂OH-HCl in 25% (v/v) HOAc solution in a water bath at 95°C with occasional agitation (Fe/Mn oxide fraction), 0.02 M HNO₃ solution, 5 mL 30% H₂O₂ solution in a water bath at 85°C with occasional agitation (organic fraction), and 5 mL of HNO₃ and 2 mL of HCl using a microwave oven (residual fraction). All of the extracted or digested solutions were passed through a 0.45 μm filter and analyzed to determine the elemental concentration using ICP-AES.

Three different microbial enzyme activities—dehydrogenase, urease, and saccharase—were measured in the soil sample. The dehydrogenase activity was determined in accordance with the method described by Tabatabai [29] using triphenyltetrazolium chloride. The triphenylformazan produced was measured using spectrophotometry at 485 nm. The urease activity was monitored using the method described by Kandeler and Gerber [30] by measuring the NH₄⁺ produced after the incubation of soil with urea. The saccharase activity was determined in accordance with the method described by Frankenberger and Johanson [31].

2.5. Statistical Analysis. Statistical analyses were performed using JMP Ver. 8.0.2 (SAS Institute Inc.). An analysis of variance was used to measure microbial enzyme activities. The differences between the mean values were determined using Tukey's honestly significant difference test at a 95% confidence level.

3. Results

3.1. Soil pH, Water-Soluble Lead, and Organic Carbon in Soil with AMC. The pH in the control soil was not significantly changed and ranged from 7.5 to 7.7 throughout the incubation period (Table 3). Moreover, the soil pH levels in all the AMCs were not significantly different from that in the control, indicating that the soil pH did not affect the enhancement or reduction in the lead mobility and bioavailability in the soil with AMC.

Figure 1(a) shows the amount of water-soluble lead in the soil with AMC. The amount of water-soluble lead in the control soil ranged from 35 to 44 mg kg⁻¹ throughout the incubation period. The amount of water-soluble lead in the soil treated with AMC with an inorganic-to-organic ratio of 0/100 was higher than that in the control soil throughout the incubation period. The amount of water-soluble lead in the soil treated by AMC with an inorganic-to-organic ratio of 25/75 was equal to or at a higher level than that in the control soil before day 30, but it decreased to 36% of that in the control soil on day 184. The amounts of water-soluble lead in the soil samples treated by AMC with inorganic-to-organic

TABLE 3: pH in soils amended with simulated compost during incubation period ($n = 3$).

Compost (Inorganic/organic)	Days of incubation				
	0	7	30	90	184
100/0	7.7 ± 0.0	7.5 ± 0.0	7.6 ± 0.1	7.8 ± 0.0	7.8 ± 0.0
75/25	7.7 ± 0.0	7.5 ± 0.0	7.7 ± 0.0	7.8 ± 0.0	7.8 ± 0.1
50/50	7.6 ± 0.0	7.6 ± 0.0	7.7 ± 0.1	7.8 ± 0.0	7.6 ± 0.0
25/75	7.4 ± 0.0	7.4 ± 0.0	7.8 ± 0.0	7.8 ± 0.0	7.6 ± 0.0
0/100	7.2 ± 0.0	7.3 ± 0.0	7.6 ± 0.1	7.8 ± 0.0	7.5 ± 0.2
Control	7.5 ± 0.1	7.6 ± 0.0	7.7 ± 0.0	7.5 ± 0.1	7.5 ± 0.2

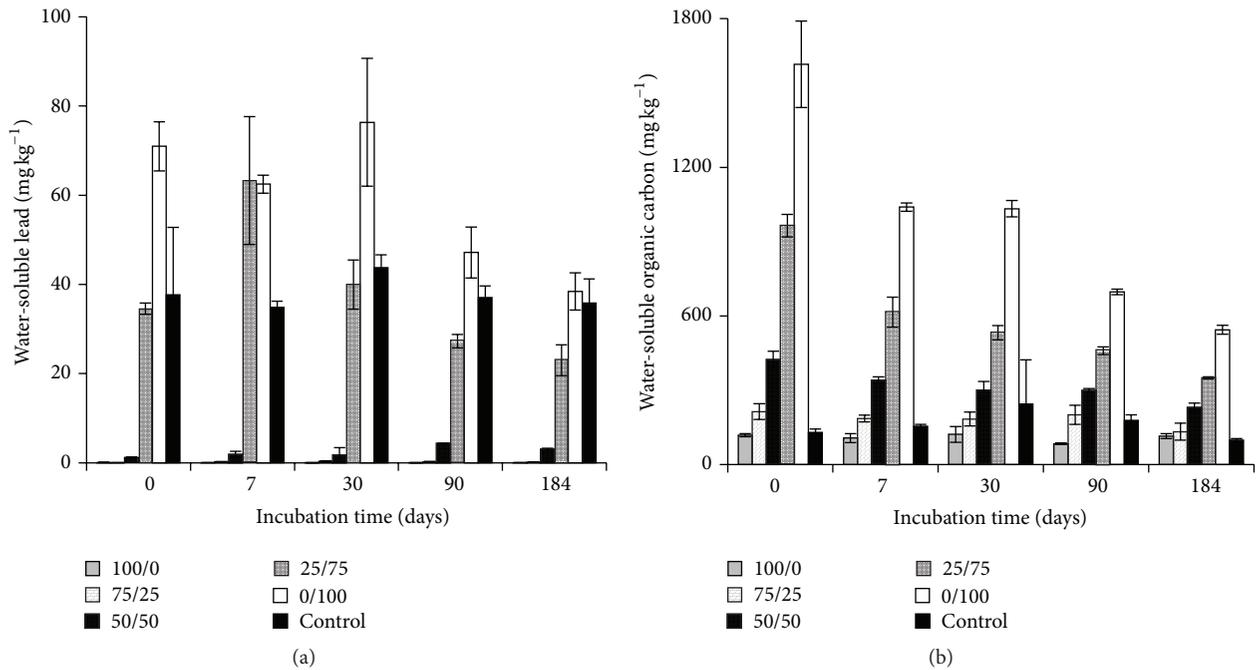


FIGURE 1: Water-soluble lead (a) and organic carbon (b) in soil amended with AMC of inorganic/organic = 100/0, 75/25, 50/50, 25/75, and 0/100 and without AMC (control). Vertical bars indicate the standard error.

ratios of 50/50, 75/25, and 100/0 were 3.4%–12%, 0.1%–0.8%, and 0.1%–0.2%, respectively, of the value in the control soil. The amount of water-soluble organic carbon in the soil is shown in Figure 1(b). At the beginning of the incubation period, the amounts of water-soluble organic carbon in the soils treated with different AMC compositions were arranged in the following order: inorganic/organic = 0/100 > inorganic/organic = 25/75 > inorganic/organic = 50/50 > inorganic/organic = 75/25 > control > inorganic/organic = 100/0. The amounts of water-soluble organic carbon in the soil treated by AMC with inorganic-to-organic ratios of 50/50, 75/25, and 100/0 remained at their initial values during the incubation period. The amounts of water-soluble organic carbon in the soil treated by AMC with inorganic-to-organic ratios of 0/100 and 25/75 had rapidly decreased between days 0 and 7, after which gradual decreases were observed. The decreases in water-soluble organic carbon between days 0 and 184 were 1,071 and 615 mg kg⁻¹ under inorganic-to-organic ratios of 0/100 and 25/75, respectively.

3.2. *CO₂ Emission from Soil Amended with AMC.* The cumulated CO₂ emission derived from AMC is shown in Figure 2. The level of CO₂ emission from the AMC with an inorganic-to-organic ratio of 0/100 increased during the early stage of incubation and then remained at approximately 500 mg-C kg⁻¹. The CO₂ emission trends from the AMC with inorganic-to-organic ratios of 50/50 and 100/0 were similar; they slightly increased at the beginning of incubation and then remained at approximately 100 mg-C kg⁻¹.

3.3. *Lead Phases by Sequential Extraction in Lead-Contaminated Soil.* Figure 3 shows the lead fraction results under sequential extraction. The average recovery, which was defined herein as the ratio of the sum total level of each fraction (Figure 3) to the total level of lead in the soil (Table 1), was 119 ± 20%. The composition of the control soil was as follows: 12.8% exchangeable fraction, 51.2% carbonate fraction, 20.7% Fe/Mn oxide fraction, 9.3% organic fraction, and 6.0% residual fraction. The percentage of organic fraction

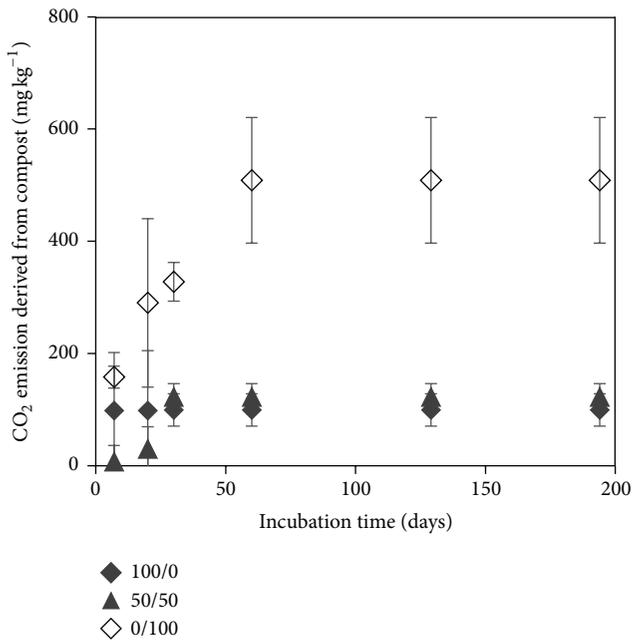


FIGURE 2: Cumulative CO₂ emission derived from AMC with inorganic/organic = 100/0, 50/50, and 0/100. Vertical bars indicate the standard error.

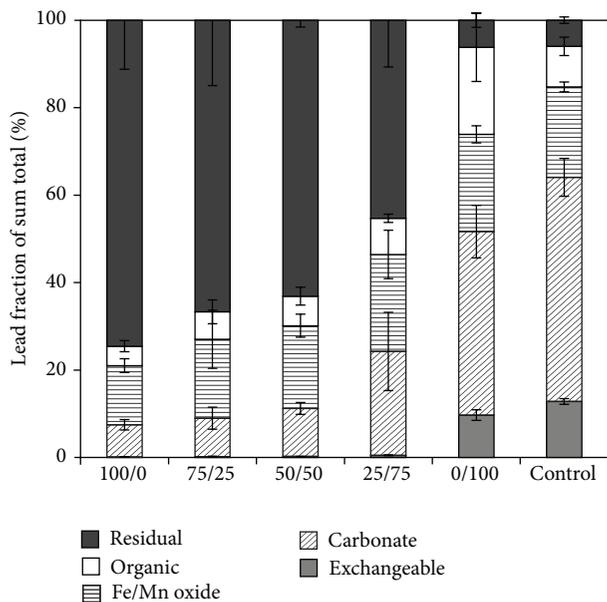


FIGURE 3: Sequential extraction of lead from soil amended with AMC of inorganic/organic = 100/0, 75/25, 50/50, 25/75, and 0/100 and without AMC (control) after 184 days of incubation. Vertical bars indicate the standard error.

by sequential extraction in the soil treated by AMC with an inorganic-to-organic ratio of 0/100 increased compared with that in the control soil, whereas that of carbonate decreased. The addition of AMC with a higher ratio of inorganic fraction resulted in a greater enhancement in the residual percentage. Furthermore, in soils with the AMCs containing an inorganic

fraction of 25% or more, the percentage of organic fraction was at the same level as that in the control soil.

3.4. *Microbial Enzyme Activities in Lead-Contaminated Soil.* The dehydrogenase and urease activities in the soil treated by AMC with inorganic-to-organic ratios of 0/100 and 25/75, respectively, were significantly higher than that in the control soil; however, those in the soil treated by AMC with inorganic-to-organic ratios of 75/25 and 100/0 were significantly lower or on the same level (Figure 4).

4. Discussion

4.1. *Role of Organic Component in Animal Manure Compost Lead Immobilization and Rehabilitation of Microbial Activity.* The water-soluble lead level in the soil treated by AMC with an inorganic-to-organic ratio of 0/100 did not become lower than that in the control soil during the incubation period (Figure 1(a)), whereas the lead phases in the soil by sequential extraction were altered to be more insoluble; the organic fraction was increased (Figure 3). Moreover, at the early stage of incubation, the water-soluble lead level remained at a higher level in the soil treated by AMC with an inorganic-to-organic ratio of 25/75. However, the water-soluble lead level decreased as the incubation time increased in soil with both composts. These observations would be explained by the higher level of water-soluble organic matter and its sorption and decomposition in the soil thereby increasing the incubation time. The water-soluble organic matter can easily form complexes with lead ions, and its complexes could enhance the lead mobility in the soil [17, 32, 33]. Therefore, at the early stage of incubation, the high level of water-soluble organic carbon would result in an enhancement of the lead mobility in the soil treated by AMC with inorganic-to-organic ratios of 0/100 and 25/75. The water-soluble organic matter was derived from the compost containing humic and fulvic acids with relatively low molecular weight [34, 35]. These organic compounds are also readily decomposable and sorbed on the soil surface [36, 37]. According to the result for CO₂ emission (Figure 2), the amount of CO₂ emission was lower than that of water-soluble organic carbon-decrease from day 0 to day 184, suggesting that some of the water-soluble organic matter derived from the compost was decomposed and some of it was sorbed in the soil with the increase in the incubation period. Thus, the level of water-soluble lead would decrease with that water-soluble organic carbon in the soil treated by AMC with inorganic-to-organic ratios of 0/100 and 25/75. It has been known that the compost amendment induced the very short-term leaching pulses of lead after the application [38], and lead was redistributed to the soil component by the decomposition of dissolved organic matter [39]. These results suggest that the organic component in the AMC does not considerably contribute to the immobilization of lead and suppression of lead mobility and bioavailability. This was comparable with the results of Schwab et al. [19] and Levonmäki et al. [40], who reported that water-soluble organic matter enhanced the lead mobility by the formation of complexation. However, all of the microbial enzyme activities

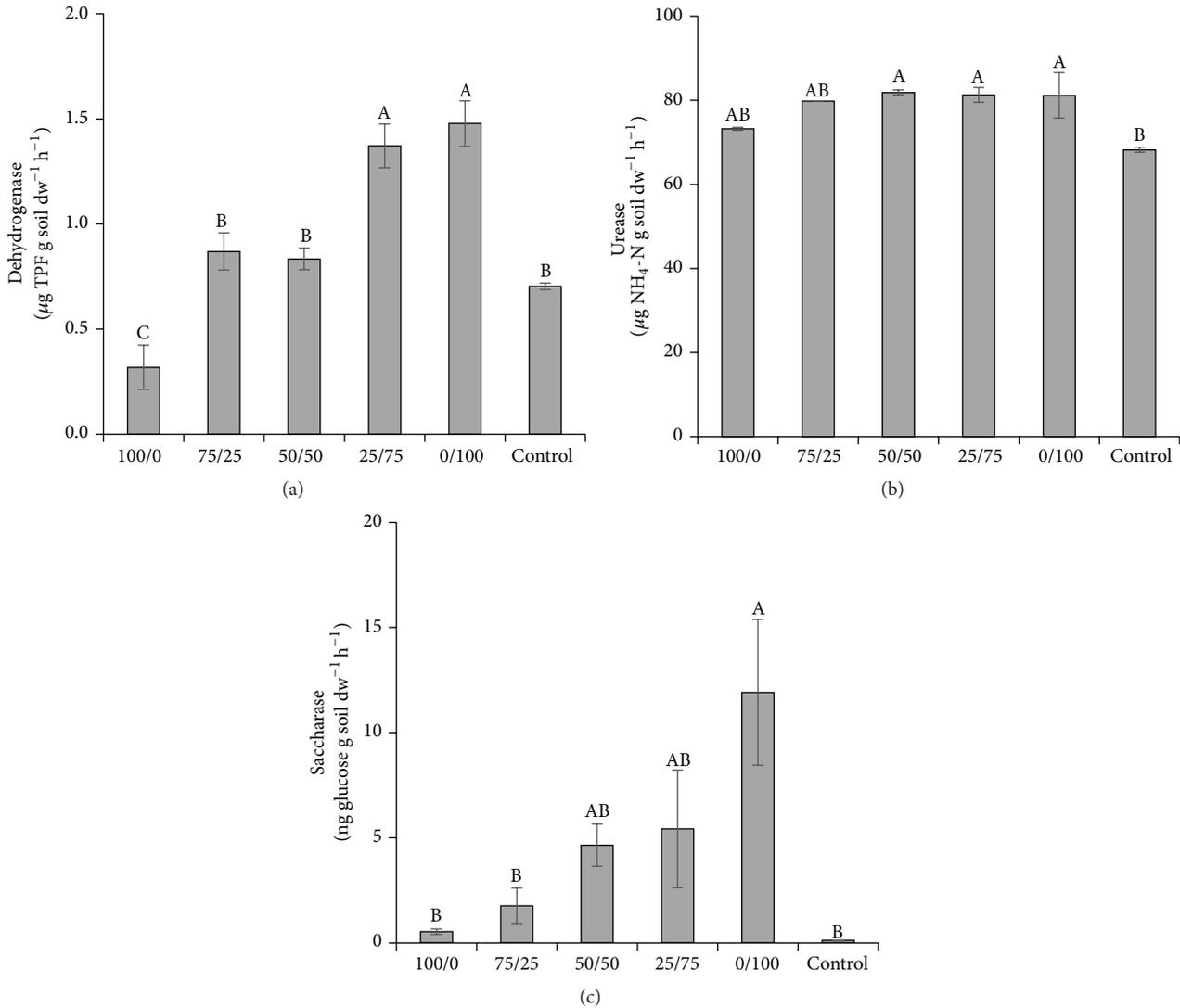


FIGURE 4: Enzyme activities of dehydrogenase (a), urease (b), and saccharase (c) in soil amended with AMC of inorganic/organic = 100/0, 75/25, 50/50, 25/75, and 0/100 and without AMC (control) after 184 days of incubation. Vertical bars indicate the standard error. Different letters indicate significant difference at $P < 0.05$.

measured herein increased in the soil treated by AMC with an inorganic-to-organic ratio of 0/100, despite the fact that the level of water-soluble lead was higher. The dehydrogenase activity, which is an indicator of the overall microbial activity [8, 9, 41–43], in the soil treated by AMC containing 50% or more inorganic fraction was the same level as that in the control soil, suggesting that the inorganic component in the AMC did not significantly contribute to the enhancement in the microbial activity, despite the fact that the lead mobility and bioavailability are greatly decreased by its addition. Farrell et al. [44] also showed that the microbial enzyme activities in the soil amended with the compost became higher than that in the inorganic material. The water-soluble organic matter derived from the compost is utilized as a nutrient source by microorganisms; thus, the addition of AMC with high organic matter content would induce the rehabilitation

of microbial activity owing to the large amount of readily decomposable organic matter.

4.2. Role of the Inorganic Component in Animal Manure Compost on Lead Immobilization. The addition of AMC containing 50% or more inorganic fraction reduced the water-soluble lead by over 88% during the incubation period (Figure 1(a)). Moreover, the addition of AMC containing 25% or more inorganic fraction could alter lead phases to be more insoluble. These results indicate that AMC containing 50% or more inorganic fraction could immobilize lead and reduce the lead bioavailability in the soil. The inorganic fraction used herein contained a considerable amount of phosphorus, which results in the precipitation of lead phosphate minerals such as pyromorphite [24]. Pyromorphite is thermodynamically stable with a solubility product of $\log K_{\text{sp}} =$

–25.05 [45]. Therefore, the phosphorus in the AMC's inorganic component was responsible for the increase in the percentage of the residual fraction and decrease in the water-soluble lead level. This is supported by the results of Walker et al. [10], Liu et al. [11], and Clemente et al. [18], who suggested that the immobilization of lead and cadmium would be due to the precipitation of insoluble phosphate salts. The percentage of Fe/Mn oxide and organic fractions by sequential extraction in the soil with AMC containing 25% or more inorganic fraction was lesser than or approximately equal to that in the control soil, although the residual fraction increased with increase in the inorganic fraction ratio in AMC. Moreover, in the soil treated by AMC containing 50% or less inorganic fraction, the level of water-soluble organic carbon was higher than that in the control soil. These results suggest that the phosphorus in the inorganic component of AMC could immobilize lead-precipitating lead phosphate minerals even if the AMC contained more organic than inorganic components. This may be because the magnitude of lead immobilization by the inorganic component of AMC suppressed the magnitude of the facilitation of lead mobility by the organic component in AMC.

The level of water-soluble lead in the soil treated by AMC with an inorganic-to-organic ratio of 25/75 was higher than that in the control soil during the first 30 days of incubation, whereas the lead phases were altered to be more insoluble. This was attributed to incomplete immobilization. Scheckel et al. [46] demonstrated that not all lead in soil could be immobilized by phosphorus material, according to extended X-ray-absorption fine-structure analysis. The percentages of exchangeable and carbonate fractions by sequential extraction in the soil treated by AMC with an inorganic-to-organic ratio of 25/75 were higher than that in the soil treated by AMC that was 50% or more inorganic fraction. The levels of water-soluble organic carbon in the soil treated by AMC with an inorganic-to-organic ratio 25/75 were also higher, particularly during the first 30 days of incubation. The higher amount of water-soluble organic matter formed complexes with lead dissolved from the exchangeable and carbonate fractions, resulting in an enhancement in the level of water-soluble lead in the early stage of incubation. With the increasing incubation time, water-soluble organic matter was decomposed and the level of water-soluble lead decreased below that in the control soil.

4.3. Optimal Ratio of Inorganic and Organic Components in Animal Manure Compost for Lead Immobilization and the Rehabilitation of Microbial Activity. Various inorganic percentages are used in the AMC, ranging from 7.3 to 82.8% [25]. The ranges of the inorganic fraction of AMC in this study fall within this range. On the basis of this study's findings, an inorganic component with a high phosphorus content of 50% or more is required to alter lead phases to be more insoluble and reduce the water-soluble lead level to less than that in the soil without compost, although the microbial activities are not enhanced. The importance of an inorganic component for the immobilization of heavy metals including lead in soil is pointed out by other researchers [21, 47, 48].

In contrast, 25% inorganic AMC can alter lead phases to be more insoluble and simultaneously enhance microbial activities, whereas the water-soluble lead level is higher than that in the soil without compost during the first 30 days after the application. This is consistent with the result of Katoh et al. [17], who indicated that the application of 25% inorganic swine manure compost could alter lead phases to be more insoluble and improve plant growth and microbial enzyme activities; however, the level of water-soluble lead was higher than that in the cattle manure compost during the early stage of incubation (90 days after application). These findings suggest that AMCs cannot immobilize both lead and restore microbial activity. Therefore, to immobilize lead and suppress the lead mobility and bioavailability using AMC, AMC that is 50% inorganic or more and contains a large phosphorus component should be applied to contaminated sites. However, in the case of low precipitation over a month, for example, during a dry season, 25% inorganic AMC should be used to both immobilize lead and restore microbial activity.

5. Conclusion

The amount of water-soluble lead in the soil treated by 100% organic AMC remained higher than that in the control soil throughout the 184-day incubation period, although it tended to decrease with increasing incubation time. The amount of water-soluble lead in the soil treated by AMC with an inorganic-to-organic ratio of 25/75 was higher than that in the soil without compost during the early stage of incubation, but it reached a lower level than that in the soil without compost after 90 days. The amounts of water-soluble lead in the soil treated by AMC containing 50% or more inorganic fraction were suppressed by over 88% from the value in the soil without compost and remained low throughout the incubation period. The reduction in the level of water-soluble lead in the soil treated by AMC with inorganic-to-organic ratios of 0/100 and 25/75 would be explained by the decomposition of water-soluble organic matter. The ratio of the residual fraction after sequential extraction was enhanced and the readily soluble lead fractions (exchangeable and carbonate fractions) were reduced in soils treated by AMC containing 25% or more inorganic fraction. In soil treated with fully organic AMC, the readily soluble lead fraction in sequential extraction did not change in comparison with that in the control soil, whereas the organic fraction in sequential extraction was enhanced. The compost containing 25% or less inorganic fraction could improve the microbial activity, but the compost containing 50% or more inorganic fraction could not. These results indicate that the compost containing 50% or more inorganic fraction with a high phosphorus content is suitable for immobilizing lead and reducing lead mobility and bioavailability in the soil. However, to immobilize lead and improve the microbial activity at the same time, the AMC with 25% inorganic and 75% organic components should be used as a lead immobilization material, but note that higher lead mobility at the initial stage after the application should be considered.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] D. J. Walker, R. Clemente, and M. P. Bernal, "Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste," *Chemosphere*, vol. 57, no. 3, pp. 215–224, 2004.
- [2] J. H. Park, N. Bolan, M. Megharaj, and R. Naidu, "Comparative value of phosphate sources on the immobilization of lead, and leaching of lead and phosphorus in lead contaminated soils," *Science of the Total Environment*, vol. 409, no. 4, pp. 853–860, 2011.
- [3] X. Cao, A. Wahbi, L. Ma, B. Li, and Y. Yang, "Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid," *Journal of Hazardous Materials*, vol. 164, no. 2–3, pp. 555–564, 2009.
- [4] X. Cao, D. Dermatas, X. Xu, and G. Shen, "Immobilization of lead in shooting range soils by means of cement, quicklime, and phosphate amendments," *Environmental Science and Pollution Research*, vol. 15, no. 2, pp. 120–127, 2008.
- [5] G. M. Hettiarachchi, G. M. Pierzynski, and M. D. Ransom, "In situ stabilization of soil lead using phosphorus and manganese oxide," *Environmental Science and Technology*, vol. 34, no. 21, pp. 4614–4619, 2000.
- [6] A. Davis, L. E. Eary, and S. Helgen, "Assessing the efficacy of lime amendment to geochemically stabilize mine tailings," *Environmental Science and Technology*, vol. 33, no. 15, pp. 2626–2632, 1999.
- [7] E. Lombi, F.-J. Zhao, G. Zhang et al., "In situ fixation of metals in soils using bauxite residue: chemical assessment," *Environmental Pollution*, vol. 118, no. 3, pp. 435–443, 2002.
- [8] P. Alvarenga, A. P. Gonçalves, R. M. Fernandes et al., "Evaluation of composts and liming materials in the phytostabilization of a mine soil using perennial ryegrass," *Science of the Total Environment*, vol. 406, no. 1–2, pp. 43–56, 2008.
- [9] P. Alvarenga, A. P. Gonçalves, R. M. Fernandes et al., "Organic residue as immobilizing agents in aided phytostabilization: (I) Effects on soil chemical characteristics," *Chemosphere*, vol. 74, no. 10, pp. 1292–1300, 2009.
- [10] D. J. Walker, R. Clemente, A. Roig, and M. P. Bernal, "The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils," *Environmental Pollution*, vol. 122, no. 2, pp. 303–312, 2003.
- [11] L. Liu, H. Chen, P. Cai, W. Liang, and Q. Huang, "Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost," *Journal of Hazardous Materials*, vol. 163, no. 2–3, pp. 563–567, 2009.
- [12] A. Sato, H. Takeda, W. Oyanagi, E. Nishihara, and M. Murakami, "Reduction of cadmium uptake in spinach (*Spinacia oleracea* L.) by soil amendment with animal waste compost," *Journal of Hazardous Materials*, vol. 181, no. 1–3, pp. 298–304, 2010.
- [13] H.-S. Chen, Q.-Y. Huang, L.-N. Liu, P. Cai, W. Liang, and M. Li, "Poultry manure compost alleviates the phytotoxicity of soil cadmium: influence on growth of pakchoi (*Brassica chinensis* L.)," *Pedosphere*, vol. 20, no. 1, pp. 63–70, 2010.
- [14] R. Clemente, C. Almela, and M. P. Bernal, "A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste," *Environmental Pollution*, vol. 143, no. 3, pp. 397–406, 2006.
- [15] E. Doelsch, A. Masion, G. Moussard, C. Chevassus-Rosset, and O. Wojciechowicz, "Impact of pig slurry and green waste compost application on heavy metal exchangeable fractions in tropical soils," *Geoderma*, vol. 155, no. 3–4, pp. 390–400, 2010.
- [16] R. P. Narwal and B. R. Singh, "Effect of organic materials on partitioning, extractability and plant uptake of metals in an alum shale soil," *Water, Air, and Soil Pollution*, vol. 103, no. 1–4, pp. 405–421, 1998.
- [17] M. Katoh, W. Kitahara, R. Yagi, and T. Sato, "Suitable chemical properties of animal manure compost to facilitate Pb immobilization in soil," *Soil and Sediment Contamination*, vol. 23, no. 5, pp. 523–539, 2014.
- [18] R. Clemente, Á. Escolar, and M. P. Bernal, "Heavy metals fractionation and organic matter mineralisation in contaminated calcareous soil amended with organic materials," *Bioresource Technology*, vol. 97, no. 15, pp. 1894–1901, 2006.
- [19] P. Schwab, D. Zhu, and M. K. Banks, "Heavy metal leaching from mine tailings as affected by organic amendments," *Biore-source Technology*, vol. 98, no. 15, pp. 2935–2941, 2007.
- [20] R. Clemente and M. P. Bernal, "Fractionation of heavy metals and distribution of organic carbon in two contaminated soils amended with humic acids," *Chemosphere*, vol. 64, no. 8, pp. 1264–1273, 2006.
- [21] A. Baghaie, A. H. Khoshgoftarmanesh, M. Afyuni, and R. Schulin, "The role of organic and inorganic fractions of cow manure and biosolids on lead sorption," *Soil Science and Plant Nutrition*, vol. 57, no. 1, pp. 11–18, 2011.
- [22] S. Deiana, C. Gressa, B. Manunza, R. Rausa, and R. Seever, "Analytical and spectroscopic characterization of humic acids extracted from sewage sludge, manure, and worm compost," *Soil Science*, vol. 150, no. 1, pp. 419–424, 1990.
- [23] M. A. A. Zaini, R. Okayama, and M. Machida, "Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons," *Journal of Hazardous Materials*, vol. 170, no. 2–3, pp. 1119–1124, 2009.
- [24] M. Katoh, W. Kitahara, and T. Sato, "Sorptions of lead in animal manure compost: contributions of inorganic and organic fractions," *Water, Air, and Soil Pollution*, vol. 225, no. 1, article 1828, 2014.
- [25] T. Yamaguchi, Y. Harada, and M. Tsuiki, "Basic data of animal waste composts," *Miscellaneous Publication of the National Agriculture Research Center*, vol. 41, pp. 1–178, 2000 (Japanese).
- [26] G. W. Gee and J. M. Bauder, "Particle-size analysis," in *Methods of Soil Analysis, Part 1*, A. L. Page, R. H. Miller, and D. R. Keeney, Eds., pp. 383–411, American Society of Agronomy, Madison, Wis, USA, 1986.
- [27] L. M. Shuman, "Fractionation method for soil microelements," *Soil Science*, vol. 140, no. 1, pp. 11–22, 1985.

- [28] A. Tessier, P. G. C. Campbell, and M. Blsson, "Sequential extraction procedure for the speciation of particulate trace metals," *Analytical Chemistry*, vol. 51, no. 7, pp. 844–851, 1979.
- [29] M. A. Tabatabai, "Soil enzymes," in *Methods of Soil Analysis, Part 2*, S. H. Mickelson and J. M. Bigham, Eds., pp. 77–83, American Society of Agronomy, Madison, Wis, USA, 1994.
- [30] E. Kandeler and H. Gerber, "Short-term assay of soil urease activity using colorimetric determination of ammonium," *Biology and Fertility of Soils*, vol. 6, no. 1, pp. 68–72, 1988.
- [31] W. T. Frankenberger and J. B. Johanson, "Method of measuring invertase activity in soils," *Plant and Soil*, vol. 74, no. 3, pp. 313–323, 1983.
- [32] S. Sauvé, M. McBride, and W. Hendershot, "Soil solution speciation of lead (II): effects of organic matter and pH," *Soil Science Society of America Journal*, vol. 62, no. 3, pp. 618–621, 1998.
- [33] H. Wang, X. Shan, T. Liu et al., "Organic acids enhance the uptake of lead by wheat roots," *Planta*, vol. 225, no. 6, pp. 1483–1494, 2007.
- [34] M. Aoyama, "Fractionation of water-soluble organic substances formed during plant residue decomposition and high performance size exclusion chromatography of the fractions," *Soil Science and Plant Nutrition*, vol. 42, no. 1, pp. 31–40, 1996.
- [35] M. Aoyama, "Properties of fine and water-soluble fractions of several composts II. Organic forms of nitrogen, neutral sugars, and muramic acid in fractions," *Soil Science and Plant Nutrition*, vol. 37, no. 4, pp. 629–637, 1991.
- [36] T. Paré, H. Dinel, M. Schnitzer, and S. Dumontet, "Transformations of carbon and nitrogen during composting of animal manure and shredded paper," *Biology and Fertility of Soils*, vol. 26, no. 3, pp. 173–178, 1998.
- [37] D. L. Jones and D. S. Brassington, "Sorption of organic acids in acid soils and its implications in the rhizosphere soil," *European Journal of Soil Science*, vol. 49, pp. 447–455, 1998.
- [38] M. Farrell, W. T. Perkins, P. J. Hobbs, G. W. Griffith, and D. L. Jones, "Migration of heavy metals in soil as influenced by compost amendments," *Environmental Pollution*, vol. 158, no. 1, pp. 55–64, 2010.
- [39] A. W. Schroth, B. C. Bostick, J. M. Kaste, and A. J. Friedland, "Lead sequestration and species redistribution during soil organic matter decomposition," *Environmental Science & Technology*, vol. 42, no. 10, pp. 3627–3633, 2008.
- [40] M. Levonmäki, H. Hartikainen, and T. Kairesalo, "Effect of organic amendment and plant roots on the solubility and mobilization of lead in soils at a shooting range," *Journal of Environmental Quality*, vol. 35, no. 4, pp. 1026–1031, 2006.
- [41] A. Pérez-de-Mora, P. Burgos, E. Madejón, F. Cabrera, P. Jaekel, and M. Schloter, "Microbial community structure and function in a soil contaminated by heavy metals: effects of plant growth and different amendments," *Soil Biology and Biochemistry*, vol. 38, no. 2, pp. 327–341, 2006.
- [42] S. Doni, C. MacCi, E. Peruzzi, M. Arenella, B. Ceccanti, and G. Masciandaro, "In situ phytoremediation of a soil historically contaminated by metals, hydrocarbons and polychlorobiphenyls," *Journal of Environmental Monitoring*, vol. 14, no. 5, pp. 1383–1390, 2012.
- [43] J. Wyszowska, J. Kucharski, and W. Lajsner, "The effects of copper on soil biochemical properties and its interaction with other heavy metals," *Polish Journal of Environmental Studies*, vol. 15, no. 6, pp. 927–934, 2006.
- [44] M. Farrell, G. W. Griffith, P. J. Hobbs, W. T. Perkins, and D. L. Jones, "Microbial diversity and activity are increased by compost amendment of metal-contaminated soil," *FEMS Microbiology Ecology*, vol. 71, no. 1, pp. 94–105, 2010.
- [45] P. Miretzky and A. Fernandez-Cirelli, "Phosphates for Pb immobilization in soils: a review," *Environmental Chemistry Letters*, vol. 6, no. 3, pp. 121–133, 2008.
- [46] K. G. Scheckel, J. A. Ryan, D. Allen, and N. V. Lescano, "Determining speciation of Pb in phosphate-amended soils: method limitations," *Science of the Total Environment*, vol. 350, no. 1–3, pp. 261–272, 2005.
- [47] P. Castaldi, L. Santona, and P. Melis, "Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth," *Chemosphere*, vol. 60, no. 3, pp. 365–371, 2005.
- [48] A. Ruttens, M. Mench, J. V. Colpaert, J. Boisson, R. Carleer, and J. Vangronsveld, "Phytostabilization of a metal contaminated sandy soil. I: influence of compost and/or inorganic metal immobilizing soil amendments on phytotoxicity and plant availability of metals," *Environmental Pollution*, vol. 144, no. 2, pp. 524–532, 2006.

Research Article

Cadmium Phytoremediation Potential of Napiergrass Cultivated in Kyushu, Japan

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Napiergrass (*Pennisetum purpureum* Schumach), a C₄ tropical species, has been used for forage since it has high dry matter productivity, sustainability over several years in low-altitudinal sites of Kyushu, and little damage from serious pests. Recently, this grass has gained attention due to its potential as a bioethanol feedstock and for phytoremediation. Napiergrass cultivar Wruk Wona was grown as an annual crop in cadmium- (Cd-) contaminated soils under two cutting frequencies. Annual dry matter yield was not affected significantly by cutting frequency, but the concentration and uptake of Cd were higher when cut twice rather than only once, due to high Cd content of the herbage from the second cutting. Therefore, the soil Cd concentration was reduced by 4.6% when managed by cutting twice in a single year of Napiergrass cultivation.

1. Introduction

Cadmium (Cd), a heavy metal, poses risks to human health through the consumption of contaminated agricultural products. Since much arable land in Japan has been polluted by Cd, mainly from mining activity, the Japanese government reduced the critical contamination level of Cd in brown rice from 1.0 to 0.4 mg kg⁻¹ in February, 2011, in conformance with the international WHO/FAO level [1]. The regulated level of 0.4 mg kg⁻¹ for brown rice is higher than that for wheat and leafy vegetables (0.2 mg kg⁻¹), which might indicate a future shift to make the regulated level for brown rice even more stringent. This new regulation should prompt remediation of Cd-contaminated land to increase the availability of arable land. Remediation techniques such as physical soil dressing and chemical washing with solvents have been applied to highly contaminated soils, such as old factory sites, but these conventional techniques have high cost, irrespective of purification efficiency. However, phytoremediation is suitable for arable lands over a wider area [2].

Napiergrass (*Pennisetum purpureum* Schumach), a C₄ tropical forage species, produces high dry matter (DM) yield up to 33 t DM ha⁻¹ yr⁻¹ in the first year of establishment in Kyushu, Japan [3]. The grass is resistant to heavy metal-contaminated substrates such as soil with a high Cu level (50 mg kg⁻¹) in a pot trial [4] and in solutions containing stable cesium-133 (¹³³Cs) [5]; although when grown on contaminated soil, it cannot be fed to livestock. Herbaceous species such as *Miscanthus sinensis* grown in paddy fields [6, 7], *Juncus subsecundus* in soil culture [8], switchgrass in hydroponic culture [9], and several energy crops such as *Arachis hypogaea*, *Brassica rapa*, and *Helianthus annuus* in pots [10] absorb contaminating Cd, while information is lacking on the Cd absorption ability of Napiergrass [11], despite its high DM production potential. In our previous study [11], Napiergrass cv. Wruk Wona showed higher potential for removing Cd contamination than cv. Merkeron.

Cutting frequency significantly affects herbage DM yield, DM composition, and concentrations of structural carbohydrates and crude protein [12], and Cd concentration in Napiergrass was markedly higher in the second cutting than

in the first, even though the second-cutting biomass was very limited [11].

Therefore, the objective of this study was to determine the phytoremediation potential of Napiergrass when cultured in Cd-contaminated hydroponic solutions and in field trials, as well as the management practices that optimize phytoremediation potential for Cd.

2. Materials and Methods

2.1. Hydroponic Test of Napiergrass in Cd Added Solutions. Stem cuttings (1-2 nodes) of nursery plants of a tall-type of Napiergrass (cv. Merkeron, the most widespread throughout the region of Kyushu), which were grown in soil before the experiments, were transferred to 180 L Cd-free Hoagland nutrient solution. The solution contained 2 M KNO₃, 2 M Ca(NO₃)₂, 2 M MgSO₄, 1 M NH₄NO₃, and 1 M KH₂PO₄ as major elements and 462.5 mM H₃BO₃, 91.45 mM MnCl₂, 7.65 mM ZnSO₄, 3.195 mM CuSO₄, and 4.96 mM Na₂MoO₄ as minor elements. The nursery plants were grown with air bubbled through the solution for 2 weeks in a glasshouse, without control over temperature, humidity, or day length, to allow shoots to emerge. The shoots were transferred to plastic containers (41 cm long, 31 cm wide, and 10 cm high) containing 3 levels of Cd (0, 50, or 100 μM Cd), supplied in the form of CdCl₂ in 4 L Hoagland nutrient solution replaced weekly with air bubbled continuously through the solution in a hot summer season, from 23 June to 25 August, 2010. Containers with 9 plants were arranged in a randomized block design with 3 replications each for 3 randomly allocated treatments, for a total of 81 plants. Growth attributes of plant height and tiller number were measured every 2 weeks after treatment. To determine DM yield, aerial plant fractions were harvested from 3 plants per replication 5 cm above the water level at 2, 4, and 8 weeks after treatment, which corresponded at 4, 6, and 10 weeks after planting in the solution media, respectively. The Cd concentration of aerial plant fractions, which were ground to pass through a 2-mm mesh plastic screen, was determined without replication by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500ce, Agilent Technology Co. Ltd, USA) using microwave decomposition equipment (ETHOS One, Milestone General Co. Ltd., Kanagawa, Japan) after predigestion in 60% HNO₃.

2.2. Field Test of Napiergrass in Cd Contaminated Soil. Napiergrass cv. Wruk Wona was subjected to field trials in Cd-contaminated paddy fields (gray lowland soil) in 2011 in Kyushu, Japan, where the previous research was carried out in 2010 [11]. The source of Cd contamination in the soil was fallout dust from a neighboring zinc-refining plant [13, 14]. The soil in these fields consists of clay loam (clay content 25%, silt content 22%, and sand content 53%). The pH and the electric conductivity (EC) of the surface soil at 0–15 cm depth were examined by twin compact pH meter (B-212, Horiba Co. Ltd., Tokyo, Japan) and twin conductivity meter (B-173, Horiba Co. Ltd, Tokyo, Japan), respectively, on 5 June, 2010, and 23 November, 2010. The total C and total N content of the soil in these fields were reported to be 24 g kg⁻¹ and 1.9 g kg⁻¹, respectively, by Ibaraki et al. [14]. The crops cultivated before

the previous [11] and present trials were sorghum as a summer crop and winter wheat as a winter crop.

After plowing, Napiergrass was vegetatively transplanted using stem cuttings at 2 plants m⁻² with 30 m² per plot on 7 May, 2011, and supplied with a basal application of slow-releasing LP compound fertilizer with 37.6 g m⁻² each of N, P₂O₅, and K₂O per season, which are levels suitable for supporting high biomass of this species [15]. The planting area was covered with biodegradable mulch film to suppress growth and Cd accumulation of weedy species, since the growth of Napiergrass is retarded severely by the invasion of weeds [16]. Plots were arranged in a randomized split-plot design with 6 replications, each containing 2 cutting frequencies (once or twice a year), for a total of 12 plots.

The growth attributes of plant height, tiller number, fresh weight, and DM of aerial fractions were determined for 2 plants per plot (total of 12 plants per treatment) at monthly intervals in the growing season on 11 June, 9 July, 5 August, 14 September, 15 October, and 26 October, 2011 (35, 63, 90, 130, 161, and 172 days after planting, resp.). Plants were harvested 10 cm above the ground and divided into fractions: leaf blade, stem inclusive of leaf sheath, and dead leaves. For treatments with two cuttings, the first cutting was on 14 September and the second was on 26 October, whereas, for single cuttings, plants were cut on 26 October. Plants were harvested into several fractions, such as aerial parts of cuts 10 cm above the ground, stubble 0–10 cm above the ground, underground stem parts, and roots in an area of 50 cm × 50 cm and 20 cm depth. On 26 October, aerial parts and stubble were divided into mother tiller and delayed tillers for the single-cutting treatment, and stubble was divided into mother tiller and tillers formed during regrowth in the two-cutting treatment. After measuring fresh weight of plant samples, subsamples (around 300–400 g) of all plant fractions were dried at 70°C for 72 h in a ventilating oven for DM determination. DM yield of plants was calculated by plant fresh weight, multiplied by percentage of DM, and plant density (2 plants m⁻²). The Cd concentration of ground plant samples was determined using the same procedure as in 2.1 for the hydroponic test.

Soils were sampled for 0–15 cm layer with 3 replications on 29 April, 14 September, and 26 October, 2011 (8 days before planting, and 130 and 172 days after planting, resp.), for both once- and twice-cutting plots. Soil Cd concentration was determined by atomic absorption spectroscopy (AA-6200, Shimadzu Corporation, Kyoto, Japan) at 2288 Å of wavelength after predigested with 5% hydrochloric acid solution gently shaking at 30°C for 1 hour and filtrated [17].

2.3. Statistical Analysis. One-way analysis of variance was carried out using Excel Statistics 2010 software (Social Information Service, Tokyo, Japan). Differences in means were evaluated using Fisher's least significant difference (LSD) test at the 5% level.

3. Results and Discussion

3.1. Culture of Napiergrass in Cd Solutions. Dry weight of the aerial herbage did not differ significantly at concentrations of 50 and 100 μM Cd ($P > 0.05$) at 2, 4, or 8 weeks after

TABLE 1: Changes in cadmium (Cd) concentration and uptake of Napiergrass plants grown in Cd-containing hydroponic conditions in 2010.

Parameter	Cd solution (μM)		
	0	50	100
Plant dry weight (g/plant)			
2 weeks after treatment	2.11 \pm 2.09	1.29 \pm 0.58	0.64 \pm 0.31
4 weeks after treatment	5.84 \pm 9.98	0.69 \pm 0.74	2.13 \pm 1.63
8 weeks after treatment	45.19 ^a \pm 37.44	4.03 ^b \pm 3.14	3.39 ^b \pm 1.15
Cd concentration (mg/kg)			
2 weeks after treatment	0	41	42
4 weeks after treatment	0	41	46
8 weeks after treatment	0.3	31	58
Cd uptake (g/plant)			
2 weeks after treatment	0 ^b	0.053 ^a \pm 0.024	0.027 ^a \pm 0.013
4 weeks after treatment	0	0.028 \pm 0.030	0.098 \pm 0.075
8 weeks after treatment	0.014 ^b \pm 0.011	0.125 ^a \pm 0.097	0.196 ^a \pm 0.066

Means in the same row followed by the same letter were not significantly different at $P < 0.05$ based on LSD test.

treatment, while it was significantly lower ($P < 0.05$) in both Cd treatments than in the control ($0 \mu\text{M}$ Cd) at any time after treatment. The Cd concentration in the aerial plant fractions tended to be higher in Cd treatments than in the control, where detection of trace Cd 8 weeks after treatment might be due to contamination from the Cd treatments. In contrast, a nonsignificant difference was observed between Cd concentrations (50 and $100 \mu\text{M}$ Cd) at 2, 4, and 8 weeks after treatment. Therefore, Cd accumulation in the aerial part tended to be higher at higher Cd concentration ($100 \mu\text{M}$), even though the difference between Cd concentrations was not significant and tended to increase with growth at 4 and 8 weeks after treatment (Table 1). The growth and Cd concentration of Napiergrass indicated that this species does not show any dose-dependent response to Cd, an effect also observed in *Miscanthus* [7]. The highest Cd uptake, occurring at the $100 \mu\text{M}$ Cd dose, suggests that this species may adapt to soils contaminated with significant levels of Cd. Even under hydroponic culture, Napiergrass was grown by bubbling with air both before and after Cd treatment to prevent reducing conditions in the solution. Reducing conditions would allow binding of Cd to divalent anions (S^{2-}), forming insoluble Cd sulfide (CdS) [14].

3.2. Response of Napiergrass to Cd-Contaminated Soils. The soil pH was 5.21 and the electrical conductivity (EC) was 7.18 mS m^{-1} on 5 June, 2010, and the values were, respectively, 5.56 and 3.69 mS m^{-1} on 23 November, 2010. Soil adsorption capacity for Cd increases with higher EC and pH, demonstrated by an increase in the capacity in amended cow manure due to higher pH [18]. In the present study, the soil chemical properties were pH values below 7 and EC values were low, which have been suggested to favor suppression of adsorption of Cd [18]. Plant height and tiller density changed similarly among treatments up to 14 September. The rapid increase from May to June was due to vegetative growth. This was followed by a marked decrease up to the early August, due to both self-thinning of tillers and a slower emergence of tillers resulting from an increase in light intensity at

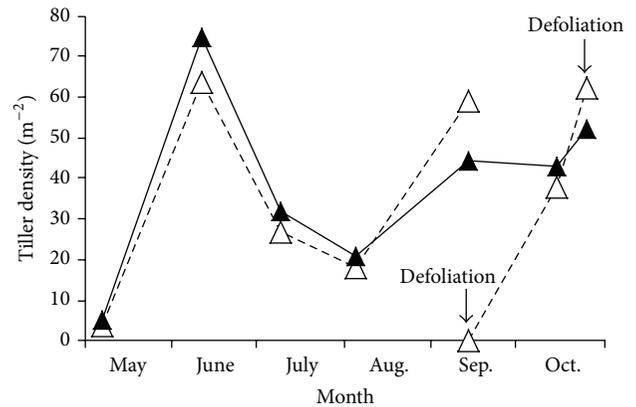


FIGURE 1: Changes in tiller density of Napiergrass after a single cutting (▲) and after two cuttings (△).

the bottom of the canopy due to rapid stem elongation. However, in the two-cutting plot after the first cutting on 14 September, tiller density increased as rapidly as in the vegetative growth phase so that the density became similar for both treatments on 26 October. The increase in tiller density after 14 September in the single-cutting plot resulted from the continued emergence of delayed tillers (Figure 1).

DM tended to be higher in the two-cutting than the single-cutting plot on 14 September, 2011, possibly due to drought stress in the elevated area of the single-cutting plot (Figure 2). However, plant DM in the single-cutting plot recovered by 26 October (Figure 2) due to the emergence of delayed tillers after sufficient precipitation in mid-September (Figure 1). Regrowth DM yield in the two-cutting plot was severely limited on 26 October, and thus annual DM yield did not differ significantly between the treatments. Underground stem DM yield was 8–10% of total plant DM yield on the two monitored dates in the single-cutting plot as well as for the first cutting of plants in the two-cutting plot on 14 September, while the percentage increased to 55% in the two-cutting plot on 26 October (Figure 2). A soil Cd concentration of

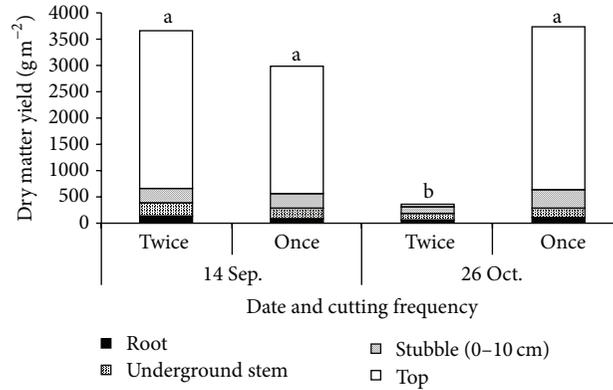


FIGURE 2: Changes in DM yield of Napiergrass after a single cutting (once) and after two cuttings (twice). Figures with the same letter were not significantly different at $P < 0.05$ based on LSD test.

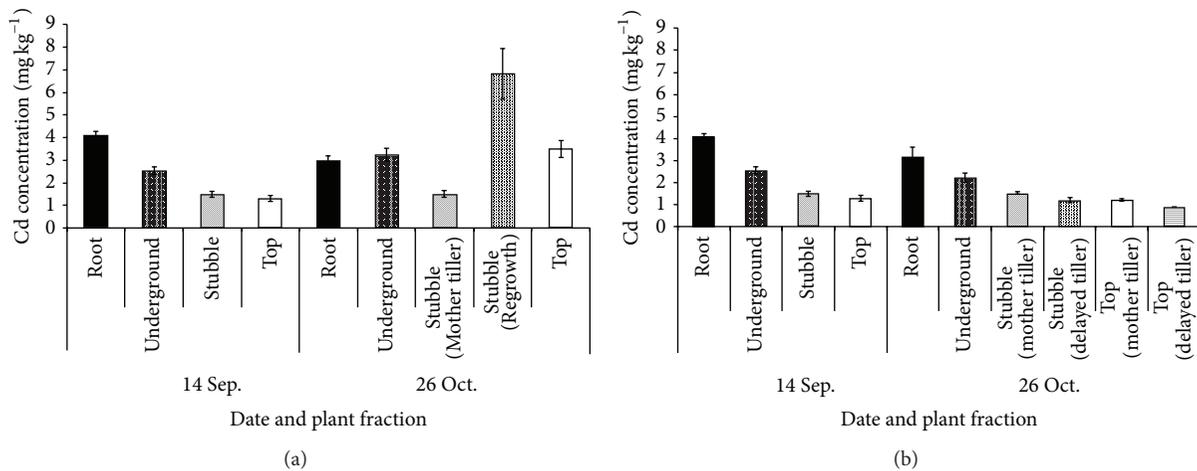


FIGURE 3: Cadmium (Cd) concentration in several plant fractions of Napiergrass after two cuttings (a) and after a single cutting (b). Mean \pm standard deviation ($n = 3$).

1.45 mg kg⁻¹, which is equivalent to 15 μ M Cd, did not cause any observable inhibition of tall-type Napiergrass growth in the heavy clay soil examined, which was consistent with the absence of a significant effect on growth of barley in pots by adding 10 mM Cd to the soil [19].

Plant Cd concentration was highest in the roots, followed by underground stems and stubble, with the lowest concentration of 1.29 mg kg⁻¹ in top parts being similar for both treatments on 14 September (Figures 3(a) and 3(b)). The Cd concentration was similar across plant fractions for the single-cutting plot on 26 October and 14 September, even after the appearance of delayed tillers (Figure 3(b)). However, in the two-cutting plot on 26 October, the Cd concentration in the stubble of regrowth tillers was highest, above 6 mg kg⁻¹, followed by the top parts at around 3 mg kg⁻¹, which was significantly higher than that in the stubble of mother tillers (Figure 3(a)).

The tendency for Cd concentration to decrease from roots to the harvested parts of aerial tillers was similar to *Miscanthus* [7], which presumably reflects the translocation of Cd from roots to aboveground parts. Indica rice (*Oryza*

sativa L.) cv. Moretsu accumulated a higher Cd concentration than the cultivar IR-8 [14], showing potential as a Cd phytoextractor for paddy fields. Napiergrass accumulated Cd in the aboveground parts at concentrations ranging from 1.30 to 7.05 mg kg⁻¹ in the two-cutting plot on 26 October (Figure 3(a)), which was lower than that in indica rice cultivated in Cd-polluted lowlands, which ranged from 31.4 to 41.0 mg kg⁻¹ [14]. However, the yield of Napiergrass, which is in the range of 3000 to 4000 g DM m⁻² under proper transplanting and infrequent cutting in southern Kyushu, even in the year of establishment [3, 12], was considerably higher than indica rice, ranging from 1100 to 1260 g DM m⁻² [14]. Therefore, Napiergrass is a potential phytoextractor for Cd-polluted lowlands in addition to being useful as a biofuel feedstuff due to its high DM productivity [3]. Napiergrass needs proper fertilization [15] and weeding [16] management combined with genotype selection [20] to exhibit its potential for Cd phytoremediation. Proper organic and inorganic fertilization is needed for Cd phytoremediation; for example, amendment of soil with quail litter biochar increased the physic nut yield and reduced Cd residue in the plants due

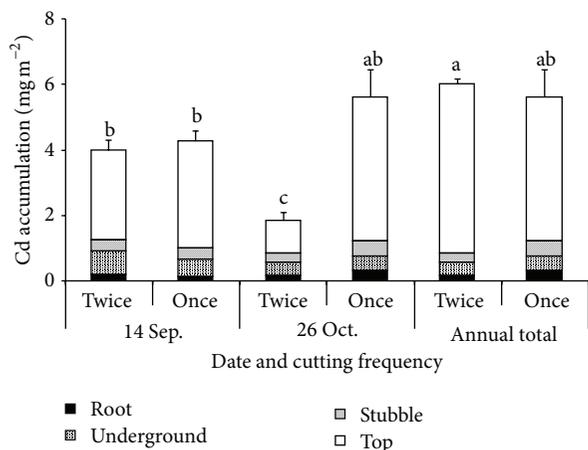


FIGURE 4: Cadmium (Cd) accumulation of Napiergrass following the first and second cuts from plots after a single (Once) or two cuttings (Twice). Mean \pm standard deviation ($n = 3$). Figures with the same letter were not significantly different at $P < 0.05$ based on LSD test.

to a reduction in bioavailability of Cd, resulting in decreased potential to remediate Cd-contaminated soil [21]. In contrast, the increase in alfalfa plant biomass as well as uptake of Cd was dependent on the supply of nitrate in pots of Cd-amended soil [22].

Annual total plant Cd accumulation tended to be 7% higher in the two-cutting plot than in the single-cutting plot (Figure 4). The Cd concentration within the first 20 cm of soil depth decreased 4.6% from 29 April to 26 October in the two-cutting plots, compared to 2.6% for the single-cutting plots in a single growing season. The remaining Cd might remain in hypogeal parts such as roots and underground stems and the aboveground stubble left by cutting stems 10 cm above the ground. The stubble had higher absolute Cd concentrations than the aerial part of *Miscanthus* [7].

In soils, Cd remains in exchangeable, dilute-acid extractable, and organically bound forms, with the exchangeable form making up a few percent of the total [1]. Soil Cd concentrations on 29 April (8 days before planting) were 1.47 and 1.30 mg kg^{-1} in once- and twice-cutting plot, respectively, and those on 26 October (second harvest) were 1.40 and 1.27 mg kg^{-1} in once- and twice-cutting plot, respectively (Figure 5). Therefore, a soil Cd concentration was reduced by 4.6% and 2.6% when managed by cutting twice and once, respectively, in a single year of Napiergrass cultivation (Figure 5), and that of 1.47 mg kg^{-1} , which is almost equivalent to 15 μM Cd, did not cause any observable inhibition of tall-type Napiergrass growth in the heavy clay soil that was examined.

4. Conclusions

Related to its phytoremediation activity, growth of tall-type Napiergrass cultured in Hoagland solution was inhibited by Cd, while the maximum Cd uptake for phytoextraction was achieved at 100 μM Cd, the highest level tested. In

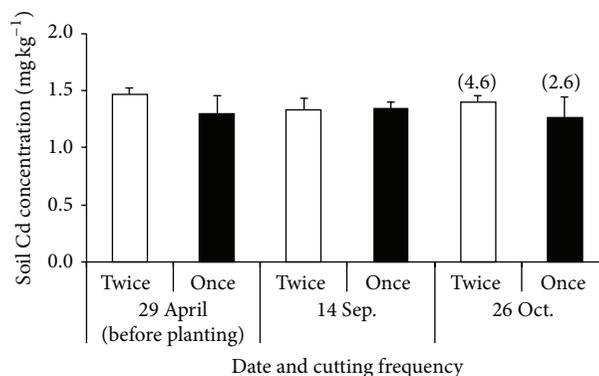


FIGURE 5: Cadmium (Cd) concentration of soils in 0–15 cm depth before planting and following the first and second cuts from plots after a single (Once) or two cuttings (Twice). Mean \pm standard deviation ($n = 3$). Figures with parenthesis show the decreasing percentage from Cd concentration before planting.

Cd-contaminated lowland fields, where soil Cd concentration was equivalent to 15 μM , tall-type Napiergrass growth was as healthy as in Cd-free soils, and Cd uptake was higher in plots cut twice than in those cut once due to higher Cd concentration in plants showing regrowth, even though it was limited. Thus, soil Cd concentration was reduced by 4.6% following two harvests in a single growing season, suggesting that Napiergrass is a potential Cd phytoextractor.

Conflict of Interests

It is declared that the authors have neither any conflict of interests nor financial gain for this paper.

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References

- [1] T. Makino, K. Sugahara, Y. Sakurai et al., "Remediation of cadmium contamination in paddy soils by washing with chemicals: selection of washing chemicals," *Environmental Pollution*, vol. 144, no. 1, pp. 2–10, 2006.
- [2] T. Arao, S. Ishikawa, M. Murakami, K. Abe, Y. Maejima, and T. Makino, "Heavy metal contamination of agricultural soil and countermeasures in Japan," *Paddy and Water Environment*, vol. 8, no. 3, pp. 247–257, 2010.
- [3] L. Khairani, Y. Ishii, S. Idota, R. F. Utamy, and A. Nishiwaki, "Variation in growth attributes, dry matter yield and quality among 6 genotypes of napier grass used for biomass in year of establishment in Southern Kyushu, Japan," *Asian Journal of Agricultural Research*, vol. 7, no. 1, pp. 15–25, 2013.
- [4] X. Liu, Y. Shen, L. Lou, C. Ding, and Q. Cai, "Copper tolerance of the biomass crops Elephant grass (*Pennisetum purpureum* Schumacher), Vetiver grass (*Vetiveria zizanioides*) and the upland reed (*Phragmites australis*) in soil culture," *Biotechnology Advances*, vol. 27, no. 5, pp. 633–640, 2009.

- [5] D. J. Kang, Y.-J. Seo, T. Saito, H. Suzuki, and Y. Ishii, "Uptake and translocation of cesium-133 in napiergrass (*Pennisetum purpureum* Schum.) under hydroponic conditions," *Ecotoxicology and Environmental Safety*, vol. 82, pp. 122–126, 2012.
- [6] I. Arduini, A. Masoni, L. Ercoli, and M. Mariotti, "Growth and cadmium uptake of *Miscanthus sinensis* as affected by cadmium," *Agricoltura Mediterranea*, vol. 133, no. 1, pp. 169–178, 2003.
- [7] I. Arduini, L. Ercoli, M. Mariotti, and A. Masoni, "Response of miscanthus to toxic cadmium applications during the period of maximum growth," *Environmental and Experimental Botany*, vol. 55, no. 1-2, pp. 29–40, 2006.
- [8] Z. Zhang, Z. Rengel, H. Chang, K. Meney, L. Pantelic, and R. Tomanovic, "Phytoremediation potential of *Juncus subsecundus* in soils contaminated with cadmium and Polynuclear Aromatic Hydrocarbons (PAHs)," *Geoderma*, vol. 175-176, no. 1, pp. 1–8, 2012.
- [9] B.-C. Chen, H.-Y. Lai, and K.-W. Juang, "Model evaluation of plant metal content and biomass yield for the phytoextraction of heavy metals by switchgrass," *Ecotoxicology and Environmental Safety*, vol. 80, no. 1, pp. 393–400, 2012.
- [10] G. Shi and Q. Cai, "Cadmium tolerance and accumulation in eight potential energy crops," *Biotechnology Advances*, vol. 27, no. 5, pp. 555–561, 2009.
- [11] Y. Ishii, K. Hamano, D. J. Kang et al., "¹⁴C₄-Napier grass cultivation for cadmium phytoremediation activity and organic livestock farming in Kyushu, Japan," *Journal of Agricultural Science and Technology A*, vol. 3, no. 4, pp. 321–330, 2013.
- [12] M. Mukhtar, Y. Ishii, S. Tudsri, S. Idota, and T. Sonoda, "Dry matter productivity and overwintering ability of the dwarf and normal napiergrasses as affected by the planting density and cutting frequency," *Plant Production Science*, vol. 6, no. 1, pp. 65–73, 2003.
- [13] T. Ibaraki, K. Kadoshige, and M. Murakami, "Evaluation of extraction methods for plant-available soil cadmium to wheat by several extraction methods in cadmium-polluted paddy field," *Soil Science and Plant Nutrition*, vol. 51, no. 6, pp. 893–898, 2005.
- [14] T. Ibaraki, N. Kuroyanagi, and M. Murakami, "Practical phytoextraction in cadmium-polluted paddy fields using a high cadmium accumulating rice plant cultured by early drainage of irrigation water," *Soil Science and Plant Nutrition*, vol. 55, no. 3, pp. 421–427, 2009.
- [15] A. Wadi, Y. Ishii, and S. Idota, "Effects of the level of fertilizer input on dry matter productivity of napiergrass and kinggrass," *Grassland Science*, vol. 48, no. 4, pp. 490–503, 2003.
- [16] R. F. Utamy, Y. Ishii, S. Idota, and L. Khairani, "Effect of weed control management on herbage yield, quality and wintering ability in the established dwarf napiergrass (*Pennisetum purpureum* Schumach)," *Journal of Warm Regional Society of Animal Science, Japan*, vol. 55, no. 1, pp. 17–26, 2012.
- [17] Ministry of Agriculture and Forestry, Ordinance of the Ministry of Agriculture and Forestry, Japan, no. 47 of 1971, 1971, <http://www.lawdata.org/law/htmldata/S46/S46F00601000047.html>.
- [18] M. Chorom, R. M. Karkaragh, B. Kaviani, and Y. K. Kalkhajeh, "Monometal and competitive adsorption of Cd, Ni, and Zn in soil treated with different contents of cow manure," *Applied and Environmental Soil Science*, vol. 2013, Article ID 510278, 8 pages, 2013.
- [19] B. B. M. Sridhar, F. X. Han, S. V. Diehl, D. L. Monts, and Y. Su, "Effects of Zn and Cd accumulation on structural and physiological characteristics of barley plants," *Brazilian Journal of Plant Physiology*, vol. 19, no. 1, pp. 15–22, 2007.
- [20] M. J. Williams and W. W. Hanna, "Performance and nutritive quality of dwarf and semi-dwarf elephantgrass genotypes in the south-eastern USA," *Tropical Grasslands*, vol. 29, no. 2, pp. 122–127, 1995.
- [21] T. Suppadit, V. Kitikoon, A. Phubphol, and P. Neumnoi, "Effect of quail litter biochar on productivity of four new physic nut varieties planted in cadmium-contaminated soil," *Chilean Journal of Agricultural Research*, vol. 72, no. 1, pp. 125–132, 2012.
- [22] S. Hattab, S. Hattab, H. Boussetta, and M. Banni, "Influence of nitrate fertilization on Cd uptake and oxidative stress parameters in alfalfa plants cultivated in presence of Cd," *Journal of Soil Science and Plant Nutrition*, vol. 14, no. 1, pp. 89–99, 2014.