

**ROLE OF HEAVY METALS AND ORGANIC MATTER ON SORPTION AND
MOBILITY OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL:
IMPLICATIONS FOR REMEDIATION**

by

Mohsen Saeedi

B.Sc., Iran University of Science and Technology, Tehran, Iran, 1994

M.A.Sc., Iran University of Science and Technology, Tehran, Iran, 1996

Ph.D., University of Tehran, Tehran, Iran, 2003

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Civil Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

September 2019

© Mohsen Saeedi, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

Role of Heavy Metals and Organic Matter on Sorption and Mobility of Polycyclic Aromatic Hydrocarbons in Soil: Implications for Remediation

submitted by Mohsen Saeedi in partial fulfillment of the requirements for
the degree of Doctor of Philosophy
in Civil Engineering

Examining Committee:

Loretta Y. Li, Department of Civil Engineering
Co-supervisor

John R. Grace, Department of Chemical and Biological Engineering
Co-supervisor

Madjid Mohseni, Department of Chemical and Biological Engineering
Supervisory Committee Member

Anthony Lao, Department of Chemical and Biological Engineering
University Examiner

Leslie Lavkulich, Faculty of Land and Food Systems
University Examiner

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a group of abundant contaminants in contaminated sites having many adverse effects on human health and the ecosystem. Due to the many common sources of PAHs and heavy metals, many sites are contaminated by both groups. Co-presence of these contaminants can affect their sorption/desorption in the soil environment, affecting their fate, transport, and remediation processes.

This research project advanced the understanding of sorption behavior of PAHs co-existing with heavy metals in soil. Three types of artificially blended clay and clay minerals (kaolinite, kaolinite+sand, kaolinite+sand+bentonite) and a real spiked clayey soil sample were investigated. The synergistic effect of organic matter (humic acid) with heavy metals on enhancing the sorption of PAHs was tested and confirmed for the first time. Different single and combined solutions were used to enhance the desorption of PAHs from the soil. Two non-ionic surfactants (Triton X-100 and Tween 80) with EDTA showed the capability to simultaneously remove these PAHs (acenaphthene, fluorene and fluoranthene) and these prominent heavy metals (Ni, Pb, and Zn) from the soil sample. Results also showed that the co-presence of metal contaminants and soil organic matter can decrease the mobility and desorption of PAHs with the results that the efficiency of soil washing/flushing remediation could decrease in such cases. Our findings also show that the rate of desorption of PAHs is reduced by the co-presence of organic matter and heavy metals in soil. This affects the cost and time of remediation of sites contaminated by mixed heavy metals and PAHs. Our findings were confirmed through column soil flushing of a real natural soil sample by combined enhancing solutions.

Lay Summary

Many contaminated sites in Canada and elsewhere are contaminated by different agents. Both aromatic hydrocarbons and heavy metals have severe adverse effects on ecosystem and human health. Most technologies to treat and remediate contaminated soil are incapable of removing both types of contaminants effectively. This research improved our understanding of these contaminants' behavior in real soils containing organic matter.

Preface

I, Mohsen Saeedi, confirm that I was primarily responsible for the design and performance of the research and analysis of the data presented in this dissertation. Several manuscripts and a conference presentation have been either submitted to, or published in, peer-reviewed journals based on this research. These contributions are as follows:

Journal Publications:

A version of chapter 2 has been accepted for publication in “Pollution” [Saeedi, M., Li, L.Y., Grace, J.R., 2019. Effect of co-existing heavy metals and natural organic matter on sorption/desorption of polycyclic aromatic hydrocarbons in soil: a review]. I was the principal investigator, responsible for major areas of concept formation, literature analysis, as well as the majority of manuscript composition. Li, L.Y and Grace, J.R. were the supervisory authors on this manuscript and were involved in concept formation and manuscript edits.

A version of chapter 3 has been published [Saeedi, M., Li, L.Y., Grace, J.R., 2018. Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals, Environ. Earth Sci. 77, 305]. I was the principal investigator, responsible for major areas of concept formation, design and conduction of experiments, data analysis, as well as the majority of manuscript composition. Li, L.Y and Grace, J.R. were the supervisory authors on this project and were involved throughout the research in concept formation and manuscript edits.

A version of chapter 4 has been published [Saeedi, M., Li, L.Y., Grace, J.R., 2018. Desorption and mobility mechanisms of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals, *J. Environ. Management* 214, 204-214]. I was the principal investigator, responsible for major areas of concept formation, design and conduction of experiments and tests, data analysis, as well as most of manuscript composition. Li, L.Y and Grace, J.R. were the supervisory authors on this project and were involved throughout the research in concept formation and manuscript edits.

A version of chapter 5 has been submitted to a peer-reviewed journal for possible publication [Saeedi, M., Li, L.Y., Grace, J.R., 2019. Desorption kinetics of acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by heavy metals at various organic matter contents]. I was again the principal investigator, responsible for major areas of concept formation, design and conduction of experiments and tests, data analysis, as well as the majority of manuscript composition. Li, L.Y and Grace, J.R. were the supervisory authors on this project and were involved throughout the research in concept formation and manuscript edits.

A version of chapter 6 has been accepted for publication in the Journal of Environmental management: [Saeedi, M., Li, L.Y., Grace, J.R., 2019. Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from natural soil by combined non-ionic surfactants and EDTA as extracting reagents: laboratory column tests. *J. Environ. Manage.*]. I was the principal investigator, responsible for major areas of concept formation, design and conduction of experiments and tests, data analysis, as well as most of the manuscript composition. Li, L.Y

and Grace, J.R. were the supervisory authors of this project, involved throughout the research in concept formation and manuscript edits.

Conference Presentation:

A conference paper related to base on this research data was presented in an international conference [Saeedi, M., Li, L.Y., Grace, J.R., 2019. Remediation and desorption kinetics of pyrene from kaolinite co-contaminated with heavy metals at various organic matter contents. Proceedings of 19th EGU General Assembly, EGU2017, 23-28 April, 2017, Vienna, Austria, p.9953]. I was the principal investigator, responsible for major areas of concept formation, experiments and tests design and conduction, as well as data analysis. Li, L.Y was the supervisory author on this project and was involved throughout the research in concept formation and manuscript composition. Grace, J.R. was the supervisory author of this project, involved throughout the research in concept formation and manuscript edits.

Versions of chapters 2, 3, 4, 5 and 6 have either been published, or have been submitted to peer-reviewed journals as listed above, for possible publication.

Table of Contents

Abstract.....	iii
Lay Summary	iv
Preface.....	v
Table of Contents	viii
List of Tables	xii
List of Figures.....	xiv
List of Abbreviations	xvii
Acknowledgements	xx
Dedication	xxii
Chapter 1: Introduction	1
1.1 Background	1
1.2 Research scope and objectives.....	4
1.3 Research contributions and novelty	7
1.4 Layout of chapters.....	8
Chapter 2: Effect of heavy metals and natural organic matter on sorption/desorption of polycyclic aromatic hydrocarbons in soil: a review	10
2.1 Introduction.....	10
2.2 Methodology	17
2.3 Sorption of PAHs in soil	17
2.3.1 Effect of soil organic matter	29
2.3.2 Effect of co-existing heavy metals on PAH sorption.....	39
2.3.3 Other factors affecting PAH sorption	44

2.4	Desorption of PAHs	48
-----	--------------------------	----

2.5	Conclusion and research needs	56
-----	-------------------------------------	----

Chapter 3: Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals 58

3.1	Introduction.....	58
-----	-------------------	----

3.2	Materials and methods	61
-----	-----------------------------	----

3.2.1	Chemicals and minerals	61
-------	------------------------------	----

3.2.2	Chemical analyses and characterization	62
-------	--	----

3.2.3	Sample preparation and experimental program	64
-------	---	----

3.2.4	Analysis of variance (ANOVA).....	70
-------	-----------------------------------	----

3.3	Results and discussion	71
-----	------------------------------	----

3.3.1	Soil characteristics	71
-------	----------------------------	----

3.3.2	Sorption of PAHs.....	72
-------	-----------------------	----

3.3.3	Effect of metals	78
-------	------------------------	----

3.3.4	Effect of organic matter	81
-------	--------------------------------	----

3.3.5	Synergistic effect of organic matter and heavy metals	83
-------	---	----

3.3.6	Analysis of variance.....	86
-------	---------------------------	----

3.4	Conclusions.....	87
-----	------------------	----

Chapter 4: Desorption and mobility of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals 89

4.1	Introduction.....	89
-----	-------------------	----

4.2	Materials and methods	91
-----	-----------------------------	----

4.2.1	Chemicals and enhancing agents	92
-------	--------------------------------------	----

4.2.2	Mineral mixtures preparation and experimental program	94
4.2.3	Batch desorption and mobility tests	95
4.2.4	Analysis of variance (ANOVA).....	97
4.3	Results and discussion	97
4.3.1	Preliminary desorption tests by single extractants	97
4.3.2	Mobility and desorption of PAHs and heavy metals	100
4.3.2.1	Kaolinite.....	100
4.3.2.2	Kaolinite and sand (KS) mixture	104
4.3.2.3	Kaolinite, sand and bentonite mixture	107
4.3.3	Analysis of variance (ANOVA).....	111
4.4	Conclusions.....	112

Chapter 5: Desorption kinetics of acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by heavy metals at various organic matter contents 114

5.1	Introduction.....	114
5.2	Materials and methods	116
5.2.1	Chemicals and materials	116
5.2.2	Desorption kinetics experiments	119
5.2.3	Chemical analysis	120
5.2.4	Desorption kinetics data evaluation	120
5.3	Results and discussion	121
5.3.1	Desorption tests with combined enhancing solutions.....	121
5.3.2	Modeling the desorption kinetics.....	126
5.4	Conclusions.....	135

Chapter 6: Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from natural soil by combined non-ionic surfactants and EDTA: laboratory column tests	136
.....	
6.1 Introduction.....	136
6.2 Materials and methods	139
6.2.1 Soil and materials.....	139
6.2.2 Soil preparation and analytical methods	141
6.2.3 Column experiments	142
6.3 Results and discussion	143
6.3.1 Removal of heavy metals.....	143
6.3.2 Removal of PAHs	146
6.3.3 Effect of volumetric flow on removal of PAHs.....	154
6.4 Conclusions.....	157
Chapter 7: Conclusions and recommendations for future works	158
7.1 Conclusions.....	158
7.2 Recommendations for further research.....	163
References	167
Appendices.....	193
Appendix A Minerals and materials characterization.....	193
Appendix B Quality assurance and quality control (QA/QC)	197
Appendix C Column tests soil particle sizing.....	199
Appendix D Comparison of final contaminants concentration with soil quality guidelines	200

List of Tables

Table 2.1 USEPA's 16 priority pollutant PAHs and selected properties	13
Table 2.2 Sites contaminated solely by metals, PAHs or both in the US, Canada and Europe (%) of total contaminated sites in each).....	15
Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals....	21
Table 2.4 Functional groups identified and observed in different NOM.....	32
Table 2.5 Summary of recent research results on the effect of soil organic matter on PAHs sorption and retention	36
Table 2.6 Summary of previous work on the effect of heavy metals on sorption of PAHs	41
Table 2.7 Effect of metals on sorption of PAHs in minerals and organic matter contained soil..	44
Table 2.8 Summary of recent studies on the effect of organic matter and heavy metals on PAHs desorption.....	52
Table 3.1 Characteristics of the three base minerals used for blending.....	65
Table 3.2 Blended clay and clay minerals for sorption experiments and their characteristics	70
Table 3.3 Sorption coefficients for ANA, FL and FLAN sorption onto different types of mineral mixtures studied	76
Table 3.4 Increments of sorption coefficient (K_d) for PAHs studied with added OM and heavy metals compared to original untreated clay mineral mixtures (%)	80
Table 3.5 Results of ANOVA analysis for sorption of FLAN onto three types of mineral and mineral mixtures	86
Table 4.1 Physical/chemical properties of surfactants used in this study.....	93
Table 4.2 Results of ANOVA analysis for desorption of ANA by EDTA+ Tween 80.....	112

Table 5.1 Properties of pure and HA-added kaolinite used in experiments	118
Table 5.2 Parameters and correlations (R^2) obtained from adjustment of kinetics models for simultaneous PAHs and heavy metals desorption from kaolinite at three added HA levels.	
.....	134
Table 6.1 Properties of the soil sample	140

List of Figures

Figure 2.1 Bay and fjord regions in PAHs molecular structures	11
Figure 2.2 Molecular structures of 16 PAHs in priority list of the USEPA	14
Figure 2.3 Structures of natural organic matter	31
Figure 2.4 Schematic of surfactant enhanced desorption of PAHs..	51
Figure 3.1 Sorption isotherms of OM on blended clay and clay mineral mixtures	67
Figure 3.2 Sorption isotherms of acenaphthene (ANA), Fluorene (FL), and Fluoranthene (FLAN) onto 18 different prepared soil types, (kaolinite: (K0) no added OM no added metals, added metals no added OM (K0M), added medium OM no added metals (K1), added medium OM added metals (K1M), added maximum OM no added metals (K2), added maximum OM added metals (K2M), kaolinite + sand: (KS0) no added OM no added metals, added metals no added OM (KS0M), added medium OM no added metals (KS1), added medium OM added metals (KS1M), added maximum OM no added metals (KS2), added maximum OM added metals (KS2M), kaolinite + sand + bentonite: (KSB0) no added OM no added metals, added metals no added OM (KSB0M), added medium OM no added metals (KSB1), added medium OM added metals (KSB1M), added maximum OM no added metals (KSB2), added maximum OM added metals (KSB2M)).	74
Figure 3.3 Synergistic effect of co-existence of heavy metals (Ni, Pb and Zn) and OM in sorption enhancement of PAHs	84
Figure 4.1 Removal efficiencies of ANA, FL and FLAN (a) and Ni, Pb and Zn (b) from spiked kaolinite (K0M) by single extractants (ANA: acenaphthene, FL: fluorene, FLAN; fluoranthene).....	98

Figure 4.2 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite with and without HA by different solutions (K0M, K1M and K2M contained heavy metals; soils K1 and K2 contained added organic matter; K0 contained neither added metals nor organic matter).....	102
Figure 4.3 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite+sand with and without HA addition by different solutions (KS0M, KS1M and KS2M contained heavy metals; KS1 and KS2 contained added organic matter; KS0 contained neither added metals nor organic matter).....	106
Figure 4.4 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite+sand+bentonie with and without HA addition (KSB0M, KSB1M and KSB2M contained heavy metals; KSB1 and KSB2 contained added organic matter; KSB0 contained neither added metals nor organic matter).	109
Figure 5.1 Removal efficiencies of ANA, FL and FLAN (a) and Ni, Pb and Zn (b) from kaolinite (K0) by a combination of enhancing agents (ANA: acenaphthene, FL: fluorene, FLAN; fluoranthene).....	124
Figure 5.2 pH of solutions at the end of batch desorption tests for spiked kaolinite (K0).	125
Figure 5.3 Kinetic profiles of PAHs and metals removal from kaolinite at different HA levels over 3-72 h period. K0: kaolinite with no added HA; K1: kaolinite containing 5.5% added HA; K2: kaolinite containing 11% added HA.....	130
Figure 5.4 Simultaneous contaminants desorption (a), and rate (b) decrease from kaolinite because of added HA to kaolinite (K1: kaolinite containing 5.5% added HA; K2: kaolinite containing 11% added HA, ANA; acenaphthene, FL; fluorene, FLAN; fluoranthene).	131

Figure 6.1 Cumulative removal efficiencies and percent removal vs. pore volume for co-existing heavy metals by flushing; a and d) Triton X-100 7.5% w/w+EDTA 0.01 M, b and e) Triton X-100 5% w/w+EDTA 0.01 M, c and f) Triton X-100 3% w/w+EDTA 0.01 M. 145

Figure 6.2 Cumulative removal efficiencies and percent removal vs. pore volume for ANA, FL and FLAN by flushing; a and d) Triton X-100 7.5% w/w+EDTA 0.01 M, b and e) Triton X-100 5% w/w+EDTA 0.01 M, c and f) Triton X-100 3% w/w+EDTA 0.01 M..... 149

Figure 6.3 Cumulative removal efficiencies and percent removal vs. pore volume for ANA, FL and FLAN by flushing; a and d) Tween 80 7.5% w/w+EDTA 0.01 M, b and e) Tween 80 5% w/w+EDTA 0.01 M, c and f) Tween 80 3% w/w+EDTA 0.01 M..... 152

Figure 6.4 Cumulative removal of PAHs by flushing Triton X-100 7.5% w/w+EDTA 0.01M at 0.456 ml min⁻¹ (LF) and 0.615 ml min⁻¹ (HF) flow rate..... 156

List of Abbreviations

AN, Anthracene

ANA, Acenaphthene

ASTM, American Society for Testing and Materials

ATSDR, Agency for Toxic Substances and Disease Registry

BAP, Benzo(a)pyrene

CCME, Canadian Council of Ministers of the Environment

CLBR, Centre for Land and Biological Resources Research

CMC, Critical Micelle Concentration

CRM, Certified Reference Materials

DCM, Dichloromethane

DOM, Dissolved organic matter

DNA, Deoxyribonucleic acid

EDTA, Ethylene Diamine Tetra Acetic Acid

FA, Fulvic acid

FAAS, Flame Atomic Absorption Spectrometer

FCSI, Federal Contaminated Sites Inventory

FL, Fluorene

FLAN, Fluoranthene

FTIR, Fourier transform infrared spectroscopy

GC, Gas Chromatography

HA, Humic Acid

HF, High flow

HLB, Hydrophile-Lipophile Balance

HM, Heavy Metal

HMW, High molecular weight

HOCs, Hydrophobic organic compounds

ILCR, Incremental lifetime cancer risk

LF, Low flow

NAP, Naphthalene

NOM, Natural Organic Matter

NRC, National Research Council of Canada

OC, Organic carbon

OM, Organic Matter

PAHs, Polycyclic Aromatic Hydrocarbons

PCBs, Polychlorinated biphenyls

PHE, Phenanthrene

PV, Pore volume

PYR, Pyrene

SDS, Sodium dodecyl sulfate

SOC, Soil organic carbon

SOM, Soil Organic Matter

USEPA, United States Environmental Protection Agency

VOCs, Volatile organic compounds

XRD, X-ray Diffraction

XRF, X-ray fluorescence

Acknowledgements

I am deeply grateful to Dr. Loretta Li, my supervisor, for all her great mentorship over the years. Beyond that, I am thankful for her support, friendship, guidance, advice, and thoughtful criticism through this journey called my PhD study. It is because of her that I undertook this project and have reached this point.

I express my appreciation and gratitude to Dr. John Grace, my co-supervisor, for all his support, patience and understanding. Without his support, it would have been impossible for me to go on. He is a great man with a great heart.

I am also grateful for Dr. Li and Dr. Grace's thoughtful criticism through research and writing process.

I would like to express my gratitude to University of British Columbia and its faculty of Applied Science for providing excellent space and support for me.

The supervisory committee provided me with great comments and useful hints on my proposal and thesis, I appreciate it.

My special gratitude and deep love go to my wife, Golara, for encouragements, persuasion, help and emotional support during my study. My beautiful, beloved daughters were always there for me also, bringing energy, hope and enthusiasm.

The Department of Civil Engineering of the Iran University of Science and Technology (IUST) is acknowledged for proving laboratory facilities and support. I especially thank those who helped me with laboratory work and tests (M. Foroughi, A. Mohammadi, S. Mohammdi, M. Rastegari, and M. Ayatinia).

I am grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding (RGPIN 185040-13, RGPIN-2018-03832, RGPIN 7111-11 and RGPIN 7111-16) as well as the Society of Contaminated Sites Approved Professionals (CSAP) of British Columbia for a graduate award scholarship. I am also thankful for a graduate award from the UBC Faculty of Applied Science.

Dedication

To my wife Golara and my beloved daughters, Salvi and Vista

To UBC, Vancouver, BC and Canada, for being so welcoming to my family and me.

Chapter 1: Introduction

1.1 Background

Soil contamination has become a major concern affecting human health and the environment.

Distributed sources of contaminants such as agricultural activities, roads, railways and atmospheric fall-out increase the amounts of contaminants in soils on large scales. Point sources of pollution, such as different industries or accidental release, also contaminate soil of small-scale areas. The soil may then function as a secondary source of these contaminants for water, air, the ecosystem food chain and humans.

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) are among the contaminants abundant in the soil of contaminated sites (UNEP, 2012; Su et al., 2014; USEPA, 2018; FCSI, 2018). These substances are rather persistent in the soil environment (EUGRIS, 2018), and they have various adverse effects on the health of humans and organisms (CCME, 2010a; CCME, 2010b) and other organisms (CCME, 2010a; CCME, 2010b).

The main anthropogenic sources of PAHs in soil are bitumen, oil and gas production plants, combustion processes, fuel and storage facilities and spills of petroleum and petroleum products during road, rail and pipeline transportation (Choi et al., 2009; CCME, 2010a). Many of those anthropogenic sources of PAHs, particularly those related to oil and gas and related industries release toxic heavy metals together with PAHs, into the environment. Therefore, in soils of many contaminated sites, PAHs coexist with heavy metals (Wang et al., 2004; Morillo et al., 2008; Thavamani et al., 2011; Thavamani et al., 2012).

Remediation of PAH-contaminated soils using traditional technologies such as pump and treat, soil vapor extraction or classical bioremediation is difficult because of the low water solubility of these contaminants and their high sorption affinities to soil particles and soil organic matter (SOM).

Co-existence of heavy metals and PAHs in contaminated soils not only may cause more toxicity, but also exhibit decreased natural attenuation and require a more complicated system for remediation (Thavamani et al., 2011; Reddy and Cameselle, 2009).

Since HMs are neither biodegraded nor transported by air in soil matrices, a technology for simultaneous remediation of PAHs co-existing with HMs in soil should be based on desorbing and solubilizing them into a liquid to carry the mixed contaminants. Previous research has shown that a washing/flushing solution containing surfactants can enhance the removal of PAHs from soils (Saichek and Reddy, 2004; Jin et al., 2013; Sánchez-Trujillo et al., 2013). On the other hand, to enhance the removal of heavy metals effectively, chelating agents and organic acids have been applied (Arwidsson et al., 2010). It seems that no single extracting solution can remove both groups of contaminants from soil effectively and economically. However, the mobility of contaminants and their subsequent removal depend on their sorption capacity, desorption behaviour and reaction kinetics in the soil.

Sorption and mobility are two important mechanisms affecting the fate of PAHs and heavy metals and their related ecological and human health risks in soil (Environment Agency, 2003;

Abdel-Shafy and Mansour, 2016). From an enhanced soil washing/flushing or electrokinetic remediation point of view, sorption/desorption and mobility of contaminants must be fully understood. The sorption/desorption behaviour of contaminants influences the remediation reaction/retention times, estimation of the efficiency and cost. While having a more realistic understanding of these mechanisms for PAHs in soil is vital, most previous studies have presented results on just one single contaminant or one group of contaminants in one type of soil.

There are many published works on the sorption of PAHs or heavy metals in soil (e.g. Peng et al., 2018a; Antoniadis and Golia, 2015; Javier Rivas et al., 2008; Luo et al., 2010). Most of them focused on either PAHs or heavy metals as target contaminants. There are some studies also on the desorption and mobility of these contaminants (e.g. Peng et al., 2018 a, b; Bezza and Nkhalambayausi-Chirwa, 2015; Covelo et al., 2007). As for the sorption studies, most of these studies have considered only one group of contaminants. Knowing that in soils of many PAH contaminated sites, there are co-existing heavy metals, there is a need to study sorption/desorption of PAHs co-existing with heavy metals in soil.

Among soil characteristics, organic matter content is vital to sorption/desorption and ultimate fate and mobility of both PAHs and HMs in soil. The composition and forms of soil organic matter, can affect the mobility and fate of mixed contaminants (Kaschl et al., 2002). PAHs and HMs both interact with organic matter in soil-water systems (Zhang and Ke, 2004; Gao et al., 2006). Therefore, in addition to soil properties, sorption/desorption of PAHs can be influenced by the presence of heavy metals (Walter and Weber, 2002). Though there are some previous studies (Yang et al., 2010; Antoniadis and Golia, 2015) on the effect of soil organic matter on

sorption and/or desorption of PAHs or heavy metals, to the best knowledge of the author, there has been no published work considering the simultaneous effects of soil organic matter and co-existing heavy metals on sorption/desorption of PAHs in soil.

Study of the effects of both heavy metals and soil organic matter on PAHs in different clay and mineral soils can give a more realistic image of targeted contaminants sorption/desorption and mobility behaviour, enabling better assessment of soil pollution risks, as well as improved design of remediation systems based on enhanced soil washing/flushing or surfactant enhanced electrokinetics.

1.2 Research scope and objectives

The first objective of this study was to extend previous work by investigating the simultaneous impact of heavy metals and humic acids, as natural organic matter, on sorption/desorption and mobility of PAHs in fine soil. The second objective was then to find an appropriate extracting solution for simultaneous removal of metals and PAHs from the soils studied. The overall goal was to enhance the removal of mixed contaminants from soil, particularly from clayey soils because fine grained and clayey soils are more challenging for mixed contaminants remediation.

To successfully achieve these objectives, research has been carried out through experiments on artificially blended clays and clay minerals, whose clay and organic matter content have been altered. The heavy metals tested in the experiments (Ni, Pb and Zn) are ones that exist in petroleum products at most contaminated sites. The PAHs chosen for experiments were acenaphthene, fluorene and fluoranthene. All three are abundant in contaminated sites and are

listed as priority PAH pollutants by USEPA. There is not much information and published work on the sorption/desorption, mobility and remediation of these three PAHs, particularly when they are mixed with HMs. To the best knowledge of the author, prior to starting this research there was only one study on the effect of co-existing heavy metals (only lead) on desorption of PAHs (only phenanthrene) (Fonseca et al., 2011). There were also only 4 published work on the sorption of PAHs co-existing with heavy metals onto soil and minerals (Saison et al., 2004; Zhu et al., 2004; Gao et al., 2006; Zhang et al., 2011a). Among these only one paper took into account the effect of organic matter and lead on phenanthrene sorption. During conduction of the present project, Liang et al. (2016) published a paper on the effect of Cu, Cr and Pb on sorption of phenanthrene , naphthalene and pyrene, while Zhang et al. (2015) published a research on the effects of lead, cadmium and organic matter on sorption of phenanthrene. Therefore, there has obviously been a gap in studying the effect of co-existing multiple metals and organic matter on sorption/desorption of multiple PAHs in soil.

In support of the objectives, the following steps have been taken:

- 1-Provide clay minerals, sand and OM for blending and preparation of different mixed clay soil samples.
- 2-Characterize the minerals in terms of physical, chemical and mineralogical properties (i.e. size fractionation, X-Ray fluorescence for chemical composition, X-Ray diffraction for mineralogy).
- 3-Spike samples to three levels (low, moderate and high) of OM by content by adding humic acid as one of the major components of NOM in soils.

- 4-Expose each type of mineral mixture (with different texture and OM content) to metal solutions of the three heavy metals of interest (Ni, Pb and Zn) through batch tests to prepare metal-contaminated soils.
- 5-Conduct PAH batch sorption tests with all metal-contaminated samples (metals-spiked soil) as well as unspiked samples.
- 6-Examine the mobility and desorption of both metals and PAHs through a series of experiments on soil-metals and soil-metals-hydrocarbons for all samples with extracting solutions.
- 7-Analyze experimental results to determine the mobility of HMs and PAHs in soils contaminated by HMs only and by mixed HMs-PAHs.
- 8-Since kaolinite has lower buffering and cation exchange capacity compared with other clay minerals and it has been widely used as the model of clayey soil in previous laboratory experiments (e.g. Yuan et al., 2006; Yuan et al., 2007; Ko et al., 1998), study of desorption efficiency and chemical kinetics of desorption was conducted on kaolinite in order to help determine the best enhancing solution and contact time for remediation.
- 9-Perform column tests to determine the mobility and desorption of HMs and PAHs in spiked kaolinite to gain a better understanding of the mobility of contaminants subject to different volumetric flows and pore volumes of extractants.

This research project is limited to three types of mineral mixtures: kaolinite, kaolinite with sand, and kaolinite with both sand and bentonite. Humic acid contents, as representative of soil natural organic matter, were tested at three levels: none added, medium level added and maximum level added. A real fine soil sample, spiked with the same PAHs and heavy metals, was used to check the results on desorption and removal of contaminants.

1.3 Research contributions and novelty

This research is novel in several respects. No previous work has been done on a group of PAHs in the presence of heavy metals in soil. Because in real mixed contaminated soil and sites, PAHs and HMs are frequently found together as contaminants, investigation of the effects of HMs on sorption and desorption of PAHs, especially taking into account the presence of soil organic matter, gives a more realistic picture of behaviour affecting remediation. Examining clay minerals other than kaolinite and a mixture of clay minerals in series in certain experiments enables different clay minerals to be compared with respect to their sorption/desorption of PAHs co-existing with metals and organic matter.

The kinetics of mixed contaminants desorption at different organic matter contents has not been investigated previously, but this is important for gaining knowledge of enhanced soil washing/flushing remediation process reaction times.

The results of this research could make a significant contribution to the environment and the scientific community. Findings could also contribute to Canadian society, since there are many mixed contaminated sites in Canada, in addition to potential cases of mixed contamination, for example along oil pipelines. This research may therefore be useful also in addressing real and potential problems related to spills and emergencies.

1.4 Layout of chapters

This dissertation is presented in seven chapters addressing the role of heavy metals and organic matter on sorption and mobility of PAHs studied with a perspective to remediation.

Chapter 1 provides a general introduction to the background of the subject, scope, objectives, and contributions of this research.

Chapters 2 presents a brief review on sorption/desorption of polycyclic aromatic hydrocarbons in soil, with the focus on the effects of co-existing heavy metals and natural organic matter. This section has been accepted for publication in the “Pollution”.

Chapters 3 to 6 are either published or have been submitted to journals. Each of these contains a brief introduction, materials and methods, results, discussion, and conclusions, for the given specific study on sorption and desorption of PAHs and heavy metals.

Chapter 3 focuses on the sorption of contaminants and the effects of humic acid and heavy metals on the sorption of PAHs in clays and clay minerals. The synergistic effects of heavy metals on PAHs sorption are examined. A version of this chapter has already been published in “Environmental Earth Sciences”.

Chapter 4 focuses on the desorption and mobility of PAHs and heavy metals in clay and clay minerals, taking into account the effect of soil organic matter. A version of this chapter has been published in the “Journal of Environmental Management”.

Chapter 5 addresses the desorption kinetics of acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by heavy metals with various organic matter contents. A version of chapter 5 is submitted to “Environmental Earth Sciences” for possible publication.

Chapter 6 provides the results of column experiments on the simultaneous removal of heavy metals and PAHs by combined enhancing solutions. A version of this chapter has been published in the “Journal of Environmental Management”.

Chapter 7 presents overall conclusions and recommendations for future studies.

Appendices are included to provide additional information on some extra experimental results and quality assurance/quality control measures.

Chapter 2: Effect of heavy metals and natural organic matter on sorption/desorption of polycyclic aromatic hydrocarbons in soil: a review¹

2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a group of chemical compounds containing benzene rings in their molecular structure. PAHs are naturally present in oil and bitumen and can form during incomplete combustion. Certain PAHs, such as benzo[a]pyrene, can interact with DNA and are genotoxic (Ewa and Danuta, 2017; Jiao et al., 2017). Other adverse health effects of PAHs include carcinogenicity, birth defects, and skin and liver damage. There is human health risk in both short and long-term exposure to PAHs (ATSDR, 2009; ATSDR, 1995).

The U.S. Environmental Protection Agency has selected sixteen PAHs as priority pollutants (USEPA, 2008; USEPA, 1993). PAHs molecular structures, can affect human health (Ewa and Danuta, 2017). For example, structural features formed between aromatic rings named as “fjord” or “bay” regions (Figure 2.1) are important in determining the health effects of PAHs. Molecules contain “fjord” regions (such as dibenzo[a,l]pyrene) prefer to bind to adenine nucleotides, whereas PAHs having a “bay” region (such as benzo[a]pyrene) bind to guanine nucleotides. PAHs contain a “fjord” region are less capable of being metabolized to form DNA-damaging adducts (Lakshman et al., 2000; Munoz and Albores, 2011). PAHs containing both four or more rings and a “bay” region in their structure can induce gene mutations that initiate

¹ A version of this chapter has been accepted for publication in the “Pollution”. Saeedi, M., Li, L.Y., Grace, J.R., Effect of heavy metals and natural organic matter on sorption/desorption of polycyclic aromatic hydrocarbons in soil: a review.

cancer whereas others with 2 to 4 aromatic rings are known as co-carcinogens, affecting cancer promotion or progression (Bostrom et al., 2002; Baird et al., 2005).

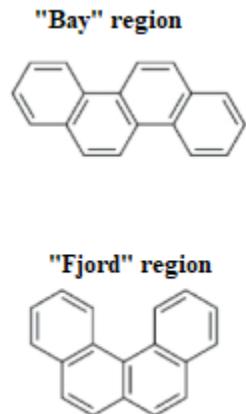


Figure 2.1 Bay and fjord regions in PAHs molecular structures

Table 2.1 and Figure 2.2 provides the names, molecular structures, properties and chemical structures of the 16 USEPA priority PAHs.

Because of toxicity, ecosystem life cycling, and non-degradability of heavy metals (HMs), they are of environmental concern. Accumulation of HMs in the environment, particularly in soil and sediment, is a common problem in many countries (Su et al., 2014), with negative impact on people on a global scale (UNEP, 2012). Although HMs are naturally present in soil as background content, they are present at much higher concentrations in heavy-metal-contaminated soils.

The major sources of PAHs in the environment are oil and gas and related products production, storage and transportation, and spills (Choi et al., 2009; CCME, 2010a). There are some natural

sources, such as volcanoes and forest fires as well. Many of these sources release both PAHs and toxic heavy metals into the environment. Therefore, due to their common sources, PAHs coexist with heavy metals in many contaminated soils (Wang et al., 2004; Morillo et al., 2008; Thavamani et al., 2011; Thavamani et al., 2012).

Table 2.1 USEPA's 16 priority pollutant PAHs and selected properties (Wick et al., 2011; CCME, 2010b)

PAH name	Number of rings	Molecular Weight G mol ⁻¹	Water solubility mg l ⁻¹	Log K _{ow} **	Log K _{oc} ***	Vapor pressure mmHg	Henry's law constant atm·m ³ mol ⁻¹
Acenaphthene	3	154.2	1.93	3.98	3.66	4.47×10 ⁻³	7.91× 10 ⁻⁵
Acenaphthylene	3	152.2	3.93	4.07	1.40	0.029	1.45×10 ⁻³
Anthracene	3	178.2	0.076	4.45	4.15	1.7× 10 ⁻⁵	1.77× 10 ⁻⁵
Benzo[a]anthracene*	4	228.2	0.01	5.61	5.30	2.2 × 10 ⁻⁸	1 × 10 ⁻⁶
Benzo[a]pyrene*	5	252.3	2.3× 10 ⁻³	6.06	6.74	5.6× 10 ⁻⁹	4.9× 10 ⁻⁷
Benzo[b]fluoranthene*	5	252.3	0.0012	6.04	5.74	5× 10 ⁻⁷	1.22× 10 ⁻⁵
Benzo[k]fluoranthene*	5	252.3	7.6× 10 ⁻⁴	6.06	5.74	9.59× 10 ⁻¹¹	3.87× 10 ⁻⁵
Benzo[g,h,i]perylene*	6	276.3	2.6× 10 ⁻⁴	6.50	6.20	1.03× 10 ⁻¹⁰	1.44× 10 ⁻⁷
Chrysene*	4	228.3	2.8× 10 ⁻³	5.16	5.30	6.3× 10 ⁻⁷	1.05× 10 ⁻⁶
Dibenz[a,h]anthracene*	6	278.3	5× 10 ⁻⁴	6.84	6.52	1× 10 ⁻¹¹	7.3× 10 ⁻⁸
Fluoranthene	4	202.3	0.2-0.26	4.90	4.58	5× 10 ⁻⁶	6.5× 10 ⁻⁶
Fluorene	3	166.2	1.68-1.98	4.18	3.86	3.2× 10 ⁻⁴	1× 10 ⁻⁴
Indeno[1,2,3-c,d]pyrene*	6	276.3	0.062	6.58	6.20	1× 10 ⁻¹⁰	6× 10 ⁻⁸
Naphthalene	2	128.2	39.06	-	-	-	-
Phenantherene	3	178.2	1.20	4.45	4.15	6.8× 10 ⁻⁴	2.56× 10 ⁻⁵
Pyrene	4	202.3	0.077	4.88	4.58	2.5× 10 ⁻⁶	1.14× 10 ⁻⁵

* The USEPA has classified these PAH as possible human carcinogens

** Octanol-Water partition coefficient

*** Organic carbon-water partition coefficient

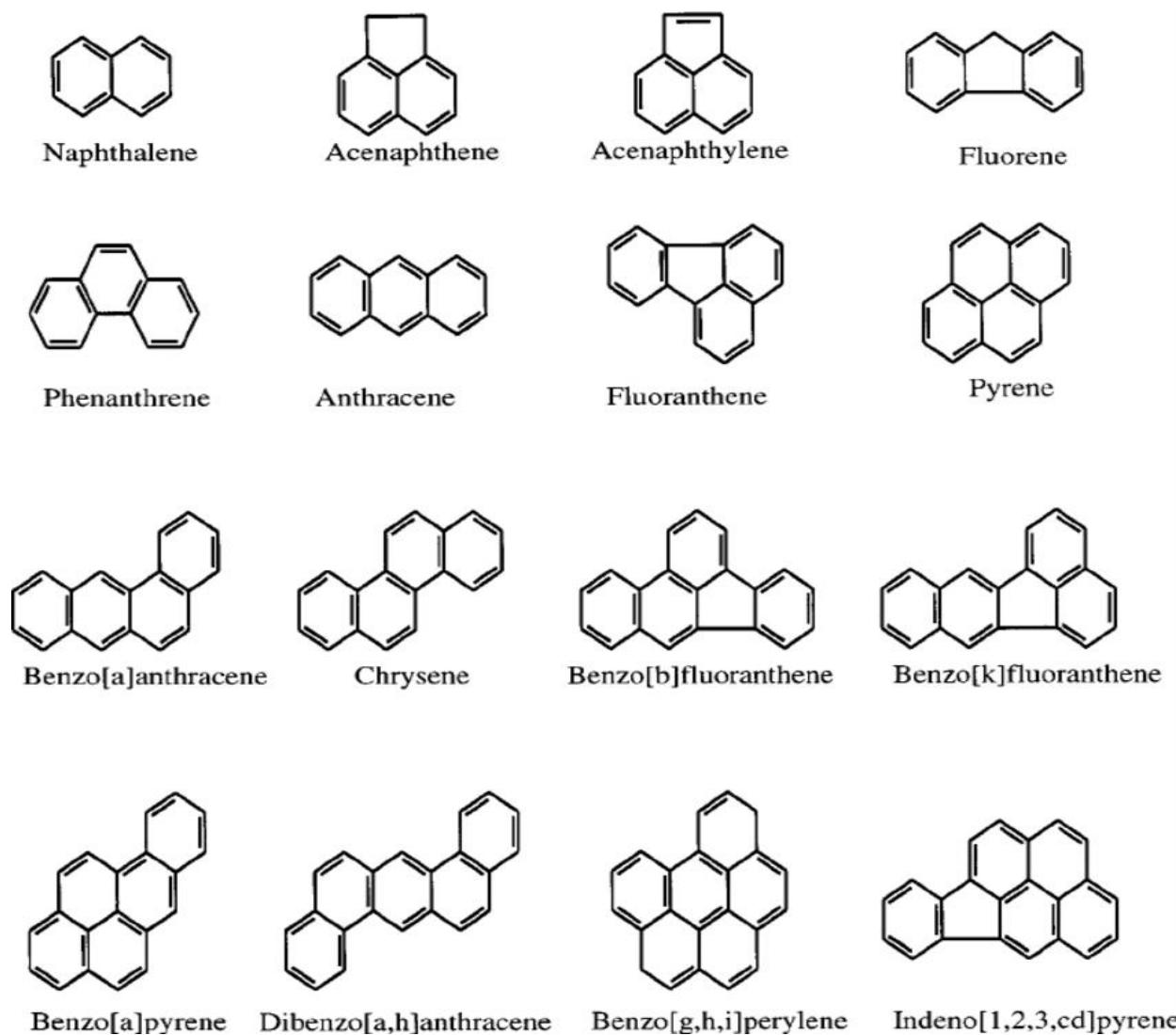


Figure 2.2 Molecular structures of 16 PAHs in priority list of the USEPA (Wick et al., 2011)

There are thousands of contaminated sites around the world. There were estimated to be 294,000 in the US (USEPA, 2004a). 1337 superfund sites are listed in a national priorities list of the United States (USEPA, 2019). In Canada, there are 22, 000 federal contaminated sites (FCSI, 2018). These numbers are likely to increase as contaminated sites continue to be identified. About 29% of contaminated sites in the US contain a single contaminant (metals, PAHs, PCBs

or VOCs), whereas 71% are contaminated by two or more types of contaminant (USEPA, 2018). Among the contaminated sites, 12.3 and 3.7% are contaminated by mixed heavy metals and PAHs in the US and Canada, respectively (USEPA, 2018; FCSI, 2018). Many other sites contain other types of contaminants in addition to HMs and PAHs. Table 2.2 summarizes the proportions of sites contaminated solely by metals, PAHs or both in the US, Canada and Europe.

Table 2.2 Sites contaminated solely by metals, PAHs or both in the US, Canada and Europe (% of total contaminated sites in each)

Region	Solely HM contamination	Solely PAH contamination	Mixed contamination by PAH+ HMs	Reference
USA	16.8%	4.3%	12.4%	USEPA (2018)
Canada	34.1%	2.6%	3.7%	FCSI (2018)
Europe	34.8%	10.9%	—	Panagos et al. (2013)

Remediating these mixed-contaminated sites poses great challenges, because of the different physicochemical properties and the broad ranges of contaminants, each requiring different technologies.

Since HMs are neither biodegraded nor transported by air in soil matrices, a technology for simultaneous remediation of PAHs co-existing with HMs in soil should be either based on desorbing and solubilizing them into a liquid to carry the mixed contaminants, or solidifying/stabilizing them into the soil matrix. However, sorption/desorption behavior and reaction kinetics influence the mobility and subsequent removal of the contaminants in soil.

Except for naphthalene, because of low solubility and high sorption affinity to soil and organic matter of PAHs, the chemical fate of PAHs is predominantly controlled by sorption and desorption processes in soil environments. From an enhanced soil washing/flushing remediation point of view, sorption/desorption and mobility of contaminants influence the remediation reaction/retention times, clean-up efficiency and cost of remediation.

Given that in the soils of many PAH contaminated sites, there are co-existing heavy metals, there is a need to study sorption/desorption of PAHs co-existing with heavy metals in soil. Among soil characteristics, organic matter content is vital to sorption/desorption, ultimate fate and mobility of both PAHs and HMs in soil (Kaschl et al., 2002). PAHs and HMs both interact with organic matter in soil-water systems (Gao et al., 2006; Zhang and Ke, 2004). Therefore, sorption/desorption of PAHs can be influenced by the presence of heavy metals in the system (Walter and Weber, 2002). Understanding these mechanisms for PAHs in soil is vital to better assess soil pollution risks, as well as to design remediation systems based on enhanced soil washing/flushing.

Among the soil properties influencing sorption of PAHs onto soil, organic matter content seems to be the most important one. From the remediation of PAH-contaminated, co-existing heavy metals point of view, the effect of heavy metals on the sorption/desorption of PAHs in soil is an essential, but less studied, subject. Therefore, the main objective of this chapter is to review and evaluate the probable effect of soil organic matter and co-existing HMs on sorption/desorption of PAHs, based on previously published literature. The contents of this chapter should help

researchers find gaps in the field of sorption/desorption of PAHs in soil, taking into account the effects of co-existing HMs and SOM.

2.2 Methodology

In this study literature on the sorption and desorption of PAHs in soil is reviewed with emphasis on the effect of soil organic matter and co-existing heavy metals on the process. References are used to explain principles of PAHs sorption and affecting factors. More recent published research (from 2006 to 2018) relevant to the aim of this chapter were collected and reviewed to be summarize and presented in the following sections; i) sorption of PAHs in soil, ii) effect of soil organic matter on PAHs sorption, iii) effect of co-existing heavy metals, iv) other factors related to PAH sorption, v) desorption of PAHs. Based on the review, conclusions and future research needs are identified.

2.3 Sorption of PAHs in soil

The term "sorption" is used to cover the adhesion of contaminants to solid particles by both adsorption and partitioning. Solids capable of sorbing PAHs in soil include minerals, particularly clay minerals, and natural organic matter. Sorption can occur by several mechanisms, including absorption into natural organic matter (partitioning); adsorption to mineral surfaces via van der Waals/London dispersion forces; adsorption through electrostatic attractive forces to sites with opposite charge on solid surfaces; and chemical sorption (covalent bonding to surface functional groups) on the soil solid particles (Hemond and Fechner-Levy, 2015).

Many sorption reactions are completely or partly reversible. Depending on the conditions, nature and composition of the sorbent and sorbate chemical, the relationship between the amounts of dissolved contaminant in the aqueous phase and the amount of sorbed (partitioning), may be linear or non-linear. The distribution coefficient (K_d) represents a ratio, indicating the amount of sorbed contaminant to its aqueous phase equilibrium concentration:

$$K_d = (C_s/C_e) \quad \text{Eq. 2.1}$$

where K_d is distribution coefficient ($L^3 M^{-1}$), C_s is the concentration of sorbed contaminant in soil ($M M^{-1}$) and C_e is the equilibrium concentration of sorbate in aqueous phase ($M L^{-3}$). There are many non-linear equations, called isotherm equations, expressing the relationship between the sorbed contaminants and sorbate concentration. Among these, the Freundlich and Langmuir isotherms are most often used to describe the sorption of contaminants in soil environments. The Freundlich isotherm equation is

$$C_s = K_f (C_e)^n \quad \text{Eq. 2.2}$$

whereas the Langmuir isotherm equation is

$$C_s = (bkC_e)/(1+kC_e) \quad \text{Eq. 2.3}$$

K_f is the Freundlich constant, n a constant reflecting the degree of non-linearity, C_s is the concentration of sorbed contaminant in soil ($M M^{-1}$) and C_e is the aqueous equilibrium concentration of sorbate ($M L^{-3}$); b and k are Langmuir constants, with k reflecting the maximum sorption capacity of a sorbent.

Table 2.3 summarizes research on the sorption of PAHs onto soil/minerals since 2006. Because sorption is a key process in the fate, transport and remediation of PAHs in contaminated soil, this information can also be useful for such studies in contaminated sites. It can be concluded that

parameters, test conditions, contaminants and results of published studies on sorption of PAHs onto soil/minerals are too scattered for there to be simple plain rules. Most previous studies on PAH sorption are conducted through batch tests, with phenanthrene, pyrene and naphthalene receiving the greatest attention. The best-fitted isotherm models have been reported to be those of Freundlich and Langmuir, in that order. Linear behavior is reported for sorption of benzo(a)pyrene onto minerals, phenanthrene onto quartz (Muller et al., 2007), phenanthrene onto poor-organic content soils and phenanthrene sorption from dilute solutions ($< 100 \mu\text{g L}^{-1}$) (Sun et al., 2010). Most tests are performed at room temperature or 20-25 °C, but some studies have examined the sorption of PAHs at 10 and 15°C (Ping et al., 2006; Kaya et al., 2013) and 40 and 50°C (Javier Rivas et al., 2008), in addition to 20°C. Overall, findings indicate that sorption is higher at lower temperatures.

Other test conditions and results are very scattered. Contact times tested have varied from 20 min to more than 48 h. Times needed to reach sorption equilibrium have been reported to be from 4 h to more than 34 h. However, it seems that in most cases there is rapid sorption in the first 10 to 90 min during which about 90% of the overall sorption takes place (Muller et al., 2007; Javier Rivas et al., 2008; Sun et al., 2010; Osagie and Owabor, 2015 a,b). Initial concentrations of PAHs in solution were in the wide range of 0.0006 to 400 mg L⁻¹. Even sorbent-to-solution ratio and amounts used in tests have varied widely. Therefore, it is not surprising that the results on PAHs sorption amounts and coefficients have varied greatly from study to study. For example, K_f values in different studies for phenanthrene have ranged from 0.21 to 220 L kg⁻¹ for different soils and minerals under different test conditions. In addition, sorption amounts of phenanthrene

have been reported to range from three to 400 mg kg⁻¹ for soils and minerals with different compositions.

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property ^c	Highlighted findings	Comments/ Limitations	Reference
PHE ^a	HA ^b and FA	Batch 1 mg L ⁻¹ PHE mixed with HA and FA 0-10 g kg ⁻¹ soil for pH range 3-6 for 24 h Temperature effect examined at pH 3 for temperatures of 15 and 25°C	Freundlich	Highest adsorption was at pH 3 for HA K _f values for HA: 221 L kg ⁻¹ for FA: 176 L kg ⁻¹	Sorption was higher at 15°C than at 25°C		Ping et al. (2006)
PHE, PYR ^d , BAP ^e	quartz, goethite-coated quartz, and quartz- montmorillonite mixture	Batch tests From 4 to 20 h at 8 time steps Initial concentration: 10% of each PAH aqueous solubility Sorbent to solution ratio: 1:5 (15 g 75 mL)	Freundlich: PHE and PYR Linear: PHE to quartz Linear: BAP	K _f values; PHE: 0.21-2.46 L kg ⁻¹ PYR: 0.36-3.43 L kg ⁻¹ K _d values; BAP: 48-154 L kg ⁻¹ PHE to quartz: 0.2 L kg ⁻¹	Equilibrium time: 4 h Instantaneous kinetics Cation-π interactions seemed an important sorption and retention mechanism for low organic matter soil environments	PHE and PYR showed the weakest sorption onto quartz-montmorillonite mixture in spite of the greatest surface area	Muller et al. (2007)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference
ANA ^f PHE, AN ^g , FLAN ^h	Natural soil	Batch Temperature 298, 313, and 333 K	Oswin, Freundlich and Caurie		<p>Three PAHs except for acenaphthene showed anomalous isotherms when tested individually</p> <p>As mixture non showed abnormal sorption trend</p> <p>Sorption kinetics was quite fast (10-20 min)</p> <p>Sorption amounts order is the same order as the solubility of PAHs (ANA > PHE > FLAN > AN)</p>	<p>trapping of PAHs by SOM released to water is the main cause</p> <p>No information given on soil properties other than SOM and particle size</p>	Javier Rivas et al. (2008)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference	
PHE, PYR	8 European soils	24 h Batch Initial concentrations: PHE: PYR: 0.0009 to 0.1 mg L ⁻¹ PHE: 0.0006 to 1.1 mg L ⁻¹	Freundlich	PYR: 3-4.5 mg kg ⁻¹ PHE: 30-50 mg kg ⁻¹	Freundlich sorption coefficients, correlated well with the soil organic carbon contents	Sorption predictions based on organic matter and one additional simple soil parameter (e.g., clay content, cation exchange capacity, or pH) yielded accurate sorption predictions of Freundlich coefficient	Sorption could not be predicted from soil organic carbon contents alone	De Jonge et al. (2008)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference
PHE	Different natural soil samples: top, aeration zone, and aquifer zone soil samples	Sorbent to solution: 3.5 g: 210 mL From 20 to 480 min in 7 time steps	Linear in OM-poor soil Linear at < 100 $\mu\text{g L}^{-1}$ of PHE in solution Nonlinear at > 100 $\mu\text{g L}^{-1}$ of PHE in solution	< 50 $\mu\text{g g}^{-1}$ in soils at < 1.5% OM 90-100 $\mu\text{g g}^{-1}$ in soils at > 1.5% OM	Equilibrium time: 8 h (90% of sorption in first 1.5 h) The more organic content the more time to reach sorption equilibrium linear relation between organic fraction of the soil and Freundlich sorption coefficient	Soil samples texture and compositions not determined Single contaminant	Sun et al. (2010)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/ Limitations	Reference
PHE	Cation modified clay minerals (smectite, kaolinite, vermiculite)	Batch Initial concentration: 0.025-1.0 mg L ⁻¹ minerals modified by Na, K and Ca cations Contact time: 48 h at 25°C	Freundlich	K _f values for Ca, K and Na modified Smectite: 20.72, 14.65, 13.72 L kg ⁻¹ for kaolinite: 7.39, 6.83, 6.61 L kg ⁻¹ for vermiculite: 7.22, 7.8 9,6.94 L kg ⁻¹			Zhang et al. (2011b)
NAP ⁱ	NB ^j and HB ^k	Batch Sorbent to solution: 0.05: 50 g mL ⁻¹ Initial concentration: 7.5-20 mg L ⁻¹ at 10, 15 and 20°C	Freundlich, Langmuir	22.45 mg g ⁻¹	K _f values; for NB: 0.397-0.706 L g ⁻¹ for HB: 1.58-3.66 L g ⁻¹		Kaya et al. (2013)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference
FL, PHE, FLAN, PYR	Silty-clay soil	Column test Test duration: 34 d Constant flow rate: 200 mL d ⁻¹ Initial concentrations: 100 µg L ⁻¹	Langmuir		1 st -order Lagergren and Bangham equation describes sorption rate. Clay minerals responsible for sorption because of low soil SOM	Types and content of soil clay minerals not determined	Yang et al. (2013)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference
PHE and PYR	Two types of natural soil; sandy loam and clay loam	Batch PAH solution concentrations: 50-400 mg L ⁻¹ contact time: 24 h	Freundlich	350-400 mg kg ⁻¹	SOM is predominant in PAHs sorption More SOM led to more sorption and less desorption		Yu et al. (2014)
NAP	Sandy soil (sieved to < 2.5 mm) Clay soil (sieved to < 220 µm)	Batch solution/sorbent: 500 mL:100 g PAH solution concentration range: 50-250	Freundlich for clay soil Langmuir for sandy soil	5.73	Equilibrium time: 20 and 24 h for sandy and clay soil Sorption kinetics fits pseudo-2 nd order model	Correlation between model and observed data was lower for sandy soil than for clay soil Correlations for kinetics model and observed data were much lower in clay soil than sandy soil Single contaminant study	Osagie and Owabor (2015a)

Table 2.3 Summary of research studies and results for sorption of PAHs onto soils/minerals (continued)

PAHs	Sorbent material	Sorption test conditions	Sorption model (isotherm)	Sorption capacity/property	Highlighted findings	Comments/Limitations	Reference
PYR	Sandy soil (sieved to < 2.5 mm) Clay soil (sieved to < 220 µm)	Batch solution/sorbent: 500 mL:100 g PAH solution concentration range: 50-250	Langmuir	0.286 mg g ⁻¹ for clay 0.225 mg g ⁻¹ for sandy soil	Sorption kinetics fits pseudo-2nd order model Equilibrium time: 28 and 34 h for sandy and clayey soil Pseudo-2nd order rate constant: 0.00088 for clay and 0.00085 for sandy soil	Single contaminant Correlations between kinetics model and observed data were lower for clay soil than sandy soil Correlation between sorption isotherm model and observed data were not very high	Osagie and Owabor (2015b)
PHE, PYR, FLAN	River sediment	Batch Initial concentration of each PAH: 10-100 mg L ⁻¹ Mixing at 25°C for 8 h sediment size with highest sorption: < 38 µm.	Freundlich	K _f values: phenanthrene: 88.54 L g ⁻¹ fluorene: 188.71 L g ⁻¹ pyrene: 91.46 L g ⁻¹			Wang et al. (2015)

^aPHE: Phenanthrene, ^bHA: Humic acid, FA: Fulvic acid, ^c K_f: Freundlich sorption coefficient, ^dPYR: Pyrene, ^e BAP: Benzo(a)pyrene, ^f ANA: Acenaphthene, ^g AN: Anthracene, ^h FLAN: Fluoranthene, ⁱNAP: Naphthalene, ^j NB: Natural bentonite, ^k HB: Modified bentonite

2.3.1 Effect of soil organic matter

Natural organic compounds entering natural systems undergo complex microbial and abiotic transformations that produce what is called natural organic matter (NOM). NOM contains fulvic, humic and humin materials. In general, NOM refers to thousands to tens of thousands of different complex chemical structures, such that no two molecules can be found to be identical (Hayes et al., 1990; Suffet and MacCarthy, 1989).

While recent research (Saeedi et al., 2018a; Zhang et al., 2011 a,b; Zhang et al., 2010) has shown that PAHs can adsorb onto clay minerals in soil matrix, it is widely believed that the partitioning (absorption) into the natural organic matters of soil (SOM) is the primary sorption mechanism of PAHs (Ping et al., 2006). Polarity, aromatic carbon and aliphatic groups of organic matter are believed to control the PAHs sorption onto soil. Aromatic domains of organic matter have also been reported to play an important role in sorption PAHs to soil and sediment (Ahangar, 2010). Based on the assumption that soil organic matter is mainly responsible for PAH sorption, methods have been developed for approximating K_d , taking both sorbate and sorbent properties into consideration. Since PAHs are mostly non-polar hydrocarbons, they have large octanol-water partitioning coefficient (K_{ow}) values, showing less tendency to dissolve in water and more tendency to sorb onto organic matter of the soil. Larger PAH molecules with higher K_{ow} are more likely to sorb onto soil particles. To predict K_d values for a given PAH in soil, the fraction of organic carbon of the soil (f_{oc}) and the K_{ow} of the PAH are used. In this method, it is assumed that the sorption occurs as soil organic matter partitioning. K_d is then calculated as;

$$K_d = f_{oc} \cdot K_{oc} \quad \text{Eq. 2.4}$$

where f_{oc} is the organic carbon fraction in the soil, and K_{oc} (chemical concentration sorbed to organic carbon/chemical concentration in water) is the organic carbon-water partition coefficient. Based on laboratory data, several regression equations have been reported in the literature for different organic chemicals to predict K_{oc} as a function of K_{ow} (Lyman et al., 1990). Based on this approach, one can calculate the K_d (sorption or distribution coefficient) values for a given PAH using K_{ow} of that PAH and the measured organic carbon of the soil.

De Jonge et al. (2008) reported that K_d values of a given PAH with different sorbents were proportional to the organic carbon contents of the soil. Important characteristics of organic matter in the sorption of PAHs are chemical properties, molecular sizes, and functional groups. Figure 2.3 depicts the two representative structures of NOM, with (a) showing the structure of fulvic acid and (b) a conceptualized NOM structure (Dunnivant and Anders, 2005). As shown in Figure 2.3, there are numerous hydrophobic centers and ionic sorption sites in such large organic matter molecules. These are key features that can enhance the sorption of polar organic compounds, HOCs such as PAHs, and ionic contaminants such as heavy metals, in soils containing NOM compared to the same soil without any NOM.

The chemical functionality of NOM is also important in its effect on the sorption of different contaminants in soil environments. The main functional groups observed and identified in NOM are summarized in Table 2.4. Water molecules in soil can form hydrogen bonds with charged and polar functional groups. The density of these groups results in hydrophobic character to organic matter on a macroscopic scale (Laird and Koskinen, 2008). On the other hand, aliphatic

groups may form localized hydrophobic regions on a molecular scale. Therefore, NOM in soil can enhance sorption of both heavy metals and PAHs.

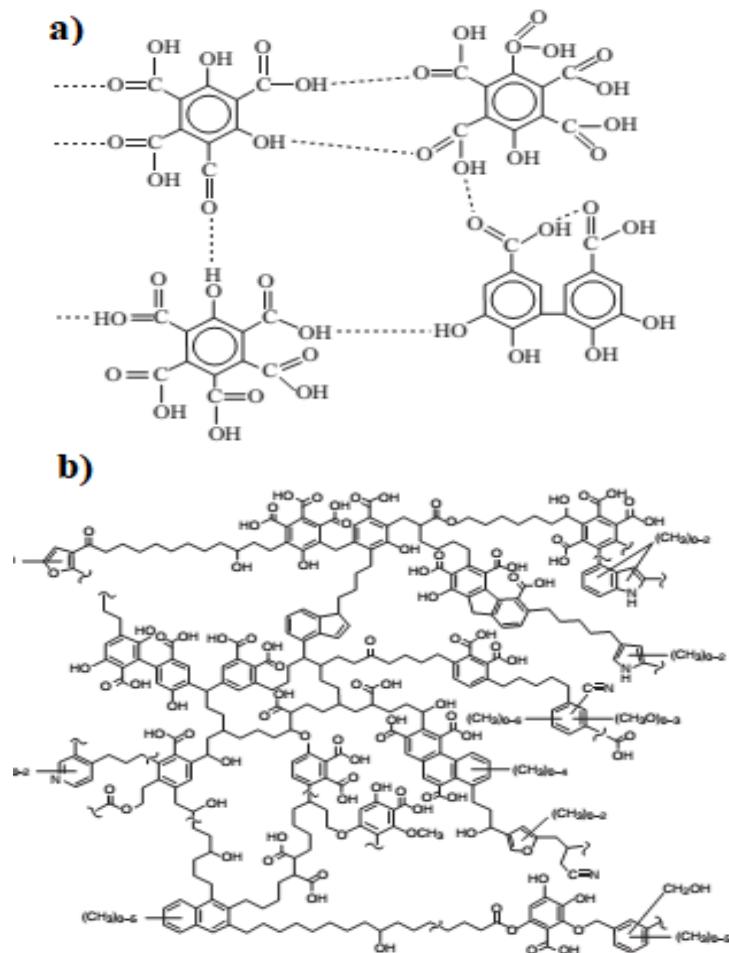


Figure 2.3 Structures of natural organic matter (Dunnivant and Anders, 2005), a) representative of fulvic acid, b) a conceptualized NOM structure

Table 2.4 Functional groups identified and observed in different NOM (Dunnivant and Anders, 2005; Killops and Killops, 1993)

Symbol/molecular structure	Name	Resulting compound
ROH	Hydroxyl	Alcohol
	Carbonyl	Phenol Aldehyde Ketone
	Carboxyl	Quinone Carboxylic acid
	Oxo	Ether
	Amino	Amine
	Amido	Amide
	Thio	Thiol
	R=CH ₂ Indenyl	Indene
	R= O Furanyl	Furan
	R= NH Pyrryl	Pyrrole
	R= S Thiophenyl	Thiophene
	R= CH Phenyl	Benzene
	R= N Pyridinyl	Pyridine
	Pyranyl	Pyran
	LAW	H ₂ LAW
	Quinone	Hydroquinone
	Iron (II) Porphyrin	Iron (II) Porphyrin

Several researchers (Hassett et al., 1980; Means et al., 1980; Delle Site, 2001; Ping et al., 2006) have shown that there are good correlations between the sorption of PAHs and other hydrophobic organic compounds (HOCs), and SOM. Hassett et al. (1980) showed that factors such as total clay content and mineralogy, cation exchange capacity, surface area and pH were not significant compared to organic matter of the soil in sorption of dibenzothiophene by soil and sediment.

Other researchers have demonstrated the role of SOM in sorption of HOCs by removing NOM from the soil by extractants or by oxidation, then investigating the sorption process (Yaron et al., 1967; Wolcott et al., 1970; Wahid and Sethunathan, 1979). They concluded that, in addition to NOM, other soil properties appear to be responsible for sorption, but their role could be masked by the SOM effect. For "organic poor" soils, at no or low organic matter content, sorption coefficients (K_d) are expected to be much lower than in the same soil at high OM contents (Schwarzenbach and Westall, 1981).

On the importance of the OM in controlling sorption of HOCs with water solubility less than 10^{-3} M (all USEPA-listed PAHs except naphthalene, acenaphthene and acenaphthylene), the following constants have been defined (Delle Site, 2001):

$$K_{om} = K_d / f_{om} \quad \text{or} \quad K_{oc} = K_d / f_{oc} \quad \text{Eq. 2.5}$$

where f_{om} and f_{oc} denote the fractions of organic matter and organic carbon (OC) in the soil, respectively. K_{om} and K_{oc} are expressed in $\text{cm}^3 \text{ g}^{-1}$ or $\text{dm}^3 \text{ kg}^{-1}$ of organic matter and organic carbon, respectively. The association of HOCs with SOM is attributable to hydrophobic bonding because of combined van der Waals forces thermodynamic gradient that drives non-polar

organics out of aqueous solution. The interactions of non-polar organic compounds with SOM are thermodynamically preferred to those of compound-water or compound-compound (Gauthier et al., 1987; Weber et al., 1991). Some previous researchers have provided a “rule of thumb” to determine if SOM or clay minerals are responsible for sorption of HOCs in a given soil. HOCs sorption on clay surfaces dominates the organic matter partitioning if the clay/OC ratio is high (Karickhoff, 1984; Weber et al., 1992). A ratio of (clay mineral)/(organic carbon) = 30 (corresponding to a clay/OM ratio of 15) was proposed by Karickhoff (1984) as a threshold. Therefore, regardless of the mineral content, if the mass ratio of clay mineral to OM in soil < 30, mineral contributions in sorption is masked by organic matter. The ratio, however, might depend on the hydrophobicity of the sorbate , type of minerals, and functional groups and chemical composition of OM.

The critical organic carbon fraction (f_{oc}), below which mineral adsorption dominates over OM partitioning of HOCs, was suggested by McCarty et al. (1981) to be:

$$f_{oc} = SA/[200 (K_{ow})^{0.84}] \quad \text{Eq. 2.6}$$

where SA is the specific surface area of the mineral.

Table 2.5 summarizes recent studies on the effect of soil organic matter on sorption of PAHs onto soil. These studies confirm the enhancing effect of SOM on sorption of PAHs. However, reports show that the composition of SOM is important in the sorption of PAHs. Ping et al. (2006) reported that fulvic acids do not enhance the sorption of phenanthrene at low pH. Wu et al. (2011) also found that pH had no significant effect on the sorption of phenanthrene onto organic matter-added montmorillonite. While PAHs tend to sorb onto fulvic and humic acids

rather than humins in soil, the fraction of larger PAH molecules sorbed onto humins is greater than the fraction sorbed onto lower molecular weight PAHs (Yang et al., 2010). On the other hand, Ukalska-Jaruga et al. (2018) reported that low-molecular-weight (two and three rings) PAHs had stronger bonds with humins in contaminated natural soil. They found no significant relationship between humic and fulvic acids for PAHs accumulation in contaminated soil. Yang et al. (2010) also noted that with increasing SOM, most PAHs tend to accumulate in fulvic acids rather than humins.

Overall, although it is well known that SOM enhances PAHs sorption, there seems to be a minimum level of SOM in soil for them to predominate. Although threshold ratios and relationships like equation 2.6 have been suggested for the minimum level, it appears to be interrelated with the properties and composition of both SOM and other components of soil, as well as mineralogy. Most previous studies indicate that the Freundlich isotherm is commonly a good model for sorption of PAHs in soil containing organic matter. It has also been found that increasing SOM content slows the rapid phase of PAH sorption towards reaching equilibrium.

Table 2.5 Summary of recent research results on the effect of soil organic matter on PAHs sorption and retention

Soil	Types of PAHs	Description of the study	Highlighted findings	Reference
Agricultural top soil treated with humic acid (HA) and fulvic acid (FA)	Phenanthrene	<p>Isotherm tests conducted at initial concentrations of 0.025, 0.050, 0.100, 0.25, 0.50, and 1.0 mg L⁻¹; 15 and 25°C temperatures tested, test duration: 24 h</p> <p>Exogenous humic acids (HAs) were added to soil to enhance the amount of soil organic carbon (SOC) by 2.5, 5.0, and 10.0 g kg⁻¹</p> <p>Sorption and desorption for pH of 3 and 6 and at 15 and 25°C were evaluated,</p>	<p>Humic acid and fulvic acid showed different effects on adsorption.</p> <p>Adsorption increased at first, then decreased with increasing fulvic acid</p> <p>At pH=3, Adsorption in FA treated soil was lower than untreated and HA treated soil</p> <p>Sorption fitted the Freundlich isotherm</p> <p>HA increased Freundlich sorption coefficients</p>	Ping et al. (2006)
8 European soils with different properties	phenanthrene, pyrene	24 h Batch tests	<p>Freundlich sorption coefficients correlated well with soil organic carbon content.</p> <p>Soil organic carbon content alone is not adequate for sorption behavior quantitative predictions.</p>	De Jonge et al. (2008)

Table 2.5 Summary of recent research results on the effect of soil organic matter on PAHs sorption and retention (continued)

Soil	Types of PAHs	Description of the study	Highlighted findings	Reference
Five surface soil samples from Shisanlin, Beijing, with different SOM and humic acids, fulvic acids and humins	acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene	Studied impact of SOM on distribution of PAHs in soils.	Humins sorbed fraction of PAHs increased with increasing PAH molecular weight Sorption of PAHs increased with increasing SOM content in soil. With increasing SOM, fraction of each individual PAH in fulvic acids increased, whereas the fraction in humins decreased.	Yang et al . (2010)
Montmorillonite (MMT) and dissolved organic matter (DOM) modified montmorillonite (DOM-MMT)	Phenanthrene	Batch sorption tests were carried out as a function of contact time, temperature, and adsorbent dose. Sorption at 25, 35 and 45°C was tested	Sorption isotherm fitted by Freundlich isotherm Sorption capacity of organic matter added montmorillonite was greatly enhanced compared to MMT. Effects on sorption could be related to changes in surface structure, specific surface area, hydrophobicity and the average pore size of MMT. Sorption is exothermic and decreased with temperature in both MMT and DOC-MMT. pH had no significant effect on sorption. Adsorption capacity of DOM–MMT decreased with increasing adsorbent dose.	Wu et al. (2011)

Table 2.5 Summary of recent research results on the effect of soil organic matter on PAHs sorption and retention (continued)

Soil	Types of PAHs	Description of the study	Highlighted findings	Reference
Commercial HAs, as well as those obtained from Umbric Andosol, Dystric Cambisol, and cow manure compost and fractionated Aldrich humic acid (AHA).	Pyrene	Relationship between the chemical properties of various types of humic acids sorption ability was investigated in batch experiments.	Positive relationship between K_{doc} and aromaticity Factors other than aromaticity may also influence the sorption of pyrene.	Kobayashi and Sumida (2015)
Potentially contaminated natural soils from southwestern Poland	16 PAHs	to evaluate the mutual relations between the soil organic matter fractions: fulvic acids, humic acids, humins, black carbon and the PAHs accumulation level in agricultural soils	Positive relations between PAH concentrations and TOC content Links between humins and PAHs were stronger for low-molecular weight (two and three rings) PAHs. Relations among PAHs, humins and black carbon were statistically significant only in soils with TOC content $\geq 12 \text{ g kg}^{-1}$. Black carbon fraction showed higher correlations with high-molecular-weight PAHs. Fulvic acids and humic acids showed no significant relationship with PAHs.	Ukalska-Jaruga et al. (2018)

2.3.2 Effect of co-existing heavy metals on PAH sorption

Recent studies demonstrate that the coexistence of heavy metals and other metals can also contribute to sorption of PAHs to soil. It is believed that this effect is greater in low organic content soils or for high metal concentrations in soil (Obuekwe and Semple, 2013; Zhang et al., 2011b; Hwang and Cutright, 2004; Walter and Weber, 2002). Some of the reports speculate on probable causes and mechanisms for this effect.

Accumulation of sorbed heavy metals on soil (particularly clay) particle surfaces can make cation- π -bonds with PAHs (Zhu et al., 2004). These authors introduced a new perspective on the sorption of PAHs onto mineral surfaces. They reported that exchangeable cations on clay mineral interlayers could condition mineral surfaces, opening more adsorption sites for strong cation- π -bonds with PAHs.

Nguyen et al. (2013) reported that larger size pores, clay fraction aggregation and more hydrophobicity are some of the effects of metal cations in clay minerals and soils, causing more PAH sorption (Zhang et al., 2011a,b). Heavy metals on clay surfaces could play a bridging role between PAHs and clay minerals.

Gao et al. (2006) showed that sorption of phenanthrene was significantly increased by the presence of heavy metals (Cu, Pb and Zn). They also found that phenanthrene sorption was intensified when concentrations of metals in soil increased. They suggested that the bridging effects of heavy metals could transform some dissolved organic matter (DOM) in the system to particulates and to the adsorbed phase in soil (soil organic matter), resulting in more

phenanthrene sorption (mainly partitioning) by the solid phase. Reducing the dissolved organic matter could also decrease the dissolved organic complexes containing phenanthrene. They also mentioned that the presence of heavy metals creates more capacity to sorb PAHs in adsorbed organic matter, than the original soil organic matter. Tao et al. (2013) reported that the sorption of phenanthrene onto biomass depended on the type and concentration of heavy metals present in the system.

Table 2.6 summarizes some previously published work on the effect of co-existing metals on PAH sorption. Overall, the few studies published on the effect of co-existing soil heavy metals show that for all PAHs/soil types/minerals tested, co-existence of heavy metals in soil enhances the sorption of PAHs. However, the extent of enhancement differs for different physical/chemical conditions. Zhang et al. (2011a) studied the effects of pH, SOM and Pb on sorption of phenanthrene onto the clay content of soil and reported that the presence of Pb and SOM increases phenanthrene sorption in soil. They also reported that changes in pH affect soil properties, influencing the capacity for phenanthrene sorption. Fonseca et al. (2011) reported that co-existence of phenanthrene could prolong the Pb retention in soil.

Table 2.6 Summary of previous work on the effect of heavy metals on sorption of PAHs

Soil/Mineral	PAHs and metal co-contaminants	Sorption Isotherm	Sorption coefficients studied	Sorption coefficient result	Reference
Montmorillonite	PHE + Pb	Linear	K_d (L kg ⁻¹)	Only PHE: 1130 PHE+Pb: 1352	Zhang et al. (2011a)
Kaolinite	PHE + Pb	Linear	K_d (L kg ⁻¹)	Only PHE: 531 PHE+Pb : 572	
Montmorillonite	PHE + Cd	Linear	K_d (L kg ⁻¹)	Only PHE: 1130 PHE +Cd : 1247	
Silty Clay	PHE/PHE + Metals	Freundlich	K_f (L kg ⁻¹)	Only PHE:8.55 PHE+Metals: 21.48	Saison et al. (2004)
Natural soil spiked with heavy metals	PHE + Pb, Zn or Cu	Linear	K_d/K_{oc}	K_{oc} values for metal spiked soils were 24% larger than for unspiked ones. Increased SOM as a result of co-existing metals enhanced phenanthrene sorption.	Gao et al. (2006)

Table 2.6 Summary of previous work on the effect of heavy metals on sorption of PAHs (continued)

Soil/Mineral	PAHs and metal co-contaminants	Sorption Isotherm	Sorption coefficients studied	Sorption coefficient result	Reference
Paddy and Black Soil	NAP	Freundlich	K_f (modified Freundlich parameter) mg kg^{-1}	(Paddy Soil: 96.5)(Black Soil: 799)	Liang et al. (2016)
	NAP+Cu			(Paddy Soil: 101)(Black Soil: 846)	
	NAP+Pb			(Paddy Soil: 116)(Black Soil: 877)	
	NAP+Cr			(Paddy Soil: 123)(Black Soil: 896)	
	PHE			(Paddy Soil: 33.7)(Black Soil: 246)	
	PHE+Cu			(Paddy Soil: 35.1)(Black Soil: 251)	
	PHE+Pb			(Paddy Soil: 40.7)(Black Soil: 270)	
	PHE+Cr			(Paddy Soil: 41.5)(Black Soil: 307)	
	PYN			(Paddy Soil: 12.6)(Black Soil: 178)	
	PYN+Cu			(Paddy Soil: 15.6)(Black Soil: 186)	
Kaolinite	PYN+Pb	Linear		(Paddy Soil: 19.5)(Black Soil: 215)	Saeedi et al. (2018a)
	PYN+Cr			(Paddy Soil: 26.1)(Black Soil: 236)	
	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)			ANA: 193, FL:213, FLAN: 2175 ANA:203, FL: 239, FLAN:2566	
Sand+kaolinite	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)	Linear	K_d (L kg^{-1})	ANA: 122, FL: 128, FLAN: 1714	
	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)			ANA: 130, FL: 140, FLAN: 1872	
	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)			ANA: 140, FL: 152, FLAN: 1607	
Sand+kaolinite+bentonite	ANA, FL, FLAN (ANA, FL, FLAN)+(Pb, Ni, Zn)	Linear		ANA: 150, FL: 159, FLAN: 1880	

As discussed in sections 2.3 and 2.3.1, in soil-water systems PAHs interact with soil organic matter and heavy metals cations to form complexes with organic molecules in soil solids (Gao et al., 2003; Zhang and Ke, 2004; Gao et al., 2006), enhancing the sorption of PAHs onto soils. Moreover, Saeedi et al. (2018a) showed that the presence of both heavy metals and organic matter in soil can enhance PAHs sorption to an even greater extent than the total of the separate effects of metals and SOM. In other words, co-existence of SOM and heavy metals causes synergistic effects on the sorption of PAHs onto soil and clay mineral mixtures (Saeedi et al. 2018a). They reported 10 to 48% increments in PAH sorption enhancement by both SOM and heavy metals compared to summation of their individual effects for different PAHs and soils. Their results showed that this effect increased with increasing PAH molecular size and aromaticity.

Metal cations can form bonds with organic matter functional groups in soil-water systems. This connects the organic molecules creating hydrophobic sites for PAH molecules sorption. Heavy metals also bridge the dissolved organic matter in the system, changing them into the solid phase of the soil. This could increase soil organic matter, reduce the association of PAHs to DOM, and consequently increase the accumulation of PAHs in the particulate phase (Obuekwe and Semple, 2013).

Table 2.7 summarizes the reported mechanisms that enhance PAH sorption when heavy metals and soil organic matter co-exist, with categorization of the type of metal cation function.

Table 2.7 Effect of metals on sorption of PAHs in minerals and organic matter contained soil

Cation functioning mechanism	Effect on PAH sorption	Result of cation interaction	Reference
Bridging among SOM molecules	Enhancement	Creating and concentrating hydrophobic sites desirable for PAH sorption	Obuekwe and Semple (2013)
Bridging between DOM and soil	Enhancement	Transforms DOM into SOM resulting in reduction of mobile PAHs Increases SOM with greater sorption capacity	Jones and Tiller (1999) Traina et al. (1989) Saison et al. (2004) Gao et al. (2006)
Bonds between soil adsorbed metals and aromatic rings	Enhancement	Cation-π bond between metal cation and PAH	Zhu et al. (2004) Zhang et al. (2011a,b)

2.3.3 Other factors affecting PAH sorption

Based on our review of previous research, the distribution and partition coefficients of PAHs can depend on multiple factors of soil and environmental conditions. Because of the multiple factors affecting sorption of PAHs in soil, there is considerable uncertainty in predicting K_d for a given PAH. That is why for PAHs and some other organic and inorganic chemicals, sorption properties are usually determined in laboratory experiments.

Other factors affecting the sorption process include temperature, pH, ionic strength, soil particle size and surface area, soil composition and mineralogy, initial concentration of PAHs, contact time and kinetics of sorption, and PAH properties such as solubility. Some of these factors and their effects on PAHs sorption in soil environments are briefly described in this section.

Surface area

The soil surface area is believed to be inversely proportional to sorption capacity of any sorbate (Wang et al., 2015). Since adsorption is a surface phenomenon, the extent of adsorption per mass of soil is proportional to the surface area. Previous work on sorption behavior of different particle sizes of adsorptive media has confirmed this general rule (Cornelissen and Gustafsson, 2004; Lemic et al., 2007; Wang et al., 2015). However, since the sorption is not exactly the same as adsorption and includes other mechanisms like ion exchange, the sorption amount and the behavior of PAHs may differ from expectations based solely on the specific surface area of the sorbent.

Ionic strength and salinity

Increasing the ionic strength and salinity of the solution has been found to increase the sorption of PAHs onto soil and sediment. Inorganic ions can decrease the solubility of PAHs, leading them onto sorbent material surfaces (Weston et al., 2010). Increasing the sorption coefficient and amount of phenanthrene in water containing higher ionic concentrations has been reported (Karickhoff et al., 1979; El-Nahhal and Safi, 2004).

Solubility

The solubility of PAHs is inversely proportional to their molecular weight and K_{ow} . Lower solubility and higher K_{ow} indicate greater hydrophobicity of a PAH. Higher hydrophobicity in turn leads to greater sorption and a higher partition coefficient. Increased sorption capacity for decreased solubility of PAHs has been reported in most previous studies (Hu et al., 2008; Balati

et al., 2015). Solubility and K_{ow} are among the main PAHs properties affecting sorption and desorption behavior.

Temperature

Most previous studies have reported increased sorption at lower temperatures and decreased sorption at higher temperatures (Table 2) (He et al., 1995; Podoll et al., 1989). For example, Hiller et al. (2008) reported decreased sorption of pyrene, phenanthrene and naphthalene with the temperature increased from 4 to 27°C. Generally, sorption is exothermic; therefore, higher temperatures result in lower sorption. However, some studies have reported the opposite effect, confirming an endothermic reaction for sorption (Balati et al., 2015). According to Kipling (1965), it is expected that compounds whose solubility increase with increasing temperature will show lower sorption capacities. For compounds whose solubility is inversely proportional to temperature, the lower the temperature, the more sorption takes place.

pH

It seems that pH affects the sorption of PAHs due to a sorbent's change in surface charge distribution and functional groups (Gao and Pedersen, 2005; Ping et al., 2006; Putra et al., 2009). However, some researchers (Mader et al., 1997; Raber et al., 1998; Zeledon-Toruno et al., 2007; Hu et al., 2014) have reported that they did not observe pH as a significant factor in the sorption of PAHs onto solid media.

Contact time and kinetics

Sorption of PAHs onto soil usually occurs in two stages. The first stage, physical adsorption onto minerals and other components of soil, is rapid. This is followed by a slower stage of chemical sorption onto organic matter (Semple et al., 2007). Most previous work (Zeledon-Toruno et al., 2007; Awoyemi, 2011; Hu et al., 2014; Gupta, 2015) confirms this two-stage kinetics. Based on this, although a considerable portion of PAH sorption onto soil may occur in the early hours, completion of the process may require much more time as it approaches the maximum sorption capacity. The equilibrium time for PAH sorption has even been reported to be 34 h, but mostly less than 24 h (Table 2.3).

Clay and minerals

For fine soils that contain clay minerals, recent research (Saeedi et al., 2018a; Zhang et al., 2010; Zhang et al., 2011a,b; Hwang et al., 2003; Zhu et al., 2004) has shown that PAHs can sorb onto the soil, even in the absence of soil organic matter.

In clay minerals, surface area may be the main factor influencing the sorption of PAHs. Hydrogen bonding between a PAH and the oxygen of the clay mineral surfaces may take place. Nevertheless, this might not be the only factor determining the sorption capacity of clay minerals for non-polar organic compounds such as PAHs. Brindley et al. (1963) surprisingly reported that the order of sorption of acetoaceticethylester and β , β - oxydipropionitrile on clay minerals per unit of surface area was gibbsite > kaolinite > montmorillonite. They explained that the hydroxyl surfaces in gibbsite and kaolinite could sorb more effectively than the oxygen surfaces in montmorillonite. However, for aromatic hydrocarbons such as benzene, toluene and xylene,

lower K_f values were reported for kaolinite than for montmorillonite and illite. This was explained based on the clay mineral surfaces of these clays: montmorillonite ($8 \times 10^6 \text{ m}^2 \text{ kg}^{-1}$), illite ($10^5 \text{ m}^2 \text{ kg}^{-1}$) and kaolinite ($3 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$) (Li and Gupta, 1994). For minerals other than clays, it seems that sorption of PAHs does not occur significantly on mineral surfaces. Mader et al. (1997) showed that PAHs interact weakly and non-specifically with some non-clay mineral surfaces ($\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$). In summary, it is clear that clay minerals can be relatively good sorbents of PAHs in soil environments. The sorption capacity of different clay minerals for PAHs seems to be proportional to the surface area of the clay and to be dependent on the clay mineralogical and crystallographic structure in terms of the number of layers and their expandability.

2.4 Desorption of PAHs

The fate of PAHs in soil is mainly controlled by sorption-desorption processes. Since some of the mechanisms that take place in sorption process are equilibrium reactions, most factors affecting sorption also affect desorption. Mobility of PAHs in soil can be influenced by soil properties, PAH physical/chemical properties and coexistence of other contaminants. As discussed above, soil organic matter and heavy metals are among the factors which play key roles in sorption-desorption processes. However, regarding hydrophobicity of PAHs, most studies on the natural desorption and mobility of PAHs have shown that their mobility is very low compared to the sorption amounts (Saeedi et al., 2018b; Olu-Owolabi et al., 2014; Yang et al., 2013; Barnier et al., 2014). On the other hand, higher amounts of desorption are needed for soil washing/flushing and electrokinetic remediation of PAH-contaminated soil.

Application of surfactants/biosurfactants and some organic and weak acids to desorb and extract PAHs or heavy metals from soil has been widely investigated (Maturi and Reddy, 2006; Alcantara et al., 2008; Song et al., 2008; Cao et al., 2013; Saichek and Reddy, 2005; Saichek and Reddy, 2004; Jin et al., 2013; Sánchez-Trujillo et al., 2013; Ling et al., 2015; Sales and Fernandez, 2016; Greish et al., 2018).

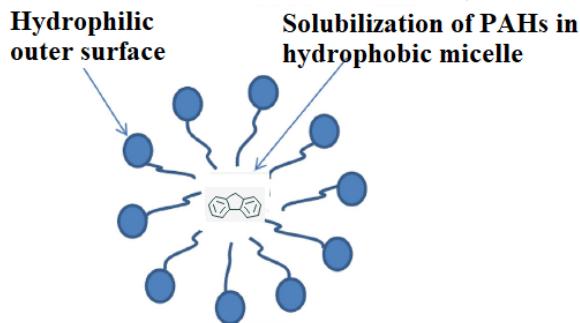
Lamichhane et al. (2017) reviewed previous studies on surfactant-enhanced remediation of PAHs. They reported that factors such as surfactant type and concentration, hydrophobicity of PAH molecules, temperature, pH, salinity, dissolved organic matter and microbial community could affect remediation of PAHs by surfactants. Cheng et al. (2017) reviewed the advantages and challenges of Tween 80-surfactant enhanced remediation for hydrophobic organic compounds. They summarized research on Tween 80 compared with other surfactants in remediation of hydrophobic organic compounds, such as PAHs. Research showed desorption and removal efficiencies in the range of 36-84% for phenanthrene, fluoranthene and benzo[a]pyrene using Tween 80, Triton X-100 and Brij 35 in soil washing (Cheng and Wong, 2006; Ahn et al., 2008; Alcantara et al. 2008, 2009). Non-ionic surfactants showed better efficiency in removing PAHs than ionic ones (Lamichhane et al., 2017; Cheng et al., 2017). These surfactants have hydrophobic and hydrophilic groups in their structure. Hydrophilic groups of surfactants enter the aqueous phase and the lipophilic groups (tails) attach to soil particles and PAHs and soil organic matter (Mao et al., 2015; Wan et al., 2011). Surfactants accumulate at solid-liquid and solid-contaminant interfaces as monomers at low concentrations. As the concentrations of surfactants increase, they replace water molecules, reducing the polarity

of the aqueous phase and the surface tension. Surfactant molecules adsorbed on the solid phase creating repulsion between soil particles and hydrophobic groups then desorb PAHs from soil (Cheng et al., 2017). If the concentrations of surfactants increase further, micelles start to form that can greatly improve the solubility and desorption of PAHs (Yeom et al., 1996; Liang et al., 2017). A schematic of surfactant enhanced desorption of PAHs is presented in Figure 2.4.

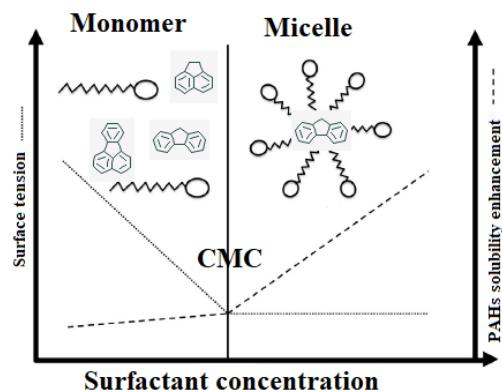
Compared to extensive research on the effect of surfactants in desorption and solubilization of PAHs, published work on the effect of soil organic matter and particularly heavy metals on desorption and removal efficiency of PAHs is limited.

Obuekwe and Semple (2013) found that the presence of Cu and Al enhanced the extraction of ¹⁴C-phenanthrene by CaCl₂ and hydroxypropyl-*b*-cyclodextrin (HPCD). They concluded that high concentrations of metals could affect phenanthrene mobility/accessibility in soil.

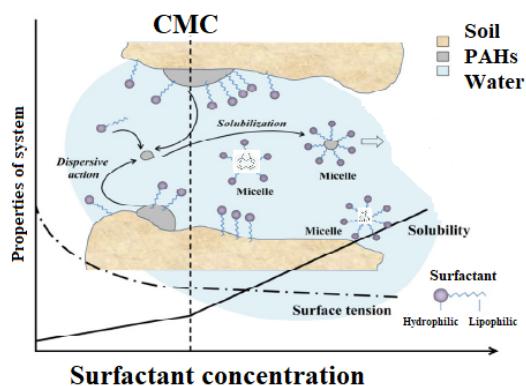
Saison et al. (2004) clearly demonstrated that the fate of PAHs in soil cannot be easily predicted because it greatly depends on co-pollution with metals. Yang et al. (2001) showed that, under the effect of complexing agents (EDTA, citric acid), other metal ions like Fe and Al are mobilized, loosening humic-cation-mineral bonds and resulting in dissolution of some soil organic matter, in turn mobilizing the PAHs in soil. Table 2.8 summarizes recent studies on the effect of soil organic matter and/or heavy metals on the desorption of PAHs from soil.



a) Modified from Lamichhane et al. (2018)



b) Modified from Trellu et al. (2016)



c) Modified from Mao et al. (2015)

Figure 2.4 Schematic of surfactant enhanced desorption of PAHs.

Table 2.8 Summary of recent studies on the effect of organic matter and heavy metals on PAHs desorption

Soil/material	Type of PAHs	Test details	Co-existing organic matter/heavy metal	Highlighted findings	Reference
Spiked three types of natural soil from Hangzhou City, China	Phenanthrene, fluorene, acenaphthene, naphthalene	Batch sorption of PAHs followed by surfactants (TX-100, TX-114 and TX-305) enhanced desorption tests. In batch desorption tests 2 g of soils mixed with 20 ml of surfactant solution at different concentrations for 48 h	Organic matter; measured as organic carbon. Organic matter contents were different in samples	Surfactants were more effective to desorb PAHs in soils with higher organic carbon content and lower clay content. Desorption by water was too low except for naphthalene, whereas the surfactants were more effective for PAHs with higher K_{ow} than water insoluble ones	Zhou and Zhu (2007)
Sediment (Yangtze River)	Phenanthrene, acenaphthene, fluorene, fluoranthene, pyrene (Multiple sorbates)	Sorption-desorption (no surfactant); Sorption with solid to liquid ratio of 1:100 (g mL ⁻¹), initial concentration: 10-100 µg L ⁻¹ , 12 h test time then desorption carried out by replacing 96% supernatant with water for 12 h test.	Natural organic matter contents in samples; measured as TOC	Sorption was affected by both carbonate and organic matter. Organic matter plays a more important role for larger PAHs with greater K_{ow} s. Lower-ring PAHs desorb faster than PAHs having more rings; more tightly sorbed PAHs desorb with more difficulty Organic matter may inhibit the diffusion of PAHs from sediment to water. Desorption of PAHs into water ranged from 0.25 to 8% of total sorption, which was rather low. However lighter PAHs showed higher desorption amounts.	Wang et al. (2008)

Table 2.8 Summary of recent studies on the effect of organic matter and heavy metals on PAHs desorption (continued)

Soil/material	Type of PAHs	Test details	Co-existing organic matter/heavy metal	Highlighted findings	Reference
Natural contaminated soil sample spiked with phenanthrene	Phenanthrene	<p>Batch tests to evaluate desorption and desorption kinetics.</p> <p>Soil-to-solution ratios of 1:2.5, 1:5 and 1:10 were tested for 24 h.</p> <p>Combined and single solutions of Tween 80, Brij 35 and EDTA were used as extractants.</p>	Lead	<p>Addition of phenanthrene to soil reduced Pb desorption from 100% to 48%.</p> <p>Combined solutions enhanced solubilisation of mixed Pb and phenanthrene.</p> <p>Desorption kinetics fitted empirical power function and pseudo-second-order equation.</p>	Fonseca et al. (2011)
Bentonite and humic/fulvic acid-coated bentonite	Phenanthrene	<p>Batch sorption and desorption/extraction experiments (no surfactant);</p> <p>0.1 g: 25 mL of solution for 72 h.</p> <p>Desorption/leachability then was assessed by deionized water, 0.1 M NaNO₃ for 60 min,</p> <p>Modified Krauss sequential extraction of phenanthrene with methanol, and Tessier (1979) extraction of Pb and Cd.</p>	Lead, Cadmium, humic/fulvic acid	<p>Co-existing phenanthrene enhanced Pb sorption.</p> <p>Enhancement was greater for humic acid-coated bentonite due to greater phenanthrene sorption.</p> <p>Phenanthrene sorption was also increased by the co-existing Pb.</p> <p>Co-existing phenanthrene and Pb redistributed each other from weak bonds to strongly bonded fractions. Humic acid coating reduced this effect.</p> <p>Presence of Pb decreased desorption of phenanthrene from bentonite.</p> <p>Presence of both humic acids and Pb reduced the desorption of phenanthrene to a greater extent.</p> <p>Desorption of phenanthrene to water was very low compared to sorption</p>	Zhang et al. (2015)

Table 2.8 Summary of recent studies on the effect of organic matter and heavy metals on PAHs desorption (continued)

Soil/material	Type of PAHs	Test details	Co-existing organic matter/heavy metal	Highlighted findings	Reference
Kaolinite, Sand+kaolinite, sand+kaolinite+bentonite	Acenaphthene, fluorene, fluoranthene	Batch desorption tests on spiked samples with added and non-added heavy metals and humic acids. Extracting solutions were CaCl ₂ (0.01M), combined EDTA (0.01M) and Tween 80, combined EDTA (0.01M) and Triton X100	Humic acid, heavy metals (Pb, Ni and Zn)	Heavy metals and humic acid decreased the desorption of PAHs. Humic acid had greater decreasing effect than heavy metals. Desorption reducing effects were greater for larger PAH than lighter ones.	Saeedi et al. (2018b)

Most previous work on co-existing contaminant has investigated either the effect of organic matter or heavy metals on desorption of PAHs. There are very few published papers on the mobility and desorption of both PAHs and heavy metals in the presence of soil organic matter. There are some discrepancies regarding the effect of heavy metals and SOM on the desorption of PAHs, but this appears to be due to the number of affecting factors and variations in the composition of the soils tested in previous research. However, some consistent findings are important with respect to fate and/or remediation of mixed-contaminated soils.

Based on the chemical properties of the PAHs and findings of previous researchers, it is clear that sorbed PAHs in soil are not desorbed in great amounts by water. Previous findings also show that SOM increases the retention of PAHs in soil. Co-existence of heavy metals reduces the extractability and desorption of PAHs. It seems also that co-existence of PAHs and heavy metals affects the chemical bonds within the soil matrix. This can affect the environmental and ecological risk of both groups of contaminants. PAHs with higher K_{ow} (i.e. larger ones with more rings) are retained by SOM in soil more than smaller PAH molecules.

Desorption kinetics of PAH removal from a mixed-contaminated soil by surfactants and enhancing solutions fit a pseudo-second-order kinetic equation and empirical function (Fonseca et al., 2011; Wang et al, 2010), whereas the sorption of PAHs to soils, particularly at higher SOM contents, has been mostly reported to follow linear kinetics.

Findings also show that application of combined surfactants and chelating agents/organic acids is effective in simultaneously desorbing PAHs and heavy metals for soil washing/flushing (Fonseca et al., 2011; Maturi and Reddy, 2008) and elecktrokinetic remediation methods.

2.5 Conclusion and research needs

Heavy metals and PAHs have totally different chemical properties in terms of sorption, desorption and remediation. Sorption and desorption of PAHs in soil are the main processes affecting remediation technologies, particularly in fine soils and soils containing natural organic matter, heavy metals or both. Given that most mixed-contaminated sites contain different types of coexisting PAHs and heavy metals, it is essential to study their combined behavior in fine and clayey soil environments in terms of sorption/desorption, as the main processes determining their environmental fate and transport, as well as remediation techniques.

The presence of either natural organic matter or heavy metals can enhance the sorption capability of fine soil, retarding the spread of PAHs in the solid matrix. Although, enhancing agents and surfactants have been reported to be able to increase the desorption and removal of PAHs from soil, at least one report (Saeedi et al., 2018a) shows that co-existing heavy metals and organic matter in soil have synergistic effects on the sorption of PAHs, leading to much lower desorption efficiencies. This can challenge remediation technologies based on removing contaminants by a liquid by electrokinetics and chemically-enhanced soil washing/soil flushing.

Overall, it is important to study the mechanisms of PAH sorption in relation to SOM composition and the interrelation with other main soil components and properties, such as types

and contents of minerals, co-existing contaminants such as heavy metals and soil physical/chemical properties. More detailed investigations are needed to determine affecting factors and conditions for heavy metals and SOM on PAH sorption and desorption, and their effects on remediation.

Chapter 3: Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals²

3.1 Introduction

As summarized in Chapters 1 and 2, PAHs often co-exist with heavy metals in contaminated soil due to having common sources (Prieto-Taboada et al., 2013; Thavamani et al., 2012; Thavamani, et al. 2011; Morillo et al., 2008; Wang et al., 2004).

Sorption strongly affects the fate and transport of PAHs in the environment. Because of their low water solubility, PAHs typically sorb onto soil and sediment (Environment Agency, 2003).

Sorption and mobility of PAHs can be influenced by the presence of other co-contaminants, such as heavy metals, particularly at high concentrations (Weber et al., 2002). Heavy metals also sorb onto fine soil particles. Both non-ionic organic contaminants such as PAHs and heavy metals interact with soil organic matter (Guo et al., 2010; Delle Site, 2001; Gao et al., 2006; Kim et al., 2006; Kim et al., 2005; Zhang et al., 2004; Gao et al., 2003). The quantity and form of organic matter in soil, can affect HM mobility, complexing and retention (Kaschl et al., 2002). Soil organic content influences sorption and consequently affects the fate and transport of mixed contaminants in soil (Delle Site, 2001).

² A version of this chapter has been published. Saeedi, M., Li, L.Y., Grace, J.R., 2018. Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals. Environ. Earth Sci. 77, 305. <https://doi.org/10.1007/s12665-018-7489-0>

Gao et al. (2006) showed that more phenanthrene sorbed in three types of natural surface soil samples from eastern China when spiked with heavy metals (Pb, Zn or Cu) than in unspiked soils. Polubesova et al. (2009) indicated that sorption of PAHs in soil is dependent on SOM and on the type and concentrations of cations. Zhang et al. (2011a) showed that the presence of Pb and soil organic matter increased phenanthrene sorption in soil. Fonseca et al. (2011) reported that phenanthrene as a co-contaminant can prolong the residence time of Pb in soil.

The effects of Zn, Cu, Al and Fe on partitioning and bioavailability of phenanthrene in soil were examined by Obuekwe and Semple (2013). The effects of other HMs (Cd, Cu, Pb and Zn) on the extractability of ¹⁴C-phenanthrene were studied by Saison et al. (2004) who reported that phenanthrene adsorption was higher in the presence of metals.

In fine soil, clay minerals are the dominant sorptive materials for contaminants such as PAHs and metals. Zhang et al. (2011a,b) showed that, in addition to metal content and soil organic matter, clay content and type affect phenanthrene sorption in soil. Therefore, knowledge of the sorptive behavior of PAHs under the influence of organic matter and heavy metals in fine and clayey soil is essential to achieve better understanding of the sorption process. While there are various types of heavy metals and PAHs present in mixed contaminated soils (Thavamani, 2012; Thavamani et al., 2011), most PAH studies focused on phenanthrene, with only a limited number of co-existing metals (Fonseca et al., 2011; Zhang et al., 2011a; Gao et al., 2006; Saison et al., 2004). While it was believed that organic matter is mainly responsible for PAHs sorption in soil (Hemond and Fechner-Levy, 2014; Environment Agency, 2003; Delle Site, 2001) there are also studies demonstrating that clay minerals and heavy metals can contribute to sorption of PAHs,

particularly in low organic content clayey soils (Zhang et al., 2011a; Hwang et al., 2003). In other words, it has been demonstrated that in low-organic-content clayey soils, there is a substantial effect of clay mineral on PAH sorption, while for higher organic contents the influence of minerals is masked by the effect of soil organic matter (Delle Site, 2001; Weber et al., 1992; Karickhoff, 1984).

Soils containing high amounts of clay minerals cover 335 million hectares world-wide (FAO, 2001). In addition, in many lowlands of the world soils are fine and contain various amounts of clays (FAO, 2001). Loamy, clayey and very fine clayey soils usually contain considerable amounts of clays, from about 27 to > 60% (OMAFRA, 2016). The proportion and type of clay particles as the most active part of soils could affect physical, chemical and biological activities (CLBR, 1993).

There is a need for studies on the sorption of less widely studied PAHs such as acenaphthene, fluorene and fluoranthene, influenced by both organic matter and metals in clay minerals and clayey soil. In addition, the effect of co-existing of both heavy metals and organic matter in clayey soils on the sorption of those PAHs has not been well documented. They may have some synergistic effects on sorption of PAHs in clays.

In this study, in a series of laboratory batch sorption experiments, we investigate the effects of organic matter (OM) (humic and fulvic acids) and the simultaneous presence of key metals (Ni, Pb and Zn) in clay mineral mixtures on the sorption of a matrix containing acenaphthene, fluorene and fluoranthene in kaolinite, blended kaolinite-sand and kaolinite-sand-bentonite

mixtures. One objective is to evaluate the probable synergistic effect of metals and soil organic matter on PAH sorption onto the soils, which has not been reported previously.

3.2 Materials and methods

3.2.1 Chemicals and minerals

Acenaphthene, fluorene, fluoranthene and zinc nitrate were purchased from Sigma-Aldrich, USA. General properties and molecular structure of the three PAHs studied are presented in Chapter 2, Table 2.1 and Figure 2.2. Nickel nitrate and lead nitrate were obtained from Merck Company, Germany. A metal standard sample (PACS-2) for quality assurance purposes was supplied by the National Research Council of Canada. All other chemicals used for sample preparation, digestion and extraction of analytes were of analytical grade obtained from Merck Co., Germany. All chemicals purchased were pure analysis and solvents tested for extraction and sample preparation for GC analyses were of HPLC grade.

Kaolinite was obtained from International Laboratory, India (product number: 1098578).

Bentonite was purchased from Iran Barite Falat (P.L.C), Tehran, Iran. Ottawa sand was obtained from Amitis Azma Co., Tehran, Iran, in accordance with standard specifications for sand (ASTM 2006). The Humax 95-WSG (CAS No. 68514-28-3), used to increase the organic matter content of the soil, was procured from JH Biotech Inc., Ventura, California, USA.

3.2.2 Chemical analyses and characterization

Minerals and mixtures were characterized in terms of particle size, mineralogy, chemical composition, Loss on Ignition (L.O.I), cation exchange capacity (CEC), pH, target heavy metals and PAH concentrations. Particle sizing was determined using a laser scattering particle size distribution analyzer (HORIBA LA-950) (Appendix A, Figures A1 and A2). X-ray diffraction and X-ray fluorescence were used to determine the mineralogy and chemical composition. X-ray analyses were performed by an XRD analyzer (PHILIPS PW1800), with Cu Ka radiation generated at 30 mA and 40 kV. Scanned angles were from 4 to 59 degrees in 0.04 steps. X-ray fluorescence analyses were conducted by an XRF analyzer (PHILIPS 1480). L.O.I was determined according to ASTM D-7348 (ASTM, 2008). The pHs of base minerals and mineral mixtures were determined according to ASTM D-4972 (ASTM, 2001) in suspensions of calcium chloride solution. CEC was measured by flame photometry following the USEPA-9081 method (USEPA, 1986a). Specific surface areas of the samples were determined by the BET method (Micromeritics ASAP 2020, accelerated surface area and porosimetry system). Clay and mineral mixture samples for heavy metals determination were acid digested (HCl, HNO₃, H₂O₂) according to USEPA-3050B (USEPA, 1996a), followed by Atomic Absorption Spectrometry (Rayleigh WFX-210) analyses. PAHs were extracted using the soxhlet method according to USEPA-3540C (USEPA, 1996b) and analyzed by Gas Chromatography (Agilent 6890- GC FID) in accordance with USEPA-8100 method (USEPA, 1986b). Some measures for quality assurance and quality control for chemical analyses are summarized in Appendix B and its Tables B1 and B2.

From manufacturer specifications, Humax 95-WSG, extracted from Leonardite, contained 80% humic acids, 15% fulvic acids and 5% K₂O. Since it is dominated by humic acids, we adopted the term HA to indicate the form of organic matter throughout the text. Humax was water soluble to a small extent; its pH was 8.5, with a relative density of 0.55. Humax pH value in CaCl₂ solution was determined to be 8.1. To ensure that the major phase of the Humax used was humic acid, Fourier Transform Infrared Spectroscopy (FTIR) of the Humax was performed using a SHIMADZU FTIR-8400-S. Comparing the resulting FTIR spectrum (Appendix A, Figure A3) with those of Stevenson and Goh (1971), Shaker et al. (2012) and Soler-Rovira et al. (2010) confirmed that the organic matter used in this research contained humic acid and was similar to the humic acid (extracted from Leonardite) reported in these three previous papers. Obtained spectrum (Figure A3 of Appendix A) shows strong and medium bands were evident; O–H stretching, N–H stretching, aliphatic C–H stretching, COO⁻ symmetric stretching, N–H bending, C=N stretching, OH deformation and C–O stretching of phenolic OH, C–O stretching of polysaccharide and polysaccharide-like substances, and Si–O of silicate impurities.

Properties of the kaolinite, bentonite and Ottawa sand used in this research are presented in Table 3.1. XRD results showed that the base kaolin contained almost 100% kaolinite (Table 3.1 and Appendix A, Figure A4). Major minerals in the bentonite were montmorillonite (54%) and quartz (23%); a minor component was cristobalite (13%) with trace amounts of gypsum (1%), calcite (3%), dolomite (2%) and illite-muscovite (3%). Based on XRD analysis of bentonite (Table S1 and Fig S2 of SI), the final mineral composition of KSB soil was calculated to be kaolinite (43.0%), quartz (45.4%), montmorillonite (8.1%), cristobalite (1.9%), calcite (0.4%), muscovite-illite (0.4%), dolomite (0.3%) and gypsum (0.15%). The major phase (> 99%) of the

sand was quartz. X-ray diffraction spectra of three base minerals are presented in Figure A4 of Appendix A.

3.2.3 Sample preparation and experimental program

18 mineral mixture samples contained (a) no added OM and no added heavy metals (K0, KS0 and KSB0); (b) added OM but no added heavy metals (K1, K2, KS1, KS2, KSB1 and KSB2); (c) added heavy metals, but no added OM (K0M, KS0M and KSB0M); or (d) added both OM and heavy metals (K1M, K2M, KS1M, KS2M, KSB1M and KSB2M). These were samples subjected to batch sorption experiments of the three combined PAHs. Three clay mineral mixtures were tested in this study: pure kaolinite (K), 60% kaolinite+40% Ottawa sand (KS), and 43% kaolinite+42% Ottawa sand+15% bentonite (KSB), prepared by thoroughly blending and homogenizing known amounts of these three base materials (kaolinite, sand and bentonite). Compared with other clay minerals, kaolinite has less buffering and cation exchange capacity. It has been widely used as the model of clayey soil in laboratory experiments (e.g. Yuan et al., 2006; Yuan et al., 2007; Ko et al., 1998). Use of bentonite in mixtures having great content of montmorillonite (with greater surface area and different chemical and mineralogical properties than kaolinite) made it possible to study the effect of different clays on sorptive behavior of the PAHs studied.

Table 3.1 Characteristics of the three base minerals used for blending

		Kaolinte	Bentonite	Sand
XRF (%)	SiO ₂	44.4	60.6	99.2
	Al ₂ O ₃	39.1	12.7	0.230
	Fe ₂ O ₃	0.360	3.76	0.030
	CaO	0.030	3.05	0.020
	Na ₂ O	0.020	2.22	0.030
	K ₂ O	0.010	0.620	0.020
	MgO	0.010	2.45	0.020
	TiO ₂	0.386	0.47	0.009
	MnO	0.005	0.086	0.002
	P ₂ O ₅	0.066	0.054	0.003
XRD (%)	SO ₃	0.012	0.421	0.009
	Kaolinite	100	-	-
	Quartz	-	23.0	99.0
	Montmorillonite	-	54.0	-
	Cristobalite	-	13.0	-
	Gypsum	-	1.00	-
	Calcite	-	3.00	-
	Dolomite	-	2.00	-
Particle Sizing	Muscovite-Illite	--	3.00	-
	Median size (μm)	0.570	8.04	384.8
	Mean size (μm)	2.60	9.89	417.7
	Mode size (μm)	0.270	9.45	369.9
	Std.Dev (μm)	3.09	7.92	165.9
	Geo. Mean size (μm)	1.04	7.10	389.7
	Skewness	1.31	1.75	1.49
	Kurtosis	4.08	7.22	6.46
Target metals content (mg kg ⁻¹)	Ni	0.7	3.5	ND
	Pb	2.4	12.1	ND
	Zn	5.3	4.1	ND
PAHs content (mg kg ⁻¹)		ND	ND	ND
pH (water)		6.9	7.6	5.80
pH (CaCl ₂)		5.6	7.3	5.30
CEC (meq/100 g)		17.2	76.9	0.80
Specific surface area (m ² g ⁻¹)		16.8	30.9	6.05

Organic matter content in fine mineral soils ranges from 1 to 6% w/w (Troeh and Thompson, 2005). Soils consist of < 1% of OM, are mostly desert soils. Organic soils generally contain 12 to 18% of OM (Troeh and Thompson, 2005). Therefore, the addition of OM to minerals and mineral mixtures were in the range of OM contents of “organic poor” to “organic rich” mineral soils.

For each blended clay mineral type, samples were prepared containing three levels of OM. The first level was the original organic content of the material and mixtures, very low (< 0.5%), since the base materials were clean and uncontaminated. Total organic matter of the three base materials was 0.25%, 0.51% and 0.36% for kaolinite, bentonite and sand, respectively. Two other levels were prepared by adding Humax to the clay minerals and mixtures to increase the OM content. A series of batch experiments were preliminarily conducted to determine the capacity of each type of clay and clay mineral mixtures for OM containment according to method presented by Shaker et al. (2012). The addition of organic matter content in clay and clay mixtures was carried out by dissolving different amounts of HA, in aqueous solution, mixing the solution with a measured amount of base soil (solid-to-liquid ratio 2 g L⁻¹ (OECD, 2000)), then stirring at 250 rpm for 24 h in Pyrex beakers. The stirrer ensured uniform humic acid distributions. Once the stirring was complete, the soils were separated and air-dried at room temperature to a constant weight. Then the loss-on-ignition carbon content method was used to determine the HA increase in each sample. The increases in LOI after HA addition compared to the initial LOI of the sample before HA addition were taken as being due to addition of HA to the clay and clay minerals. The results of batch experiments are depicted in Figure 3.1, showing that each type of blended soil had a maximum specific capacity to adsorb HA. The maximum

capacities for kaolinite, kaolinite+sand and kaoloinite+sand+bentonite were 11.0, 7.0 and 5.8% (w/w), respectively for this study. Shaker et al. (2012) reported that the maximum capacity of humic acid sorption onto kaolinite ranges from 5 to about 12% (w/w), depending on solution cations and pH. For the same experimental conditions of solution cations and pH, we obtained similar results for HA (Humax 95-WSG) sorption onto kaolinite (11% w/w). Based on the maximum OM capacity results, two levels of organic contents for each clay mineral mixture were selected: level corresponding to maximum capacity of OM and half of that capacity for each mineral mixture type.

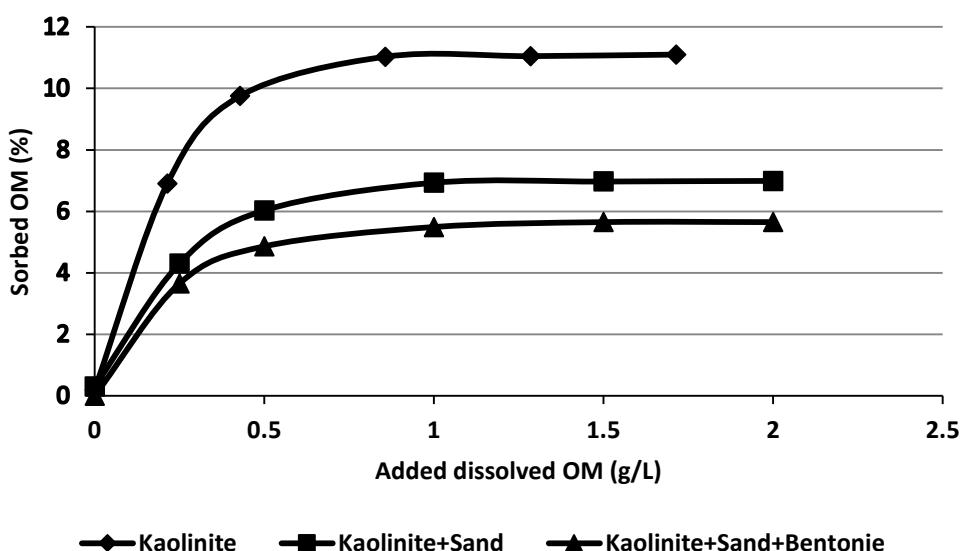


Figure 3.1 Sorption isotherms of OM on blended clay and clay mineral mixtures

All nine mineral mixtures, with and without heavy metals addition, were subjected to PAH batch sorption experiments. This allowed the three basic prepared mineral mixtures to be investigated for both organic matter and effect of heavy metals on their sorptive behavior. To spike soils with

heavy metals (5000, 1000 and 700 mg kg⁻¹ of Pb, Zn and Ni, respectively), appropriate amounts of Ni, Pb and Zn were added as nitrate solution to blended mineral mixture samples, followed by stirring for 24 h to reach equilibrium. The spike concentration of metals were based on their relative abundance at contaminated sites (Fonseca et al., 2011), exceeding the recommended contents for protection of environmental and human health in the Canadian environmental quality guidelines (CCME, 1999a, 1999b, 1999c) to have samples co-contaminated by metals.

The pH of the spiking solutions was adjusted to 5.5 (Bhattacharyya and Gupta, 2008). Each spiked sample was then separated by centrifugation and dried at room temperature to a constant weight, then they left to age for 14 days.

The main characteristics of the 18 prepared (blended and/or spiked) mineral mixtures for the sorption experiments are summarized in Table 3.2.

The sorption of PAHs onto prepared mineral mixture samples from aqueous solutions was examined through a series of batch equilibrium experiments (18 prepared samples each at six initial concentrations of mixed PAHs). All batch experiments for PAH sorption were carried out in glass vials with screw caps. Appropriate volumes of ANA, FL and FLAN dichloromethane (DCM) stock solution were added to each vial. The vials were next shaken to completely evaporate the DCM and disperse the PAHs at their bottoms. Then 0.5 g mineral sample and 250 ml background solution containing 0.01 M NaCl to maintain ionic strength, and 100 ppm NaN₃ (as biocide to inhibit bacterial growth) were added to each vial.

Since in the batch experiments of OM and heavy metals sorption onto minerals metals the pH was adjusted to 5.5, the pH in the PAH sorption tests was also adjusted to 5.5, in accordance with Zhang et al. (2011 a and b). Initial concentrations of PAHs in the solids ranged from zero to 50 mg kg⁻¹. The vials were shaken in the dark for 24 h at 25±1°C and 250 rpm on a rotary shaker to reach sorption equilibrium (Yu et al., 2011). Finally, the suspension was centrifuged at 4000 rpm for 30 min to separate supernatant. The PAH contents of the samples were determined by GC-FID. The amounts of PAHs sorbed for each mineral mixture sample were then calculated from mass balances. Analysis of the mineral free blank samples showed that there was negligible vial wall adsorption loss.

Synergistic effects of co-existing metals and OM on the sorption of PAHs were determined by comparing the summation of sorption coefficient increases for separate metals and OM with that increase in the presence of co-existing metals and OM in each type of mineral mixture sample.

Sorption coefficients (K_d), representing the ratio of sorbed contaminant to its equilibrium concentration in aqueous phase, were calculated from;

$$K_d = (C_s/C_e) \quad \text{Eq. 3.1}$$

where K_d is the sorption coefficient (L kg⁻¹), C_s is the concentration of sorbed contaminant in mineral mixtures (mg kg⁻¹) and C_e is the aqueous equilibrium concentration of sorbate (kg L⁻¹).

Table 3.2 Blended clay and clay minerals for sorption experiments and their characteristics

Mineral mixture*	Soil**	Added OM*** (w/w %)	pH (CaCl ₂)	Surface area (m ² g ⁻¹)	CEC (meq/100 g)	Added Ni mg kg ⁻¹	Added Pb mg kg ⁻¹	Added Zn mg kg ⁻¹
K	K0	0.0	5.6	16.85	17.2	-	-	-
	K0M	0.0			-	700	5000	1000
	K1	5.5	5.8		30.7	-	-	-
	K1M	5.75			-	700	5000	1000
	K2	11.0	6.0		44.2	-	-	-
	K2M	11.0			-	700	5000	1000
KS	KS0	0.0	5.4	12.54	10.6	-	-	-
	KS0M	0.0			-	700	5000	1000
	KS1	3.5	5.6		19.5	-	-	-
	KS1M	3.5			-	700	5000	1000
	KS2	7.0	5.7		28.3	-	-	-
	KS2M	7.0			-	700	5000	1000
KSB	KSB0	0.0	5.8	14.45	19.3	-	-	-
	KSB0M	0.0			-	700	5000	1000
	KSB1	2.9	6.0		26.3	-	-	-
	KSB1M	2.9			-	700	5000	1000
	KSB2	5.8	6.1		33.4	-	-	-
	KSB2M	5.8			-	700	5000	1000

*K: Pure kaolinite, KS: 60% kaolinite+40% sand, KSB: 43% kaolinite+42% sand+15% bentonite

**Soil label, K – Kaolinite; S – Sand; B – Bentonite; M – Metal added; 0 – no OM. 1– low OM; 2– high OM

***OM –added Humax 95-WSG (humic acid)

3.2.4 Analysis of variance (ANOVA)

Factorial ANOVA, using Microsoft Excel 2016, was performed on sorption coefficients of three PAHs onto three mineral and mineral mixtures at different test conditions, with a significance level of 0.05, to identify statistically significant factors.

3.3 Results and discussion

3.3.1 Soil characteristics

Properties of blended clay mineral mixtures are presented in Table 3.2. Among the three base minerals (kaolinite clay mineral, bentonite clay mineral and sand) used to make mixtures, bentonite had the highest surface area ($30.95 \text{ m}^2 \text{ g}^{-1}$). However, kaolinite had the highest surface area ($16.85 \text{ m}^2 \text{ g}^{-1}$) among the three types of blended mineral samples studied. KSB blended minerals also had greater surface area than KS because of the 8.1% montmorillonite contained in its composition.

KSB has greater CEC (19.3 meq/100g) than K and KSB blended samples. The montmorillonite and illite contained in the KSB mineral mixtures explain why they had the greatest CEC. Results presented in Table 3.2 also show that with increasing organic matter content of each of the blended mineral soils, the CEC increased. There are numerous ionic sorption sites and functional groups such as hydroxyls, carbonyls and carboxyls in large natural organic matter molecules (Dunnivant and Anders, 2005; Killops and Killops, 1993). These are key factors that could enhance the cation exchange capacity of the blended minerals with the addition of OM. Regarding higher OM sorption by kaolinite, its CEC after OM addition was higher than that of the other two other blended clay mineral mixtures.

Our results for OM sorption onto three clay and blended clay minerals studied show that the blended minerals containing more kaolinite had more capacity to sorb OM (K > KS > KSB) (see Figure 3.1 and Table 3.2 above). Kaolinite showed greater surface sorption of organic molecules than montmorillonite. Delle Site (2001) suggested that sorption onto clays may take place

through hydrogen bonding from the hydroxyl surfaces of clay toward oxygen atoms in the organic molecules. Brindley et al. (1963) indicated that hydroxyl surfaces, which comprise half the basal area of kaolinite, could sorb more effectively than the oxygen surfaces which occur in montmorillonite and comprise half the basal area of kaolinite. Because of the competition of water molecules, oxygen surfaces of montmorillonite are less effective in sorption of organic molecules by hydrogen bonding. Furthermore, the exchangeable cations of montmorillonite, Ca and Na, readily form hydration complexes which may screen an appreciable portion of the available surface. Kaolinite is thought to have relatively few exchangeable cations in its extended basal surfaces (Delle Site, 2001). Therefore, from this point of view, it is reasonable that these minerals should exhibit higher surface sorption than montmorillonite. Although the pH of the mineral mixtures showed a slight increase after OM addition, these changes were not significant (Table 3.2). At the greatest level of OM addition, the increase in pH was less than 0.3.

3.3.2 Sorption of PAHs

Differences between results for duplicate batch experiments for sorption were always less than 5%. Average results were used in sorption isotherms and calculations. Sorption isotherms of ANA, FL and FLAN for the 18 prepared clay mineral mixtures are presented in Figure 3.2. The sorption process for all three PAHs could be represented by linear fits. Soil and sediments containing high proportions of clay (30-68%) and OM (0.4-2.5% organic carbon) have been reported to show linear sorptive behavior for phenanthrene (Gao et al., 2006), pyrene, 7,12-dimethylbenz[a] alanthracene, 3-methylcholanthrene, and dibenzanthracene (Means et al., 1980). Gao et al. (2006) suggested that this was related to organic partitioning governance in sorption of phenanthrene in soil-water systems.

Sorption coefficients for all three PAHs tested and all types of blended minerals are presented in Table 3.3. Sorption of all three PAHs onto the mineral mixtures without added OM and metals (K_0 , K_{S0} and K_{SB0}) also occurred. Sorption coefficients (K_d) of PAHs in each mineral sample show an increase with increasing PAH molecular weight. This increment shows a great jump in the case of fluoranthene (a four-ring molecular structure in which there are three benzene rings) ($K_d = 2174.8$) compared with fluorene ($K_d = 213.4$) and acenaphthene ($K_d = 193.7$) (three ring molecular structures in which two of them are benzene rings). So the ranking of sorption coefficients of the three PAHs studied was FLAN >> FL > ANA. In clay minerals, surface area may play an important role in sorption of PAHs. It has been reported that hydrogen bonding may occur with oxygen on the clay surfaces (Delle Site 2001). At low OM content and "organic poor" sorbents, sorption coefficients (K_{ds}) were expected to be very low compared with the same sorbent at high OM contents (Schwarzenbach and Westall, 1981).

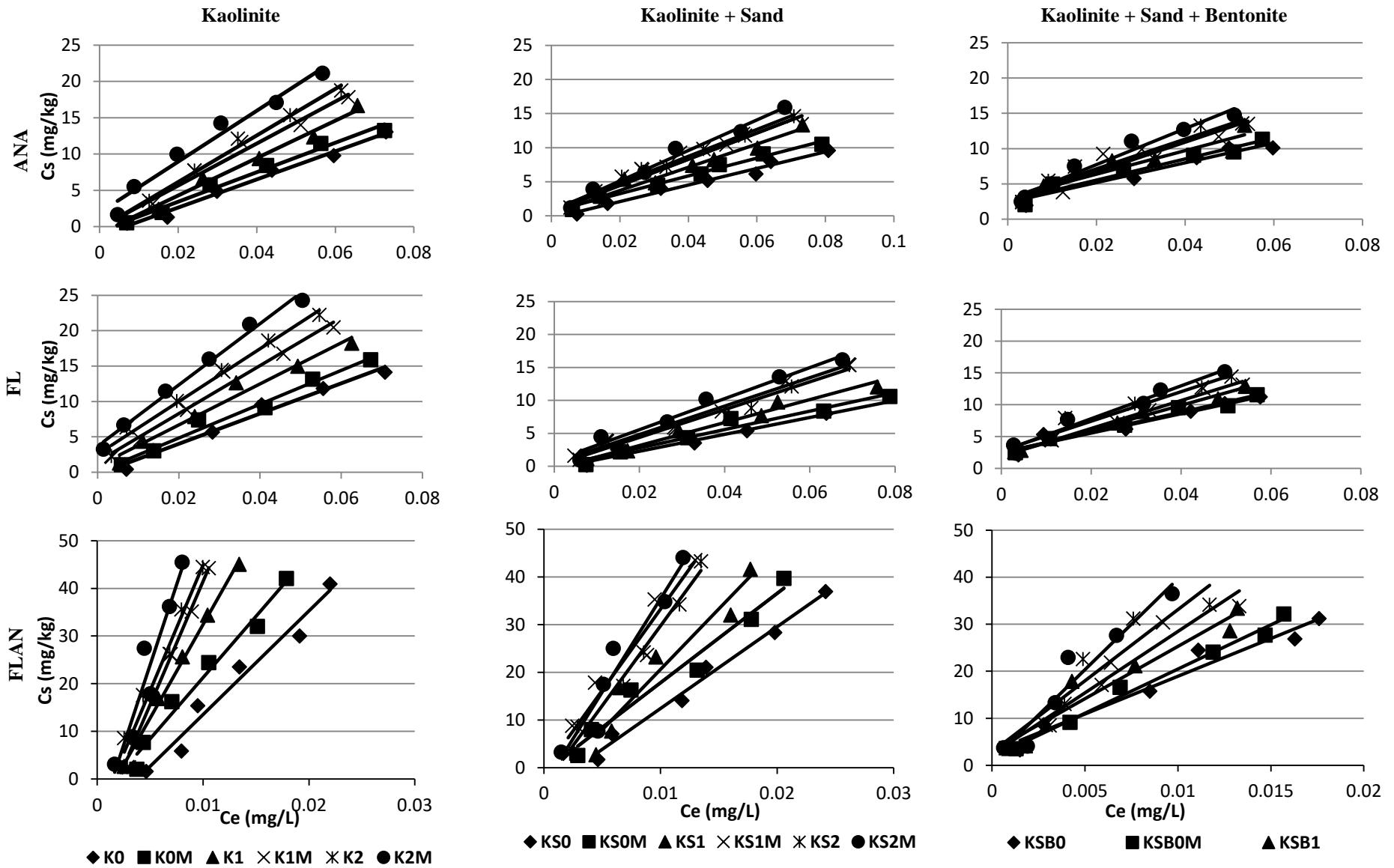


Figure 3.2 Sorption isotherms of acenaphthene (ANA), Fluorene (FL), and Fluoranthene (FLAN) onto 18 different prepared soil types.

Our results in Table 3.3 also show that for each PAH tested, the sorption coefficient for each blended clay mineral soil is much lower than for the same soil at high OM content. For all PAHs studied, sorption coefficients (K_d) onto blended minerals soils are in order $K_0 > K_{SB0} > KS_0$. This is the order of the blended mineral surface areas, indicating that in "organic poor" minerals, surface area is an important factor in the sorption of PAHs. It has been reported that the adsorption on clay surface dominates the organic matter partitioning at high clay/OM ratios (Weber et al., 1992; Karickhoff, 1984). A threshold ratio of (clay mineral)/(organic carbon) =30 was defined by Karickhoff (1984), indicating that if the mass fraction of clay mineral to organic carbon in sorbent > 30, the mineral contribution in sorption would not be masked by organic matter. This ratio, however, depends on the hydrophobicity of the sorbate. In our study, blended clay mineral soils without OM addition (K_0 , KS_0 and K_{SB0}) are all sorbents in which mineral surface sorption is a dominant process according to the Karickhoff ratio (Karickhoff, 1984). In our study, the Karickhoff ratios for K , KS_0 and K_{SB0} are 499, 200 and 193.3, respectively, all much higher than 30.

Table 3.3 indicates that KSB blended mineral samples containing 8.1% montmorillonite and 0.45% illite show higher sorption coefficients for any given PAH than KS mineral samples. Montmorillonite is a 2:1 layered expandable clay with very great surface area ($8 \times 10^6 \text{ m}^2 \text{ kg}^{-1}$). Illite is also 2:1 layered, but non-expandable, with relatively high surface area ($10^5 \text{ m}^2 \text{ kg}^{-1}$), whereas kaolinite is a 1:1 non-expandable clay with approximate surface area $3 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ (Li and Gupta, 1994). In clay mineral mixtures with (clay mineral)/(organic carbon) ratio > 30, mineral surface interactions are predominant, and surface area is an important factor in PAH sorption.

Table 3.3 Sorption coefficients for ANA, FL and FLAN sorption onto different types of mineral mixtures studied

Soil	ANA		FL		FLAN	
	K _d L kg ⁻¹	R ²	K _d L kg ⁻¹	R ²	K _d L kg ⁻¹	R ²
K0	193.7	0.988	213.4	0.980	2175	0.966
K0M	202.7	0.982	238.8	0.980	2566	0.976
K1	257.8	0.988	289.7	0.973	3927	0.997
K1M	289.7	0.981	338.8	0.976	5161	0.988
K2	320.1	0.991	372.7	0.984	5280	0.967
K2M	350.2	0.969	432.1	0.987	6723	0.919
KS0	121.8	0.980	128.3	0.979	1715	0.986
KS0M	129.9	0.981	139.6	0.960	1872	0.967
KS1	170.2	0.970	174.3	0.968	2534	0.930
KS1M	191.8	0.951	215.5	0.988	3408	0.939
KS2	197.0	0.978	211.2	0.977	3345	0.986
KS2M	223.7	0.981	235.8	0.974	3917	0.930
KS0B	139.9	0.923	151.9	0.946	1608	0.958
KS0BM	150.3	0.952	158.5	0.974	1880	0.987
KS1B	167.6	0.887	197.0	0.990	2225	0.936
KS1BM	210.8	0.905	219.3	0.988	2618	0.945
KS2B	210.2	0.925	232.3	0.950	3033	0.892
KS2BM	254.5	0.964	257.5	0.971	3863	0.931

K=kaolinite, M=Heavy metals, S=sand, B=bentonite, ANA=Acenaphthene, FL=Fluorene, FLAN=Fluoranthene

KSB blended mineral samples containing 8.1% montmorillonite and 0.45% illite, show higher sorption coefficients for any given PAH than KS mineral samples (Table 3.3). Montmorillonite is a 2:1 layered expandable clay with very great surface area ($8 \times 10^6 \text{ m}^2 \text{ kg}^{-1}$). Illite is also 2:1 layered, but non-expandable, with relatively high surface area ($10^5 \text{ m}^2 \text{ kg}^{-1}$), whereas kaolinite is

a 1:1 non-expandable clay with approximate surface area of $3 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ (Li and Gupta, 1994).

In clay mineral mixtures with (clay mineral)/(organic carbon) ratio > 30 , mineral surface interactions are predominant, and surface area is an important factor in PAH sorption.

Our results suggest that blended minerals with higher clay mineral contents (K_0) and higher surface area showed the greatest PAH sorption coefficient among the three basic blended clay minerals studied (Table 3.3). Greater sand content in the soil is seen to have led to less sorption affinity for PAHs (Figure 3.2).

In all three basic types of blended mineral soil, increasing both OM and heavy metals led to increased sorption affinity of PAHs to mineral mixtures. The effect of soil organic matter on enhancement of PAH sorption in soil has been reported previously (Chen et al., 2009; Means et al., 1980). Addition of OM can provide more sorption sites, as shown in Table 3.2 where it is seen that CEC of each mixture increases by $\sim 2.6 \text{ meq}/100 \text{ g}$ for every 1% (w/w) Humax added, resulting in enhancement of PAH sorption in soil.

The ranking of sorption coefficients for the three PAHs studied was FLAN $>$ FL $>$ ANA for all mineral mixtures, whether spiked with OM and heavy metals or unspiked. Overall, PAHs with less water solubility and greater K_{ow} showed more sorption to blended mineral soils. High molecular weight (HMW) PAH (PAHs having four or more rings) showed a sharp rise in sorption affinity relative to low molecular weight (LMW) PAHs (i.e. PAHs having three or fewer aromatic rings). In minerals containing no added OM, those with more surface area showed higher PAH sorption.

3.3.3 Effect of metals

Table 3.4 shows the increments in PAHs sorption coefficients to mineral mixtures upon the addition of metals, OM at two levels and both metals and OM for the three mineral mixture groups. These results reveal that the presence of heavy metals (Ni, Pb and Zn) slightly increased the sorption of all three PAHs studied onto all three basic mineral groups. Minimum and maximum sorption coefficient increments caused by coexistence of all three heavy metals were 4.3 and 17.9%, respectively. Even when there was no organic matter added to mineral mixtures, the coexistence of heavy metals increased the sorption of PAHs onto all types of minerals studied (K, KS and KSB). Obuekwe and Semple (2013) and Zhang et al. (2011a) reported that the sorption of phenanthrene increased as a result of adding some metals (Cu, Zn, Pb) to soil.

Adsorbed heavy metal ions accumulate on the clay surface providing sites for cation- π bonds with PAHs. Zhu et al. (2004) suggested that exchangeable cations, concentrated on montmorillonite clay mineral interlayers by conditioning of mineral surfaces, might open more adsorption sites for strong cation- π bonds with PAHs. Previous work on various clay minerals (Karnland et al., 1992; Push, 2001; Villar, 2005; Castellanos et al., 2008) provides evidence that an increase in cation concentration in pore water, increases the hydraulic conductivity of clay. According to Castellanos et al. (2008), the mechanisms that can be involved are (i) clay matrix swelling, leading to modification of pore size distribution; and (ii) exchangeable cations in the diffuse double layer or adsorbed on the clay sheet surfaces can cause variations in the mobility of water molecules. Consequently, cations reduce the swelling capacity of clay particles and increase the clay aggregation and the size of large pores. Therefore, the presence of metal cations in clay minerals can also increase the size of pores in clay, causing aggregation and more

hydrophobicity of the clay (Nguyen et al., 2013), resulting in more PAH sorption (Zhang et al., 2011a). The bridging effect of heavy metals with clay surface can lead to more PAH sorption (Zhu et al., 2004).

Tables 3.3 and 3.4 show that in minerals studied at very low soil organic matter contents (K0, KS0 and KSB0), the ability of heavy metals to enhance PAH sorption is relatively low, compared to the effect of OM addition. For instance, the enhancement of FLAN sorption onto K0 by heavy metals addition is 17.9% while it is 80.5% by OM addition to K0. In two other types of mineral mixtures, this pattern also observed (9.2% increased sorption of FLAN onto KS0 by heavy metals and 47.8% increase by OM). These amounts are 16.9 and 38.4% for FLAN in KSB0 by heavy metals and OM, respectively.

Table 3.4 suggests that the three studied heavy metals are more effective in sorption enhancement of FLAN than for ANA and FL. It seems that for a larger PAH molecule, containing more benzene rings and having lower water solubility and higher K_{ow} , heavy metals have greater sorption enhancement onto clay minerals. This could be related to more benzene rings in FLAN than in the two other PAHs studied, and more negative electrostatic charge over the rings of the molecule that may lead to more cation- π interactions between exchangeable metals on the mineral surface and the PAH.

Table 3.4 Increments of sorption coefficient (K_d) for PAHs studied with added OM and heavy metals compared to original untreated clay mineral mixtures (%)

Soil	ANA	FL	FLAN
K0 (kaolinite, no added OM and heavy metals)	-	-	-
K0M (kaolinite, heavy metals spiked)	4.7	11.9	17.9
K1(kaolinite, moderate added OM)	33.1	35.7	80.5
K1M (kaolinite, moderate added OM and heavy metals spiked)	49.5	58.7	137.3
Synergistic effect of added OM (at moderate level) and metals on PAH sorption (%)	11.7	11.1	38.9
K2 (kaolinite, maximum added OM)	65.3	74.6	142.8
K2M (kaolinite, maximum added OM and heavy metals spiked)	80.8	102.5	209.1
Synergistic effect of added OM (at maximum level) and metals on PAH sorption (%)	10.8	16.0	48.4
KS0 (kaolinite and sand, no added OM and heavy metals)	-	-	-
KS0M (kaolinite and sand, heavy metals spiked)	6.6	8.8	9.2
KS1(kaolinite and sand, moderate added OM)	39.8	35.8	47.8
KS1M (kaolinite and sand, moderate added OM and heavy metals spiked)	57.5	68.0	98.7
Synergistic effect of added OM (at moderate level) and metals on PAH sorption (%)	11.1	23.4	41.7
KS2 (kaolinite and sand, maximum added OM)	61.7	64.6	95.1
KS2M (kaolinite and sand, maximum added OM and heavy metals spiked)	83.6	83.8	128.4
Synergistic effect of added OM (at maximum level) and metals on PAH sorption (%)	15.3	10.4	24.1
KS _B 0 (kaolinite, sand and Bentonite, no added OM and heavy metals)	-	-	-
KS _B 0M (kaolinite, sand and Bentonite, heavy metals spiked)	7.4	4.3	16.9
KS _B 1 (kaolinite, sand and Bentonite, moderate added OM)	19.8	29.6	38.4
KS _B 1M (kaolinite, sand and Bentonite, moderate added OM and heavy metals spiked)	50.7	44.3	62.8
Synergistic effect of added OM (at moderate level) and metals on PAH sorption (%)	23.5	10.4	7.5
KS _B 2 (kaolinite, sand and Bentonite, maximum added OM)	50.3	52.9	88.6
KS _B 2M (kaolinite, sand and Bentonite, maximum added OM and heavy metals spiked)	81.9	69.5	140.3
Synergistic effect of added OM (at maximum level) and metals on PAH sorption (%)	24.2	12.3	34.8

ANA=Acenaphthene, FL=Fluorene, FLAN=Fluoranthene

3.3.4 Effect of organic matter

Organic matter (mostly humic acid), added at moderate level to each mineral mixture in the absence of heavy metals, led to significant enhancement of PAH sorption (Tables 3.3 and 3.4). Sorption of ANA upon moderate OM addition to soil, increased by 19.8, 33.1 and 39.8% for the KSB1, KS1 and K1 mineral mixture groups, respectively (Table 3.4). For FL, the percentage sorption increments for all soil groups were about 29-35% under moderate containment of OM in samples. These enhancements were from 38 to 80% for FLAN. The most significant effect was observed for FLAN in kaolinite.

Organic matter at the highest levels in soils led to dramatic increases in sorption of all PAHs onto minerals, from 50% for ANA in KSB mineral mixture to 140% for FLAN in kaolinite. Our results showed a consistent pattern in this case, indicating that the sorption enhancement increased in larger, less water-soluble, more benzene-ring-containing and higher K_{ow} PAH molecules. Comparing the sorption coefficients of FLAN, FL and ANA for each type of mineral mixture studied reveals that the increment of sorption coefficients of FLAN in comparison with the two other PAHs investigated increased with increasing organic matter content of each soil type. This is in agreement with the suggestion of McCarty et al. (1981) that soil organic matter content becomes more important in sorption as the K_{ow} of the sorbate increases. In our study, fluoranthene had the greatest K_{ow} ($10^{5.22}$) and lowest water solubility among the three PAHs studied. Its sorption coefficient increments resulting from OM addition to the minerals were much higher than for FL and ANA. It was also observed that FL had higher K_{ow} ($10^{4.18}$) compared with ANA ($K_{ow}=10^{3.92}$).

These findings all occurred because humic organic matter contains various hydrophobic functional groups (Dunnivant and Anders, 2005; Saichek and Reddy, 2005; Killops and Killops, 1993). Therefore, addition of humic substances could provide the soil with more hydrophobic sites for adsorption of PAHs (Ping et al., 2006).

Adding organic matter to clay mineral could lead to a change in the structure of clay, making it more porous and aggregated with larger pores, increasing the sorption capacity (Wu et al., 2011). Wu et al. (2011) also showed that the presence of aromatics, alcohols and hydroxybenzene in organic matter bonded to the mineral along with other mentioned changes of the clay caused more phenanthrene sorption to montmorillonite clay mineral.

Yu et al. (2014) also reported that organic matter was the most important factor affecting phenanthrene and pyrene in two soil samples from a contaminated site. Chen et al. (2009) showed that by chemical oxidation of three types of natural soil organic matter, the sorption capacity of those soils for naphthalene and phenanthrene decreased, emphasizing the importance of OM in PAH sorption in soil.

Our results indicate that the organic matter content of the clay mineral mixtures is more effective for PAH molecules with higher K_{ow} for the same sorbent. This can be seen in Table 3.4 where sorption coefficient enhancements are much higher for FLAN than for FL and ANA with OM addition. The results also reveal that the amount of OM added to the clays and blended clay minerals is important in sorption enhancements. When the OM content of the mineral is at a level of masking the mineral role in sorption (Karickhoff, 1984), the amount of OM plays the

main role in sorption of PAHs. This justifies the higher sorption coefficient increments under the effect of OM addition in kaolinite (with 5.5 and 11% added OM) compared with the other two blended minerals (with about 3 and 6% added OM) for all three PAHs studied.

The results of this study on the enhancing effects of organic matter and heavy metals on PAH sorption are in agreement with most previous reported works for phenanthrene or other PAHs, (Obuekwe and Semple, 2013; Zhang et al., 2011a; Gao et al., 2006; Saison et al., 2004; Zhu et al., 2004; Jones and Tiller, 1991; Traina et al., 1989) although in most previous works, different PAHs were investigated.

3.3.5 Synergistic effect of organic matter and heavy metals

It has been reported that adding cations to clay minerals causes more PAH sorption (Gao et al., 2006; Zhang et al., 2011a). This was confirmed in this study for simultaneous sorption of ANA, FL and FLAN onto various clay minerals because of the presence of Ni, Pb and Zn. The enhancing effect of soil organic matter on PAH sorption is also well documented. In the presence of organic matter, metal cations form bonds with some OM functional groups connecting the organic molecules and more hydrophobic sorption sites for PAH molecules (Obuekwe and Semple, 2013). Heavy metals also decrease the dissolved organic matter in the system, reducing the association of PAHs to dissolved organic matter and consequently accumulation of the PAHs on the particulate phase (Saison et al., 2004; Jones and Tiller, 1999). They can make complexes with hydroxyl and carboxyl functional groups in soil organic matter, leading to Cation Bridges which affect the polar parts of organic matter, creating more hydrophobic sorption sites for

PAHs (Saison et al., 2004). Therefore, stronger bridging chains of organic matter-heavy metal-PAH form, leading to enhanced sorption.

Taking account of all of these findings, it is hypothesized that the co-existence of organic matter and heavy metals in clay minerals shows synergistic effects on enhancing PAH sorption.

Therefore, in this study, the possibility of synergistic effects of OM and heavy metals on the sorption coefficient of PAHs in soil-water systems was examined. Results presented in Table 3.4 and plotted in Figure 3.3 show that all three PAHs studied (ANA, FL and FLAN) have higher sorption coefficients to all mineral mixtures (K, KS and KSB) in the presence of soil OM and co-existing heavy metals (Ni, Pb and Zn). While the separate presence of metals was found to cause a slight increase in PAH sorption, and organic matter content had a significant increasing effect, the co-existence of metals and organic matter had an even greater influence than the summation of the effects of the separate metals and OM (see Table 3.4).

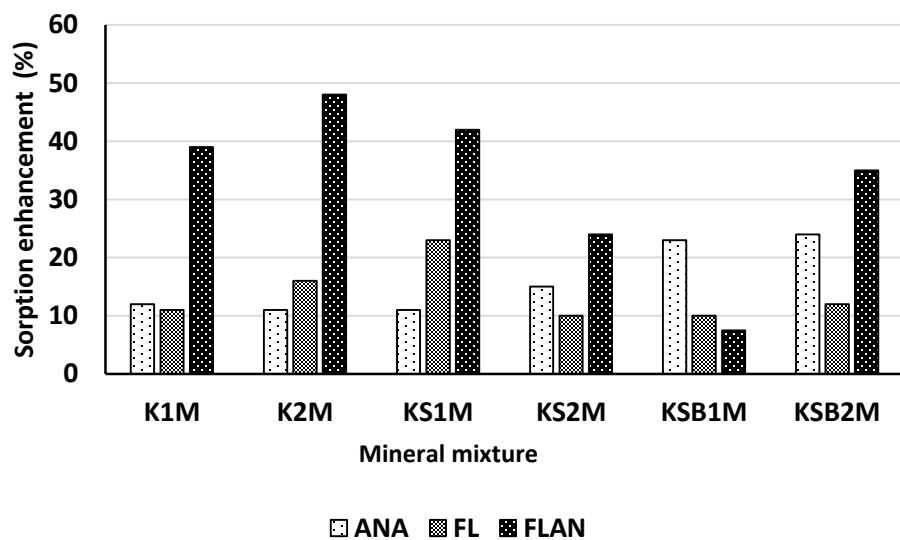


Figure 3.3 Synergistic effect of co-existence of heavy metals (Ni, Pb and Zn) and OM in sorption enhancement of PAHs

Our results reveal that this synergy can enhance the sorption of PAHs from about 10% for ANA in kaolinite to more than 48% for FLAN in kaolinite. This increment is greater than the increment of sorption under the effect of separate metals and OM. Except for the KSB soil, a general pattern of sorption is observed, even in the synergistic effect, revealing that the synergistic effect of metals and OM increases with increasing PAH molecule size and with aromaticity (number of benzene rings). More aromaticity could provide the system with more cation- π bonds between metals and PAHs. At the same time, metals also make Cation Bridges among functional groups of OM. These effects could lead to even greater enhancement of PAH sorption compared to the sum of the separate effects of OM and metals.

An important finding that might be applied to the environmental fate and transport of PAHs is that, depending on the organic matter content and the co-existence of heavy metals of the soil, the sorption and retention of target PAHs in soil might be much higher (e.g. twice) than what is usually assumed in such cases. This could retard the mobilization of targeted PAHs and undermine the remediation plan.

Greater accumulation and sorption affinities of PAHs in soils with co-existing organics and metals can make contaminated clay-soil sites challenging to remediate. At the same time, the soils of such sites may show long-term release of both heavy metals and PAHs into the environment. This suggests that it is important to consider synergistic effects in environmental mobility, fate and remediation studies.

3.3.6 Analysis of variance

The factorial ANOVA can also be used infer that one or more factors (independent variables) can cause a significant difference in one or more dependent variable. It has been used in PAH remediation of contaminated soil studies (Ravanipour et al., 2015). In this study, factorial ANOVA was performed on sorption coefficient data of each PAH onto all three mineral mixtures tested at different HA levels with and without the presence of metals. Table 3.5 shows the results of the analysis for sorption of FLAN at different test conditions. In the table, rows are for three mineral mixture types, whereas columns show the effect of HA at three content levels, spiked/unspiked metals, and metals addition to HA added minerals. As presented in Table 3.5, F values for both rows and columns are well above the critical F, while p-values are well below 0.05, indicating that the type of soil, presence of heavy metals and HA solely or together are all important with respect to sorption coefficients, with statistically significant differences among their effects on sorption. Factorial ANOVA for all three PAHs tested show similar results.

Table 3.5 Results of ANOVA analysis for sorption of FLAN onto three types of mineral and mineral mixtures

ANOVA						
Source of Variation	SS	df	MS	F	p-value	F crit.
Rows	10932546	2	5466273	18.6997	0.000418	4.1
Columns	19736837	5	3947367	13.5036	0.000353	3.3
Error	2923187	10	292318.7			
Total	33592571	17				

3.4 Conclusions

The main findings of this chapter can be summarized as:

- Larger PAH molecules containing more benzene rings having higher K_{ow} and less water solubility were found to have the greatest sorption coefficients for the clay mineral mixtures studied.
- In the organic poor clay and clay mineral mixtures studied, the minerals having more specific surface area had greater sorption affinities to the three PAHs studied.
- Heavy metals in soil were found to slightly enhance the sorption of PAHs onto "organic poor" clays and clay minerals.
- In "organic rich" clays and clay minerals, sorption enhancement by heavy metals was found to be highly intensified.
- Soil organic matter can significantly enhance the sorption of PAHs onto blended clay minerals. This effect was greatest for larger PAH molecules having lower water-solubility and higher K_{ow} .
- The simultaneous presence of heavy metals and organic matter in clays and blended clay minerals was shown to have synergistic effects on the enhancement of sorption of PAHs. These effects were much greater for larger PAH molecules with higher K_{ow} .

As pH-dependent charges of different organic (e.g. carboxyl) and inorganic (e.g. Al-OH and Si-O) functional groups may vary in nature and acidity, microscopic understanding of all detailed mechanisms contributing to PAH sorption and the synergistic effect of metals and organic matter seem to be complicated, needing more in-depth research. The effects of soil type and solution pH

on the sorption capacity and behavior of PAHs co-existing with heavy metals also require further investigation.

Chapter 4: Desorption and mobility of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals³

4.1 Introduction

Although in many contaminated sites, soil is co-contaminated by PAHs and heavy metals (e.g. 3.7% and 12.4% of contaminated sites in Canada and the US, respectively) (Wang et al., 2004; Morillo et al. 2008; Thavamani et al. 2011; Thavamani et al. 2012; FCSI, 2018; USEPA, 2018), current remediation technologies are mostly intended and designed for either organic or inorganic compounds. Rarely can they be applied efficiently for both organics and inorganics (Wick et al., 2011). Technologies to treat mixed PAHs (organic) and HMs (inorganic) contaminants are limited and more challenging for low-permeability soils due to high clay content (Reddy and Cameselle, 2009).

To devise an appropriate technological approach to remediate mixed contaminants in soil based on the extraction and mobilization of contaminants, synergistic effects among HM and PAH mobility, bio-degradation and desorption in soil must be better understood. The mobility of contaminants and their subsequent removal depend on their sorption affinities and reaction kinetics in the soil. Soil properties, mineralogy and organic content also influence desorption and mobility of mixed contaminants in soil.

³ A version of this chapter has been published. Saeedi, M., Li, L.Y., Grace, J.R., 2018. Desorption and mobility mechanisms of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals. *J. Environ. Manage.* 214, 204-214.

Saison et al. (2004) showed that the fate of PAHs in soil depends on the co-pollution with heavy metals. Fonseca et al. (2011) showed that the presence of phenanthrene as a co-contaminant can prolong the residence time of Pb in soil.

Other studies (Zhou and Zhu, 2007; Cao et al., 2013) have also found that desorption of organics and some inorganics could be enhanced by chelating and surfactant solutions. Limitations of this enhancement include low soil permeability, heterogeneity and insoluble contaminants such as PAHs (Bezza and Nkhalambayausi-Chirwa, 2015). Another limitation is that surfactants are mostly effective on PAHs and chelating solutions on metals. None of the single solutions showed good efficiencies for both types of contaminants. Most recent work focuses on removal/desorption of specific PAHs (particularly phenanthrene), solely, or in the presence of a limited number of metals, using a variety of chelating agents, surfactants and other chemicals (Bezza and Nkhalambayausi-Chirwa, 2015; Song et al., 2008; Wang et al., 2010).

The clay-size components greatly influence the physical, chemical and biological activities of soil (CLBR, 1993). Clay minerals are dominant components of many Canadian soils (CLBR, 1993). Loamy, clayey and very fine clayey soils usually contain considerable amounts of clays, from about 27 to > 60% (OMAFRA, 2016). Therefore, it can be expected that clay minerals are major components in many contaminated sites.

The aim of this chapter is to investigate the impact of heavy metals (Ni, Zn and Pb, abundant in petroleum-contaminated sites) and humic acids, solely and together, on desorption of both HMs

and PAHs (acenaphthene, fluorene and fluoranthene) to improve the understanding of desorption and mobility of co-existing contaminants in various clay and blended clay minerals.

Our research tested artificially blended clay minerals. Blending proportions of kaolinite, bentonite and sand were selected so that all resulting mixtures could still be classified as clayey soils. There is little information and published work on the mobility and desorption/remediation of these three PAHs, and no information when they are mixed with heavy metals.

The findings may be useful in remediation of fine contaminated soils containing co-existing metals and natural organic matter content, particularly when chemical desorption technologies are considered. It is shown that, even when the metal contents are less than those of soil criteria, the desorption efficiency of extracting solutions for PAHs removal may be considerably lower than expected. This chapter also indicates decreased desorption efficiency resulting from the co-existence of selected heavy metals and humic acids.

4.2 Materials and methods

Two common clay minerals (kaolinite and bentonite) were tested with sand. By blending different proportions of these three base materials, three types of fine-grained clay mineral mixtures containing different proportions of clay were prepared. The first was pure kaolinite. The second mineral mixture was kaolinite+sand, a coarser mixture with a lower content of kaolinite (60% w/w), but still clayey. The third type was a mixture of 43% w/w kaolinite, 42% w/w sand and 15% w/w bentonite, blended in such a way that the resulting mixture was clayey, but containing a small proportion of montmorillonite (the major constituent of bentonite). Details

on chemical analysis and mixtures preparation are presented in sections 3.2.2 and 3.2.3 of Chapter 3.

4.2.1 Chemicals and enhancing agents

Chemicals and minerals used for this part of study are mostly the same as ones described in section 3.2.1, Chapter 3. A PAH standard sample was purchased from Sigma-Aldrich, USA, whereas a metals standard sample (PACS-2) for quality assurance purposes was supplied by the National Research Council of Canada. Analytical grade chemicals from Merck Co., Germany were used for sample preparation, digestion and extraction of analytes. HPLC grade solvents were used for extraction and sample preparation for GC analyses. Non-ionic surfactants, Triton X-100 and Tween 80 (Sigma-Aldrich), and EDTA (Merck) were selected as enhancing agents for desorbing PAHs from the spiked samples tested. Table 4.1 presents the properties of Triton X-100 and Tween 80 were used in desorption studies.

Table 4.1 Physical/chemical properties of surfactants used in this study

Surfactant	Formula	Molecular structure	Average molecular weight	CMC ^a mM (mg L ⁻¹)	HLB ^b	Solubility (mg L ⁻¹)
Triton X-100	C ₁₄ H ₂₂ O(C ₂ H ₄ O) _n n=9-10		625	0.22- 0.24 (137- 150)	13.4	soluble
Tween 80	C ₆₄ H ₁₂₄ O ₂₆	 HO(CH ₂ CH ₂ O) _w (OCH ₂ CH ₂) _x OH CH(OCH ₂ CH ₂) _y OH CH ₂ O-(CH ₂ CH ₂ O) _{z-1} -CH ₂ CH ₂ O-C(=O)-CH ₂ (CH ₂) ₅ CH ₂ CH=CHCH ₂ (CH ₂) ₆ C Sum of w + x + y + z = 20	1310	0.01- 0.12 (13-15)	15.0	Soluble

^a. CMC, critical micelle concentration provided by Sigma-Aldrich

^b. HLB, hydrophile-lipophile balance (Cheng et al., 2017)

4.2.2 Mineral mixtures preparation and experimental program

The three clay mineral mixtures were prepared by thoroughly blending and homogenizing the pre-determined mass proportions of kaolinite, sand and bentonite. Each clay mineral mixture contained three levels of HA, without and with two different concentrations of Humax being added to increase the HA content. Batch experiments were first conducted to determine the capacity of each type of mineral mixture for HA as presented in sections 3.2.2 and 3.2.3 of Chapter 3. The maximum capacities of HA for kaolinite, kaolinite+sand and kaoloinite+sand+bentonite were 11.0, 7.0 and 5.8% (w/w), respectively for this study.

Given that there were three types of mineral mixtures and three levels of HA for each mixture, nine mineral mixtures were prepared containing either different clays or different levels of HA. Finally, two identical sets of these nine sample types were prepared. Nine sample types in one set were then spiked with the three heavy metals (Ni, Pb and Zn), and nine similar samples were left without metal spiking. Therefore, a total of 18 blended mineral samples were prepared (three types of mineral mixtures at three levels of HA, spiked and unspiked with heavy metals). The procedure was repeated to prepare the required number of each sample type to investigate the effect of different enhancing agents on the mobility and desorption of contaminants in each mixture.

The spike concentrations were the same as those for sorption tests. Spiking procedure is explained in section 3.2.3 of Chapter 3. These levels of metal spiking in soils exceed the recommended contents for protection of environmental and human health in the Canadian

environmental quality guidelines (CCME, 1999a, 1999b, 1999c) to ensure that the samples were co-contaminated by metals to a level typical of contaminated soil.

All mixture samples, with and without added heavy metals, were spiked with 500 mg kg⁻¹ each of acenaphthene, fluorene and fluoranthene. These concentrations were selected based on reported PAH concentrations in PAH- and mixed-contaminated soils (USEPA, 2004a, Fonseca et al., 2011), as well as the levels tested by previous researchers (Gomez et al., 2010, Fonseca et al., 2011). This allowed all three PAHs to be investigated for the influence of both HA and heavy metals on desorption and mobility in the three types of mineral mixtures. The spiking of PAHs followed a traditional method described by Khodadust et al. (2004) and Saichek and Reddy (2004). The PAH-spiked samples were then left to age for 14 days (Luo et al., 2012). The concentrations of metals and PAHs after spiking and aging showed < 3% deviation from the targeted spiked concentrations. Sample labels and spiking conditions are summarized in Table 3.2.

4.2.3 Batch desorption and mobility tests

Batch experiments were conducted to evaluate the desorption and mobility of selected PAHs and heavy metals for all 18 contaminated mineral mixture types. 5 g of contaminated mineral was placed into a brown glass vial, to which 25 ml of desorbing/enhancing solution was added (solid to liquid ratio of 1:5 g mL⁻¹ (Fonseca et al., 2011), and the vial was sealed with a Teflon screw-top. The vials were next agitated on a rotary shaker table at 300 rpm for 24 h at room temperature (22-24°C). The solution and solid phase were separated by centrifuging at 4000 rpm for 30 min and analyzed for the concentrations of selected contaminants. The pH was monitored

during all experimental tests. Final pH values of suspensions of all batch tests were between 4.5 and 5.5.

Trion X-100 and Tween 80, non-ionic surfactants having low toxicity and widely used in remediation research and practices (Gomez et al., 2010; Saichek and Reddy, 2004), were selected. EDTA, shown to be efficient in metals removal (Zhang and Lo, 2006; Wong et al., 1997), was selected as a chelating agent.

Preliminary batch tests, tested the removal efficiencies of selected contaminants from mineral (metals spiked kaolinite, K0M) by single chelating and extracting agents at different ranges of concentrations (0.01 to 0.1 M EDTA, 5 to 10% (w/w) Tween 80 and 5 to 10% (w/w) Triton X-100). Then different combinations of those agents were examined in a series of preliminary batch desorption tests to find the optimal combination of extracting agents to attain the highest desorption efficiencies of contaminants. Based on these preliminary tests, the combined extracting solutions were selected for desorption and mobility assessment of PAHs and metals in batch experiments. Solutions tested were as 0.01 M CaCl₂, with either a mixture of 0.01 M EDTA and Tween 80 at a concentration of 7.5% (w/w), or a mixture of 0.01 M EDTA and Triton X-100 at a concentration of 7.5% (w/w). All aqueous solutions for the soil tests contained 0.01 M CaCl₂ to maintain constant ionic strength. The concentration of EDTA selected (0.01 M) was also in agreement with optimal concentrations reported by Zhang and Lo (2006) and Wong et al. (1997). A control experiment with 0.01M CaCl₂ was carried out to establish the baseline level of desorption and mobility enhancement for comparison with agent-containing solutions for each

mineral mixture studied. Quality control and assurance measures for desorption experiments are explained in Appendix B.

4.2.4 Analysis of variance (ANOVA)

To identify the statistically significant factors, factorial ANOVA was performed on desorption of three PAHs from three mineral and mineral mixtures at different tested conditions, with a significance level of 0.05, using Microsoft Excel 2016.

4.3 Results and discussion

4.3.1 Preliminary desorption tests by single extractants

As preliminary tests, spiked kaolinite (K0M) samples were subjected to desorption by each extractant individually. Results presented in Figure 4.1 show that both citric acid and EDTA were effective in removing heavy metals from mixed-contaminated kaolinite. Overall assessment of the effect of EDTA and citric acid at different concentrations indicated that 0.01 M EDTA was most effective in metals removal among the extractants tested. Khodadoust et al. (2004) also reported removal efficiency of 90% for nickel from pure kaolinite by EDTA and 60% by citric acid. Other researchers (Song et al. 2008; Maturi and Reddy 2006) have reported greater effectiveness of EDTA than citric acid for removing nickel, zinc, lead and cadmium. However, EDTA and citric acid showed negligible removal of PAHs from mixed-contaminated kaolinite.

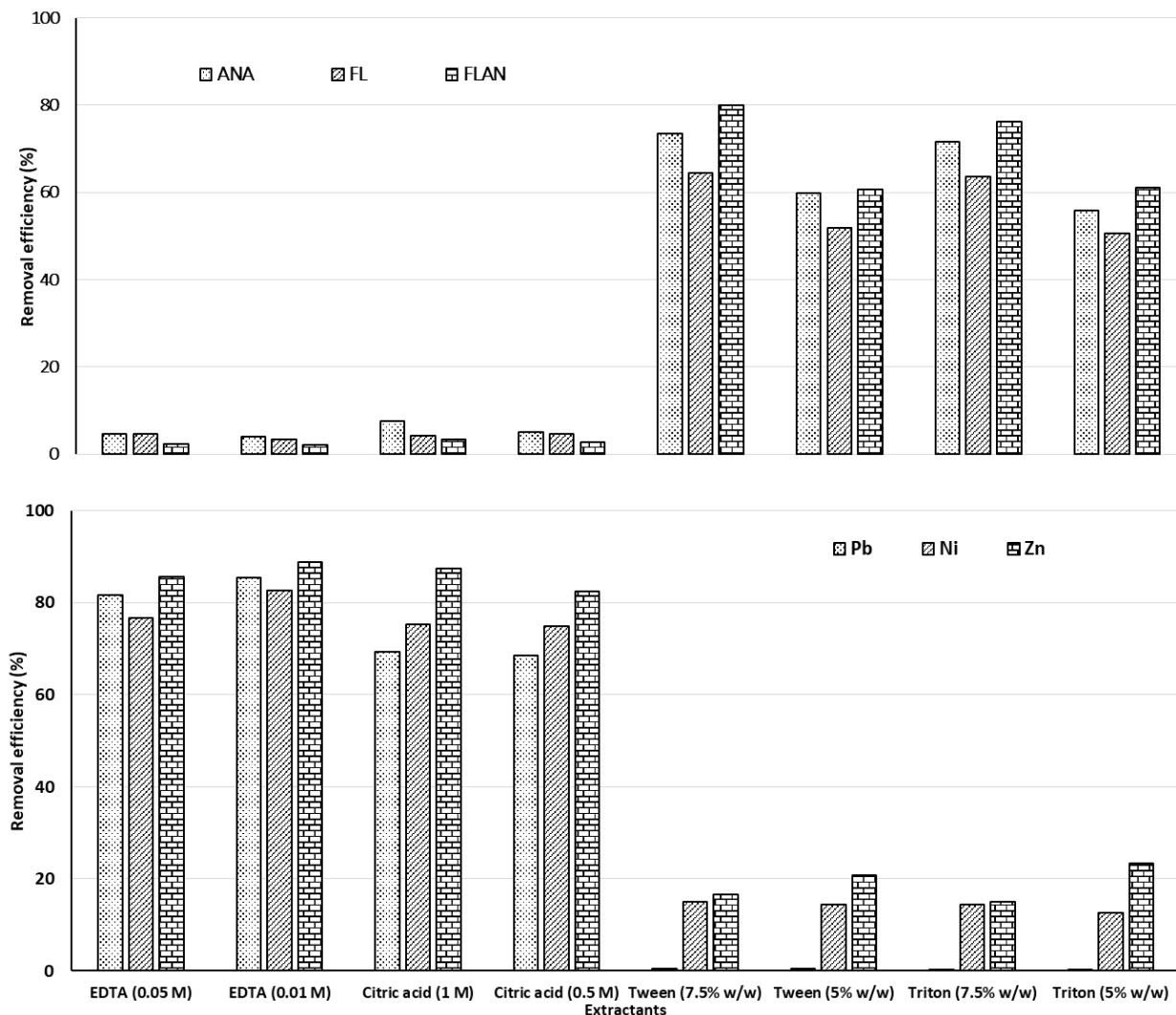


Figure 4.1 Removal efficiencies of ANA, FL and FLAN (a) and Ni, Pb and Zn (b) from spiked kaolinite (K0M) by single extractants (ANA: acenaphthene, FL: fluorene, FLAN; fluoranthene).

On the other hand, the individual surfactants tested proved to be quite effective in removing PAHs (> 60% removal), with negligible effect on the heavy metals. Higher surfactant concentrations (7.5% compared to 5% w/w) led to greater PAH removal from kaolinite.

Triton X-100 and Twin 80 as non-ionic surfactants, contain both hydrophilic and lipophilic groups. The hydrophilic (head) groups of non-ionic surfactants in soil-water systems likely enter

the aqueous phase, mainly because hydrogen bonds form between surfactants and water molecules, whereas the lipophilic (tail) groups combine with soil particles and with PAHs as hydrophobic contaminants (Mao et al. 2015) and HA present in the solid phase (Wan et al. 2011). At low concentrations, surfactants accumulate at solid-liquid and solid-contaminant interfaces in the form of monomers (Mao et al. 2015). With increasing surfactant concentrations, they replace water molecules, decreasing the aqueous phase polarity and changing the wettability of the system. In this phase, surfactant molecules adsorbed on the solid phase cause repulsion between soil particles and head groups of the surfactants, releasing hydrophobic contaminant molecules such as PAHs from soil particles (Cheng et al. 2017). When the concentration of surfactants further increases, micelles start to form in the surfactant-water-soil system. The concentration of a surfactant at which micelles start to form, is the critical micelle concentration (CMC). Micelles consist of lipophilic cores and a hydrophilic surfaces. They can greatly improve the solubility and desorption of hydrophobic contaminants (Yeom et al. 1996; Liang et al. 2017), such as for PAHs, in the soil. The concentrations of Triton X-100 and Tween 80 (7.5% w/w) tested in this study were well above their CMC (Table 4.1) concentrations. Figure 2.4 of Chapter 2 depicts a schematic of the mechanism.

It has been reported (Chi 2011; Li et al. 2016) that when non-ionic surfactants such as Triton X-100 and Tween 80 form a micellar pseudo-phase, they are more effective in solubilizing and desorbing hydrophobic contaminants from soil. However, one important negative aspect is the adsorption of non-ionic surfactants onto soil, creating more hydrophobicity that consequently increases the partitioning and retention of PAHs in the soil phase. This would decrease the

effectiveness of surfactant-enhanced PAH desorption from soil. The adsorbed surfactants are usually more effective in hydrocarbon partitioning in soil than humic matter (Li et al., 2016).

The main factors affecting the adsorption of surfactants are the molecular structure of the surfactants and soil properties. The greater the chain length of the surfactant, the more the increase in surfactant adsorption onto the solid phase (Mao et al., 2015). Soil organic matter such as HA enhances the adsorption of surfactants. Wan et al. (2011) reported that the distribution coefficients for Triton X-100 sorption onto HA were larger than that of Triton X-100 onto kaolin, up to 1.8-2.9 orders of magnitude.

4.3.2 Mobility and desorption of PAHs and heavy metals

4.3.2.1 Kaolinite

Figure 4.2 depicts the desorption of contaminants from pure kaolinite, HA added kaolinite and metals-spiked kaolinite, all containing 500 mg kg⁻¹ of each of these PAHs. From 8.4 to 11.0% of the total contents of Ni and 12.4 -13.8% of Zn proved to be mobile upon the addition of a solution such as CaCl₂. Pb was less mobile under similar conditions, revealing that the mobility of Pb in kaolinite is very low. Previous studies on multiple-metals adsorption-desorption onto different clay minerals have shown that Pb has greater affinity to adsorb onto kaolinite compared to other metals (e.g. Cu, Cd, Ni, Zn) due to its small hydrated radius (Li, 2006; Fischer et al., 1992). Thus, it could be expected that Pb would be the least mobile and extracted metal. For the pH range of our desorption tests (~4.5-5.5) the kaolinite surface charge remains negative and metals cations are held by the surface of the clay particles.

EDTA+Tween simultaneously removed about 67, 78 and 84% of Pb, Ni and Zn, respectively from pure kaolinite whereas EDTA+Triton also desorbed 70, 79 and 89% of Pb, Ni and Zn respectively from pure kaolinite. Increasing HA content of the kaolinite decreased desorption of metals, in agreement with previous work (Fischer et al., 1992, Strawn and Sparks, 2000). This decrease was no more than 10%, even for the kaolinite mixtures with maximum HA contents. Less lead was removed than Ni and Zn, demonstrating that the affinity of Pb for the solid phase is greater than for the other metals. This indicates that removal of Pb may be challenging in mixed contaminated fine kaolinite soils. Sherene (2010) also reported that Pb leached less than other heavy metals in contaminated sites. The extent of Pb desorption decreased as the soil HA increased. The reason is that the complexes formed in soil with and without HA differ.

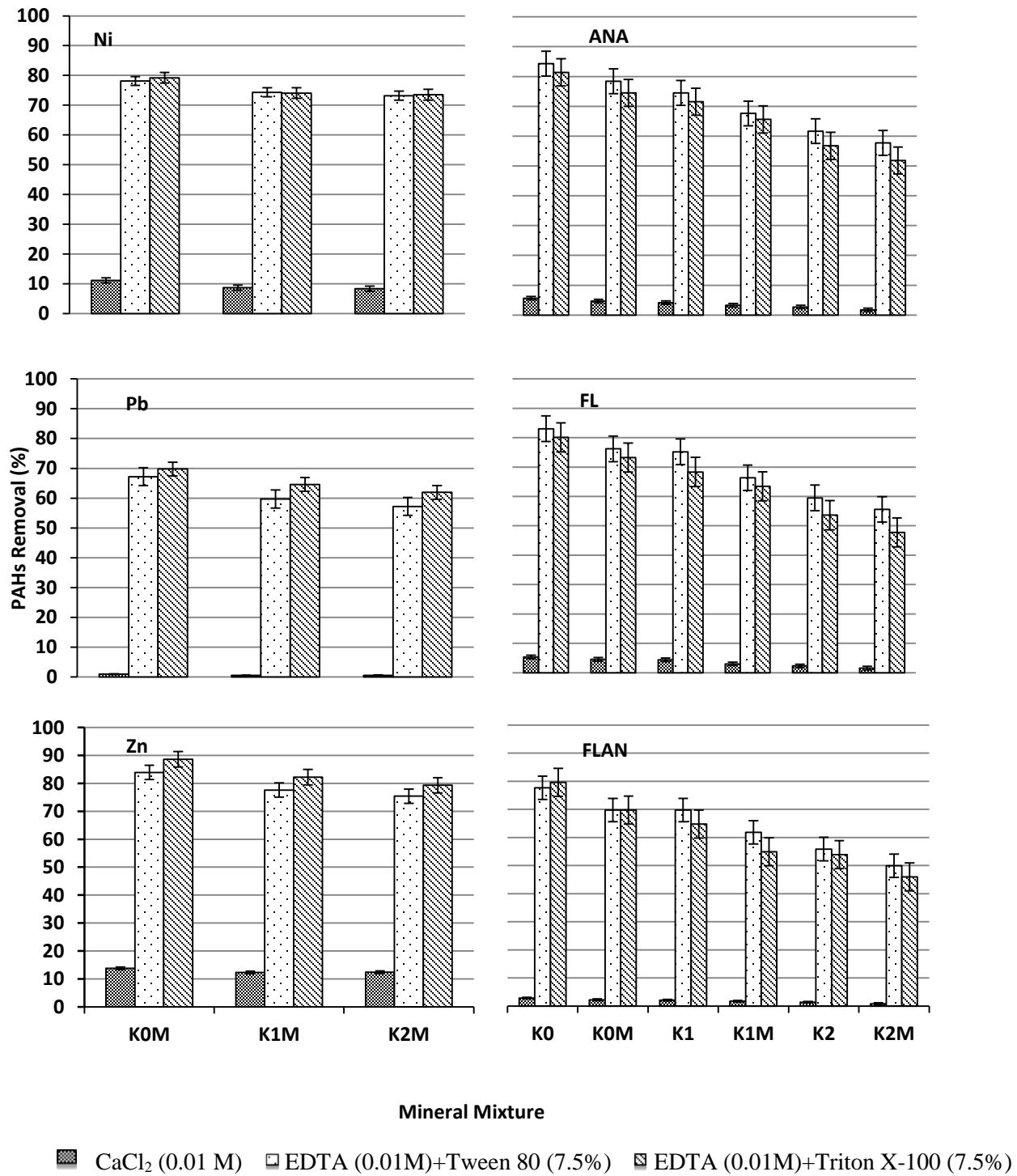


Figure 4.2 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite with and without HA by different solutions (K0M, K1M and K2M contained heavy metals; soils K1 and K2 contained added organic matter; K0 contained neither added metals nor organic matter).

Organic content could block the mineral surface from sorbing Pb. Thus, most Pb sorbs onto HA, resulting in stronger bonds which are more resistant to desorption (Strawn and Sparks, 2000).

The mobility (with 0.01 M CaCl₂ as extracting solution) of all three PAHs studied was less than 7% of their contents in soil, with a slight decrease with increasing contents of HA and heavy metals. Extracting solutions (EDTA 0.01 M+Tween 80 and EDTA 0.01 M+Triton X-100) were able to remove more than 80% of the PAHs from pure kaolinite (K0). Coexistence of both HA (5.5% w/w) and heavy metals led to a decrease of 15-20% in PAHs desorption. In kaolinite-containing heavy metals at a maximum level of HA (K2M), PAH desorption fell to about 50%. This shows that there was approximately 30% more retention of PAHs in co-contaminated kaolinite containing HA. Zhang et al. (2011a) and Yu et al. (2014) also reported that desorption of phenanthrene, as a representative PAH, decreased with increasing organic content of the soil and with the presence of Pb. Organic matter in soil enhances the sorption and affinity of PAHs due to partitioning into the soil organic phase rather than clay minerals surfaces (Wang et al., 2008). PAHs with a greater octanol-water partition coefficient (K_{ow}) tend to be highly affected by partitioning into organic matter, resulting in more difficult desorption from soil. The order of desorption and mobility of the three PAHs studied in kaolinite was found to be ANA > FL > FLAN, consistent with the order of their K_{ow} values.

EDTA 0.01 M+Tween 80 and EDTA 0.01 M+Triton X-100 showed no significant difference in desorbing metals and PAHs in kaolinite soils, although EDTA+Tween 80 provided slightly greater desorption for PAHs, whereas EDTA+Triton X-100 showed slightly greater mobilization of Pb and Zn in mixed contaminated kaolinite.

4.3.2.2 Kaolinite and sand (KS) mixture

Figure 4.3 portrays the removal of contaminants from a kaolinite+sand mineral mixture (KS) containing 500 mg kg⁻¹ of each of the three PAHs investigated. It is seen that replacement of very fine clay particles by coarse silica sand particles (inactive, with no or few charged particles) led to more mobility of heavy metals in a 0.01M CaCl₂ solution. In this case, the mobility of Ni and Zn increased to 15.0 and 13.5% of their content, respectively, while Pb adhered to the mineral mixture and was resistant to mobilization. This is related to the higher Pb absorbability to sand (SiO₂) compared to the other two metals. According to Murray (1994), the extent of metals adsorption is directly related to the metal properties that favor its hydrolysis, such as high charge, small radius and polarizability. Of the three metals studied, Pb can be most easily hydrolyzed in water, favoring more chemisorption to sand (Murray, 1994; Awan et al., 2003), resulting in more retention in kaolinite+sand compared to Ni and Zn. Awan et al. (2003) also showed that Pb shows more affinity to adsorb onto sand in aqueous solutions containing mixtures of other metals (Pb, Cu, Cr and Zn).

Application of mixed solutions of the nonionic surfactants (Tween 80 and Triton X-100) and EDTA to enhance the desorption of contaminants from the KS (kaolinite+sand mineral mixture) showed about 10% more removal of metals from the base mixture (KS0) compared to the base kaolinite (K0), with more than 80% removal for Pb and 90% for Ni and Zn achieved. This indicates that the presence of coarser particles in clay mineral can facilitate metals removal. Our preliminary results on the separate application of each solution (EDTA, Tween 80 and Triton X-100) to remove contaminants showed that EDTA played the major role in metals removal, whereas the other two agents had the main effect with respect to PAH removal. As for kaolinite

soil, with increasing HA contents in kaolinite and sand (KS1M and KS2M), the removal efficiencies and mobility of metals decreased slightly, by 10% from the efficiencies for the base mineral mixture at the maximum HA content (7% w/w). Decreasing effects of soil organic matter on metal desorption and removal from soils were previously identified by Strawn and Sparks (2000), Hizal and Apak (2006), Chorom et al. (2013). According to Strawn and Sparks (2000), bonds between soil organic matter and metals are stronger than those between soil mineral particles and metals, resulting in less desorption of metals in the presence of greater concentrations of organics.

In the base kaolinite+sand mixture (KS0), more than 90% of ANA and FL were removed with the aid of the enhancing solutions. The efficiency for the larger FLAN molecule was less than for the other two PAHs, a little more than 80%. Increasing HA and heavy metals led to a decrease in PAH removal. Detrimental effects of metals and soil organic content have been reported previously (Obuekwe and Semple, 2013, Yu et al., 2014). Zhang et al. (2011a,b) found that the decreased desorption of phenanthrene in the presence of metals in soil is related to π -cation bonds between organic and inorganic contaminants. However, the extent of the effect of soil HA and metals on decreasing the removal efficiencies of PAHs from kaolinite+sand soil was less than for pure kaolinite soil, indicating that clay particles play a key role in bonding PAH contaminants to HA and metals and in determining their affinity to remain in the soil matrix. This behavior is more evident for the two lighter PAHs (ANA and FL) than for FLAN.

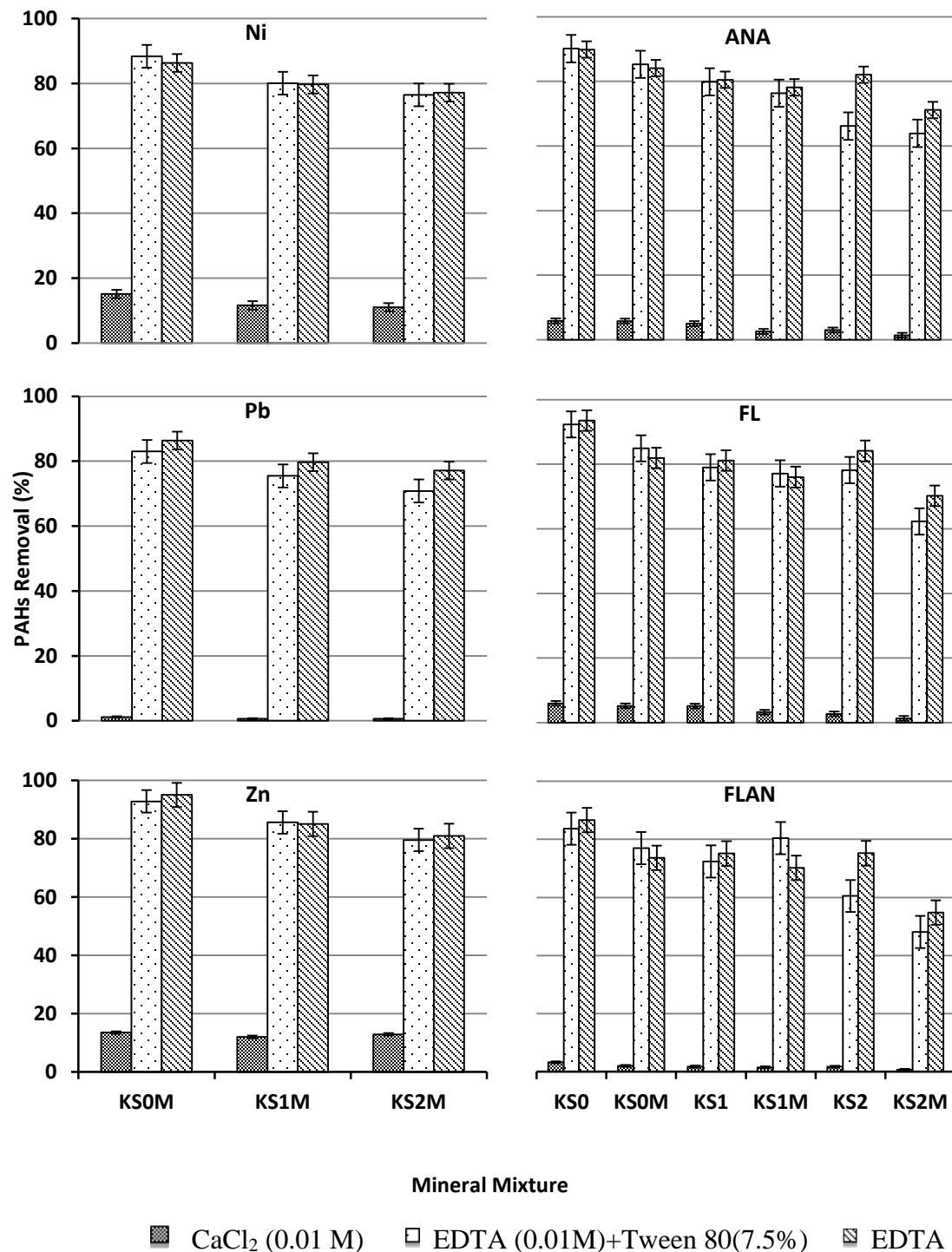


Figure 4.3 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite+sand with and without HA addition by different solutions (KS0M, KS1M and KS2M contained heavy metals; KS1 and KS2 contained added organic matter; KS0 contained neither added metals nor organic matter).

Our results revealed that at least 70% removal efficiency could be achieved in KS for ANA and FL, even in the presence of retarding compounds such as heavy metals and HA. The concentration of Triton X-100 utilized in this research exceeded the critical washing concentration (CWC) of this surfactant for all three of the PAHs studied, resulting in greater desorption and mobility of PAHs (Zhou and Zhu, 2005).

4.3.2.3 Kaolinite, sand and bentonite mixture

The impact of adding coarser inactive soil with no or low charged sand particles on the simultaneous desorption and mobility of metals and PAHs is examined in Figure 4.4. Based on XRD analysis of bentonite (Table 3.1, Chapter 3 and Figure A4, Appendix A), the final mineral composition of the KSB mineral mixture was kaolinite (43.0%), quartz (45.4%), montmorillonite (8.1%), cristobalite (1.9%), calcite (0.4%), muscovite-illite (0.4%), dolomite (0.3%) and gypsum (0.15%). Although this material contained 1.9% of cristobalite, this mineral, like quartz, has little or no reactivity (Harris and Rossington, 1968) and would not contribute significantly to surface reactions of the contaminants.

Metals were more mobile in mineral mixtures containing kaolinite+sand+bentonite than for a system containing only kaolinite clay. This is related to the larger surface area of the clays and cations exchange capacity that makes them adsorb more metals than sand. Consequently, the desorption of sorbed metals could be easier onto sand than onto clayey particles.

Enhancing solutions containing EDTA and Tween, or EDTA and Triton X-100, showed 80-90, 70-80 and 90% removal efficiencies for Ni, Pb and Zn, respectively, from base mineral mixture

(KSB0M). Increasing the HA content of this soil led to a slight decrease in metals removal, with less than a 10% decrease for all metals (Figure 4.4 KSB1M and KSB2M). It should be pointed out as the kaolinite proportion in mineral mixtures decreases, the maximum HA content of the mixture also decreases, leading to less retention of contaminants.

The extracting agents used in this study assisted in achieving greater efficiencies to desorb PAHs (Figure 4.4, KSB0). For all three PAHs studied, 90% or more of the initial PAH contaminants in the base sample (KSB0; unspiked metals and HA) could be removed by either EDTA+Tween 80 or EDTA+Triton X-100. Similar results were obtained for the other three mineral mixtures studied, with reduced PAH mobility and removal efficiencies upon the addition of heavy metals and HA. This reduction intensified with increasing HA content and when there were co-existing metals in the system. In the worst case, enhancing agents led to desorption of about 70% of each of the three PAHs from the soil containing metals and HA (Figure 4.4, KSB2M for ANA, FL and FLAN).

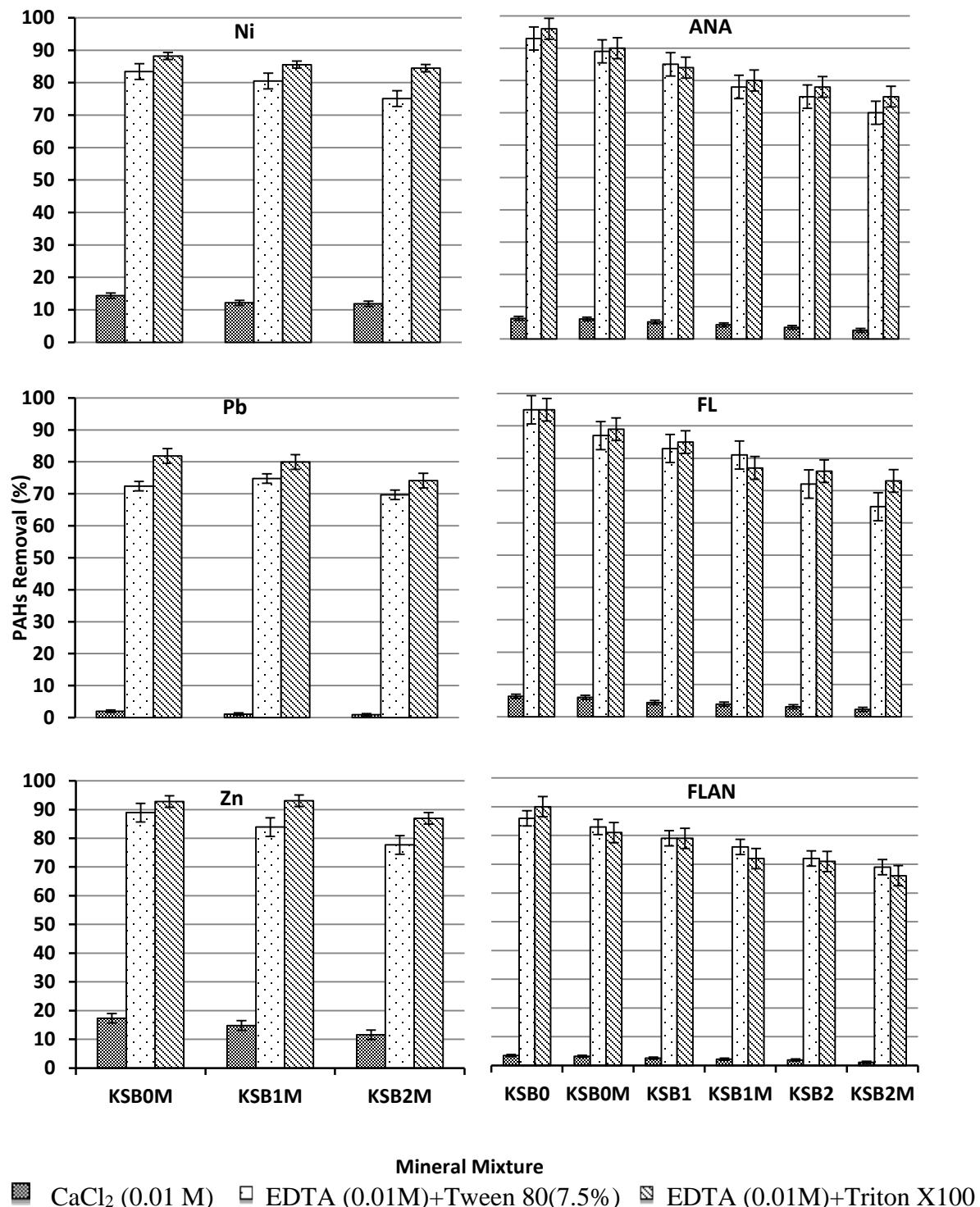


Figure 4.4 Simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite+sand+bentonite with and without HA addition (KSB0M, KSB1M and KSB2M contained heavy metals; KSB1 and KSB2 contained added organic matter; KSB0 contained neither added metals nor organic matter).

Overall, the results show that both combined solutions were effective in simultaneously removing heavy metals (Ni, Pb and Zn) and PAHs (ANA, FL and FLAN) from mineral mixtures containing kaolinite and bentonite. Contaminant mobility and the extent of removal both decreased with increasing HA content. HA addition to the soils raised the pH (Table 3.2 of Chapter 3) and also led to organometallic chemical bonds, increasing the retention of metals in the mineral mixture. The decreases in mobility by HA addition were more significant for PAHs than for heavy metals. Co-existence of metals and soil HA, particularly with HA at higher concentrations, led to considerably greater retention of PAHs. The presence of metal cations in clay minerals leads to larger pores, aggregation and more hydrophobicity of clay (Nguyen et al., 2013), resulting in more PAH retention (Zhang et al., 2011b), consequently reducing the desorption of PAHs. The effect of metals on decreasing PAHs extractability was highly intensified for mixtures containing more HA and having higher clay content (Figure 4.2, K2M for ANA, FL and FLAN). Metal cations in soil-water systems make complexes with hydroxyl and carboxyl functional groups in soil organic matter, making a Cation Bridge, affecting polar parts of organic matter, creating more hydrophobic sorption sites (Saison et al., 2004; Jones and Tiller, 1999). This mechanism could increase the retention of PAHs in soil and cause a substantial decrease in PAH desorption in the presence of co-existing metals and high HA content (Figures 4.2, 4.3 and 4.4).

These findings are important with respect to remediation of mixed-contaminated clayey soils containing natural organic matter. The results indicate that PAH removal efficiencies by enhancing solutions could decrease by 20-35% from the expected efficiencies for the base mineral mixtures without high metals and HA contents. The results also demonstrate that in

clayey mineral mixtures containing sand, desorption of PAHs by enhancing agents, even in the presence of co-existing metals and high HA contents, is higher than for samples containing solely clays and clay minerals. Decreased desorption of PAHs by cation bridging and metal complexes with HA in samples containing higher proportions of kaolinite and bentonite clays is greater than for those containing sand with lower proportions of clays. Since kaolinite can sorb more organic matter than montmorillonite, the effect of heavy metals cation bridging and complexing with functional groups of HA on decreasing of PAHs desorption from mineral mixtures having a higher proportions of kaolinite is more than for mixtures containing less kaolinite, even if the mixtures contain bentonite.

From the remediation point of view, our results demonstrate that in fine clay soils, more organic matter led to less removal of contaminants by enhancing solutions. Clay minerals such as kaolinite and montmorillonite with lower particle size, higher CEC and greater surface specific area in fine soil also make PAHs and metals more resistant to remediation. In addition, co-present heavy metals adversely affect the removal of PAHs from all mineral mixtures studied. The inhibiting effect of metals and HA content of the samples on PAH removal by enhancing solutions was greatest for larger-molecule PAH contaminants with higher K_{ow} (e.g. FLAN).

4.3.3 Analysis of variance (ANOVA)

The factorial ANOVA is used to compare means across two or more independent variables. It can also be used to check the cause- effect relationship. It infers that one or more factors (independent variables) can make a significant difference of one or more dependent variable. It is used in PAH remediation of contaminated soil studies (Ravanipour et al., 2015). In this study

factorial ANOVA was performed on the desorption data of each enhancing solution on all three mineral mixtures tested at different HA levels and metal presence/non-presence. Table 4.2 shows the results of the analysis for desorption of ANA by EDTA+Tween 80. In the table, rows are for three mineral mixture types, whereas columns show the effect of HA at two levels of content, spiked/unspiked metals, and metals addition to HA added minerals. As presented in Table 4.2, F values for both rows and columns are well above F_{crit} , while p-values are well below 0.05, indicating that the type of soil, presence of heavy metals and HA solely or together are all effective with respect to desorption, with statistically significant differences among their effects on desorption. Factorial ANOVA for all three enhancing solutions and each PAH tested showed similar results.

Table 4.2 Results of ANOVA analysis for desorption of ANA by EDTA+ Tween 80

ANOVA						
Source of Variation	SS	df	MS	F	p-value	F crit.
Rows	249.1	2	124.5	25.3	0.000122	4.1
Columns	15681.2	5	3136.2	637.8	3.49E-12	3.3
Error	49.2	10	4.9			
Total	15979.4	17				

4.4 Conclusions

Simultaneous mobility and desorption of Ni, Pb, Zn, acenaphthene, fluorene and fluoranthene in different mineral mixtures containing kaolinite, sand and bentonite in the presence and absence of HA were studied. The mobility and desorption of the PAHs in the presence and absence of the heavy metals and HA were also studied. The presence of HA reduced the desorption of metals, as a result of greater pH and more organometallic bonds, and PAHs.

HA had greater impact on the retention of PAHs than heavy metals for all mineral mixtures studied. The presence of heavy metals decreased the mobility and desorption of PAHs from all samples studied. This decreasing effect was greater for samples containing both heavy metals and HA. The combined effect of organic matter partitioning, cation bridging and more hydrophobicity of clays by co-existing metals and HA made the PAHs significantly less mobile and desorbable. A high molecular weight less water-soluble PAH (fluoranthene) was retained more than two other PAHs in all mixtures. The order of PAHs retention by HA and soil heavy metals was FLAN > FL > ANA in all mineral mixtures studied. This pattern follows the order of molecular weight and K_{ow} with lower water solubility. In higher clay content samples, the decreasing desorption of metals and PAHs was higher than for mixtures containing sand and less clay. Because of the structure of kaolinite compared to montmorillonite, higher HA sorption by kaolinite occurs, and the co-presence of heavy metals results in greater PAH retention compared to samples containing bentonite.

Applying extracting solutions containing both non-ionic surfactants and chelating agents can effectively and simultaneously desorb PAHs and co-existing heavy metals from samples.

In PAH desorption studies, one needs to consider the presence and concentrations of co-existing metals and natural organic matter content (e.g. HA), even if the metal contents are less than those of soil criteria. In the presence of metals and HA in clayey soils, the desorption efficiency of extracting solutions for PAHs removal can be considerably lower than expected on the basis of results for cases where there is no co-presence.

Chapter 5: Desorption kinetics of acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by heavy metals at various organic matter contents⁴

5.1 Introduction

The high hydrophobicity of PAHs results in interactions between them and soil organic matter. Many of remediation technologies to remove PAHs and heavy metals are based on an extracting solution to enhance the removal. Different types of enhancing solutions have been utilized for desorption and removal of mixed metals and organic contaminants from soil (Maturi and Reddy, 2006; Alcantara et al., 2008; Song et al., 2008; Cao et al., 2013; Yuan et al., 2010; Saichek and Reddy, 2005).

Previous research was shown that surfactants can enhance the removal of PAHs from soils (Saichek and Reddy, 2004; Jin et al., 2013; Sánchez-Trujillo et al., 2013). On the other hand, to enhance the removal of heavy metals effectively, application of chelating agents and organic acids has been practiced (Arwidsson et al., 2010). Simultaneous removal of PAHs and heavy metals could not be performed effectively and economically by a single extracting solution.

⁴ A version of this chapter is submitted to Environmental Earth Sciences: Saeedi, M., Li, L.Y., Grace, J.R., Desorption kinetics of acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by heavy metals at various organic matter contents.

The remediation cost of such mixed-contaminated sites also depend on the kinetics of desorption of contaminants from soil. Recent reports (Fonseca et al., 2011; Rhodes et al., 2012; Barnier et al., 2014; Bezza and Nkhalambaya-Chirwa, 2015) have shown that PAHs desorption first took place rapidly then at a much slower rate.

Natural organic matter like humic acids have been widely found to affect the fate and transport of metals and aromatics in soil environments (Hwang et al., 2003; Petrovic et al., 1999).

Different functional groups such as carboxylic and phenolic hydroxyl groups substituted on the aromatic rings lead to a high capacity of complexation with metals in humic acids (Stevenson, 1994; Güngör and Bekbölet, 2010). Acids and chelating agents that can solubilize organic matter in organic matter-metal-mineral linkages enhance the desorption of PAHs sorbed on soil organic matter (Yang et al., 2001; Zhang et al., 2011a,b; Wen et al., 2012).

While the kinetics of PAH desorption is an important factor in remediation design and cost estimation, there is little research on the desorption kinetics of PAHs co-existing with heavy metals (Wang et al., 2010; Fonseca et al., 2011). Both Fonseca et al. (2011) and Wang et al. (2010) reported that Pb and phenanthrene desorption from natural soils follow a pseudo-second-order kinetics model. To the best knowledge of the author, there is no published study on simultaneous desorption kinetic of PAHs from soils and minerals, especially when they co-exist with heavy metals considering the effect of soil organic matter.

In this study, for the first time, simultaneous desorption and desorption kinetics of three selected less-studied PAHs (acenaphthene, fluorene, and fluoranthene) and three heavy metals (Ni, Pb

and Zn), from kaolinite using different enhancing agents are evaluated. The three PAHs studied in this research are among USEPA's 16 priority pollutant PAHs likely found in most PAH- and mixed-contaminated sites (USEPA, 2008). Desorption and kinetics were examined through batch experiments. In the batch experiments, artificially contaminated kaolinite at three different humic acid content levels was used.

EDTA, citric acid, non-ionic surfactants of Tween 80, and Triton X-100 and their combinations were used to enhance removal of PAHs and heavy metals. Desorption kinetics of the contaminants were examined with the solution containing (Triton X-100+EDTA), which provided the high removal efficiency of both metals and PAHs.

Parabolic diffusion, Elovich, pseudo-second-order, and empirical power function kinetic models were evaluated based on data from desorption kinetics study.

5.2 Materials and methods

5.2.1 Chemicals and materials

Tween 80 and Triton X-100 from Sigma-Aldrich, EDTA and citric acid from Merck, zinc nitrate, acenaphthene, fluorene, fluoranthene from Sigma-Aldrich, zinc and lead nitrate from the Merck Company, Germany were used for the experimental tests. Humax 95-WSG, from JH Biotech Inc. Ventura, California, USA, was used to add humic acid content to the kaolinite.

Pure kaolinite was supplied by International Laboratory India. X-ray diffraction analysis of purchased kaolinite, performed by an XRD analyzer (PHILIPS PW1800) showed that it contained pure kaolinite, with negligible organic matter (~ 0.2% w/w). Chemical and mineral characteristics of the kaolinite used are reported in Chapter 3.

Desorption experiments were conducted with kaolinite at three levels of organic matter by adding Humax: K0 was the base kaolinite without addition of any organic matter; HA was added to K1 and K2 to provide medium and high levels of HA (5.5 and 11% w/w increase in loss on ignition of K0).

Pure (K0, no HA added) and HA-added kaolinite (K1 5.5% w/w HA added and K2 11% w/w HA added) samples were spiked with Ni, Pb, Zn, acenaphthene, fluorene and fluoranthene to obtain concentrations of 700, 5000 and 1000 mg kg⁻¹ for Ni, Pb and Zn and 500 mg kg⁻¹ for each of the three PAHs. The relative abundance of selected heavy metals at contaminated sites was the base for their spiked concentrations (Fonseca et al., 2011). Spiked concentrations were also greater than recommended by Canadian environmental quality guidelines for protection of environment and human health (CCME, 2010a, b; CCME, 1999a, b, c). In addition, in most research on PAH desorption in spiked soils, spiking concentrations have been in the range of 300-800 mg kg⁻¹ (Bezza and Nkhalambayausi-Chirwa, 2015; Fonseca et al., 2011; Zhou and Zhu, 2007). Heavy metals spiking was carried out by mixing kaolinite samples (K0, K1, and K2) with metal nitrate solutions, then dried and aged for 14 days. Key properties of pure (K0), HA-added

kaolinite (K1 and K2) are presented in Table 5.1. The properties of the surfactants used in this study are presented in Table 4.1 of Chapter 4.

Table 5.1 Properties of pure and HA-added kaolinite used in experiments

Property	K0	K1	K2
pH	5.6	5.8	6.0
Added HA (w/w %)	0	5.5	11
Cation exchange capacity (mEq/100 g)	17.2	30.7	44.2
Specific surface area ($\text{m}^2 \text{ g}^{-1}$)	16.85	-	-
Added Ni (mg kg^{-1})	700	700	700
Added Pb (mg kg^{-1})	5000	5000	5000
Added Zn (mg kg^{-1})	1000	1000	1000
Added acenaphthene (mg kg^{-1})	500	500	500
Added fluorene (mg kg^{-1})	500	500	500
Added fluoranthene (mg kg^{-1})	500	500	500

K1: Moderately added OM kaolinite, K2: Maximum added OM kaolinite

Spiking of PAHs and preparation for desorption tests were carried out following the method used by Khodadoust et al. (2004), and Saichek and Reddy (2004). After dissolving ANA, FL and FLAN were first dissolved in acetone, the solution was mixed and stirred with heavy metal-contaminated kaolinite samples. The spiked samples were next air dried at room temperature for 15 days until the samples were dry and the acetone had completely evaporated. The spiked soils

aged for 14 days in brown glass bottles. (Luo et al., 2012). Analysis of the three PAHs in the spiked and aged samples showed the deviations from the targeted concentration were < 3%.

5.2.2 Desorption kinetics experiments

Firstly, some preliminary batch experiments were conducted to evaluate the desorption efficiency of each individual enhancing agent (EDTA, citric acid, Triton X-100 and Tween 80). Since there were both metals and PAHs in the kaolinite samples, none of the desorption-enhancing agents was individually expected to show satisfactory efficiency to desorb both types of contaminants simultaneously (Figure 4.1, Chapter 4). Therefore, combinations of these agents, [(i) Triton X-100 (7.5% w/w)+EDTA (0.01 M), (ii) Triton X-100 (7.5% w/w)+citric acid (1 M), (iii) Triton X-100 (5% w/w)+EDTA (0.01 M), (iv) Tween 80 (7.5% w/w)+EDTA (0.01 M), (v) Tween 80 (7.5% w/w)+citric acid (1 M) and (vi) Tween 80 (5% w/w)+EDTA (0.01 M)] were used in preliminary assessment of desorption capabilities in pure kaolinite. Based on the results (Figure 5.1), Triton X-100 (7.5% w/w)+EDTA (0.01 M), was selected for kinetics studies.

The desorption batch experiments were conducted using 5 g of spiked kaolinite and 25 ml of enhancing agent as described in section 4.2 of Chapter 4. The final pH of desorption test solutions was measured after completing all experiments.

For kinetics experiments, the required number of pure and spiked kaolinite samples (K0, K1 and K2) were prepared following the same procedure as for desorption tests with vials shaken for up

to 72 h. Desorption of mixed contaminants was calculated based on analyses of shaken samples after 3, 6, 12, 24, 48 and 72 h.

5.2.3 Chemical analysis

The Soxhlet method was used to extract ANA, FL and FLAN (USEPA, 1996a). An extraction procedure was adopted to determine the PAH concentrations in solution (Saichek and Reddy, 2004). 12 ml of methylene chloride was added to 4 ml of centrifugation supernatant and shaken at 300 rpm for 24 h, in order to complete the PAHs extraction. They were next extracted from solutions into methylene chloride. Methylene chloride samples were then analyzed by a GC-FID (Agilent model 6890) following the USEPA-8100 method (USEPA, 1986b).

For determination of heavy metals (Ni, Pb and Zn), samples were digested by HCl, HNO₃ and H₂O₂ according to method 3050B (USEPA, 1996b). Elemental analysis of digested samples was performed by a Flame Atomic Absorption Spectrometer (Rayleigh Wfx-210).

5.2.4 Desorption kinetics data evaluation

Four kinetic models (Empirical power function, Elovich model, Pseudo second order equation, and Parabolic Diffusion equation) were used to evaluate the kinetics data. Models used were:

a) Pseudo second order equation: $\frac{t}{Q_t} = \frac{1}{k_1 Q_e^2} + \frac{t}{Q_e}$ Eq. 5.1

b) Empirical power function: $Q_t = k_2 t^\nu$ Eq. 5.2

c) Elovich: $Q_t = a + k_3 \ln(t)$ Eq. 5.3

$$d) \text{ Parabolic Diffusion: } Q_t = b + k_4 \sqrt{t} \quad \text{Eq. 5.4}$$

where Q_t (mg kg^{-1}) is the desorption at time t (h), K_1 ($\text{kg mg}^{-1} \text{h}^{-1}$), K_2 ($\text{mg kg}^{-1} \text{h}^{-v}$), K_3 ($\text{mg kg}^{-1} \text{ln(h)}$) and k_4 ($\text{mg kg}^{-1} \text{h}^{-1/2}$) are the rate constants. v , a and b are constants of the models and Q_e (mg kg^{-1}) is the amount of desorption at equilibrium.

A log-log graph of Q_t versus t would give the values of K_2 and v for the empirical power function model. A graph of t/Q_t versus t gives the values of Q_e (slope) and K_1 (intercept) for the pseudo second order equation. Plotting Q_t versus $\ln(t)$ gives the values of a and K_3 in the Elovich model and for the parabolic diffusion model, plotting Q_t versus $t^{1/2}$ allows b and k_4 to be evaluated (Wang et al., 2010; Fonseca et al., 2011; Ho, 2006).

5.3 Results and discussion

5.3.1 Desorption tests with combined enhancing solutions

As depicted in Figure 4.1 (Chapter 4), selected single agents tested were not capable of simultaneously removing selected PAHs and heavy metals significantly. Among the most efficient enhancing agents, six combinations were tested to achieve greater simultaneous removal of PAHs and heavy metals from kaolinite. The concentrations of Triton X-100 and Tween 80 (7.5% w/w) tested in this study were well above their CMC (Table 4.1, Chapter 4) concentrations.

Figure 5.1 depicts the removal efficiency of PAHs and heavy metals by combined enhancing agents. Combining EDTA or citric acid with surfactants resulted in > 80% removal efficiencies

for ANA, FL and FLAN (Figure 5.1a). While removal efficiencies of metals by single citric acid or EDTA applied individually were in the range of 70-80%, and removal efficiencies for PAHs by all surfactants used individually were in the 60-80% range (Chapter 4, Figure 4.1), the efficiencies for both metals and PAHs simultaneously increased as a result of utilization of combined enhancing agents to 70-90% for the three heavy metals and 80-85% for the three PAHs tested (Figure 5.1). This means that combinations of chelating agents and surfactants can raise the removal efficiency of each group of contaminants to a higher level for the related extractants of each contaminant acting alone (e.g. Triton X-100+EDTA > EDTA for metals, and Triton X-100+EDTA > Triton X-100 for PAHs).

Tween 80 has a longer hydrophobic tail in its structure than Triton X-100, and it is expected that the extracting solution containing Tween 80 will desorb PAHs more efficiently than Triton X-100. However, no significant differences were observed between the two combined solutions for PAHs removal, both proving to have favorable desorption efficiencies for the PAHs studied in kaolinite.

On the one hand, the longer hydrophobic chain of Tween 80 might lead to better desorption of PAHs; on the other hand, the longer tail of Tween 80 provides more adsorption onto soil, resulting in more PAH retention. In addition, the lower hydrophile-lipophile balance (HLB) of Triton X-100 and the benzene structure of its molecule could cause more affinity of Triton X-100 to PAHs, improving its performance in removing PAHs from kaolinite relative to Tween 80 (Chi, 2010). The balance of these properties affecting each surfactant resulted in similar removal efficiencies.

Published results comparing the efficiency of non-ionic surfactants in removing hydrophobic organic compounds from soil lack consistency. Some researchers (Wei et al., 2015; Chi 2010) have reported Triton X-100 to be the most efficient surfactant in removal of hydrophobic compounds from soil, whereas others (Cheng et al., 2017) found Tween 80 to be one of the best extracting surfactants in removing hydrophobic organic compounds.

For the heavy metals studied, both combined solutions desorbed Ni, Pb and Zn with high efficiencies (70 to 90%). Overall, the observed differences in simultaneous desorption efficiencies of contaminants for the two solutions were too small to differentiate significantly between these two combined solutions.

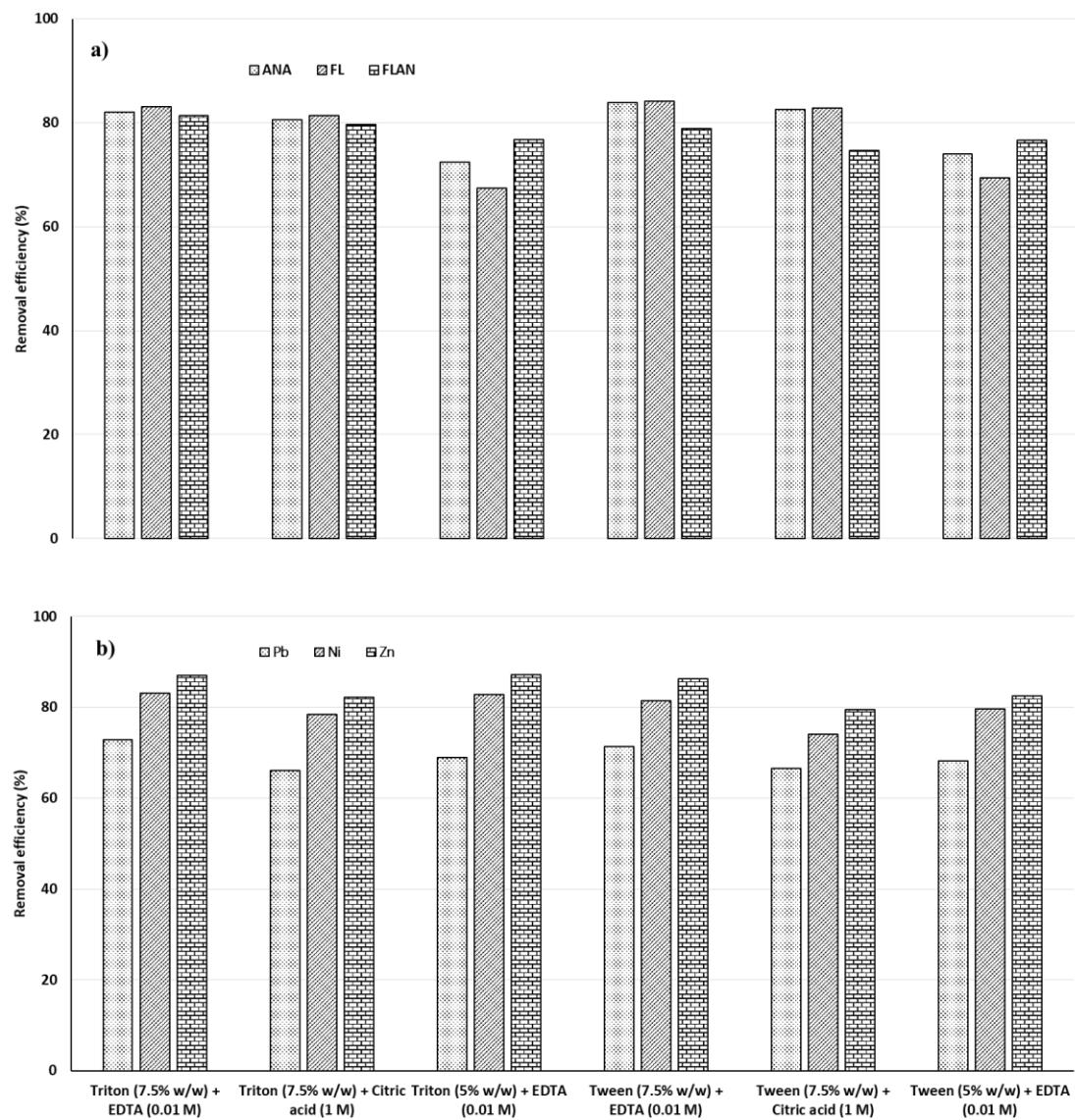


Figure 5.1 Removal efficiencies of ANA, FL and FLAN (a) and Ni, Pb and Zn (b) from kaolinite (K0) by a combination of enhancing agents (ANA: acenaphthene, FL: fluorene, FLAN; fluoranthene).

Figure 5.2, shows the pH of combined solutions at the end of the batch desorption tests. The final pH of the solutions containing citric acid was about 2, whereas it was about 4 for EDTA combined with Triton X-100 and Tween 80 surfactants.

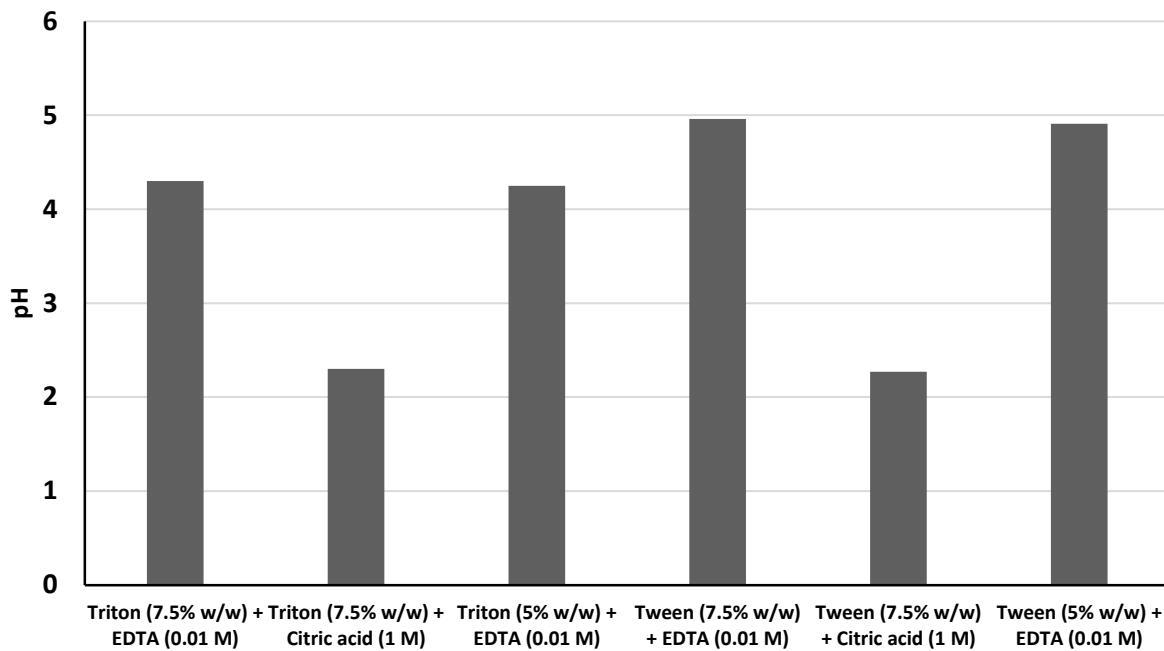


Figure 5.2 pH of solutions at the end of batch desorption tests for spiked kaolinite (K0).

The effectiveness of H⁺ ion on the desorption of Pb from contaminated kaolinite as a variable charge clay mineral was shown clearly in previous work (Li and Li, 2000). It is expected to have similar results for desorption of other metals from kaolinite by increasing the H⁺ ion concentration in soil systems. However, acidification has adverse effects on soil chemical, physical, and microbial characteristics (Reed et al., 1996). For remediation purposes, methods that would lead to soil acidification should be avoided because of the adverse environmental impact, in addition to the cost of adjusting the pH of the remediated soil. Therefore, based on the removal efficiencies achieved in desorption tests and the pH side effects on tested kaolinite, EDTA was selected as the enhancing agent to be combined with the two surfactants studied.

5.3.2 Modeling the desorption kinetics

Based on the results from preliminary tests, desorption kinetics of the PAHs were examined for the solution studied containing Triton X-100 7.5% w/w+0.01 M EDTA. Batch tests for the desorption kinetic study were carried out for times between 3 to 72 h. Figure 5.3 shows the time profiles of PAH removal from contaminated kaolinite at three levels of HA. As organic matter contents of kaolinite increased the removal efficiencies of all three PAHs studied decreased.

In kaolinite containing higher levels of HA, clay-bound HAs increase the partitioning of surfactants (Wan et al., 2011), causing them to adsorb onto kaolinite. Since HA contains both hydrophilic and hydrophobic groups, HA added to kaolinite could adsorb greater amounts of surfactants, decreasing the amount of surfactants reacting in the system, leading to more retention of PAHs and hence to greater resistance to desorption. Organic matter in soil enhances the sorption and affinity of PAHs due to partitioning into the soil organic phase, rather than onto clay minerals surfaces (Wang et al., 2008). Overall, this leads to (i) reduced amount of dissolved surfactants, because of adsorption onto soil organic matter; (ii) more sorption capacity of samples for PAHs because of surfactants adsorbed onto kaolinite; and (iii) more PAHs partitioning (to functional groups) in samples containing higher levels of OM, leading to decreased removal efficiency of PAHs from kaolinite as a result of an increase in OM content.

Maximum desorption efficiencies of ANA, FL and FLAN from mixed-contaminated kaolinite (K0) after 72 h were 94.6, 95.1 and 89.8%, respectively. In K1 (kaolinite containing 5.5% added HA), removal efficiencies were reduced to 74.1, 76.8 and 66.3% for ANA, FL and FLAN,

respectively. In kaolinite (K2) at maximum added HA (11%) the removal efficiencies fell to 52.8, 53.7 and 42.8% for ANA, FL and FLAN, respectively.

Decreases in the mobility and desorption of PAHs in soils affected by organic matter were reported previously (Saeedi et al., 2018a; Yu et al., 2014). Partitioning into organic phase enhances the sorption of PAHs rather than mineral surfaces (Wang et al., 2008). PAHs with higher octanol-water partition coefficient (K_{ow}) are more affected by partitioning into organic matter. This would result in more desorption reduction of kaolinite.

Data plotted in Figure 5.2 show that during the first 24 h, desorption of the three PAHs studied were rapid, then declined and reached a plateau over the 72 h duration of the experiment. Previous research (Fonseca et al., 2011; Rhodes et al., 2012; Barnier et al., 2014; Bezza and Nkhalambayausi-Chirwa, 2015) also reported two-step kinetics. PAHs and heavy metals make stronger bonds with soil components as contaminants age. As a result, contaminants near the surface desorb more rapidly (Bezza and Nkhalambayausi-Chirwa, 2015), leading to two-stage desorption kinetics.

Comparison of fractional PAHs desorption during the first 24 h as part of the total mass desorbed over 72 h shows that the three PAHs studied desorbed at nearly their maximum desorption capacity, though in organic-added kaolinite it took more than 24 h for the PAH desorption profile to reach a plateau. Diffusion through organic matter and intraparticle pores result in slow desorption (Pignatello and Xing, 1995; Janos et al., 2010). In the case of kaolinite, with increasing organic content, the fraction of PAHs that might be absorbed more deeply into the organic components of the soil due to various hydrophobic functional groups associated with HA

strongly bonded to PAHs, (Saeedi et al., 2018 a,b) would be greater, resulting in a reduction of the rapid desorption phase in the first hours of the reaction.

Based upon this, it seems that in soil washing, using a combined solution of Triton X-100 (7.5% w/w)+EDTA (0.01M), the provisional contact time for remediation of PAHs and metals co-contaminated kaolinite could be about 24 h. Other operating conditions such as temperature, mixing power and speed need to also be investigated to reduce contact time for practical purposes. However, acceptable desorption efficiencies from a real contaminated soil, depending on the particular pollutant to be extracted, can be achieved after several hours of contact time or even days, while desorption in artificially contaminated soil might be faster (Vandevivere et al., 2001).

Desorption kinetic profiles of PAHs also show that desorption of FLAN, a larger PAH molecule (with a lower water solubility of 0.2 mg L^{-1}), takes place more slowly than for ANA, a smaller PAH molecule (with a greater water solubility of 1.93 mg L^{-1}) in the first 12 h of the reaction. FLAN, with a greater K_{ow} , tends to be more affected (McCarty et al., 1981) by partitioning into organic matter and consequently less desorbed than ANA and FL.

It has been reported that the affinity of PAHs to soil organic matter is directly related to hydrophobicity and K_{ow} (McCarthy and Jimenez, 1985; Saparpakorn et al. 2007). There are reports stating that H-bonding, π - π interactions, cation- π bonds and covalent bonding interactions have essential effects on the intermolecular forces between PAH complexes and soil organic matter (Saparpakorn et al., 2007; Kacker et al., 2002; Zhang et al., 2011a,b).

The order of desorption kinetic rate of the three PAHs studied here was ANA > FL > FLAN for the kaolinite at three HA levels. The final pH of solutions of kinetic experiments were in the ranges of 4.3-4.4, 4.9-5.1 and 5.3-5.4 for K0, K1 and K2, respectively.

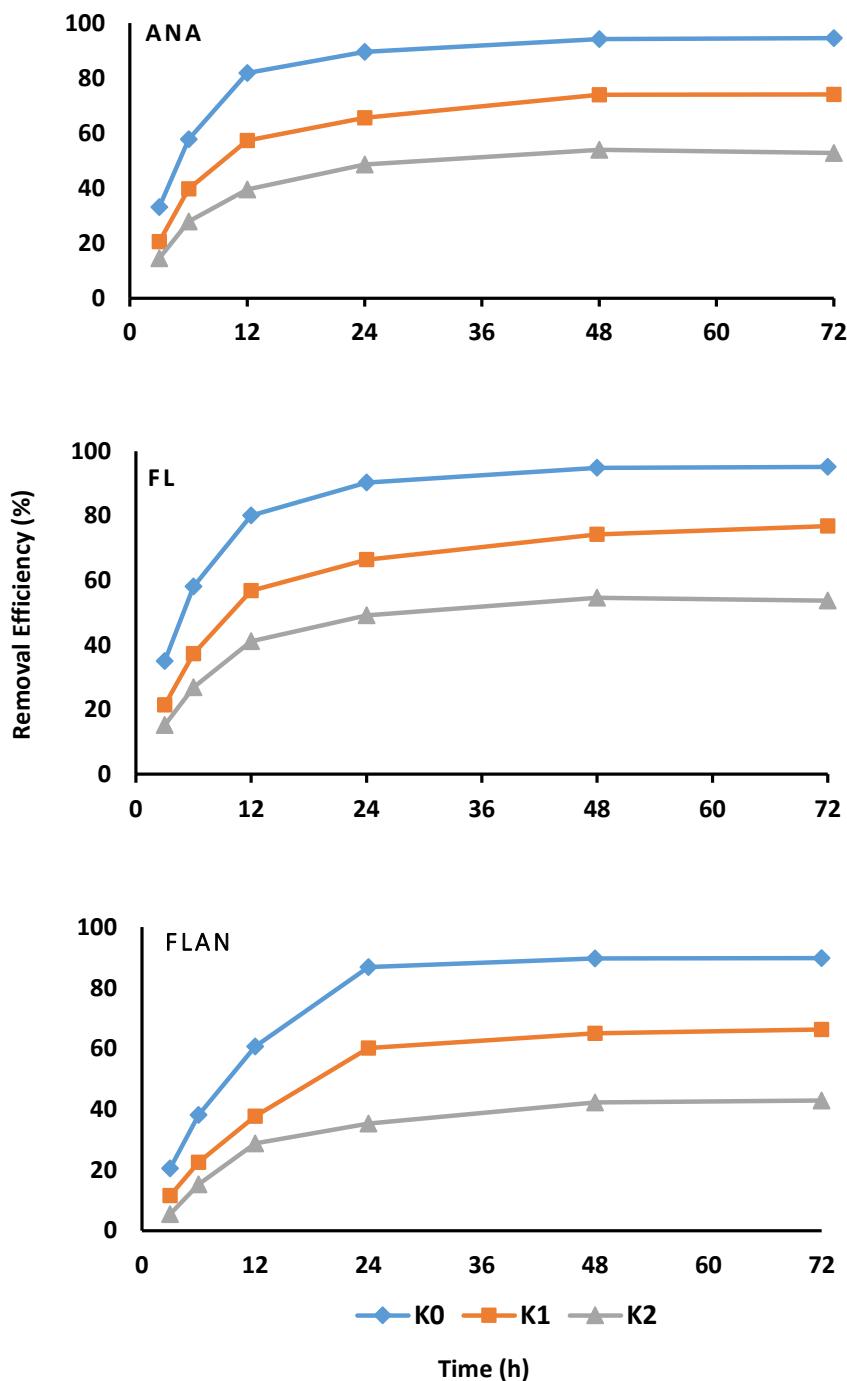


Figure 5.3 Kinetic profiles of PAHs and metals removal from kaolinite at different HA levels over 3-72 h period. K0: kaolinite with no added HA; K1: kaolinite containing 5.5% added HA; K2: kaolinite containing 11% added HA.

Percent reduction in desorption amounts and kinetic rate for each PAH studied with increasing organic matter, are presented in Figure 5.4.

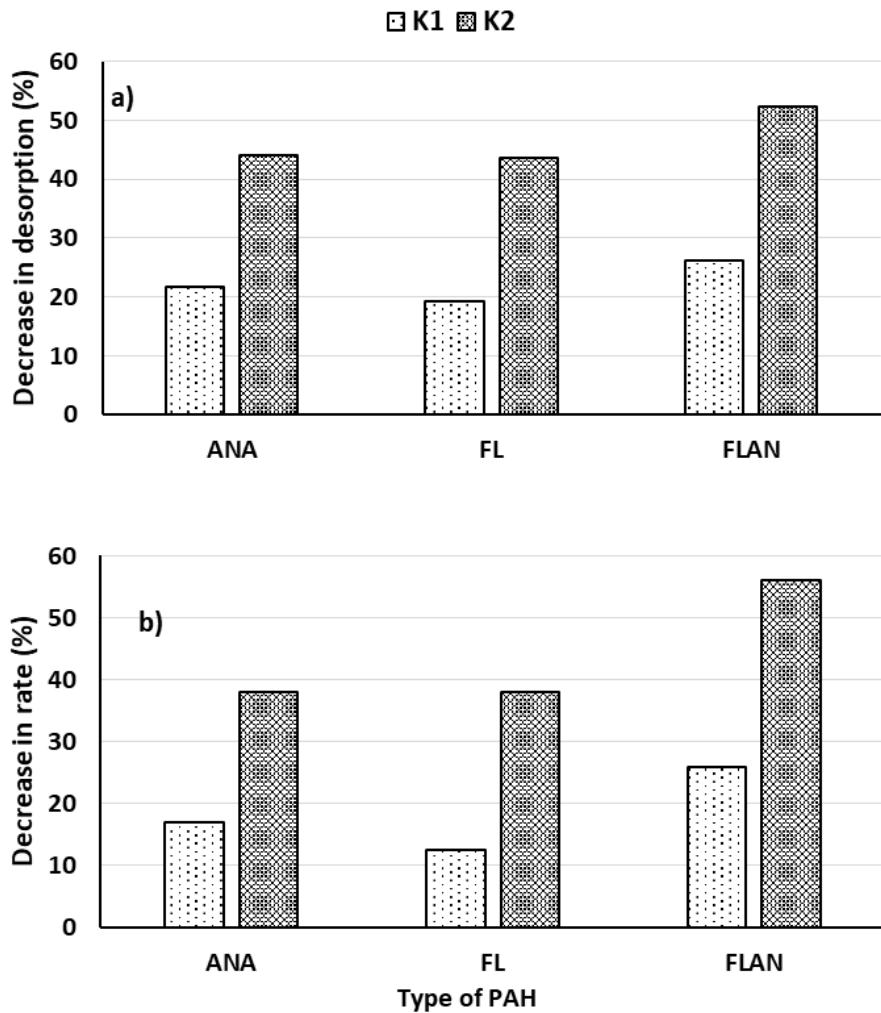


Figure 5.4 Simultaneous contaminants desorption (a), and rate (b) decrease from kaolinite because of added HA to kaolinite (K1: kaolinite containing 5.5% added HA; K2: kaolinite containing 11% added HA, ANA; acenaphthene, FL; fluorene, FLAN; fluoranthene).

Increasing the organic matter of in kaolinite to a moderate level (5.5% w/w) decreased PAHs desorption by 20, 21 and 26% for ANA, FL and FLAN, respectively. For the same conditions,

desorption of heavy metals decreased by 10, 8 and 6% for Pb, Ni and Zn. With increasing soil organic matter to its maximum level (11%), ANA and FL desorption decreased by about 45% while FLAN desorption decreased more dramatically by 55%.

Although added organic matter led to decreased desorption of all contaminants studied, the decreasing effect was greater for PAHs than for metals. Among the three heavy metals, the affected one was Zn, which was the most mobile metal of the three in this study. On the other hand, Pb was the least affected metal in the experiments. Overall, a high molecular weight PAH (FLAN) and Pb seem to be more resistant to enhanced soil washing/flushing remediation in high organic content fine soils.

The rate of desorption in the first 24 h of reaction during which most of desorption takes place decreased by increasing the organic matter content. At maximum organic matter level of kaolinite (11%), the rate of desorption in rapid phase (first 24 h) decreased about 40% for low molecular weight PAHs and about 55% for high molecular weight PAH (FLAN). This is important in PAH and metal mixed contaminated fine/clayey soils remediation leading to prolong the removal of contaminants, especially the larger PAHs.

Data obtained from fitting of the four kinetics models to simultaneous desorption of three studied PAHs and heavy metals are presented in Table 5.2. Pseudo-second-order equation and the Elovich model fit the data better than the other two models tested. For the contaminants studied and all types of kaolinite samples (K0, K1 and K2), the average correlation coefficients of the pseudo-second-order and Elovich models were ~0.993 and 0.924, respectively. Better fit of a

pseudo-second-order compared to a pseudo-first-order kinetic model for phenanthrene and lead desorption is reported before (Wang et al., 2010). On the other hand, better fitting of an empirical power function model than a pseudo-second-order equation for desorption of Pb and phenanthrene by a combined solution of EDTA+Tween 80 was reported by Fonseca et al. (2011). The discrepancy between the results of different studies may have originated from differences among enhancing agents, types, number and concentrations of contaminants and their properties, as well as soil physical/chemical/mineralogical properties (Luthy et al., 1997; Shor et al., 2003).

Results presented in Table 5.2 also show that the observed data for the desorption of PAHs and heavy metals fits best with a pseudo-second-order equation. Therefore, kinetics of simultaneous desorption of PAHs and heavy metals by combined solutions of Triton X-100 (10% w/w)+EDTA (0.01M) exposed to kaolinite and HA-added kaolinite follows the pseudo-second-order equation better than an empirical power function, parabolic diffusion and Elovich models. This indicates that the desorption of PAHs by the extracting solutions used in this study is a reaction that is mostly chemically rate controlled so that the mechanism is controlled by the concentrations of reactants rather than diffusion/physical surface exchange of contaminants (Ho and McKay, 1998, 1999).

Table 5.2 Parameters and correlations (R^2) obtained from adjustment of kinetics models for simultaneous PAHs and heavy metals desorption from kaolinite at three added HA levels.

Contaminant	Sample	Q_{72}	Kinetics model											
			Pseudo-second-order			Empirical power function			Elovich			Parabolic Diffusion		
			Q_e	k_1	R^2	v	k_2	R^2	a	k_3	R^2	b	k_4	R^2
ANA	K0	473	500	0.00047	0.99	0.30	2.2	0.80	112.7	94.5	0.87	191.8	39.5	0.71
	K1	371	416	0.00035	0.99	0.37	1.9	0.85	41.2	84.1	0.93	107.9	36.1	0.79
	K2	264	294	0.00051	0.99	0.38	1.8	0.86	25.1	62.1	0.93	73.8	26.6	0.80
FL	K0	476	500	0.00048	0.99	0.29	2.2	0.83	116.8	93.7	0.89	194.0	39.5	0.73
	K1	384	434	0.00030	0.99	0.38	1.9	0.88	32.8	87.8	0.95	99.7	38.1	0.83
	K2	269	303	0.00048	0.99	0.38	1.8	0.87	24.6	63.2	0.93	74.3	27.1	0.79
FLAN	K0	449	526	0.00020	0.99	0.46	1.9	0.88	-4.7	117.2	0.93	86.2	50.5	0.80
	K1	331	416	0.00016	0.98	0.55	1.6	0.91	-41.9	93.8	0.95	26.8	41.3	0.86
	K2	214	277	0.00021	0.95	0.60	1.3	0.85	-27.5	0.9	0.96	18.1	26.4	0.85
Pb	K0	463	500	0.00039	0.99	0.31	4.9	0.91	88.5	96.2	0.93	162.4	41.6	0.81
	K1	415	455	0.00029	0.99	0.37	4.6	0.92	35.0	94.1	0.96	104.7	41.2	0.86
	K2	336	385	0.00036	0.99	0.42	4.2	0.84	19.7	83.5	0.90	87.3	35.3	0.75
Ni	K0	498	526	0.00046	0.99	0.29	5.1	0.84	123.8	97.3	0.88	203.5	41.0	0.72
	K1	455	500	0.00034	0.99	0.34	4.8	0.88	70.4	98.1	0.94	146.3	42.3	0.81
	K2	408	455	0.00032	0.99	0.38	4.6	0.86	41.6	93.2	0.92	114.8	39.9	0.79
Zn	K0	491	526	0.00053	0.99	0.27	5.2	0.81	140.7	92.9	0.85	218.9	38.7	0.68
	K1	461	500	0.00038	0.99	0.32	4.9	0.87	86.3	95.3	0.92	161.6	40.7	0.78
	K2	401	435	0.00039	0.99	0.36	4.6	0.86	51.7	90.4	0.91	124.0	38.4	0.76

ANA: acenaphthene, FL: fluorene, FLAN: fluoranthene, K0: No added HA kaolinite, K1: kaolinite containing 5.5 % added HA, K2: kaolinite containing 11 % added HA

5.4 Conclusions

Our experimental results reveal that Triton X-100+EDTA and Tween 80+EDTA were both effective in simultaneously removing acenaphthene, fluorene and fluoranthene from kaolinite co-contaminated by Ni, Pb and Zn at different humic acid levels in kaolinite. The maximum desorption capability of Triton X-100 (7.5 % w/w)+EDTA (0.01 M) decreased with increasing humic acid content in the kaolinite. The greatest decrease in desorption due to humic acid among the three PAHs studied was observed for fluoranthene. The addition of Triton X-100 (7.5 % w/w)+EDTA (0.01 M) caused rapid desorption of PAHs and metals in the first 24 h, then slowly approximately to a maximum level. The rate of the desorption of all PAHs and metals studied in the first 24 h decreased as the humic acid content of kaolinite increased. Modeling of the desorption test data showed that, for the contaminants and operating conditions studied, a pseudo-second-order equation best fitted the experimental desorption kinetic data. This indicates that the process was controlled by chemical desorption, and the concentrations and ratios of extractants and contaminants influence both the efficiency and the rate of removal of PAHs.

Chapter 6: Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from natural soil by combined non-ionic surfactants and EDTA: laboratory column tests⁵

6.1 Introduction

Soil washing and flushing are among the technologies used to remediate contaminated soils.

Depending on the type and composition of the washing/flushing solutions, these technologies are applied to remediate PAHs, as well as other contaminants such as heavy metals. Surfactants have been used as washing/flushing solutions to increase the solubility and desorption of PAHs (Jin et al., 2013; Sánchez-Trujillo et al., 2013). Partitioning to hydrophobic groups of surfactants increases PAH solubilities and enhances their desorption from soil particles into the aqueous phase (Cheng et al., 2017; Liang et al., 2017; Li et al., 2016).

To investigate different aspects of surfactant-enhanced soil washing, researchers conduct batch experiments. Numerous studies have been published on surfactants and important factors to remove PAHs and heavy metals from soils and minerals (e.g. Chen et al., 2008; Chang et al., 2000; Saichek and Reddy, 2004; Jin et al., 2013; Sánchez-Trujillo et al., 2013; Ling et al., 2015). In the case of mobility, desorption and removal of mixed contaminants containing PAHs and heavy metals from soil, there have been several recent publications (Ye et al., 2015; Obuekwe

⁵ A version of this chapter has been published in the Journal of Environmental Management: Saeedi, M., Li, L.Y., Grace, J.R., 2019. Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from natural soil by non-ionic surfactants and EDTA: laboratory column tests. *J. Environ. Manage.* 248, 109258.
<https://doi.org/10.1016/j.jenvman.2019.07.029>

and Semple, 2013; Song et al., 2008; Maturi and Reddy, 2008), though far fewer than those on single contaminant groups such as PAHs. In addition, many of these works are limited in terms of the number of co-existing contaminants, soil composition and other key factors.

Column experiments are often used to study soil flushing, with or without surfactants,. For contaminant removal from soil, column flushing is believed to have advantages over batch soil washing, leaving the soil structure intact, providing that the flow-through pattern is similar to what would be found in the field (Hauser et al., 2005; Lee et al., 2002; Bassi et al., 2000; Neale et al., 1997). Column experiments may be used for simulation and study of in-situ soil flushing remediation system design and effectiveness, as well as for evalutaton of the environmental fate and behavior of contaminants in soil by using weak solutions as washing liquids (Banzhaf and Hebig, 2016; Ecologic Institute, 2012). Flushing by enhancing agents in column tests has been investigated to remove heavy metals (Mukhopadhyay et al. 2013; Yang et al., 2012; Hauser et al., 2005) or organic contaminants including PAHs (Salehian et al., 2012; Chi, 2010; Gong et al., 2006; Shin et al., 2006; Chu, 2003; Lee et al., 2002). However, there have been fewer column tests than batch experiments on PAH removal by enhancing solutions. Mukhopadhyay et al. (2013) used 20 mM L⁻¹ sodium dodecyl sulfate (SDS) as a washing solution to remove arsenic from natural spiked soil. Arsenic removal efficiency of 78% was the best that could be achieved in column test experiments. Yang et al. (2012) removed 90% and 50% of Cd and Pb, respectively, from natural spiked soil with 0.12 M EDTA as washing solution in column experiments. Shin et al. (2006) investigated the removal of phenanthrene using rhamnolipid biosurfactant at 150 mg L⁻¹ concentration. The best removal efficiency they reported was 17.3%. They indicated that the volume of washing liquid up to 10 times the pore volume had a

significant effect on the removal efficiencies. Lee et al. (2002) removed 73 and 95% of organic contaminants in batch and column experiments, respectively. Salehian et al. (2012) reported that the soil permeability in column tests decreased when they used SDS surfactant in washing solutions to remove petroleum hydrocarbons from sandy soil.

To achieve better removal efficiencies in mixed contaminated soils, the washing solution may contain enhancing agents for both heavy metals and PAHs. Although some research has been carried out on the desorption of PAHs co-existing with heavy metals from soil through batch experiments, column test studies on the mobility and desorption of PAHs co-existing with heavy metals are scarce.

Overall, to the best knowledge of the authors, this is the first study focusing on column tests in flushing of combined surfactants and chelants for simultaneous removal of acenaphthene (ANA), fluorene (FL) and fluoranthene (FLAN), together with heavy metals, from natural soil. Although batch tests showing the effects of these combined solutions on simultaneous removal of ANA, FL, FLAN, Ni, Pb and Zn from kaolinite and artificially blended mineral mixtures, considering the effect of soil organic matter, were reported (Saeedi et al., 2018), column experiments on the effectiveness of these solutions flushing through real contaminated soil have not been reported previously.

In this chapter, we examine, for the first time, simultaneous removal of heavy metals and PAHs from spiked real natural soil by two combined solutions, Triton X-100+EDTA and Tween 80 + EDTA, in column experiments. The removals of nickel, lead and zinc, representative of

dominant metals in contaminated sites, and acenaphthene, fluorine and fluoranthene, as abundant, but less-studied PAHs, are investigated. The main objective was to assess the simultaneous removal efficiencies of PAHs co-existing with heavy metals from spiked real soil using two extractive agents which combined non-ionic surfactants (Tween 80 and Triton X-100) with 0.01 M EDTA as chelating agent. Tables 2.1 (Chapter 2) and 4.1 (Chapter 4) contain information on the key properties of PAHs and surfactants tested in this study.

6.2 Materials and methods

6.2.1 Soil and materials

Top soil was collected from a potential impact area outside and adjacent to an oil refinery located northeast of the city of Shiraz, Iran. This soil was characterized (Table 6.1) in terms of particle size (laser scattering particle size distribution analyzer- HORIBA LA-950), mineralogy (XRD-PHIPILS PW-1800), elemental chemical composition (XRF-PHILIPS PW-1480), organic matter content (as loss on ignition, LOI), cation exchange capacity (CEC) (flame photometer Biocotek-FP 6410), pH (EUTECH-PC510) and the concentrations of contaminants. Characterization of this soil showed that it was within the range of heavy metals in natural environment and was considered uncontaminated (Table 6.1). Chemicals obtained from Sigma-Aldrich, USA, (acenaphthene, fluorene and fluoranthene, and zinc nitrate) and Merck, Germany (lead and nickel nitrate) were used to spike the soil. Non-ionic surfactants (Triton X-100 and Tween 80 from Sigma-Aldrich) combined with EDTA were explored as possible enhancing solutions for removal of PAHs and heavy metals in soil column tests. A Sigma-Aldrich PAHs standard sample and a metals standard sample (PACS-2) were purchased from Sigma-Aldrich, USA, and the National Research Council of Canada (NRC), respectively for quality assurance purposes.

Table 6.1 Properties of the soil sample

Texture	Lean clay (silty loam)
Particle size	Silt (80%)
(Particle size distribution is presented in Appendix C, Figure C1)	Clay (20%) $D_{90}= 11$, $D_{60}= 7.1$, $D_{50}= 6.5$ and $D_{10}= 2.5 \mu\text{m}$
XRD analysis (% w/w)	
Quartz	38
Calcite	26
Illite	15
Albite	7
Kaolinite	5
Dolomite	6
XRF analysis (% w/w):	
SiO_2	48.4
CaO	17.2
Al_2O_3	11.9
Fe_2O_3	6.8
MgO	4.7
K_2O	2.3
TiO_2	0.8
Na_2O	0.3
MnO	0.1
LOI	5.7
pH	7.9
Organic matter (% w/w)	5.7
CEC (mEq/100 g) ^a	35.7
$\text{Pb} (\text{mg kg}^{-1})$	9.9
$\text{Ni} (\text{mg kg}^{-1})$	29.5
$\text{Zn} (\text{mg kg}^{-1})$	42.4
$\sum \text{PAHs} (\text{mg kg}^{-1})$	15

a. Based on the CEC of the soil and the added concentration of metals, the soil had much more capacity to adsorb spiked metals

6.2.2 Soil preparation and analytical methods

Soil was sieved through a #60 sieve at room temperature to separate debris and grains, then ground and sieved again to obtain soil particles < 250 µm (Carter, 1993). The soil was spiked based on methods used by Khodadoust et al. (2004) and Saicheck and Reddy (2005). Heavy metals nitrate solution was added to the soil and stirred gently to spike the soil to 5000, 1000, and 700 mg kg⁻¹ of Pb, Zn and Ni, respectively. Metal-spiked soil was left for one week to reach equilibrium. After drying and gently grinding the dried soil, appropriate amounts of PAHs were mixed with acetone and added to the soil to prepare mixtures containing 500 mg kg⁻¹ each of ANA, FL and FLAN in soil. The spiked concentrations are within the range of contaminated soils from industrial areas (Fonseca et al., 2011; Reddy and Camselle, 2009; Maturi and Reddy, 2008; Maturi and Reddy, 2006) and the contamination range presented by the Canadian Council of Ministers of Environment (CCME, 2010a, b). The spiked soil was then left to age for 15 days (Luo et al., 2012).

Soil pH was measured according to the USEPA 9045D method (USEPA, 2004b). LOI as a measure of organic matter content was determined following ASTM- D 7348 (ASTM, 2008). CEC was measured in accordance with USEPA-9081 method (USEPA, 1986a).

Heavy metals in soil were digested by HNO₃/HCl/H₂O₂ according to the USEPA 3050 B method. Heavy metals in washing solutions were digested according to the USEPA 3010A method (USEPA, 1992), and concentrations were determined by a Flame Atomic Absorption Spectrophotometer (WFX-210).

A liquid-liquid extraction method (Saicheck and Reddy, 2005) was used to extract PAHs from solution. A GC-FID (Beifen-3420A) was used to determine the PAH concentrations.

6.2.3 Column experiments

Columns with inner diameter 40 mm and soil bed height 100 mm were used in the experiments. The soil was inserted into the column in eight identical steps. After each addition, the bed was consolidated by eight similar impactions.

Non-ionic surfactants have shown better efficiency in removing PAHs than ionic ones (Lamichhane et al., 2017; Cheng et al., 2017). These surfactants have hydrophobic and hydrophilic groups in their structures. Hydrophilic surfactants enter the aqueous phase, while the lipophilic groups (tails) attach to soil particles, PAHs and soil organic matter (Mao et al., 2015; Wan et al., 2011). Tween 80 and Triton X-100 at different concentrations, each combined with EDTA 0.01 M, were used as extracting solutions. Spiked soil in the columns was flushed by the enhancing solutions at different concentrations up to about 21-bed pore volumes (pv) (each pore-volume was about 38 mL). The volumetric flow of flushing solutions was maintained at 0.534 mL min⁻¹ with a constant hydraulic head. The 21-pore-volume-flushing took about 22 h. The effect of volumetric flow on desorption was examined by testing two other flow rates, one lower (0.456 mL min⁻¹) and the other higher (0.615 mL min⁻¹), with constant hydraulic heads. Two other flow rates were selected to be approximately 15% lower and 15% greater than the base test value in order to check the effect of volumetric flow on the removal of contaminants. The hydraulic conductivities of packed soil in the different tests were between 8.2×10^{-7} and 8.5×10^{-7} m s⁻¹, indicating that the compactions of soil samples in the columns were consistent and similar.

6.3 Results and discussion

6.3.1 Removal of heavy metals

Our results showed no significant difference in metals removal efficiency by flushing Triton X-100+EDTA or Tween 80+EDTA from contaminated soil. Therefore, results for cumulative and stepwise desorption of co-existing heavy metals from mixed contaminated soil by Triton X-100 (at three different concentrations)+EDTA (0.01 M) after flushing by 21 pore volumes (each pore volume was about 38 mL) are presented here (Figure 6.1). While the concentration of chelating agent (EDTA) in three combined solutions was constant, there was a small increase in the removal efficiency of all three metals with increasing surfactant concentration. Our preliminary studies on the effect of single solutions on removal of mixed contaminants had shown that addition of the surfactants had a small positive effect on metals removal, possibly due to the solubilizing effect of surfactants on PAHs in metal-PAH-soil bonds.

The maximum heavy metal removals achieved by Triton X-100 7.5%+EDTA (0.01 M) were 75, 85 and 90% for Pb, Ni and Zn, respectively. These removal efficiencies of co-existing metals in the presence of PAHs from a natural soil containing 5.7% w/w organic matter are surprisingly high. The order and values of approximate removal are the same as reported by Saeedi et al. (2018) for the same contaminants in clay mineral mixtures. Lead had a greater affinity for adsorption onto soil particles and organic matter than Zn and Ni, probably because of its smaller hydrated radius (Li, 2006; Fischer et al., 1992). Also, in soils containing organic matter, the removal of Pb is less (Fischer et al., 1992, Strawn and Sparks, 2000). Less leaching of Pb compared to other heavy metals in contaminated sites has also been reported previously (Sherene, 2010). The patterns of desorption of metals by all three solutions tested were similar.

For all three metals and all enhancing solutions, the maximum removal per pore volume flushing occurred between 6 to 12 pore volumes. Overall and stepwise removal efficiencies approached minimum values after 21 pore volume flushing (Figures 6.1 d, e and f).

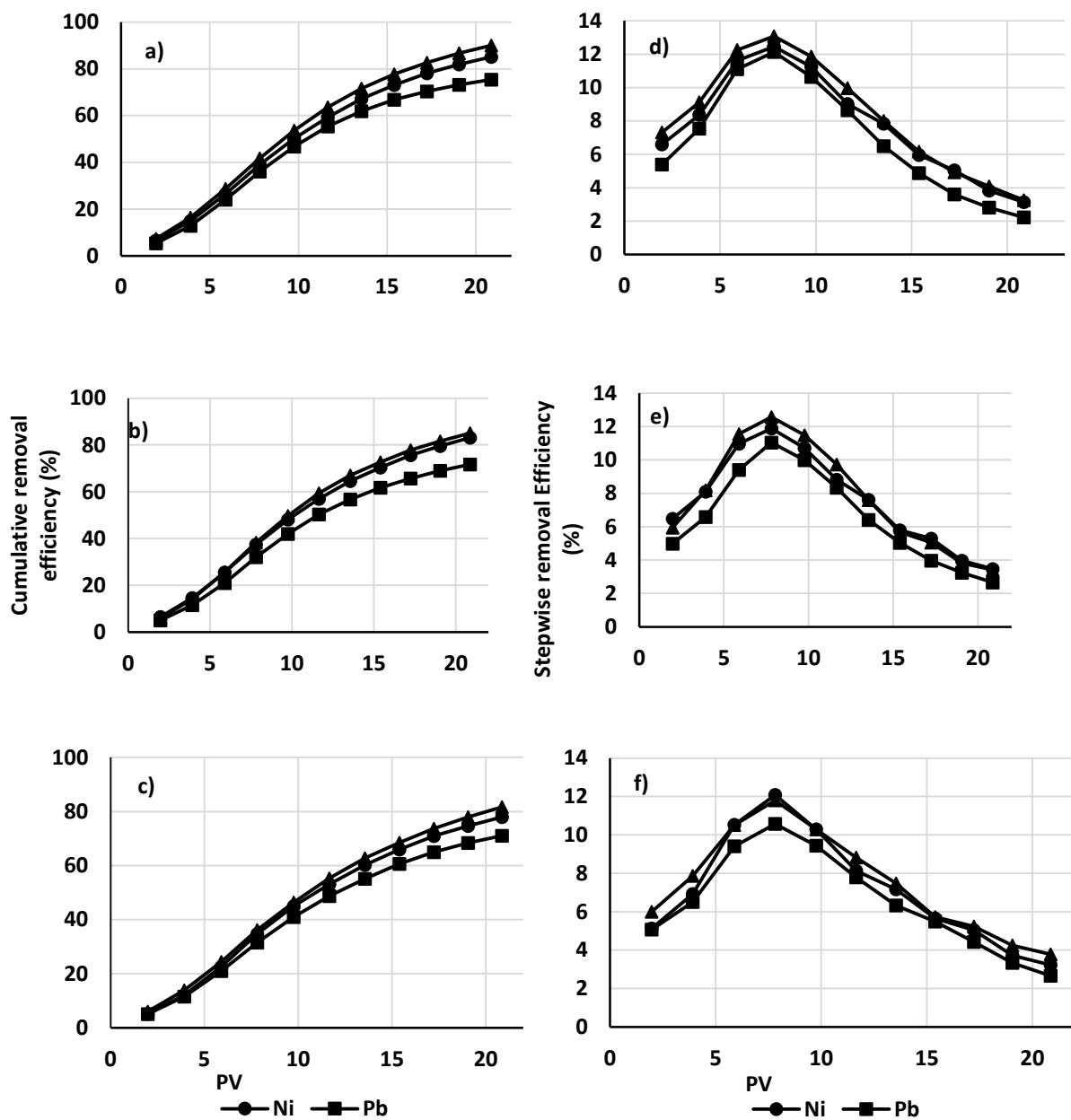


Figure 6.1 Cumulative and stepwise removal efficiencies and percent removal vs. number of pore volumes of flushing (PV) for co-existing heavy metals; a and d) Triton X-100 7.5% w/w+EDTA 0.01 M, b and e) Triton X-100 5% w/w+EDTA 0.01 M, c and f) Triton X-100 3% w/w+EDTA 0.01 M.

6.3.2 Removal of PAHs

Cumulative and stepwise removal efficiency and percent removal with each pore volume step of ANA, FL, and FLAN co-existing with heavy metals from a natural soil column are presented in Fig 6.2. After 21 pore volume flushing of enhancing solution (Triton X-100 7.5%+EDTA 0.01 M) 54, 47 and 40% of ANA, FL and FLAN were removed from the soil column. Flushing of Tween 80 7.5% w/w+EDTA 0.01 M at the same conditions removed 42, 38 and 37% of ANA, FL and FLAN (Figure 6.3 a-c). These are the highest removal efficiencies achieved by this solution in this study. The removal efficiency of each PAH decreased as the concentration of surfactant decreased.

Triton X-100 and Twin 80, non-ionic surfactants, contain both hydrophilic and lipophilic groups. The hydrophilic (head) groups of non-ionic surfactants in soil-water systems likely enter the aqueous phase, whereas the lipophilic (tail) groups combine with soil particles and with PAHs as hydrophobic contaminants (Mao et al. 2015), as well as with organic matter present in the solid phase (Wan et al. 2011). At low concentrations, surfactants accumulate at solid-liquid and solid-contaminant interfaces in the form of monomers (Mao et al. 2015). With increasing surfactant concentration, they replace water molecules, decreasing the aqueous phase polarity and changing the wettability of the system. In this phase, surfactant molecules adsorbed on the solid particles cause repulsion between soil particles and head groups of the surfactants, releasing hydrophobic contaminant molecules such as PAHs from soil particles (Cheng et al. 2017). When the concentration of surfactants increases further, micelles start to form in the surfactant-water-soil system. The concentration of a surfactant at which micelles start to form is the critical micelle concentration (CMC). The micelles consist of lipophilic cores and hydrophilic surfaces. They can

greatly improve the solubility and desorption of hydrophobic contaminants (Yeom et al., 1996; Liang et al., 2017), such as for PAHs in soil. The concentrations of Triton X-100 and Tween 80 tested in this study were well above their CMC concentrations (see Table1).

Greater removal efficiencies for the same contaminants and the same extracting solutions were reported by Saeedi et al. (2018) through batch experiments on kaolinite, kaolinite+sand and kaolinite+sand+bentonite. They reported 65, 63 and 55% removal for ANA, FL and FLAN from kaolinite containing the same concentrations of metals and quite similar organic matter content. For the mineral mixture of sand and kaolinite, they reported 78, 76, and 70% removal of ANA, FL and FLAN, while the removal efficiencies were 80, 77 and 72%, respectively from a kaolinite+sand+bentonite mineral mixture. These greater reported efficiencies may be related to the artificial mineral mixtures and the use of batch experiments. Natural soil contains a much greater variety of constituents that can compete and affect desorption, utilizing a portion of surfactants and chelating agents for processes other than desorption. The pattern of PAHs removal shows that when they were all present in soil at equal concentrations, the order of removal by the enhancing solution was directly related to the PAH molecular weights.

As a result, the PAH with the highest octanol-water partitioning coefficient (K_{ow}) showed the least removal by both Triton X-100+EDTA and Tween 80+EDTA (acenaphthene > fluorene > fluoranthene). Saeedi et al. (2018) reported the same order of removal for simultaneous desorption of these contaminants from kaolinite, kaolinite and sand, and kaolinite+sand+bentonite mineral mixtures. With decreasing concentration of surfactant in the flushing solution, the differences between the PAH removal efficiencies decreased.

Figure 6.2 (d, e and f) depict the sequential amounts of removal of each PAH during the test at 2-pore volume flushing steps. Flushing solutions containing 7.5% Triton X-100 led to greater removal amount of all three PAHs studied.

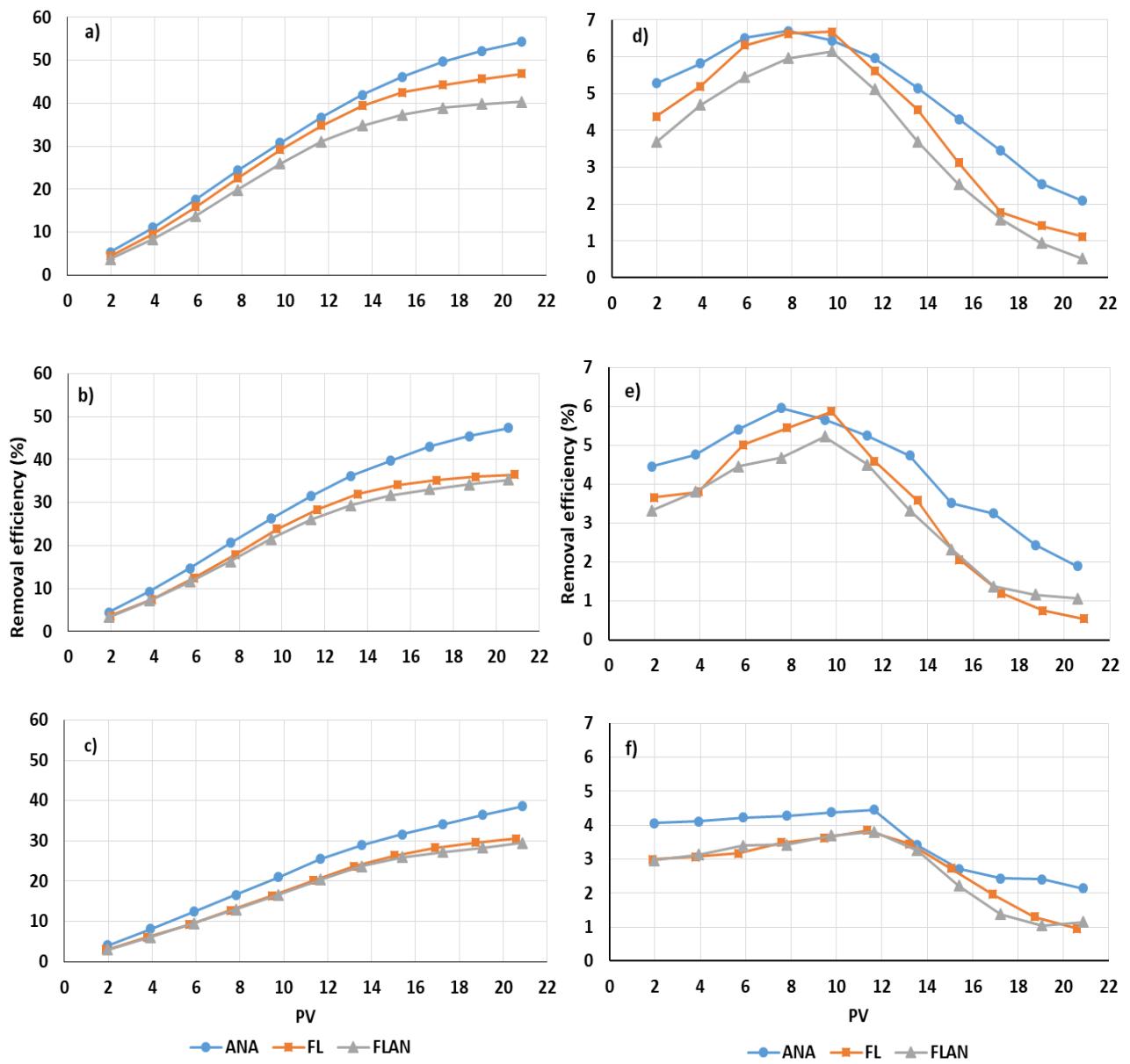


Figure 6.2 Cumulative and stepwise removal efficiencies and percent removal vs. number of pore volumes of flushing (PV) for ANA, FL and FLAN by flushing; a and d) Triton X-100 7.5% w/w+EDTA 0.01 M, b and e) Triton X-100 5% w/w+EDTA 0.01 M, c and f) Triton X-100 3% w/w+EDTA 0.01 M

The removal started from the beginning of flushing and increased to a peak at about 10 pore volumes of flushing. Beyond that, the PAHs removal per pore volume flushing decreased. At the end of the experiment, removal efficiencies of FL and FLAN were about 1% or less, but ANA was removed at an efficiency of 2% in the final step. Curve fitting indicated that FL and FLAN were not removed any more significantly by flushing solutions, with 21 pore volumes flushing yielding the maximum achievable efficiency for the conditions studied. For solutions containing 5 and 7.5% of Triton X-100, the maximum stepwise removal occurs at 8 to 10 pore volume flushing.

It was also observed that for the heavier and larger PAHs (FL and particularly FLAN), with up to 17 pore volume flushing (about 20 h of contact time) gave the maximum achievable removal efficiency, while more flushing could still remove additional ANA, the lightest of the PAHs investigated. Based on this, it can be implied that for remediation of contaminated sites, if there are mixed contamination of different PAHs, to gain maximum simultaneous remediation efficiencies of all PAHs, a flushing time of ~22 h might be needed. Since surfactant flushing for a greater number of pore volumes might cause clogging of soil pores due to colloid mobilization (Chi, 2010), achieving the maximum efficiency of simultaneous contaminants removal during 22 pore volume flushing with Triton X-100 (7.5%)+EDTA 0.01 M provided good performance.

The patterns for PAH removal by Tween 80+EDTA were similar to those observed for Triton X-100+EDTA. The main differences were that the removal efficiencies for all three PAHs studied were greater for Triton X-100+EDTA than for Tween 80+EDTA at equal concentrations of each surfactant. Tween 80 has a longer tail in its molecular structure, which may enable more

adsorption of this surfactant onto soil particles and organic matter. This might lead to lower affective micelle concentrations of Tween 80 in the system, particularly at 3% w/w content of this surfactant, and more PAH retention in the soil, due to increased soil hydrophobicity. Triton X-100 has a benzene ring structure that may provide more π - π bonds between the surfactant and PAHs. The lower hydrophile-lipophile balance (HLB) of Triton might also lead to greater desorption of ANA, a lighter (and more soluble) PAH.

While the concentration of both surfactants in all flushing solutions tested exceeded the critical micelle concentration (CMC, 137-150 mg L⁻¹ for Triton and 13-15 mg L⁻¹ for Tween 80), the efficiencies of the solutions containing 3% w/w surfactants were significantly lower than for the solutions containing 7.5% surfactant.

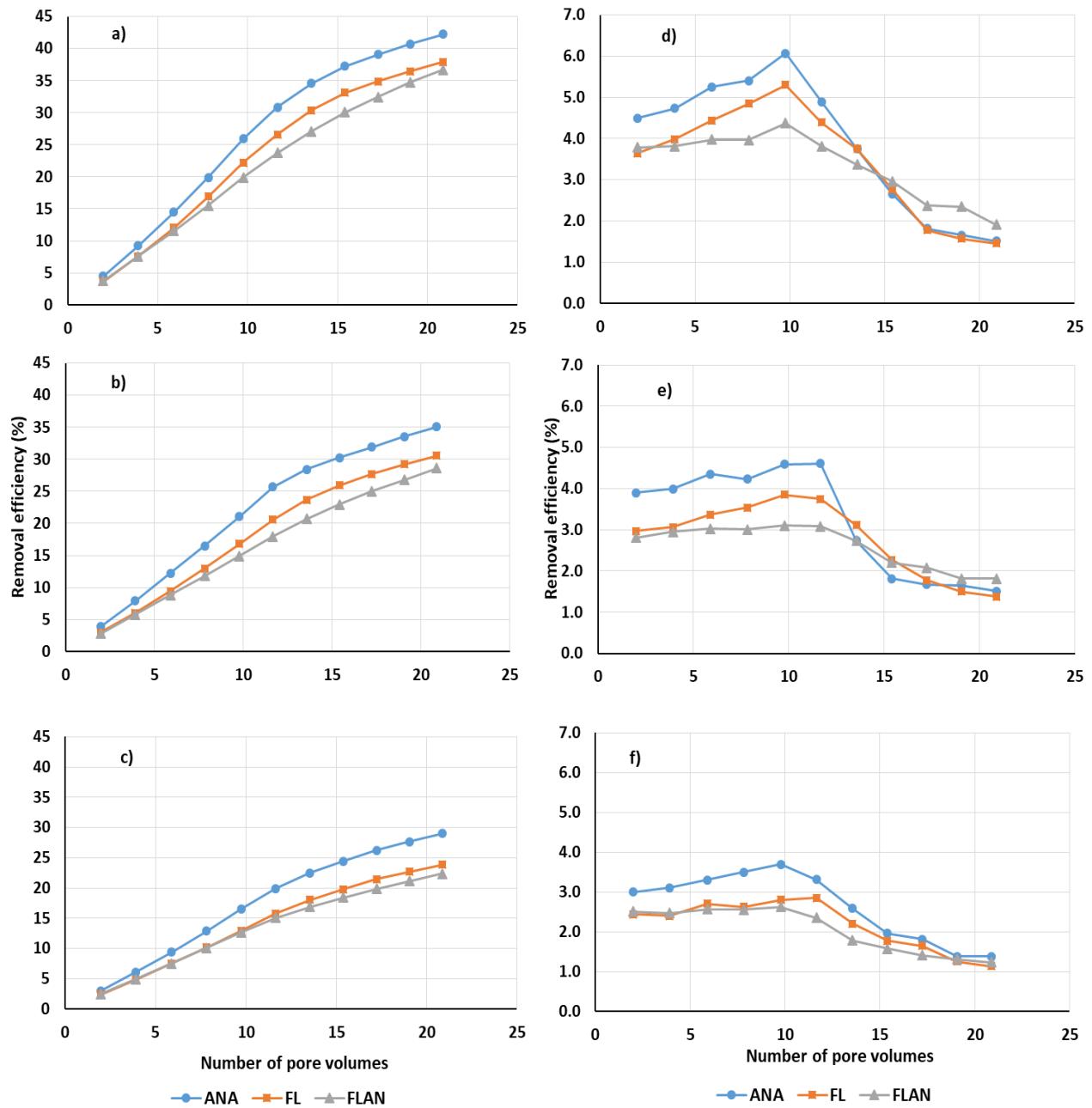


Figure 6.3 Cumulative and stepwise removal efficiencies and percent removal vs. number of pore volumes of flushing (PV) for ANA, FL and FLAN by flushing; a and d) Tween 80 7.5% w/w+EDTA 0.01 M, b and e) Tween 80 5% w/w+ EDTA 0.01 M, c and f) Tween 80 3% w/w+EDTA 0.01 M

The organic matter content of the soil tested was quite high (5.7%). Because of the hydrophobic tail of non-ionic surfactants, and high soil organic matter content, part of surfactant molecules utilized adsorbed onto soil organic matter. This would increase the hydrophobicity and increase the retention of PAHs in the soil. Wan et al. (2011) showed that sorption of Triton X-100 into humic natural organic matter of soil such as humic acids is much greater than sorption onto kaolinite. Adsorbed surfactants are retained more strongly in hydrocarbons than soil organic matter itself (Li et al., 2016). The retention of more hydrophobic PAHs would then be greater than for those with lower K_{ow} . That is why the removal efficiency of FLAN is significantly lower than that of ANA. The effect of soil organic matter on decreasing the desorption of PAHs was reported previously by Wang et al. (2008).

Therefore, the effective surfactant content in systems containing flushing solutions at lower concentrations would be much less than for a solution containing 7.5% surfactant. Surfactant adsorption also seems to be the reason why, in the system flushed by the solution containing 3% surfactant, there was no major peak in stepwise removal efficiencies, and, until 12 pore volume flushing, there was only a gradual increase in the removal efficiency at each step. That is why a slower rate of desorption was observed for FLAN than for ANA for both flushing solutions at 3% surfactant concentration. This also indicates slower kinetics of PAH desorption, particularly for the larger PAH molecules, by flushing solutions at lower concentrations of surfactants, compared to solutions containing higher surfactant concentrations (Figures 6.2 f and 6.3 f). Therefore, for remediation purposes, it seems that if a combined flushing solution of lower surfactant concentration (Triton X-100 or Tween 80) were used, flushing of more pore volumes of solution over a longer time would be needed to achieve the target removal efficiency

compared to solutions at higher surfactant concentrations. The choice of surfactant would then be based on cost-benefit tradeoffs.

Soil properties such as organic matter content and CEC, as well as the pH of the soil-water system, can also influence the removal efficiency of metals and PAHs. Lower pH would increase the solubilization of metals into the extracting solution. Greater CEC will also retain metals in soil, resulting in decreased removal. Organic matter in soil enhances the sorption and affinity of PAHs, due to partitioning into the soil organic phase (Wang et al., 2008). Overall, the PAH removal efficiency could decrease due to: (i) reduction in the amount of dissolved surfactants because of adsorption onto soil organic matter, and (ii) more PAH partitioning (to functional groups).

6.3.3 Effect of volumetric flow on removal of PAHs

All of the above experiments were conducted at a base flushing flow rate of $0.534 \text{ mL min}^{-1}$ (approximate hydraulic conductivity of $8.5 \times 10^{-7} \text{ m s}^{-1}$). Two different volumetric flows lower and greater than the base flow rate of flushing solution with the best efficiency (Triton X-100 7.5 % w/w+EDTA 0.01 M) through a contaminated soil column were tested. Figure 6.4 shows the cumulative removal of the three PAHs studied during ~ 22 pore volume flushing.

For a higher flushing rate of $0.615 \text{ mL min}^{-1}$ (approximate hydraulic conductivity of $8.2 \times 10^{-7} \text{ m s}^{-1}$), the removal efficiency of all three PAHs decreased. The efficiency of removal of ANA, FL and FLAN after 22 pore volume, fell from 54.3, 46.8 and 40.3% in the base experiments to 46.3, 39.9 and 34.4%, respectively, for the higher flushing rate.

On the other hand, the removal efficiency of PAHs for the lower flushing rate of $0.456 \text{ mL min}^{-1}$ (approximate hydraulic conductivity of $8.3 \times 10^{-7} \text{ m s}^{-1}$) increased to 58, 50 and 43% for ANA, FL and FLAN, respectively. Results show that PAH removal at each 2-pv step were higher for the first 10-12 pv, after which the incremental removals started to decrease step-by-step, reaching a plateau. Though this change in the rate of removal with total flushing volume (or time) is not very significant, some previous researchers (Bezza and Nkhalambayausi-Chirwa, 2015; Barnier et al., 2014; Rhodes et al., 2012; Fonseca et al., 2011) reported two-step kinetics of PAH desorption, related to the nature of the desorption of contaminants from soil, particularly for soils containing great amounts of organic matter.

Heavy metals and PAHs adsorbed onto the surface of soil particles could be removed more easily and rapidly than contaminants absorbed at depth onto soil particles and organic matter (Cornelissen and Gustafsson, 2004; Bezza and Nkhalambayausi-Chirwa, 2015). This explains why the desorption and removal of PAHs and heavy metals from soil follow a two-step-like pattern.

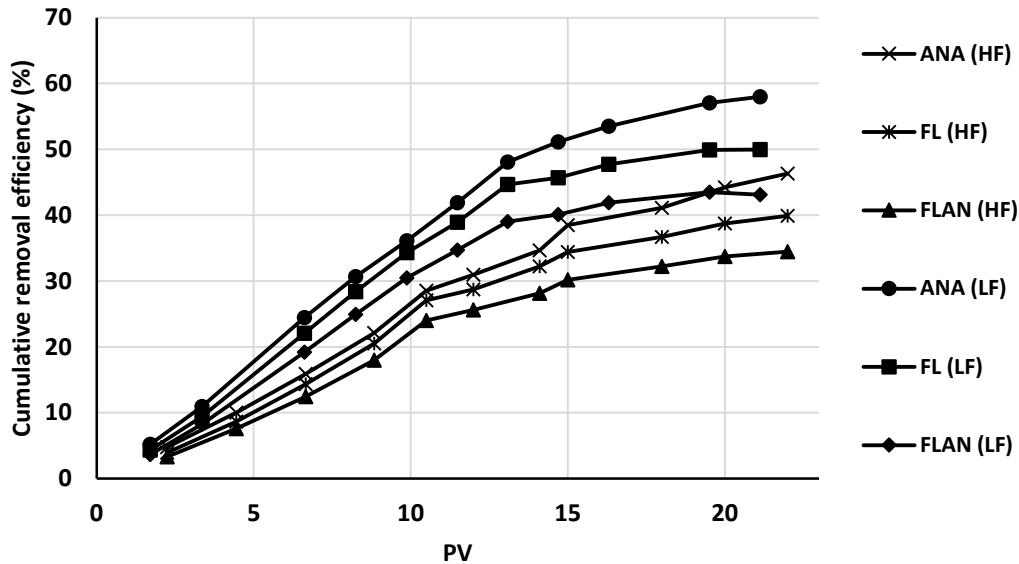


Figure 6.4 Cumulative removal of PAHs by flushing Triton X-100 7.5% w/w+EDTA 0.01 M at $0.456 \text{ ml min}^{-1}$ (LF) and $0.615 \text{ ml min}^{-1}$ (HF) flow rates.

Although the total volume of flushing solution was almost equal in each experiment, the better performance for the lower flushing flow rate indicates that the contact time is also important. For a total of approximately 800 mL solution flushing at flow rates of 0.615, 0.534 and $0.456 \text{ mL min}^{-1}$, the flushing time was about 22.5, 25 and 29 h, respectively.

The contaminant concentrations in soil after flushing of 800 mL of Triton X-100 7.5 %+EDTA 0.01 M at $0.456 \text{ mL min}^{-1}$ are compared with the recommended maximum concentrations in Canadian guidelines in Table D1 of appendix D. Most contaminants concentrations after removal are below recommended values from different standards.

6.4 Conclusions

The ability of combined solutions of Triton X-100+EDTA and Tween 80+EDTA at three surfactant concentrations to serve as flushing agents for simultaneous removal of 3 PAHs (ANA, FL and FLAN) and three heavy metals (Ni, Pb and Zn) from spiked natural fine-grained soil containing organic matter was examined. The results revealed that solutions at the three surfactant concentrations (3, 5 and 7.5% w/w) tested, were capable of removing heavy metals and PAHs. Combined flushing solutions containing Triton X-100 removed PAH contaminants more efficiently than solutions containing Tween 80. The removal rates and amounts were greater for solutions containing 7.5% w/w surfactant. ANA, the lightest molecular weight PAH of the three studied, was removed most quickly and to a greater extent through soil column flushing by enhancing solutions than two heavier-molecular-weight PAHs having greater K_{ow} (FL and FLAN). For almost equal volumes of flushing solution, lower volumetric flow of flushing solution led to greater efficiency of PAHs removal. Most contaminants were removed from soil by up to 12 pore volumes of enhancing solution flushing. It seems that, in addition to other factors, the surfactant concentration affects the kinetics of PAH desorption. Our results clearly showed that combining non-ionic surfactants and chelating agent at higher concentrations of surfactant can significantly remove multiple PAHs and heavy metals from a real clay soil. From a remediation point of view, two-step removal of contaminants via soil flushing can provide remediation in less time using less chemicals.

Chapter 7: Conclusions and recommendations for future works

7.1 Conclusions

Sorption, desorption/mobility are important processes affecting the fate of PAHs and heavy metals in soil environments (Environment Agency, 2003; Abdel-Shafy and Mansour, 2016).

Efficiency and applicability of remediation technologies like soil washing/soil flushing and electrokinetics depend on the sorption and desorption of these contaminants in soil.

The simultaneous presence of both organic matter and heavy metals affects the sorption and desorption of PAHs in soil. To the best knowledge of the author there has been no published research reporting these simultaneous effects and very few reports on simultaneous desorption/removal of PAHs and heavy metals. Previous research on the sorption of multi-PAHs onto soil in the presence of multi-metals and organic matter is also rare.

Based on the knowledge on the sorptive behaviour of metals and PAHs in clayey soil containing organic matter, it was hypothesized that there should be a synergistic enhancement in sorption of PAHs onto soil by heavy metals and organic matter.

Research was conducted to investigate the effect of soil organic matter and heavy metals individually and together on the sorption, and desorption/mobility of three selected PAHs in clay mineral and mineral mixtures, representative of fine clay soils. Having a soil washing/soil flushing remediation technology in perspective, batch and column tests were conducted towards

desorption and removal of PAHs from soils containing added and no added heavy metals and organic matter.

Review of the literature on the topic (Chapter 2) revealed that there were only four published papers on the effect of co-existing with heavy metal/s in sorption of a PAH onto soil and minerals (Saison et al., 2004; Zhu et al., 2004; Gao et al., 2006; Zhang et al., 2011a). To the time of starting this research there was also only one study on the effect of co-existing heavy metals (only lead) on desorption of PAHs (only phenanthrene) (Fonseca et al., 2011). Therefore, there was obviously a gap in studying the effect of co-existing multiple metals and organic matter on sorption/desorption of multiple PAHs in soil. Regarding important effects on the cost and efficiency of remedial technologies, it is essential to study the mechanisms of PAH sorption in relation to SOM composition and the interrelation with other main soil components and properties, such as types and contents of minerals, co-existing contaminants such as heavy metals and soil physical/chemical properties.

Chapter 3 evaluated the sorption of acenaphthene, fluorene and fluoranthene onto clay and clay mineral mixtures considering the effects of co-existing heavy metals (Ni, Pb and Zn) and humic acid as organic matter. In total, 108 batch sorption tests of PAHs were conducted for three types of clay mineral mixtures with six possible combinations of soil organic matter and heavy metal contents from no heavy metals and organic matter added to maximum organic matter added with spiked heavy metals. Results showed that the existence of metals increased the sorption of PAHs onto kaolinite from 5% for acenaphthene to 18% for fluoranthene. Organic matter in a kaolinite-sand-bentonite matrix could increase PAH sorption by up to 140% for fluoranthene. Synergistic

effects of organic matter and heavy metals on PAH sorption increments in the studied mixtures were such that the overall sorption could be 10 to 41% higher than that based on summation of the separate effects of metals and organics. A high molecular weight PAH (fluoranthene) had much greater sorption coefficients in the clay mineral mixtures studied. In the organic poor clay and clay mineral mixtures, specific surface area was found to influence the sorption affinities of the three PAHs studied. Heavy metals in soil, even in organic poor soil enhanced the sorption of PAHs onto clays and clay minerals. Humic acid as representative of organic matter also enhanced the sorption of PAHs to a great extent. The more organic matter content and the larger the PAH, the enhancing effect on sorption of PAH onto minerals tested was greater. Co-existence of heavy metals and humic acid showed a substantial synergistic effect on PAHs sorption. This effect was greater for larger PAH molecules and at higher humic acid content of the soil. These effects can influence the fate and retention of PAHs in natural fine-grained soils containing organic matter and in contaminated soils co-contaminated by heavy metals.

In the next study (Chapter 4), desorption and mobility of PAHs and heavy metals, as well as the effects of soil components such as clay minerals, as humic acids, and co-existing metals, were examined. Three types of artificially blended clay and clay mineral mixtures (pure kaolinite, kaolinite+sand and kaolinite+sand+bentonite), each with different humic acid content, were tested for desorption and mobility of acenaphthene, fluorene and fluoranthene by three extracting solutions CaCl_2 (0.01 M) and EDTA (0.01M) with non-ionic surfactants (Tween 80 and Triton-X 100). Heavy metals (Ni, Pb and Zn) were also studied for desorption and mobility. The influence of co-present metals on simultaneous desorption and mobility of PAHs was investigated as well. Less than 10% of metals in the clay mineral mixtures were mobile. Combined EDTA and non-

ionic solutions could enhance the desorption and mobility of PAHs to > 80% in clay mineral mixtures containing no sand, while in the same soils containing ~40% sand, the desorption exceeded 90%. Heavy metals, as well as increasing humic acids content in the clay mineral mixtures, decreased the desorption and mobility of PAHs, especially for soils containing no sand, and for fluoranthene compared with fluorene and acenaphthene. Effect of humic acid on the retention of PAHs was greater than the effect of heavy metals. However, the presence of heavy metals in all mineral and mineral mixtures studied decreased the desorption of PAHs. Higher molecular weight PAHs showed greater retention. Desorption of PAHs decreased because of the combined effect of organic matter partitioning, cation bridging and more hydrophobicity of clays by co-existing metals and humic acid. The order of retention for PAHs by both humic acid and soil heavy metals was FLAN > FL > ANA. This pattern of decrease in desorption followed the order of molecular weight and K_{ow} of PAHs. The clay content also influenced the extent of desorption. Clay minerals that can adsorb more humic acid (such as kaolinite compared to montmorillonite) retain PAHs to a greater extent with and without containing added heavy metals. Our results revealed that for high organic content soils contaminated by mixed PAHs and heavy metals, remediation technologies based on desorbing solutions such as soil washing/flushing and enhanced elektrokinetics, might not be as efficient as expected.

Chapter 5 focused on simultaneous desorption kinetics of PAHs and heavy metals (Ni, Pb and Zn) from co-contaminated kaolinite containing three levels of humic acid. Desorption was carried out using enhancing agents including non-ionic surfactants (Triton X-100, Tween 80), a chelating agent (EDTA). Parabolic diffusion, Elovich,

pseudo-second-order, and empirical power function kinetic models were evaluated for desorption kinetics of the contaminants studied. PAHs desorbed mostly within 24 h, with maximum desorption reached between 48 and 72 h. Humic acid, representative of natural organic matter content in kaolinite, reduced the kinetic rate of contaminant desorption in the first 24 h. A pseudo-second-order equation fitted the kinetic data better than three models with $R^2 > 0.95$ for all contaminants tested at all three humic acid kaolinite content levels. It can be implied that for fine soils containing high contents of organic matter and contaminated with both heavy metals and PAHs, not only the efficiency of desorption-based remediation techniques would decrease, but also the time needed to remediate to a certain level would increase. This increases the remediation costs for high organic content fine soils compared to lower organic content soil utilizing the same technique.

The effectiveness of combined solutions tested and proposed in Chapters 4 and 5, was examined by column flushing of those combined solutions of Triton X-100 and Tween 80 with EDTA to simultaneously remove of PAHs and heavy metals from a natural fine grained spiked soil. While the effectiveness of both combined solutions in heavy metals removal was not significantly different, Triton X-100+EDTA was more efficient in removing PAHs. Results showed that after 21 pore volume flushing of enhancing solution (Triton X-100 7.5%+EDTA 0.01 M) at flow rate of $0.534 \text{ mL min}^{-1}$ through the column with hydraulic conductivity $8.5 \times 10^{-7} \text{ m s}^{-1}$. 54, 47 and 40% of acenaphthene, fluorene, and fluoranthene were

removed simultaneously. At the same conditions, 75, 85 and 90% of Pb, Ni and Zn, were also removed simultaneously. Increasing the flow rate of flushing solution decreased the removal efficiency of the contaminants. Lower volumetric flow of flushing solution led to greater removal of target contaminants. By up to 12 pore volumes of enhancing solution flushing, most contaminants had been removed from the soil. In addition to influencing the removal efficiency, the concentration of surfactant in enhancing solution affects the rate and kinetics of contaminant removal from soil.

7.2 Recommendations for further research

In subsurface transport studies and modeling of PAHs including modeling for the purposes of natural attenuation, it is important to use the corrected sorption coefficients of PAHs, because the observed synergistic effect of heavy metals and soil organic matter on PAHs sorption can be significant.

The effects of soil organic matter, heavy metals and co-existence of them in contaminated soil need to be considered in remediation design studies. These influencing factors decrease the efficiency and increase the time of remediation.

This research is one of the first studies focusing on sorption/desorption of multiple PAHs addressing the effect of co-contaminants and soil organic matter. Interactions between PAHs, soil components and heavy metals influencing sorption/desorption are complicated. Therefore, regarding the importance of sorption/desorption of PAHs in fate and transport, remedial, and

environmental risk studies other research is need to acquire better understanding and documentation.

In this study, humic acid was used as an organic matter representative. The effects of other major types of natural organic matter, such as fulvic acid and humin, solely and co-existing with heavy metals on sorption/desorption of PAHs need to be investigated.

The effects of three heavy metals (Ni, Pb and Zn) were examined in this study showing major effect on both sorption and desorption of PAHs. Because in contaminated sites there are often multiple heavy metals in soil, it is required to study the effect of multiple abundant metals, as well as individual metals (particularly ones that might be found in sites at high concentration as main contaminants such as chromium or lead). Equivalent content of metals might be important in their interactions affecting sorption/desorption of PAHs. Hence examining metals equivalent content is also important.

Rarely is a single PAH the sole contaminant. They are instead found as mixtures of PAHs. In highly contaminated soils containing limited clay content and organic matter, there may be competition for sorption sites and then preference in desorption and remediation among PAHs. This study examined simultaneous presence of three less-studied PAHs. It is required to study their competitive behavior and interactions in fine-grained soil in terms of organic matter content and type, clay minerals and co-existing heavy metals.

This research studied the sorption and desorption of PAHs from a macroscopic point of view.

Results showed that different mechanisms and properties might be involved in the processes.

From a microscopic point of view, the underlying mechanisms of humic acid and heavy metals effects on sorption/desorption of PAHs in clayey and fine soils need to be studied. The effect of properties like cation exchange capacity of organic matter, different functional groups in organic matter structure as well as metals speciation in soil-water system and metal fractionation in soil are also important factors to be investigated.

As pH-dependent charges of different organic (e.g. carboxyl) and inorganic (e.g. Al-OH and Si-O) functional groups may vary in nature and acidity, microscopic understanding of all detailed mechanisms contributing to PAH sorption/desorption seems to be complicated and in need of in-depth research. Effects of soil and solution pH changes on the sorption/desorption capacity and behavior of PAHs studied co-existed with heavy metals may also need to be studied.

Part of the non-ionic surfactants used in this study, can adsorb onto soil depending on the soil organic matter composition and content. To study the adsorption of Triton X-100 and Tween 80 combined with EDTA, onto soil and influencing factors in adsorption not only will help achieve better efficiency using less enhancing solution, but also can help to minimize the possible impact of applied solutions on the soil environment.

This study shows that PAHs and heavy metals can be simultaneously removed by application of combined enhancing solutions of non-ionic surfactants and EDTA. Probable synergistic effect of EDTA and surfactants on the desorption of PAHs and heavy metals, and the mechanisms

involved, can also be examined to find optimum proportion and combination of enhancing agents to gain the best removal and the least chemical consumption/environmental effects and cost.

Environmental effects and impacts of the combined enhancing solutions on soil environment, and other effects on soil properties also need to be studied.

References

- Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* 25, 107-123.
- Agency for Toxic Substances and Disease Registry (ATSDR), 1995. Public Health Statement Polycyclic Aromatic Hydrocarbons (PAHs), 6 pp.
- Agency for Toxic Substances and Disease Registry (ATSDR), 2009. Case Studies in Environmental Medicine, Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs), 68pp.
- Ahangar, A.G., 2010. Sorption of PAHs in the soil environment with emphasis on the role of soil organic matter: A review. *World Appl. Sci. J.* 11, 759-765.
- Ahn, C., Kim, Y., Woo, S., Park, J., 2008. Soil washing using various nonionic surfactants and their recovery by selective adsorption with activated carbon. *J. Hazard. Mater.* 154, 153–160.
- Alcantara, M.T., Gómez, J., Pazos, M., Sanromán, M.A., 2008. Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant-electrochemical degradation. *Chemosphere* 70, 1438-1444.
- Alcantara, M.T., Gómez, J., Pazos, M., Sanromán, M.A., 2009. PAHs soil decontamination in two steps: desorption and electrochemical treatment. *J. Hazard. Mater.* 166, 462–468.
- American Society for Testing and Materials (ASTM), 2008. Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues. ASTM D 7348.
- American Society for Testing and Materials (ASTM), 2006. Standard Specification for Standard Sand. ASTM C778.

American Society for Testing and Materials (ASTM), 2001. Standard Test Method for pH of Soils. ASTM D 4972.

Antoniadis, V., Golia, E.E., 2015. Sorption of Cu and Zn in low organic matter-soils as influenced by soil properties and by the degree of soil weathering. Chemosphere 138, 364-369.

Arwidsson, Z., Elgh-Dalgren, K., von Kronhelm, T., Sjöberg, R., Allard, B., van Hees, P., 2010. Remediation of heavy metal contaminated soil washing residues with amino polycarboxylic acids. J. Hazard. Mater. 173, 697-704.

Awan, M.A., Qazi, I.A., Khalid, I., 2003. Removal of heavy metals through adsorption using sand. J. Environ. Sci. 15, 413-416.

Awoyemi, A., 2011. Understanding the Adsorption of PAHs from Aqueous Phase onto Activated Carbon. MSc Thesis, University of Toronto, Canada

Baird, W. M., Hooven, L. A., Mahadevan, B., 2005. Carcinogenic polycyclic aromatic hydrocarbon-DNA adducts and mechanism of action. Environ. Mol. Mutagen. 45, 106–114.

Balati, A., Shahbazi, A., Amini, M.M., Hashemi, S.H., 2015. Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic-inorganic nanohybrid material. J. Water Reuse Desalin. 5, 50-63.

Banzhaf, S., Hebig, K.H., 2016. Use of column experiments to investigate the fate of organic micropollutants-a review. Hydrol. Earth Syst. Sci. 20, 3719–3737.

Barnier, C., Ouvrard, S., Robin, C., Morel, J. L. 2014. Desorption kinetics of PAHs from aged industrial soils for availability assessment. Sci. Total Environ. 470, 639-645.

Bassi, R., Prasher, S.O., Simpson, B.K., 2000. Extraction of metals from a contaminated sandy soil using citric acid. Environ. Prog. 19, 275-82.

Bezza, F. A., Nkhalambayausi-Chirva, E. M., 2015. Desorption kinetics of polycyclic aromatic hydrocarbons (PAHs) from contaminated soil and the effect of biosurfactant supplementation on the rapidly desorbing fractions. *Biotechnol. Biotechnol. Equip.* 29, 680-688.

Bhattacharyya, K.G., Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv. Colloid Interface Sci.* 140, 114-131.

Bostrom, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* 110, 451–488.

Brindley, G. W., Bender, R., Ray, S., 1963. Sorption of non-ionic aliphatic molecules from aqueous solutions on clay minerals clay-organic studies-VII. *Geochim. Cosmochim. Acta.* 27, 1129-1137.

Cao, M., Hu, Y., Sun, Q., Wang, L., Chen, J., Lu, X., 2013. Enhanced desorption of PCB and trace metal elements (Pb and Cu) from contaminated soils by saponin and EDDS mixed solution, *Environ. Pollut.* 174, 93-99.

Canadian Council of Ministers of the Environment (CCME), 2010a. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Polycyclic Aromatic Hydrocarbons.

Canadian Council of Ministers of the Environment (CCME), 2010b. Canadian Soil Quality Guidelines; Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs) (Environmental and Human Health Effects), PN1445.

Canadian Council of Ministers of the Environment (CCME), 1999a. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Zinc.

Canadian Council of Ministers of the Environment (CCME), 1999b. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Lead.

Canadian Council of Ministers of the Environment (CCME), 1999c. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Nickel.

Carter, M. R., 1993. Soil Sampling and Methods of Analysis, CRC Press.

Castellanos, E., Villar, M.V., Romero, E., Lloret, A., Gens, A., 2008. Chemical impact on the hydro-mechanical behaviour of high-density FEBEX bentonite. Phys. Chem. Earth 33, 516-526.

Centre for Land and Biological Resources Research (CLBR), 1993. Clay Mineralogical Database of Canadian Soils, Technical Bulletin 1993-1E, Ottawa, Ontario.

Chang, M.C., Huang, C.R., Shu, H.Y., 2000. Effects of surfactants on extraction of phenanthrene in spiked sand. Chemosphere 41, 1295–1300.

Chen, W.J., Hsiao, L.C., Chen, K.K.Y., 2008. Metal desorption from copper(II)/nickel(II)-spiked kaolin as a soil component using plant-derived saponin biosurfactant. Process Biochem. 43, 488–498.

Chen, W., Hou, L., Luo, X., Zhu, L., 2009. Effects of chemical oxidation on sorption and desorption of PAHs in typical Chinese soils. Environ. Pollut. 157, 1894-1903.

Cheng, K., Wong, J., 2006. Effect of synthetic surfactants on the solubilization and distribution of PAHs in water/soil-water systems. Environ. Technol. 27, 835–844.

Cheng, M., Zeng, G., Huang, D., Yang, Y., Lai, C., Zhang, C., Liu, Y., 2017. Advantages and challenges of Tween 80 surfactant-enhanced technologies for the remediation of soils contaminated with hydrophobic organic compounds. Chem. Eng. J. 314, 98-113.

- Chi, F-H., 2010. Remediation of polycyclic aromatic hydrocarbon contaminated-soil by nonionic surfactants: column experiments. Environ. Eng. Sci. 28, d.o.i:10.1089/ees.2010.0223
- Choi, S.D., Shunthirasingham, C., Daly, G.L., Xiao, H., Lei, Y.D., Wania, F., 2009. Levels of polycyclic aromatic hydrocarbons in Canadian mountain air and soil are controlled by proximity to roads. Environ. Pollut. 157, 3199-206.
- Chorom, M., R. M. Karkaragh, B. Kaviani, and Y. k. Kalkhajeh. 2013. Monometal and competitive adsorption of Cd, Ni, and Zn in soil treated with different contents of cow manure. Appl. Environ. Soil Sci. 510278, <http://dx.doi.org/10.1155/2013/510278>
- Chu, W., 2003. Remediation of contaminated soils by surfactant-aided soil washing. Pract. Period. Hazard. Toxic Radioact. Waste Manage. 7, 19-24.
- Cornelissen, G., Gustafsson, O., 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. Environ. Sci. Technol. 38, 148-155.
- Covelo, E.F., Vega, F.A., Andrade, M.L., 2007. Heavy metal sorption and desorption capacity of soils containing endogenous contaminants. J. Hazard. Mater. 143, 419-30.
- De Jonge, L. W., Moldrup, P., De Jonge, H., Celis, R., 2008. Sorption and leaching of short-term-aged PAHs in eight European soils: Link to physicochemical properties and leaching of dissolved organic carbon. Soil Sci. 173, 13-24.
- Delle Site, A., 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. a review. J. Phys. Chem. Ref. Data 30, 187-439.

Dunnivant, F. M., Anders, E., 2005. A Basic Introduction to Pollutant Fate and Transport: An Integrated Approach with Chemistry, Modeling, Risk Assessment, and Environmental Legislation, John Wiley & Sons.

Ecologic Institute (Demonstration of Promising Technologies to Address Emerging Pollutants in Water and Waste water, DEMEAU), 2012. Guidelining Protocol for Soil-Column Experiments Assessing Fate and Transport of Trace Organics.

El-Nahhal, Y.Z., Safi, J.M., 2004. Adsorption of phenanthrene on organoclays from distilled and saline water. *J. Colloid Interface Sci.* 15, 269, 265-73.

Environment Agency, 2003. Review of the Fate and Transport of Selected Contaminants in the Soil Environment. Draft Technical Report P5-079/TR1.

Ewa, B., Danuta, M-S., 2017. Polycyclic aromatic hydrocarbons and PAH-related DNA adducts. *J. Appl. Genet.* 58, 321-330.

Federal Contaminated Sites Inventory (FCSI), 2018. <http://www.tbs-sct.gc.ca/fcsi-rscf/home-accueil-eng.aspx>, Accessed Feb. 10, 2018.

Fischer, K., Rainer, C., Bieniek, D., Kettrup, A., 1992. Desorption of heavy metals from typical soil components (clay, peat) with glycine. *Int. J. Environ. Anal. Chem.* 46, 53-62.

Fonseca, B., Pazos, M., Figueiredo, H., Tavares, T., Sanroman, M.A., 2011. Desorption kinetics of phenanthrene and lead from historically contaminated soil. *Chem. Eng. J.* 167, 84–90.

Food and Agriculture Organization of the United Nations (FAO), 2001. Lecture Notes on the Major Soils of the World. World Soil Resources Reports.

Gao, Y.Z., He, J.Z., Ling, W.T., Hu, H.Q., Liu, F., 2003. Effects of organic acids on copper and cadmium desorption from contaminated soils. *Environ. Int.* 29, 613–618.

- Gao, J.A., Pedersen, J.A., 2005. Adsorption of sulfonamide antimicrobial agents to clay minerals. *Environ. Sci. Technol.* 39, 9509-9516.
- Gao, Y., Xiong, W., Ling, W., Xu, J., 2006. Sorption of phenanthrene by soils contaminated with heavy metals. *Chemosphere*, 65, 1355–1361.
- Gauthier, T. D., Seitz, W. R., Grant, C. L., 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene KQC values. *Environ. Sci. Technol.* 21, 243-48.
- Gomez, J., Alcantara, M. T., Pazos, M., Sanroman, M. A., 2010. Remediation of polluted soil by a two-stage treatment system: desorption of phenanthrene in soil and electrochemical treatment to recover the extraction agent. *J. Hazard. Mater.* 173, 794-798.
- Gong, Z., Wilke, B.-M., Alef, K., Li, P., Zhou, O., 2006. Removal of polycyclic aromatic hydrocarbons from manufactured gas plant-contaminated soils using sunflower oil: Laboratory column experiments. *Chemosphere* 62, 780-787.
- Greish, S., Rinnan, A., Marcussen, H., Holm, P.E., Christensen, J.H., 2018. Interaction mechanisms between polycyclic aromatic hydrocarbons (PAHs) and organic soil washing agents. *Environ. Sci. Pollut. Res.* 25, 299-311.
- Güngör, E. B. Ö., Bekbölet, M. 2010. Zinc release by humic and fulvic acid as influenced by pH, complexation and DOC sorption. *Geoderma* 159, 131-138.
- Guo, X., Luo, L., Ma, Y., Zhang, S.H., 2010. Sorption of polycyclic aromatic hydrocarbons on particulate organic matters. *J. Hazard. Mater.* 173, 130-136.
- Gupta, H., 2015. Removal of phenanthrene from water using activated carbon developed from orange rind. *Int. J. Sci. Res. Environ. Sci.* 3, 248-255.

- Harris, J.R., Rossington, D.R., 1968. Comparison of surface states of quartz, cristobalite, and silicic acid. *J. Am. Ceram. Soc.* 51, 511-518.
- Hassett, J.J., Means, J. C. , Banwart, W. L. , Wood, S. G. , Ali, S., Khan, A., 1980. Sorption of dibenzothiophene by soils and sediments. *J. Environ. Qual.* 9, 184-186.
- Hauser, L., Tandy, S., Schulin, R., Nowack, B., 2005. Column extraction of heavy metals from soils using the biodegradable chelating agent EDDS. *Environ. Sci. Technol.* 39, 6819-24.
- Hayes, M. H. B., MacCarthy, P., Malcolm, Jr., R. L., Swift, S., 1990. Humic Substances II: In Search of Structure, Wiley-Interscience.
- He, Y.W., Yediler, A., Sun, T.H., Kettrup, A., 1995. Adsorption of fluoranthene on soil and lava-effects of the organic-carbon contents of adsorbents and temperature. *Chemosphere* 30, 141-150.
- Hemond, H.F., Fechner-Levy, E.J., 2014. Chemical Fate and Transport in the Environment, Academic Press.
- Hiller, E., Jurkovic, L., Bartal, M., 2008. Effect of temperature on the distribution of polycyclic aromatic hydrocarbons in soil and sediment. *Soil Water Res.* 3, 231–240.
- Hizal, J., Apak., R., 2006. Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. *J. Colloid Interface Sci.* 295, 1-13.
- Ho, Y.S., 2006. Review of second-order models for adsorption systems. *J. Hazard. Mater.* 136, 681-689.
- Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451-465.
- Ho, Y.S., McKay, G., 1998. A comparison of chemisorption kinetics model applied to pollutants removal on various sorbents. *Process Saf. Environ. Prot.* 76, 322-340.

- Hu, X.L., Liu, J.F., Mayer, P., Jiang, G., 2008. Impacts of some environmentally relevant parameters on the sorption of polycyclic aromatic hydrocarbons to aqueous suspensions of fullerene. *Environ. Toxicol. Chem.* 27, 1868-1874.
- Hu, Y., He, Y., Wang, X., Wei, C., 2014. Efficient adsorption of phenanthrene by simply synthesized hydrophobic MCM-41 molecular sieves. *Appl. Surf. Sci.* 311, 825-830.
- Hwang, S., N. Ramirez, T. J. Cutright, and L. K. Ju., 2003. The role of soil properties in pyrene sorption and desorption. *Water Air Soil Pollut.* 143, 65-80.
- Hwang, S.C., Cutright, T.J., 2004. Adsorption/desorption due to system nonequilibrium and interaction with soil constituents. *J. Environ. Sci. Health Part A* 39, 1147–1162.
- Janos, P., Vavrova, J., Herzogova, L., Pilarova, V., 2010. Effects of inorganic and organic amendments on the mobility (leachability) of heavy metals in contaminated soil: a sequential extraction study. *Geoderma* 159, 335-341.
- Javier Rivas, F., García de la Calle, R., Alvarez, P., Acedo B., 2008. Polycyclic aromatic hydrocarbons sorption on soils: some anomalous isotherm. *J. Hazard. Mater.* 158, 375-8.
- Jiao, H., Bian, G., Chen, X., Wang, S., Zhouang, X., Bai, Z., 2017. Distribution, sources, and potential risk of polycyclic aromatic hydrocarbons in soils from an industrial district in Shanxi, China. *Environ. Sci. Pollut. Res.* 24, 12243-12260.
- Jin, H., Zhou, W., Zhu, L., 2013. Utilizing surfactants to control the sorption, desorption, and biodegradation of phenanthrene in soil-water system. *J. Environ. Sci.* 25, 1355-1361.
- Jones, K. D., Tiller, C. L., 1999. Effect of solution chemistry on the extent of binding of phenanthrene by a soil humic acid: a comparison of dissolved and clay bound humic. *Environ. Sci. Technol.* 33, 580-587.

- Kacker, T., Haupt, E. T., Garms, C., Francke, W., Steinhart, H., 2002. Structural characterisation of humic acid-bound PAH residues in soil by ^{13}C -CPMAS-NMR-spectroscopy: evidence of covalent bonds. *Chemosphere* 48, 117-131.
- Karickhoff, S., 1984. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.* 110, 707-735.
- Karickhoff, S.W., Brown, D.S., Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. *Water. Res.* 13, 241-248.
- Karnland, O., Pusch, R., Sandén, T., 1992. The importance of electrolyte on the physical properties of MX-80 bentonite (Report AR 92-35). SKB, Stockholm (in Swedish).
- Kaschl, A., Römhild, V., Chen, Y., 2002. Cadmium binding by fractions of dissolved organic matter and humic substances from municipal solid waste compost. *J. Environ. Qual.* 31, 1885 – 1892.
- Kaya, E.M.O., Ozcan, A.S., Gok, O., Ozcan, A., 2013. Adsorption kinetics and isotherm parameters of naphthalene onto natural and chemically modified bentonite from aqueous solutions. *Adsorpt.* 19, 879-888.
- Khodadoust, A. P., Reddy, K. R., Maturi, K., 2004, Removal of nickel and phenanthrene from kaolin soil using different extractants. *Environ. Eng. Sci.* 21, 691-704.
- Kim, D., Petrisor, I.G., Yen, T.F., 2005. Evaluation of biopolymer-modified concrete systems for disposal of cathode ray tube glass. *J. Air Waste Manage. Assoc.* 55, 961-969.
- Kim, D., Lai, H-T., Chilingar, G.V., Yen, T.F., 2006. Geopolymer formation and its unique properties. *Environ. Geol.* 51, 103-111.
- Killops, S.D., Killops, V. J., 1993. An Introduction to Organic Geochemistry, Longman Scientific & Technical, John Wiley & Sons.

- Kipling, J.J., 1965. Adsorption from Solution of Non-electrolytes. Academic Press, London.
- Ko, S.O., Schlautman, M.A., Carraway, E.R., 1998. Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. experimental studies. Environ. Sci. Technol. 32, 2769-2775.
- Kobayashi, T., Sumida, H., 2015. Effects of humic acids on the sorption and bioavailability of pyrene and 1,2-dihydroxynaphthalene. Soil Sci. Plant Nutr. 61, 113-122.
- Laird, D.A., Koskinen, W.C., 2008, Triazine soil interactions. In: LeBaron, H.M., McFarland, J.E., Burnside, O.C. (Eds), 2008. The Triazine Herbicides 50 Years Revolutionizing Agriculture.
- Lakshman, M.K., Kole, P.L., Chaturvedi, S., Saugier, J.H., Yeh, H.J.C., Glusker, J.P., Carrell, H.L., Katz, A.K., Afshar, C.E., Dashwood, W-M., Kenniston, G., Baird, W.M., 2000. Methyl group-induced helicity in 1,4-dimethylbenzo[c]phenanthrene and its metabolites: synthesis, physical, and biological properties. J. Am. Chem. Soc. 122, 12629-12636.
- Lamichhane, S., Bal Krishna, K.C., Sarukkalige, R., 2017. Surfactant-enhanced remediation of polycyclic aromatic hydrocarbons: A review. J. Environ. Manage. 199, 46-61.
- Lee, D.H., Cody, R.D., Kim, D.J., Choi, S., 2002. Effect of soil texture on surfactant-based hydrophobic organic remediation of contaminated soil. Environ. Int. 27, 681–688.
- Lemic, J., Tomasevic-Canovic, M., Adamovic, M., Kovacevic, D., Milicevic, S., 2007. Competitive adsorption of polycyclic aromatic hydrocarbons on organo-zeolites. Microporous Mesoporous Mater. 105, 317-323.
- Li, L.Y., 2006. Removal of multiple-metals from contaminated clay minerals. Environ. Technol. 27, 811-822.

- Li, L.Y., Li, R.S., 2000. The role of clay minerals and the effect of H⁺ ions on removal of heavy metal (Pb²⁺) from contaminated soils. *Can. Geotech. J.* 37, 296–307.
- Li, Y., Gupta, G., 1994. Adsorption/desorption of hydrocarbons on clay minerals. *Chemosphere* 28, 628-637.
- Li, G., Guo, S., Hu, J., 2016. The influence of clay minerals and surfactants on hydrocarbon removal during the washing of petroleum-contaminated soil. *Chem. Eng. J.* 286, 191-197.
- Liang, X., Guo, C., Liao, C., Liu, S., Wick, L.Y., Peng, D., Yi, X., Lu, G., Yin, H., Lin, Z., Dang, Z., 2017. Drivers and applications of integrated clean-up technologies for surfactant-enhanced remediation of environments contaminated with polycyclic aromatic hydrocarbons (PAHs). *Environ. Pollut.* 225, 129-140.
- Liang, X., Zhu, L., Zhuang, S., 2016. Sorption of polycyclic aromatic hydrocarbons to soils enhanced by heavy metals: perspective of molecular interactions. *J. soils sediments* 16, 1509-1518.
- Ling, W., Sun, R., Gao, X., Xu, R., Li, H., 2015, Low-molecular-weight organic acids enhance desorption of polycyclic aromatic hydrocarbons from soil. *Eur. J. Soil Sci.* 66, 339–347.
- Luo, L., Zhang, S. Z., Christie, P., 2010. New insights into the influence of heavy metals on phenanthrene sorption in soils. *Environ. Sci. Technol.* 44, 7846-7851.
- Luo, L., Lin, S., Huang, H., Zhang, S., 2012. Relationships between aging of PAHs and soil properties. *Environ. Pollut.* 170, 177-182.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber W.J. Westall, J.C., 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* 31, 3341-3347.

- Lyman, W. J., Reehl, W. F., Rosenblatt, D. H., 1990. Handbook of Chemical Property Estimation Methods. 2nd printing. American Chemical Society, Washington, DC.
- Mader, B.T., Goss, K.U., Eisenreich, S.J., 1997. Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. Environ. Sci. Technol. 31, 1079-1086.
- Mao, X., Jiang, R., Xiao, W., Yu, J., 2015. Use of surfactants for the remediation of contaminated soils: a review. J. Hazard. Mater. 285, 419-35.
- Maturi, K., Reddy, K.R., 2006. Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin. Chemosphere 63, 1022-1031.
- Maturi, K., Reddy, K.R., 2008. Extractants for the removal of mixed contaminants from soils. Soil Sediment Contam. 17, 586-608.
- McCarthy, J.F., Jimenez, B.D., 1985. Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation. Environ. Sci. Technol. 19, 1072-1076.
- McCarty, P.L., Rittmann, B.E., Reinhard, M., 1981. Trace organics in groundwater. Environ. Sci. Technol. 15, 40-51.
- Means, J.C., Wood, S.G., Hassett, J.J., Banwart, W.L., 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol. 14, 1524-1528.
- Morillo, E., Romero, A.S., Madrid, L., Villaverde, J., Maqueda, C., 2008. Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (Southern Spain). Water Air Soil Pollut. 187, 41–51.

- Mukhopadhyay, S., Mohd, A.H., Sahu, J.N., Yusoff, I., Sen, G.B., 2013. Comparison of a plant based natural surfactant with SDS for washing of As (V) from Fe rich soil. *J. Environ. Sci. (China)* 1, 247-256.
- Muller, S., Totsche, K.U., Kogel-Knabner, I., 2007. Sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Eur. J. Soil Sci.* 58, 918–931.
- Munoz, B., Albores, A., 2011. DNA damage caused by polycyclic aromatic hydrocarbons: mechanisms and markers. In: Chen, C. (ed.) *Selected Topics in DNA Repair*. InTech.
- Murray, B.M., 1994, Environmental Chemistry of Soils, Oxford University Press.
- Neale, C.N., Bricka, R.Y., Chao, A.C., 1997. Evaluating acids and chelating agents for removing heavy metals from contaminated soils. *Environ. Prog.* 16, 274-80.
- Nguyen, X.P., Cui, Y.J., Tang, A.M., Deng, Y.F., Li, X.L., Wouters, L., 2013. Effects of pore water chemical composition on the hydro-mechanical behavior of natural stiff clays. *Eng. Geol.* 166, 52-64.
- Obuekwe, I.S., Semple, K.T., 2013. Impact of Zn, Cu, Al and Fe on the partitioning and bioaccessibility of ¹⁴C-phenanthrene in soil. *Environ. Pollut.* 180, 180-189.
- Olu-Owolabi, B.I., Diagboya, P.N., Adebawale, K.O., 2014. Evaluation of pyrene sorption-desorption on tropical soils. *J. Environ. Manage.* 137, 1-9.
- Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), 2016. Classifying Prime and Marginal Agricultural Soils and Landscapes: Guidelines for Application of the Canada Land Inventory in Ontario. <http://www.omafra.gov.on.ca/english/landuse/classify.htm>, Accessed, 26.08.2016.

Organization for Economic Cooperation and Development (OECD), 2000. Adsorption - Desorption Using a Batch Equilibrium Method. OECD Guideline for the Testing of Chemicals.

Osagie, E.I., Owabor, C.N., 2015a. Adsorption of naphthalene on clay and sandy soil from aqueous solution. *Adv. Chem. Eng. Sci.* 5, 476-483.

Osagie, E.I., Owabor, C.N., 2015b. Adsorption of pyrene from aqueous solution by clay and sandy soil. *Adv. Chem. Eng. Sci.* 5, 345-351.

Panagos, P., Van Liedekerke, M., Yigini, Y., Montanarella, L., 2013. Contaminated sites in Europe: review of the current situation based on data collected through a European network. *J Environ. Public Health* 158764.

Peng, L., Liu, P., Feng, X., Wang, Z., Cheng, T., Liang, Y., Lin, Z., Shi, Z., 2018a. Kinetics of heavy metal adsorption and desorption in soil: developing a unified model based on chemical speciation. *Geochim. Cosmochim. Acta* 224, 282–300.

Peng, L., Shi, Z., Wang, P., Li W., Lin, Z., Dang, Z., Sparks, D.L., 2018b. A novel multi-reaction model for kinetics of Zn release from soils: Roles of soil binding sites. *J. Colloid Interface Sci.* 514, 146-155.

Petrovic, M., Kastelan-Macan, M., Horvat, A. J., 1999. Interactive sorption of metal ions and humic acids onto mineral particles. *Water Air Soil Pollut.* 111, 41-56.

Pignatello, J.J., Xing, B., 1995. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* 30, 1-11.

Ping, L., Luo, Y., Wu, L., Qian W., Song, J., Christie, P., 2006. Phenanthrene adsorption by soils treated with humic substances under different pH and temperature conditions. *Environ. Geochem. Health* 28, 189-195.

Podoll, R.T., Irwin, K.C., Parish, H.J., 1989. Dynamic studies of naphthalene sorption on soil from aqueous-solution. Chemosphere 18, 2399-2412.

Polubesova, M., Chen, Y., Stefan, C., Selle, M., Werner, P., Chefetz, B., 2009. Sorption of polycyclic aromatic compounds by organic matter-coated Ca^{2+} and Fe^{3+} montmorillonite. Geoderma 154, 36-41.

Portal for Soil and Water Management in Europe (EUGRIS), 2018.

Prieto-Taboada, N., Ibarrodo, I., Gómez-Laserna, O., Martínez-Arkarazo, I., Olazabal, M.A., Madariaga, J.M., 2013. Buildings as repositories of hazardous pollutants of anthropogenic origin. J. Hazard. Mater. 248-249, 451-460.

Push, R., 2001. Experimental study of the effect of high porewater salinity on the physical properties of a natural smectitic clay (Technical Report TR-01-07). SKB, Stockholm.

Putra, E.K., Pranowo, R., Sunarso, J., Indraswati, N., Ismadji, S., 2009. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics. Water Res. 43, 2419-2430.

Raber, B., Kogel-Knabner, I., Stein, C., Klem, D., 1998. Partitioning of polycyclic aromatic hydrocarbons to dissolved organic matter from different soils. Chemosphere 36, 79-97.

Ravanipour, M., Kalantary, R.R., Mohseni-Bandpi, A., Esrafili, A., Farzadkia, A., Hashemi-Najafabadi, S., 2015. Experimental design approach to the optimization of PAHs bioremediation from artificially contaminated soil: application of variables screening development. J. Environ. Health Sci. Eng. 13, 22. <https://doi.org/10.1186/s40201-015-y>

- Reddy, K.R., Cameselle, C., 2009. Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater. John Wiley & Sons
- Reed, B.E., Carriere, P.C., Moore, R., 1996. Flushing of a Pb (II) contaminated soil using HCl, EDTA, and CaCl₂. *J. Environ. Eng.* 122, 48-50.
- Rhodes, A.H., Riding, M.J., McAllister, L.E., Lee, K., Semple, K.T., 2012. Influence of activated charcoal on desorption kinetics and biodegradation of phenanthrene in soil. *Environ. Sci. Technol.* 46, 12445-1245.
- Saeedi, M., Li, L.Y., Grace, J.R., 2018a. Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals. *Environ. Earth. Sci.* 77, 305.
- Saeedi, M., Li, L.Y., Grace, J.R., 2018b. Desorption and mobility mechanisms of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals. *J. Environ. Manage.* 214, 204-214.
- Saichek, R.E., Reddy, K.R., 2005. Electrokinetically enhanced remediation of Hydrophobic Organic Compounds in soils: A Review. *Crit. Rev. Environ. Sci. Technol.* 35, 115-192.
- Saichek, R.E., Reddy, K.R., 2004. Evaluation of surfactants/cosolvents for desorption/solubilization of phenanthrene in clayey soils. *Int. J. Environ. Stud.* 61, 587-604.
- Saison, C., Perrin-Ganier, C., Amellal, S., Morel, J.L., Schiavon, M., 2004. Effect of metals on the adsorption and extractability of ¹⁴C-phenanthrene in soils. *Chemosphere* 55, 477–485.
- Salehian, E., Khodadadi, A., Hosseini, B., 2012. Remediation of diesel contaminated soils using surfactants: column study. *Am. J. Environ. Sci.* 8, 352-359.

- Sales, P.S., Fernandez, M.A., 2016. Synergism in the desorption of polycyclic aromatic hydrocarbons from soil models by mixed surfactant solutions. Environ. Sci. Pollut. Res. 23, 10158–10164.
- Sánchez-Trujillo, M.A., Morillo, E., Villaverde, J., Lacorte, S., 2013. Comparative effects of several cyclodextrins on the extraction of PAHs from an aged contaminated soil. Environ. Pollut. 178, 52-58.
- Saparpakorn, P., Kim, J.H., Hannongbua, S., 2007. Investigation on the binding of polycyclic aromatic hydrocarbons with soil organic matter: a theoretical approach. Mol. 12, 703-715.
- Shor, L.M., Rockne, K.J., Taghon, G.L., Young, L.Y., Kosson, D.S., 2003. Desorption kinetics for field-aged polycyclic aromatic hydrocarbons from sediments. Environ. Sci. Technol. 37, 1535-1544.
- Schwarzenbach, R.P., Westall, J., 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. Environ. Sci. Technol. 15, 1360-1367.
- Semple, K.T., Doick, K.J., Wick, L.Y., Harms, H., 2007. Microbial interactions with organic contaminants in soil: definitions, processes and measurement: a review. J. Environ. Pollut. 150, 166-176.
- Shaker, A.M., Komy, Z.R., Heggy, S.E.M., El-Sayed, M.E.A., 2012. Kinetic study for adsorption humic acid on soil minerals. J. Phys. Chem. A. 116, 10889-10896.
- Sherene, T., 2010. Mobility and transport of heavy metals in polluted soil environment. Biol. Forum Int. J. 2, 112-121.
- Shin, K.H., Kim, K.W., Ahn, Y., 2006. Use of biosurfactant to remediate phenanthrene-contaminated soil by the combined solubilization-biodegradation process. J. Hazard. Mater. 137, 1831–1837.

- Soler-Rovira, P., Madejon, E., Madejon, P., Plaza, C., 2010. In situ remediation of metal-contaminated soils with organic amendments: Role of humic acids in copper bioavailability. *Chemosphere* 79, 844-849.
- Song, S., Zhu, L., Zhou, W., 2008. Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin a plant-derived biosurfactant. *Environ. Pollut.* 156, 1368–1370.
- Stevenson, F., Goh, K., 1971. Infrared spectra of humic acids and related substances. *Geochim. Cosmochim. Acta* 35, 471-483.
- Strawn, D. G., Sparks, D. L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb (II) sorption and desorption in soil. *Soil Sci. Soc. Am. J.* 6, 144-156.
- Su, C., Jiang, L.Q., Zhang, W.J., 2014. A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. *Environ. Skeptics Critics* 3, 24-38.
- Suffet, I.H., MacCarthy, P., 1989. Aquatic Humic Substances: Influence of Fate and Treatment of Pollutants. American Chemical Society.
- Sun, D., Li, X., Lou, L., 2010. On the Research of adsorption of polycyclic aromatic hydrocarbons (Phenanthrene) in soil-groundwater in Zhangshi irrigation district. *Procedia Environ. Sci.* 2, 824–83.
- Tao, Y., Li, W., Xu, B., Zhong, J., Yao, Sh., Wu, Q., 2013. Different effects of copper (II), cadmium (II) and phosphate on the sorption of phenanthrene on the biomass of cyanobacteria. *J. Hazard. Mater.* 261, 21–28.

- Thavamani, P., Megharaj, M., Krishnamurti, G.S.R., McFarland, R., Naidu, R. 2011. Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: implications to bioremediation. *Environ. Int.* 37, 184–189.
- Thavamani, P., Megharaj, M., Naidu, R., 2012. Multivariate analysis of mixed contaminants (PAHs and heavy metals) at manufactured gas plant site soils. *Environ. Monit. Assess.* 184, 3875–3885.
- Traina, S.J., Spontak, D.A., Logan, T., 1989. Effects of cations on complexation of naphthalene by water-soluble organic carbon. *J. Environ. Qual.* 18, 221-227.
- Troeh, F.R., Thompson, L.M., 2005. Soils and soil fertility. 6th ed. Ames, Iowa: Blackwell Pub.
- Ukalska-Jaruga, A., Smreczak, B., Klimkowicz-Pawlas, A., 2018. Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons. *J. Soils Sediments* 19,1890-1900.
- United Nations Environment Program (UNEP), 2012. GEO5 Global Environment Outlook, Environment for the Future We Want.
- United States Environmental Protection Agency (USEPA), 2019. National priorities list. <https://www.epa.gov/superfund/superfund-national-priorities-list-npl>. Accessed Feb. 16, 2019.
- United States Environmental Protection Agency (USEPA), 2018. <https://www.epa.gov/cleanups/cleanups-where-you-live>, Accessed 10, Feb. 2018.
- United States Environmental Protection Agency (USEPA), 1993. Provisional Guidance for Quantitative Risk Assessment of PAH, EPA/600/R-93/089. Washington, DC.

United States Environmental Protection Agency (USEPA), 2008. Polycyclic Aromatic Hydrocarbons (PAHs). Available online at:

<http://www.epa.gov/wastes/hazard/Wastemin/minimize/factshts/pahs.pdf>.

United States Environmental Protection Agency (USEPA), 2004a. Cleaning up the Nation's Waste Sites : Markets and Technology Trends, Washington, DC.

United States Environmental Protection Agency (USEPA), 2004b. Soil and Waste pH. Method 9045 D.

United States Environmental Protection Agency (USEPA), 1986a. Cation Exchange Capacity of Soils (Sodium Acetate). EPA-Method 9081.

United States Environmental Protection Agency (USEPA), 1986b. Method 8100, Polynuclear Aromatic Hydrocarbons. EPA-Method 8100.

United States Environmental Protection Agency (USEPA), 1996a. Acid Digestion of Sediments, Sludges and Soils. EPA-Method 3050B.

United States Environmental Protection Agency (USEPA), 1996b. Soxhlet Extraction EPA-Method 3540C.

United States Environmental Protection Agency (USEPA), 1992. Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy. EPA-Method 3010A.

Vandevivere, P., Hammes, F., Verstraete, W., Feijtel, T., Chowanek, D., 2001. Metal decontamination of soil, sediment, and sewage sludge by means of transition metal chelant [S,S]-EDDS. *J. Environ. Eng.* 127, 802–811.

Villar, M.V., 2005. MX-80 bentonite. Thermo-hydro-mechanical characterisation performed at CIEMAT in the context of the prototype project. (Informes Técnicos 1053). CIEMAT, Madrid, Departamento de Impacto Ambiental de la Energía.

Wahid, P.A., Sethunathan, N., 1979. Sorption-desorption of .alpha., .beta., and .gamma. isomers of hexachlorocyclohexane in soils. *J. Agric. Food Chem.* 27, 1050-1053.

Walter, J., Weber, W.J. Jr., 2002. Distributed reactivity model for sorption by soils and sediments: 15. High-concentration co-contaminant effects on phenanthrene sorption and desorption. *Environ. Sci. Technol.* 36, 3625–3634.

Wan, J., Wang, L., Lu, X., Lin, Y., Zhang, S., 2011. Partitioning of hexachlorobenzene in a kaolin/humic acid/surfactant/water system: combined effect of surfactant and soil organic matter. *J. Hazard. Mater.* 196, 79-85.

Wang, G., Mielke, H., Quach, V., Gonzales, C., Zhang, Q., 2004. Determination of polycyclic aromatic hydrocarbons and trace metals in New Orleans soils and sediments. *Soil Sediment Contam.* 13, 1–15.

Wang, G., Zhou, Y., Wang, X., Chai, X., Huang, L., Deng, N., 2010. Simultaneous removal of phenanthrene and lead from artificially contaminated soils with glycine- β -cyclodextrin. *J. Hazard. Mater.* 184, 690–695.

Wang, L., Niu, J., Yang, Z., Shen, Z., Wang, J., 2008. Effects of carbonate and organic matter on sorption and desorption behavior of polycyclic aromatic hydrocarbons in the sediments from Yangtze River. *J. Hazard. Mater.* 154, 811-817.

Wang, J., Wang, C., Huang, Q., Ding, F., He, X., 2015. Adsorption of PAHs on the sediments from the yellow river delta as a function of particle size and salinity. *Soil Sediment Contam.* 24, 103-115.

- Weber, W.J. Jr, Kim, S.H., Johnson, M.D., 2002. Distributed reactivity model for sorption by soils and sediments: 15. High-concentration co-contaminant effects on phenanthrene sorption and desorption. Environ. Sci. Technol. 36, 3625–3634.
- Weber, W.J. Jr., McGinley, P.M., Katz, L.E., 1991, Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport. Water Res. 25, 499-528.
- Weber, W.J. Jr., McGinley, P.M., Katz, L.E., 1992. Distributed reactivity model for sorption by soils and sediments.1. Conceptual basis and equilibrium assessments. Environ. Sci. Technol. 26, 1955-1962.
- Wei, Y.F., Liang, X.J., Lin, W.J., Guo, C.L., Dang, Z. 2015. Clay mineral dependent desorption of pyrene from soils by single and mixed anionic-nonionic surfactants. Chem. Eng. J. 264, 807-814.
- Wen, Y., Ehsan, S., Marshall, W. D., 2012. Simultaneous mobilization of macro-and trace elements (MTEs) and polycyclic aromatic hydrocarbon (PAH) compounds from soil with a nonionic surfactant and [S,S]-ethylenediaminedisuccinic acid (EDDS) in admixture: PAH compounds. J. Hazard. Mater. 199, 240-246.
- Wick, A.F., Haus, N.W., Sukkariyah, B.F., Haering, K.C., and Daniels, W.L., 2011. Remediation of PAH-contaminated soils and Sediments: a literature review. Virginia Polytechnic Institute and State University.
- Weston, N.B., Giblin, A.E., Banta, G.T., Hopkinson, C.S., Tucker, J., 2010. The effects of varying salinity on ammonium exchange in estuarine sediments of the parker river, Massachusetts. Estuaries Coasts 33, 985-1003.
- Wolcott, A. R., Shin, Y-Oh, Chodan, J. J., 1970. Adsorption of DDT by soils, soil fractions, and biological materials. J. Agric. Food Chem. 18, 1129-1133.

- Wong, J. S., R. E. Hicks, and R. F. Probstein, 1997. EDTA-enhanced electroremediation of metal-contaminated soils. *J. Hazard. Mater.* 55, 61-79.
- Wu, P., Tang, Y., Wang, W., Zhu, N., Li, P., Wu, J., Dang, Z., Wang, X., 2011. Effect of dissolved organic matter from Guangzhou landfill leachate on sorption of phenanthrene by Montmorillonite. *J. Colloid. Interface Sci.* 361, 618–627.
- Yang, Y., Ratte, D., Smets, B.F., Pignatello, J.J., Grasso, D., 2001. Mobilization of soil organic matter by complexing agents and implications for polycyclic aromatic hydrocarbon desorption. *Chemosphere*, 43, 1013-1021.
- Yang, Y., Tao, S., Zhang, N., Zhang, D.Y., Li, X.Q., 2010. The effect of soil organic matter on fate of polycyclic aromatic hydrocarbons in soil: a microcosm study. *Environ. Pollut.* 158, 1768-74.
- Yang, Y., Zhang, N., Xue, M., Tao, S., 2010. Impact of soil organic matter on the distribution of polycyclic aromatic hydrocarbons (PAHs) in soils. *Environ. Pollut.* 158, 2170-2174.
- Yang, Z., Zhang, S., Liao, Y., Li, Q., Wu, B., Wu, R., 2012. Remediation of heavy metal contamination in calcareous soil by washing with reagents: A column washing. *Procedia Environ. Sci.* 16, 778-785.
- Yang, L., Jin, M., Tong, C., Xie, S., 2013. Study of dynamic sorption and desorption of polycyclic aromatic hydrocarbons in silty-clay soil. *J. Hazard. Mater.* 244-245, 77-85.
- Yaron, B., Swoboda, A.R., Thomas, G.W., 1967. Aldrin adsorption by soils and clays. *J. Agric. Food Chem.* 15, 671–675.
- Ye, M., Sun, M., Wan, J., Fang, G., Li, H., Hu, F., Jiang, X., Kengara, F.O., 2015. Evaluation of enhanced soil washing process with tea saponin in a peanut oil-water solvent system for the

- extraction of PBDEs/PCBs/PAHs and heavy metals from an electronic waste site followed by vetiver grass phytoremediation. *J. Chem. Technol. Biotechnol.* 90, 2027-2035.
- Yeom, I.T., Ghosh, M.M., Cox, C.D., 1996. Kinetic aspects of surfactant solubilization of soil-bound polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 30, 1589-1595.
- Yu, H., Xiao, H., Wang, D., 2014. Effects of soil properties and biosurfactant on the behavior of PAHs in soil-water systems. *Environ. Sys. Res.* 3, 6.
- Yu, H., Huang, G.H., An, C.J., Wei, J., 2011. Combined effects of DOM extracted from site soil/compost and biosurfactant on the sorption and desorption of PAHs in a soil-water system. *J. Hazard. Mater.* 190, 883-890.
- Yuan, S., Tian, M., Lu, X.H., 2006. Electrokinetic movement of hexachlorobenzene in clayed soils enhanced by Tween 80 and beta-cyclodextrin. *J. Hazard. Mater.* 137, 1218–1225.
- Yuan, S., Wu, X., Wan, J., Long, H., Lu, X., Wu, X., Chen, J., 2010. Enhanced washing of HCB and Zn from aged sediments by TX-100 and EDTA mixed solutions. *Geoderma* 156, 119-125.
- Yuan, S., Shu, Z., Wan, J., Lu, X., 2007. Enhanced desorption of hexachlorobenzene from kaolin by single and mixed surfactants. *J. Colloid Interface Sci.* 314, 168-175.
- Zeledon-Toruno, Z.C., Lao-Luque, C., de Las Heras, F.X., Sole-Sardans, M., 2007. Removal of PAHs from water using an immature coal (leonardite). *Chemosphere* 67, 505-512.
- Zhang, M.K., Ke, Z.X., 2004. Copper and zinc enrichment in different size fractions of organic matter from polluted soils. *Pedosphere* 14, 27–36.
- Zhang, W., Lo, I. M., 2006. EDTA-enhanced washing for remediation of Pb-and/or Zn-contaminated soils. *J. Environ. Eng.* 132, 1282-1288.

- Zhang, W., Cao, J., Huang, H., Zhang, R., 2010. Effect of coexisting lead and phenanthrene on their individual sorption on a clayish soil. *Soil Sediment Contam.* 19, 322-337.
- Zhang, W., Zhuang, L., Yuan, Y., Tong, L., Tsang, D.C.W., 2011a. Enhancement of phenanthrene adsorption on a clayey soil and clay minerals by coexisting lead or cadmium. *Chemosphere* 83, 302–310.
- Zhang, L.C., Luo, L., Zhang, S.Z., 2011b. Adsorption of phenanthrene and 1,3-dinitrobenzene on cation-modified clay minerals. *Colloids Surf. A Physicochem. Eng. Asp.* 377, 278-283.
- Zhang, W., Zheng, J., Zheng, P., Tsang, D.C.W., Qiu, R., 2015. The roles of humic substances in the interactions of phenanthrene and heavy metals on the bentonite surface. *J. Soils Sediments* 15, 1463–1472.
- Zhou, W., Zhu, L., 2007. Efficiency of surfactant-enhanced desorption for contaminated soils depending on the component characteristics of soil-surfactant PAHs system. *Environ. Pollut.* 14, 66-73.
- Zhou, W., Zhu, L., 2005. Distribution of polycyclic aromatic hydrocarbons in soil-water system containing a nonionic surfactant, *Chemosphere* 60, 1237-1245.
- Zhu, D., Herbert, B.E., Schlautman, M.A., Carraway, E.R., Hur, J., 2004. Cation-Pi bonding: a new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *J. Environ. Qual.* 33, 1322-1330.

Appendices

Appendix A Minerals and materials characterization

HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name	:	100NM	Median Size	:	384.82361(μm)
ID#	:	201405061009723	Mean Size	:	417.71686(μm)
Data Name	:	201405061009723	Variance	:	27534(μm ²)
Transmittance(R)	:	87.2(%)	Std.Dev.	:	165.9349(μm)
Transmittance(B)	:	90.6(%)	Mode Size	:	369.9059(μm)
Circulation Speed	:	5	Span	:	0.9946
Agitation Speed	:	5	Geo.Mean Size	:	389.6725(μm)
Ultra Sonic	:	00:20 (7)	Geo.Variance	:	1.0606(μm ²)
Form of Distribution	:	Auto	Skewness	:	1.4934
Distribution Base	:	Volume	Kurtosis	:	6.4617
Material	:		Diameter on Cumulative %	:	(1)5.000 (%) - 216.0999(μm)
Source	:			:	(2)10.00 (%) - 245.5742(μm)
Lot Number	:	BCL		:	(3)20.00 (%) - 286.4708(μm)
Test or Assay. Number	:			:	(4)30.00 (%) - 319.9784(μm)
Refractive Index (R)	:	1.60-0i in water[RI=1.60(1.600 - 0.000i), Water(1.333)]		:	(5)40.00 (%) - 352.3098(μm)
Refractive Index (B)	:	1.60-0i in water[RI=1.60(1.600 - 0.000i), Water(1.333)]		:	(6)60.00 (%) - 421.7077(μm)
				:	(7)70.00 (%) - 465.3403(μm)

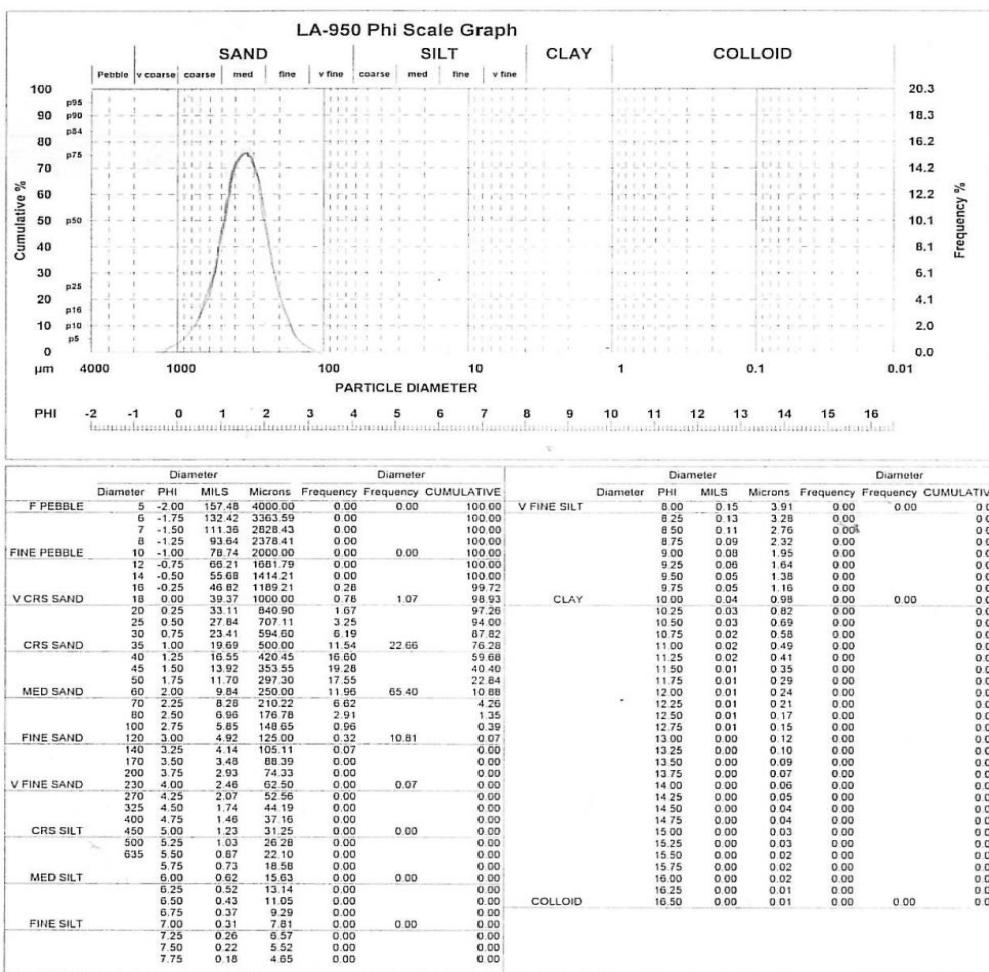


Figure A1 Particle sizing results for sand used in experiments

HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name	100NM	Median Size	8.03936(μm)
ID#	201405061031727	Mean Size	9.89867(μm)
Data Name	MMT-D	Variance	62.810(μm ²)
Transmittance(R)	89.7(%)	Std.Dev.	7.9253(μm)
Transmittance(B)	80.2(%)	Mode Size	9.4526(μm)
Circulation Speed	5	Span	2.1934
Agitation Speed	5	Geo Mean Size	7.1227(μm)
Ultra Sonic	01:20 (7)	Geo.Variance	1.40956(μm ²)
Form of Distribution	Auto	Skewness	1.7589
Distribution Base	Volume	Kurtosis	7.2237
Material		Diameter on Cumulative %	(1)5.000 (%) - 1.5138(μm)
Source			(2)10.00 (%) - 2.1404(μm)
Lot Number	BCL		(3)20.00 (%) - 3.5156(μm)
Test or Assay. Number			(4)30.00 (%) - 5.0549(μm)
Refractive Index (R)	1.60-0i in water[Ri=1.60(1.600 - 0.000i),Water(1.333)]		(5)40.00 (%) - 6.5328(μm)
Refractive Index (B)	1.60-0i in water[Ri=1.60(1.600 - 0.000i),Water(1.333)]		(6)60.00 (%) - 9.7172(μm)
			(7)70.00 (%) - 11.7287(μm)

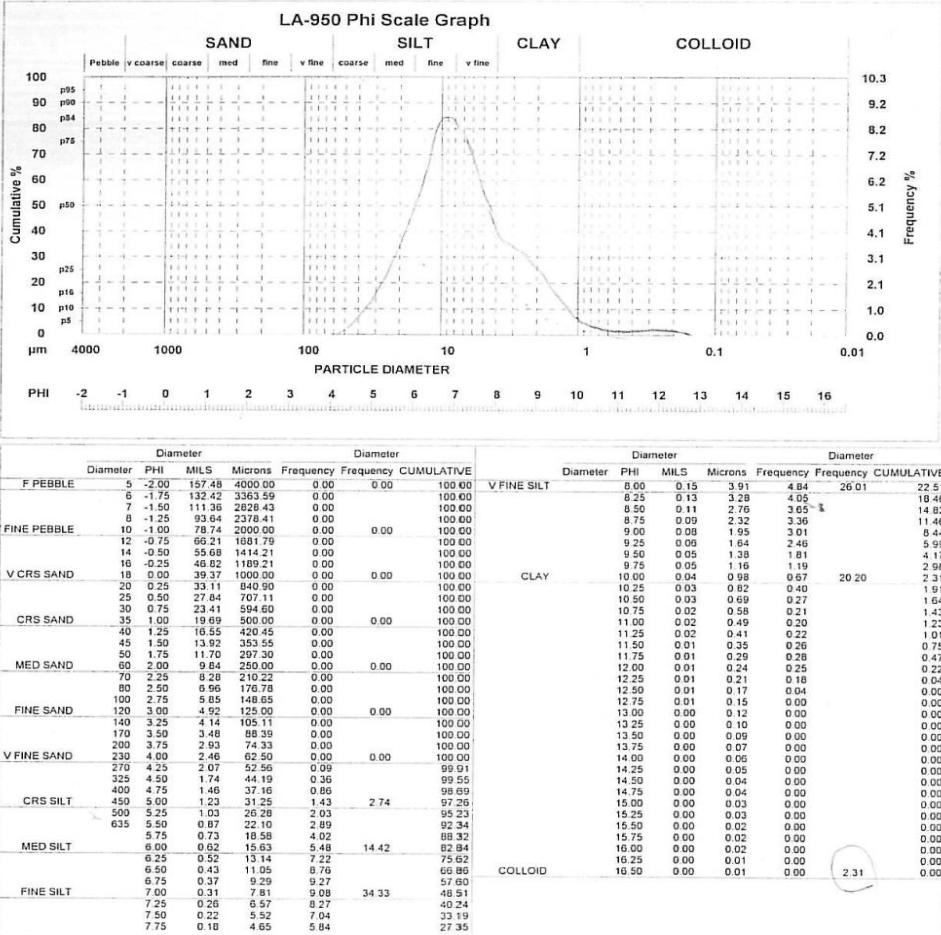


Figure A2 Particle sizing results for bentonite used in the experiments

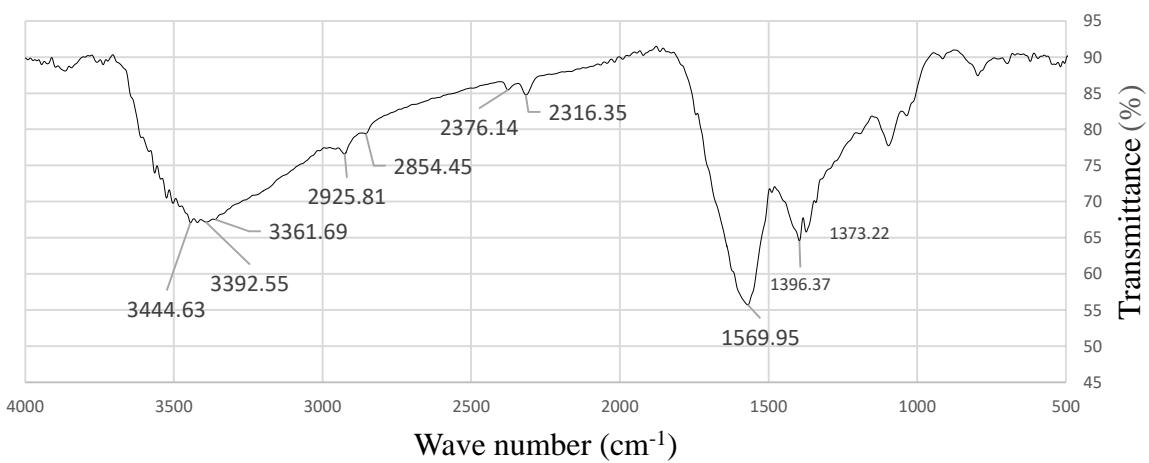


Figure A3 FTIR spectrum of Humax used in this research

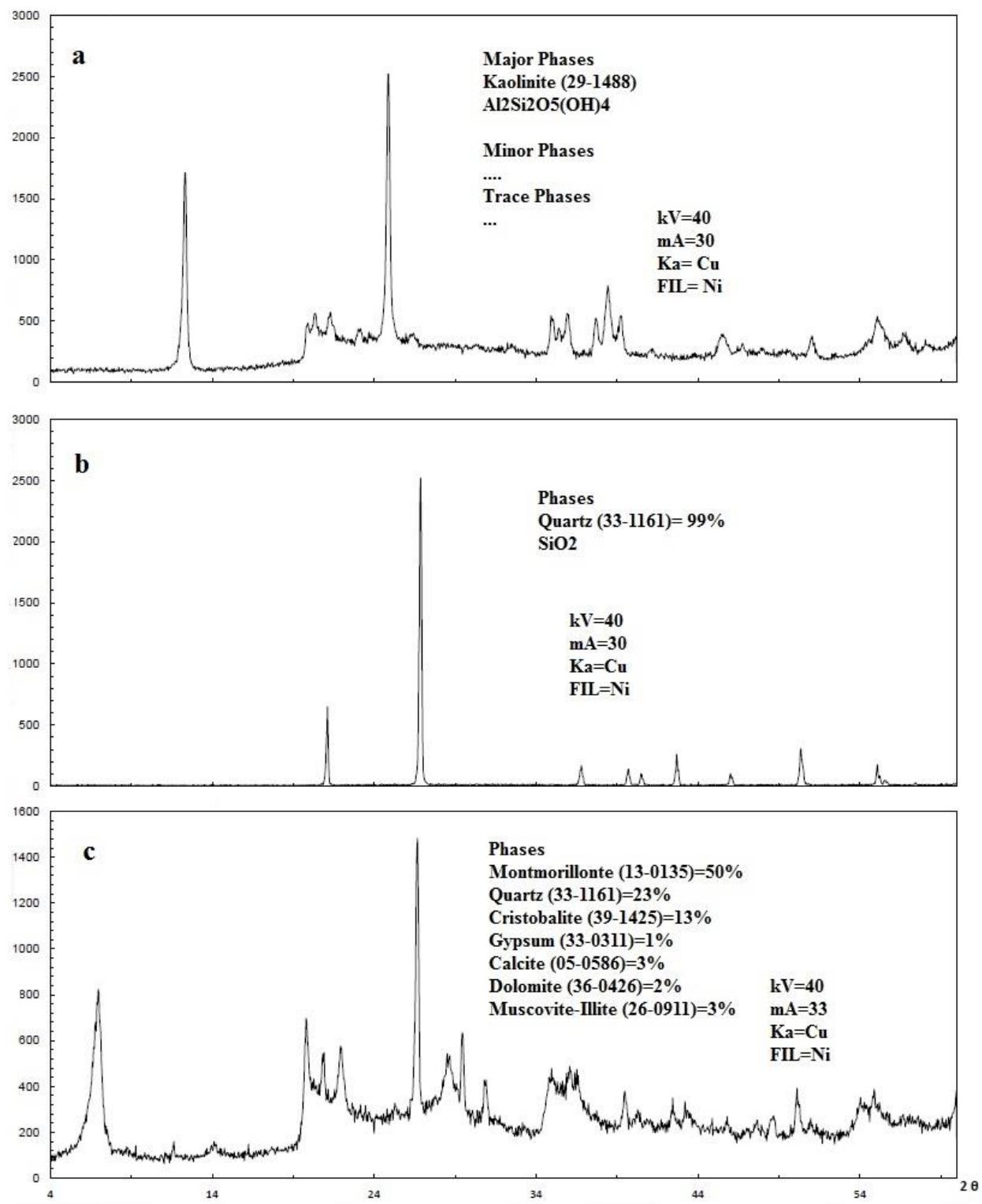


Figure A4 XRD spectra of three base soils used for blending, a) Kaolin, b) Ottawa sand, c) Bentonite

Appendix B Quality assurance and quality control (QA/QC)

A PAH standard (CRM 47940, Supelco) was used to confirm the GC calibration. The detection limits were obtained from triplicate analysis blanks prepared with the same procedure as the actual samples. For heavy metal measurement quality assurance, the certified reference material, PACS-2, was used. Analyzed metal concentrations were within the range recommended by NRC (2000) (Table B1). Calibration curves with $R^2 > 0.99$ were used for metal analysis. Repeatability of instrumental analyses was confirmed by triplicate reading of concentrations in digested samples with relative standard deviation (RSD) $< 1.5\%$. Duplicate column experiments showed precision of 93-96%. Accuracy was evaluated by recovery tests of sample spikes, with the percentage recoveries calculated based on:

$$\% \text{ Recovery} = [(\text{concentration in spiked sample} - \text{concentration in unspiked sample})/\text{actual spike concentration}] \times 100\%$$

Recoveries for spiked heavy metals and PAHs are presented in Table B2. Concentrations of contaminants used to calculate removal efficiencies were corrected for their recoveries.

Table B1 Published and measured heavy metals in PACS-2 samples (mg kg^{-1})

Heavy metal	Published concentration	Average measured concentration
Ni	39.5 ± 2.3	38.7
Pb	183 ± 8.0	184.3
Zn	364 ± 23.0	371.3

Table B2 Recovery test results of contaminants for a soil matrix spiked sample

Contaminant	Initial concentration in soil (mg kg ⁻¹)	Target concentration (mg kg ⁻¹)	Added concentration (mg kg ⁻¹)	Measured concentration in spiked sample (mg kg ⁻¹)	Recovery ^a (%)
Ni	29.5±0.30	700	670.5	680±9.0	97.1±1.2
Pb	9.9±0.10	5000	4990	4755±45	95.1±1.0
Zn	42.4±0.60	1000	957.5	975±12	97.5±1.2
ANA	1.1±0.0	500	499.0	459±17	91.7±3.4
FL	1.2±0.0	500	499.0	458±21	91.5±4.2
FLAN	1.4±0.0	500	498.6	456±23	91.2±4.6

^a Recovery= (measured concentration in spiked sample)/(initial concentration+added concentration)

All batch experiments were conducted in duplicate for quality control of the experiments. For all batch experiments, vials containing the PAHs in the absence of solid materials were also tested based on the same procedure to account for possible losses resulting from degradation, photolysis, volatilization and wall adsorption. Losses were found to be negligible.

Appendix C Column tests soil particle sizing

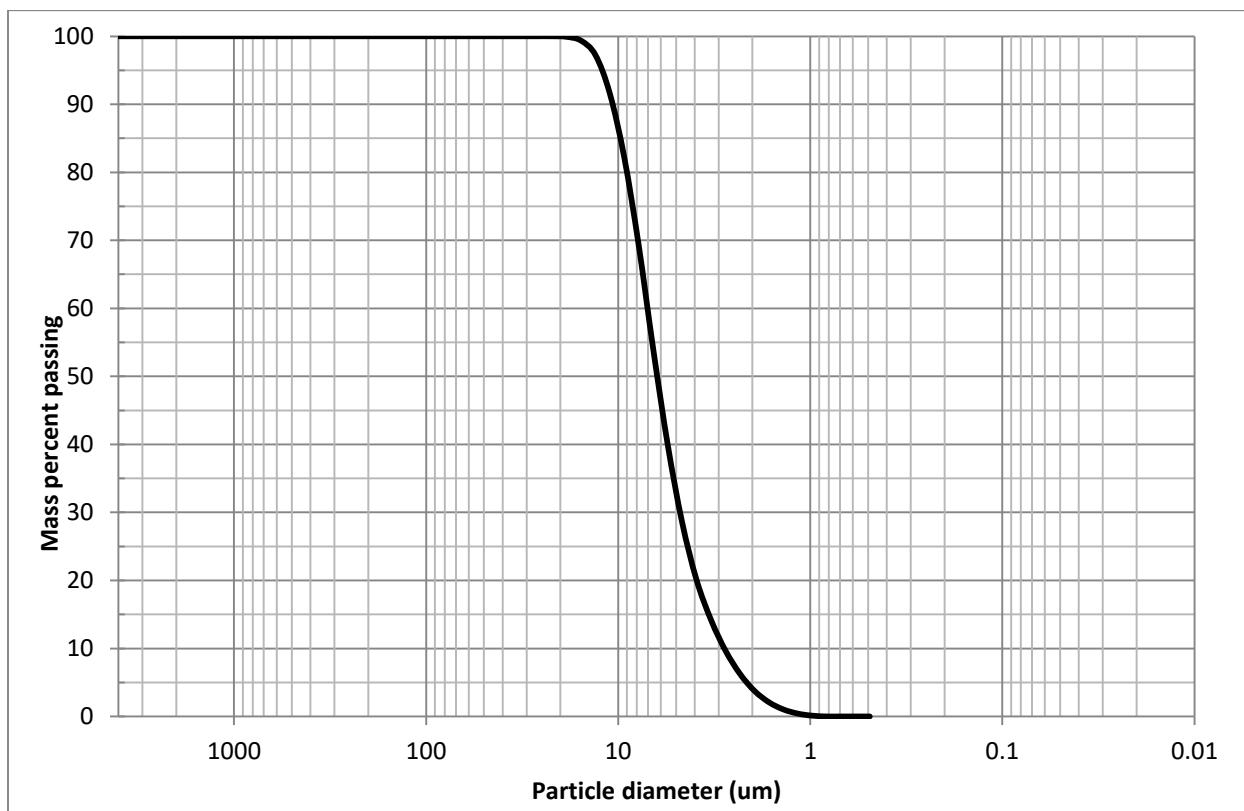


Figure C1 Particle size distribution for soil used in column experiments

Appendix D Comparison of final contaminants concentration with soil quality guidelines

Table D1 compares the concentrations of ANA, FL, FLAN, Ni, Pb and Zn in real spiked soil after 21 pore volume flushing of Triton X-100 (7.5 %)+EDTA (0.01 M) at a low flow rate (0.456 mL min⁻¹) in column experiments with values from British Columbia (BC) numerical soil standards of contaminated sites for industrial land use.

Table D1 Comparison of contaminants concentration in treated soil and BC contaminated sites standards^a for industrial land use

	Contaminant (mg kg ⁻¹)					
	Ni	Pb	Zn	ANA	FL	FLAN
Soil flushing column test, soil concentration after treatment	102	1188	98	197	229	257
<hr/>						
Standards						
Numerical soil standard (toxicity to soil invertebrates and plants)	250	1000	450	-	-	200
Generic numerical soil standard to protect human health (residential low density)	-	-	-	950	600	-

^aSource: Environmental Management Act, Contaminated Sites Regulation, B.C. Reg. 375/96, Deposited December 16, 1996 and effective April 1, 1997, Last amended January 24, 2019 by B.C. Reg. 13/2019.