CHARACTERIZATION AND REMEDIATION OF TOXIC METALS IN WASTEWATER REUSE FOR AGRICULTURAL IRRIGATION

BY

STEPHEN MATHIAS ANDERSON

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Agricultural and Biological Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2010

Urbana, Illinois

Master's Committee:

Professor Prasanta K. Kalita, Chair
Associate Professor Richard A. C. Cooke
Professor Michael C. Hirschi
Dr. Khajanchi Lal, Central Soil Salinity Research Institute, Karnal, India

ABSTRACT

Expanding agricultural water demand has led to the reuse of wastewaters for irrigation purposes. Left untreated, these reused wastewaters may contaminate agricultural land, plants, and thereby food products. Common contaminants include toxic metals, which are conservative within the soil-plant-water system.

While conventional treatment of these waste streams is possible the treatment is resource intensive leaving it beyond the reach of many developing nations. Inventory of metals in the plant-soil-water system may reveal health exposure risks, or may suggest metal buildup is below levels of concern. Accurate inventory takes into account the chemical pool into which soil metals are bound, and thus resultant mobility within the soil system.

Where reduced soil metal loadings are desirable, a variety of inexpensive sorbents have been suggested to remove toxic metals in place of activated carbon. While involved research efforts have evaluated the field of possible sorbents in great depth little comparative research has been done, and the methods utilized have eased laboratory distinctions at the cost of modifying the system from its native conditions.

This research utilizes Tessier's method of sequential extractions to inventory metals in different chemical pools (Tessier et al., 1979). A field of inexpensive and widely available sorbents, including sugarcane bagasse, ground rice husk, and sawdust, is compared against the conventional metal removal techniques of activated carbon sorption and gypsum pH modification for chemical precipitation.

A large percentage of metals present are bound to the soil reducible fraction, which may be mobile due to repetitive anoxic conditions under flood irrigation practices. Metal concentrations were higher in fields irrigated with groundwater over contaminated surface waters, suggesting metal groundwater contamination is present. Overall, bagasse, rice husk, and sawdust performed similarly but well below the performance of the activated carbon standard.

The results indicate possible treatment methods and materials for industrial wastewater that can be used for irrigation or used as supplemental irrigation in Indian conditions. Locally available low-cost materials show great promise to be used as metal removal media. Further investigation with small plots or field scales would be necessary to confirm the benefit of results found in this study to make a realistic impact on Indian agriculture.

For those who taught me about boundaries.

ACKNOWLEDGMENTS

I would like to acknowledge the following for the assistance and support shown to me during this graduate work:

Dr. Prasanta Kalita, my advisor and mentor;

The staff at CSSRI, and particularly **Dr. Khajanchi Lal**, who were kind to a farmboy from Illinois in a foreign land;

Dr. Inayat Khan, who tolerated an engineer’s never-ending questions in a chemistry lab;

Rachel McDaniel, who spent a long Indian summer away from her family to help gather the data for this work; and

My family, who have remained steadfastly supportive.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
AIC	Akaike’s Information Criterion
AKI	US-India Agricultural Knowledge Initiative
BCF	Bioconcentration Factor
BIC	Bayesian Information Criterion
CF	Carbonate fraction
CSSRI	Central Soil Salinity Research Institute
EC	Electrical Conductivity
EF	Exchangeable fraction
EPA	Environmental Protection Agency
ET	Evapotranspiration
IARI	Indian Agricultural Research Institute
ICAR	Indian Council of Agricultural Research
IUPAC	The International Union of Pure and Applied Chemistry
MS-ICP	Inductively Coupled Plasma Mass Spectrometer
NIH	National Institute of Health
OF	Organic fraction
PI	Principal Investigator
PFR	Plug Flow Reactor
RF	Reducible fraction
ResF	Residual fraction

CHAPTER 1: INTRODUCTION

Resource scarcity is an increasing concern across the globe. Among energy and food, access to adequate and high-quality water is of highest importance. Particularly in rapidly developing regions, ever-increasing volumes of contaminated industrial and domestic wastewater have been generated by growing industries and cities.

Where regulations and treatment processes are not adequate, these untreated waste streams are introduced into the riparian environment. At the same time, growing domestic and industrial demand for water coupled with declining groundwater tables has resulted in the increased use of riparian streams as sources of agricultural irrigation.

A multitude of concerns exist with the use of these irrigation sources. While acute pathogen outbreaks are of concern, a more subtle impact is heightened toxic metal concentrations. In particular, toxic metals accumulation in the plant-soil-water environment can affect soil structure and quality and heavy metal concentrations in plant tissues. Toxic metal presence in agricultural lands is a first step in a transport chain leading to chronic human exposure. Chronic low-level exposure to metals can lead to human and animal health risks.

Once introduced into the soil environment, metals are difficult to remove and can remain present at low environmental concentrations indefinitely. Metals sorb strongly in the soil onto a variety of sites. Metals may be bound onto exchangeable sites, carbonates, reducible Al- and Fe-hydroxides, in soil biomass (organic portion), or be irreversibly bound within the soil matrix. The way in which the metals are bonded to the soil can dramatically affect the mobility of the metals to leach to groundwater or be taken up by plants.

In developing countries such as India, possibly the most effective way to prevent metals introduced in peri-urban wastewaters from entering the food chain is to treat wastewater streams utilized for irrigation before entering the complex soil-water system. Toxic metal-contaminated waters have been extensively treated by a variety of methods, possibly the most common of which are sorption onto activated carbon and precipitation by pH modification. While effective, these methods are generally expensive. The areas in which untreated wastewaters are being released generally have neither access to adequate capital to build treatment plants nor a regulatory scheme able to consistently force emitters to treat waste streams. Viable low-cost, low-tech removal methods have the ability to strongly reduce the prevalence of metals in these agricultural systems.

Commonly proposed solutions involving low cost and low-tech approaches are generally based on sorption principles, typically onto a variety of lignacious biomasses. Sorption processes are generally well understood and documented, especially where the contaminant to be removed is present at relatively high concentration. However, in the wastewater reuse for agricultural irrigation scenario, the fundamental sorption processes are complicated by high-volume low-concentration (chronic low-level) metal levels in environmental wastewater-contaminated irrigation streams, wastewater solutions of varied composition (pH, EC, hardness, etc), and treatment media for which consistent standards and characterizations have not been developed.

This work attempts to address some of the complexities showcased above. Novel approaches used in this work include the following:

- Fractionating metals in soils under wastewater irrigation between different chemical pools
- Sampling deep into the soil profile (90cm) as opposed to the more common 30cm
- testing sorbents simultaneously under the same conditions to allow for a true comparison;
- utilizing native environmental wastewater (as opposed to DI water)
- spiking the water with relatively low levels of heavy metals to better simulate realistic conditions yet allow for meaningful detections

This work was funded in part through a grant from the US-India Agricultural Knowledge Initiative (AKI). The USA and India have had a previous formal agricultural research partnership dating back to the 1970’s and the Green Revolution. That partnership was highly successful in achieving a goal of increasing yields to reduce food shortages.

The current renewed AKI partnership aims to continue the successes of the Green Revolution in a new EverGreen Revolution focusing on sustainability and economic viability. Research efforts are focused in the areas of biotechnology, food processing, and the area of this research, sustainable water use.

CHAPTER 2: OBJECTIVES

The overall objective of this research is to develop a better understanding of wastewater reuse for agricultural irrigation.

The specific objectives of this research are to:

- Characterize the extent of toxic metal contamination in agricultural plant-soil-water systems irrigated with wastewater near Karnal, India.
- Assess the effectiveness of gypsum, sugarcane bagasse, sawdust, and rice husk in removing toxic metals from native wastewater through sorption capacity and provide a recommendation of best practices for low-cost low-tech treatment.
- Use simple models to quantify the effects of treatment practices on toxic metal concentrations under the experimental conditions encountered in researching the above objective.

CHAPTER 3: REVIEW OF LITERATURE

3.1 Toxic Metals Nomenclature

The wide range of toxic elements combined with the variety of their respective chemical attributes has made a precise nomenclature difficult. ‘Heavy metals’ is an often used term to describe toxic metals and metalloids present in the environment. The International Union of Pure and Applied Chemistry (IUPAC) has addressed some of the complexities inherent with the use of these terms (Duffus, 2002) and suggested the term ‘toxic metals’ to be the most suitable and reasonable for scientific writing. It has been thus used in this thesis report.

3.2 Toxic Metals in the Plant-Soil-Water System

The increasing levels of toxic metals in the biosphere are not all equally bioavailable and thus threatening to human and animal health (Ahmad et al., 2005). Although toxic metals are conservative in the environment, they are readily complexed in soils and sediments, where they naturally gravitate as they settle out of the air and water. In the northern Indian agricultural irrigation context, the majority of toxic metal loading on agricultural soils is expected to come from metal-rich wastewaters applied as irrigation. Resultant mobility, including leaching risks to groundwater and plant uptake, depends primarily on the way in which metals are complexed within the soil.

3.2.1 Irrigation Waters

Significant metal contamination has been detected in Northern India due to rapid industrialization, particularly attributed to the textile and dye industry. Metal-rich industrial wastewaters join with domestic wastewaters and often receive inadequate secondary treatment, leaving high levels of metals in wastewater canals. These waters are often used by farmers, for both nutrient-providing capability and also in lieu of declining alternative irrigation sources due to the falling water table and increasing consumptive use of canal waters due to growing urban centers (Ahmad et al., 2005). Among other authors finding heavy metal pollution a concern in northern India (Krishna and Govil, 2004), Yadav et al. (2002) and Sharma et al. (2007) have documented cadmium, chromium, and nickel as metals of elevated concentration in agricultural fields after applications of metal-rich wastewaters. Yadav et al. (2002) found Cd and Ni at levels of 0.02 and 0.12 mg/l, respectively, in sewage irrigation waters. Sharma et al. (2007) found Cd, Cr, and Ni at levels of 0.01-0.02, 0.03-0.09, and 0.03-0.05 mg/l, respectively, in sewage irrigation waters in northern India.

3.2.2 Soil Binding

Metals within soils have been characterized by widely varying means, including as broadly as total metal elemental content and as narrowly as plant bioavailability under given environmental conditions (Ahmad et al., 2005). Whereas the broad characterization of total metal content fails to account for background levels of metals in soil parent materials, the narrow definition of plant bioavailability under defined conditions also fails to allow for release and mobility under changing environmental conditions.

3.2.2.1 Chemical Pool Approaches

Tessier et al. (1979) addressed some of the above issues by characterizing metals within soils according to the different ‘chemical pools’ or fractions in which metals are bound, affecting resultant release and mobility. The sequential extraction procedure developed first removes metals bound on exchange surfaces, then those bound to carbonates, then reducible metal oxides, then those metals found in organic material within the soil, then finally the remaining irreversibly-bound metals within the soil. Tessier’s method has several shortcomings, not least of which is the labor- and time-intensive procedure itself. Under some conditions, it may also under – or over-represent the metals bound to a particular soil fraction.

Alternative approaches include single-extractant approaches; one popular reagent is the Mehlich-III reagent. The Mehlich-III reagent attempts to show bioavailable soil elements, including metals, available for plant uptake (Mehlich, 1984). However, large pools of non-bioavailable metals could be present in the soil undetected by the Mehlich test. As mentioned above, bioavailability approaches fail to account for changing metal mobility under potentially differing environmental conditions. Such conditions are often experienced in the rice/wheat cropping systems of northern India, where soil redox potential changes drastically between flooded rice paddy conditions and arid winter conditions.

3.2.2.2 General Characteristics of Metals in Soils

Kabata-Pendias (1993) characterized the general behavior of trace metals within the soil-plant-water system, drawing distinctions between the behavior of lithogenic, pedogenic and anthopogenic metals in the system and the resultant soil phases in which they are most prevalent, depending on soil conditions. Kabata-Pendias suggested that, in general, lithogenic metals are fairly immobile, while pedogenic metal behavior depends greatly on soil composition and chemical state. In particular, however, mobile metals such as Cd may be expected to be found primarily in soil organic matter (OM) and on exchangeable surfaces while less mobile metals such as Ni and Cr would be expected to be bound more firmly to silicates (Tessier's residual fraction). Anthropogenic metals would be expected to be mobile under most soil conditions, with significant correlations between plant metal and soil mobile (exchangeable and OM-bound) metal concentrations. Overall, the effect of origin on mobility risk is expected to be significant for Cd and Ni, with anthropogenic origin leading to increased risk. Cr mobility risk is expected to be relatively independent of metal origin.

3.2.2.3 Use of Tessier's Method

Tessier's method has been used in the Indian context to analyze metal fractions in surface water bed sediments (Singh et al., 2005; Jain, 2004; Jain and Chakrapani, 2008), finding metals present in varying amounts throughout the different fractions depending on surface water and sediment characteristics.

The use of Tessier's method in the wastewater irrigation context is not yet widespread. Lucho-Constantino et al. (2005) used a modified version of the method to characterize cadmium and chromium fractionation and accumulation in soils under wastewater irrigation in Mexico, simply adding an initial fraction of 'easily soluble' metals. The site in question had been irrigated with raw wastewater for some 20 years, with accumulated overall metal concentrations in the first 30cm of topsoil found to be 0.51-1.89 and 11.59-27.42 ug/g of Cd and Cr, respectively. The cadmium and chromium were principally found bound in the residual fraction.

Jjemba has compiled the allowable soil metal limits for various countries (Ahmad et al., 2005). The chart is shown in Table 1. Note the values between countries, often spanning over an order of magnitude difference. The US has rather liberal requirements relative to European and other countries. India's guidelines are not included.

Table 1. Permissible limits for various heavy metals in agricultural soils in selected countries (modified from Ahmad et al., 2005).

Jurisdiction	Permissible Concentration (mg/kg soil)		
	Cr	Ni	Cd
General Benchmark	--	15	0.1
Australia	100	60	1
Belgium (sandy soil)	100	30	1
Belgium (clay-loam soils)	150	75	3
China (pH<6.5)	600	100	5
China (pH>6.5)	1000	20	20
Netherlands	75	30	1.25
Republic of South Africa	80	15	2
United Kingdom	400	75	3
USA	1200	420	39
Sweden	30	30	0.4
New Zealand	--	35	--

3.2.3 Plant Uptake and Bioconcentration

Observations of increased metals in plants grown in metal-rich soils and/or under metal-rich irrigation are widespread. In relevant soils in southern Asia, Yadav et al. (2002) observed increased concentrations of metals including Cd and Ni in such crops as wheat, berseem clover, rice, and sweet sorghum. Bahmanyar (2008) found Cd, Cr, and Ni in industrially irrigated crops in southern Asia at levels 2-5 times above the control treatments, while noting metal concentrations in roots higher than those in shoots, suggesting inter-plant mobility of such metals was low.

3.3 Treatments for Metal Removal from Wastewater

While agricultural soils can be managed to minimize human exposure risk to metals, and to remove metals from the complex system, another way to minimize exposure risk is to capture metals before entering the soil system. In the northern Indian irrigation context, a principal possibility of slowing metal flow towards the soil sink is to remove metals from industrial wastewaters before entering agricultural fields as irrigation waters.

A variety of methods have been utilized to remove toxic metals from industrial wastewaters. Included among them are chemical precipitation, ion exchange, and electrochemical methods. These methods tend to be either costly, ineffective at low environmental metal concentrations, or both, and are particularly stymied by the presence of organics when domestic wastewaters are mixed with industrial wastewaters (Bailey et al., 1998; Babel and Kurniawan, 2003).   Other methods abound, with various strengths, weaknesses, and costs.

3.3.1 Traditional Approach

The common solution adopted by the wastewater treatment industry involves primary and secondary settling followed by, when necessary, tertiary treatment via activated carbon filtration. This process handles organics well.

Activated carbon is a desirable filtration medium due to its homogeneity, the high removal density (mg metal/kg carbon), and ability to scavenge metals at low concentrations (Terdbiatburana and Wang, 2008). While effective, such treatment is expensive, requires a substantial up-front investment, and perhaps more significantly requires a network of piping to deliver wastewater to the treatment facility – untenable factors in developing and resource-poor areas (Ahmad et al., 2005). Thus, metal-rich wastewaters are frequently introduced into the riparian environment.

3.3.2 Alternative Approaches

Dilution of metal-rich waste streams by the large amounts of irrigation waters flowing through these contaminated canals does nothing to reduce the metal load, but does complicate removal attempts via sorption methods. Nevertheless, extensive work characterizing metal removal ability has been performed on a wide variety of inexpensive and readily available ‘biosorbents’ suitable for deployment for metal removal from waters. Bailey et al. (1998) reviewed the spectrum of ‘potentially low-cost sorbents for heavy metals’ including a variety of biomass- and some mineral-based sorbents, finding chitosan, zeolites, lignin and lignin-based sorbents, and seaweed to have high observed metal absorbency. Bailey et al. particularly noted the variety of methods used to measure the various sorbents precluded comprehensive comparisons and definitive conclusions.

Babel and Kurniawan (2003) confirmed in their review that chitosan, zeolites, and lignin were particularly effective in removing metals from wastewaters, additionally noting some substances (ie lignacious biosorbents) often required some chemical modification to improve performance. The lignacious substances reviewed included sawdust, ground rice husk, and sugarcane bagasse.

These authors cite but a few of the vast array of literature written on the topic of metal sorption onto unconventional sorbates. The literature, in general, seems confined to those either (1) maximizing the removal density of sorbates, generally by increasing the beginning metal concentration and/or chemically modifying the underlying substrate, (2) meticulously documenting the sorption parameters via extensive kinetics and isotherms at differing temperatures and by using lab-bench column studies, generally using pristine metal-spiked DI water, and/or (3) documenting precise sorption mechanisms through high-powered microscopy and chemical deconstruction of the underlying sorbate. Very few authors have generated work on comparative sorption, allowing for more fair comparison of material efficacy for metal removal. No authors this reviewer has encountered have performed experiments to quantify metal removal effectiveness of inexpensive substrates using environmental wastewater.

Based on availability and cost, sawdust, ground rice husk (GRH), and sugarcane bagasse seem likely candidates for further suitability analysis. Activated carbon and gypsum seem useful standards against which to test these other materials, based on the homogeneity of the medium. Gypsum has the additional advantage of being inexpensive to procure, particularly in India, where it is widely used to lower high pH soils.

Typical methods used to compare the efficacy of materials for sorptive removal are kinetics, isotherms, and breakthrough curves from column studies.

3.4 Cadmium

The United States Environmental Protection Agency (USEPA 2000a, 2006, and 2009a) has extensively summarized and categorized the environmental characteristics and health effects of cadmium. The National Institute of Health (NIH 2005) has further codified the health effects of cadmium. The information is presented in the sections below.

3.4.1 Environmental Release

Cadmium (atomic number 112) is naturally found in metal ores in the earth's crust, and is commonly found with zinc, lead, and copper ores. While more general releases of cadmium into the environment may come through mining and smelting activities, the rapid industrialization in northern India, particularly in the textile and dye industries, is thought to release significant amounts of cadmium into surface waters .

3.4.2 Health Effects

Notable short-term health effects include livery injury, convulsions, and renal (kidney) failure. Long-term exposure may result in kidney, liver, bone, and/or blood damage. Reproductive effects may include skeletal defects and neurological issues. USEPA classifies cadmium as a probable human carcinogen, meaning USEPA has no definitive evidence associating chronic cadmium exposure with increased incidences of cancer. However, NIH considers cadmium and cadmium compounds as known human carcinogens based on observances of lung tumors in human and animal studies. It is likely NIH's definition includes exposure to cadmium via inhalation, while EPA's definition focuses on oral cadmium ingestion via drinking water.

3.4.3 Environmental Fate

Cadmium solubility varies widely according to the compound in which it is found. In soils, adsorption is strongly pH-dependent, desorbing below pH 6-7. Mobility is expected to be higher than for such other metals as Cu, Zn, and Pb. However, Cd bound to carbonates and/or precipitated with iron oxides is expected to be less mobile than Cd bound to exchangeable surfaces.

3.5 Nickel

In much the same way as cadmium, USEPA (2000b, 2009c) has characterized nickel in regards to environmental characteristics and possible health effects.   USEPA remanded the MCL/MCLG for nickel in 1995, but is currently reconsidering regulating nickel in drinking water. The US National Institute for Health (2005) has further characterized carcinogenic health effects of nickel. The information is presented in the following subsections.

3.5.1 Environmental Release

Nickel (atomic number 28) is found in a variety of ores and is introduced to the environment through smelting and petroleum refining. As with cadmium above, nickel is of particular interest in the wastewater irrigation context due to its use in textile and dyeing industries.

3.5.2 Health Effects

Food consumption is generally the primary source of nickel exposure. Beyond minor dermatitis, chronic exposure can lead to heart and liver damage. USEPA has not found nickel acetates to be carcinogenic. Soluble nickel salts have not been evaluated by USEPA for potential human carcinogenity. However, NIH has found soluble nickel salts to cause cancer in animal studies.

3.5.3 Environmental Fate

Nickel is extremely mobile in the aquatic environment. In organic-rich environments, such as found in industrial/sewage wastewater mixes, nickel will remain soluble. Where reducing environments are found, nickel will likely become insoluble. Eventual fate is dependent upon such physical and chemical interactions through precipitation/dissolution, adsorption/desorption, oxidation/reduction, and complexation onto active groups. While it is bioaccumulated, nickel uptake into biomass is not considered a significant removal pathway from the soil/water system.

3.6 Chromium

USEPA and NIH have also characterized the environmental characteristics and health effects of chromium (USEPA 2009b; NIH 2005); applicable information is summarized in the below subsections.

3.6.1 Environmental Release

Chromium occurs naturally in the soils and plants in a trivalent (+3) form. The hexavalent (+6) forms are commercially generated for pigment manufacture and textile dyeing among other uses.

3.6.2 Health Effects

Trivalent chromium is an essential trace element for humans, while hexavalent chromium is strongly toxic to humans. Chronic exposure can result in organ damage and skin irrigation. Hexavalent chromium is further considered a known human carcinogen.

3.6.3 Environmental Fate

Both trivalent and hexavalent forms of chromium are fairly stable, although hexavalent chromium will eventually be reduced to chromium (III).

Chromium is unlikely to migrate to surface or groundwaters. Once present, however, chromium is persistent in water systems, particularly in particulates and sediments.

Chromium sorbs strongly to the soil and is relatively immobile. Plant uptake occurs, but is strongly favored by extremely basic conditions as opposed to mere calcareous (pH 7.5-8) soils.

CHAPTER 4: METHODS AND MATERIALS

Research activities were conducted in Karnal, Haryana, India during 2008-2009. Karnal and the surrounding areas may be considered a peri-urban environment wherein industrial and sewage waste streams are commonly used as irrigation sources. Likewise, the materials tested for use in remediation, such as rice husk and bagasse, are readily available in India. Experiments were conducted at the main research station of the Central Soil Salinity Research Institute (CSSRI) of the Indian Council of Agricultural Research (ICAR).

4.1 Toxic Metals in Agricultural Lands

Field samples were collected from sites near Paniput, Haryana, India. Paniput is a center for textile and dye industries in northern India. Metals are commonly used in dyes, such as cadmium orange and cadmium yellow. When untreated, the resultant wastewater streams have high toxic metal concentrations and mix into the larger environmental water streams.

4.1.1 Site Selection

Sites were selected based on irrigation water source and crop type. Sites were identified as using wastewater-irrigation (W), tube-well water irrigation (T), or conjunctive-irrigation of both tube-well and wastewaters (C). The primary criterion was a site that was identifiably irrigated by an obvious water source as evidenced by topography and water availability. These observations were corroborated where possible by the local farmer or a neighbor.

Secondary criteria were crop type and field history, as evidenced by present flora and as explained by local farmers, respectively. Sorghum was chosen as a typical, in-season crop likely available across the gamut of irrigation types. Past cropping and irrigation patterns were established by interviewing local farmers.

Soil, water, and crop foliage samples were taken from two general regions near Paniput. The site locations are shown in Figure 1. Sites 1-7 were clustered closely near the exit pipe for wastewater effluent from a wastewater treatment plant near Paniput. Sites 8-12 were more scattered, located in two clusters approximately 1.5 and 3km downstream from the effluent exit point, to minimize localized effects and potentially show some metals/transport distance relationships.

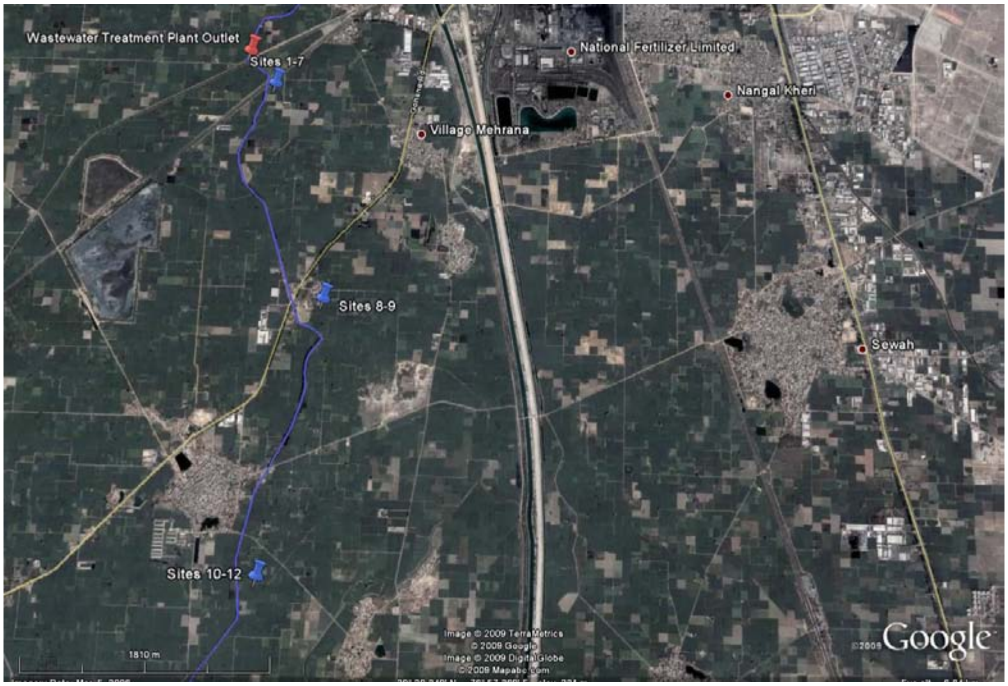


Figure 1. GIS map of field sample site near Panipat, Haryana, India.

4.1.2 Sampling Protocol

One sample location was randomly selected from within each selected field, generally less than 0.25 ha. GPS coordinates were recorded and are shown in Table 2. Soil samples were taken with a manual screw-type auger to a depth of 90cm.

Table 2. Soil and foliage sample site locations.

Site	Latitude		Longitude	
	deg (N)	minutes (N)	deg (E)	minutes (E)
1	29	21.246	76	56.155
2	29	21.260	76	56.120
3	29	21.199	76	56.191
4	29	21.169	76	56.179
5	29	21.180	76	56.224
6	29	21.118	76	56.009
7	29	21.119	76	56.002
8	29	20.221	76	56.489
9	29	23.304	76	56.497
10	29	19.109	76	56.217
11	29	19.235	76	56.234
12	not recorded (near 11)		not recorded (near 11)	

Soil samples were taken in 4 depth-increments of 0-15, 15-30, 30-60, and 60-90 cm, respectively, and then stored in plastic bags. The 60 and 90cm sampling depths cover a greater portion of the soil profile than is generally found in the literature. Figure 2 shows the sampling apparatus. Some field sampling conditions were less than ideal, with recent tillage performed to prepare for the summer rice crop.

Figure 2. Soil sampling apparatus. Note some fallow sites had been recently tilled in preparation for rice planting.

Water samples were taken from nearby identifiable irrigation sources (see **4.1.1 Site Selection**), either canal wastewater or tubewell irrigation groundwater. One hundred-mL samples were collected in nalgene bottles labeled with the corresponding site. Figure 3 shows the wastewater canal from which surface irrigation wastewater samples were collected. The wastewater was noticeably murky with visible suspended sediments, and smelled somewhat sulfurous indicating a reducing environment (high BOD/COD and low DO levels).

Figure 3. Wastewater-contaminated stream utilized for irrigation. Note the murky water.

A sample of crop foliage was collected where possible. Table 3 shows the sample site irrigation type, water sample type, and current (as of sampling) crop type. Samples were collected by removing all above-ground foliage for fodder species (berseem and sorghum) and/or, where identifiable, by removing the edible fruit of a crop (gourds and melons, etc). In some fields where multiple crops were growing multiple foliage samples were taken. In the fallow fields a sample of grasses growing as weeds was taken. Samples were stored in plastic bags.

Table 3. Sample site irrigation and crop types at time of sampling. Irrigation types include tube-well (T), wastewater (W), and conjunctive usage (C).

Site	Irrigation Type	Water Sample	Crop Common Name	Crop Latin Name
1	C	WW	Berseem	*Trifolium alexandrinum*
2	C	(same as 1)	Sorghum	*Sorghum bicolor*
3	W	(same as 1)	Sorghum	*Sorghum bicolor*
4	W	(same as 1)	Indian round gourd - leaves Indian round gourd - fruit Round gourd - leaves Grass	*Praecitrullus fistulosus* *Praecitrullus fistulosus* *Praecitrullus fistulosus* *unknown*
5	W	(same as 1)	Sorghum	*Sorghum bicolor*
6	T	TW	Berseem	*Trifolium alexandrinum*
7	T	(same as 6)	Sorghum	*Sorghum bicolor*
8	C	WW	Sorghum	*Sorghum bicolor*
9	T	TW	Sorghum	*Sorghum bicolor*
10	W	WW	Fallow (weeds) Fallow (weeds)	*unknown* *unknown*
11	T	TW	Sorghum	*Sorghum bicolor*
12	W	WW	Round gourd - fruit Round gourd - leaves Berseem Round gourd - fruit round gourd (Tinda)	*Praecitrullus fistulosus* *Praecitrullus fistulosus* *Trifolium alexandrinum* *Praecitrullus fistulosus* *Praecitrullus fistulosus*

4.1.3 Analytical Procedures

Standard analytical procedures were followed. While variations abound in the analytical methods, many of procedures are set forth in the Soil Plant Water Analysis manual published by IARI (Singh et al., 1999). Where other methods were used attribution is listed.

The majority of lab exercises were performed at CSSRI in Karnal, Haryana, India. CSSRI, an analogue to a USDA-ARS research station, is a premier research institution of IARI. The laboratories are fully equipped to handle a wide variety of soil, plant, and water analyses.

Some sample analysis was performed using UIUC's laboratory facilities. Soil total and fraction metal samples, expected to be present at levels below the detectible limit for flame AAS, were conveyed from India to be analyzed using MS-ICP.

4.1.3.1 Soil Sample Analysis

Soil samples were stored in plastic bags from the field to the CSSRI laboratory. Soil samples were spread on trays and air-dried for 48 hours to achieve uniform moisture content before being ground with a wooden pestle and mortar. Samples were ground to fit through a 2-mm screen. Samples were stored in plastic bags for the remainder of the experiment.

Soil pH and electrical conductivity (EC) were tested from a 1:2 soil-water suspension using a LiCor 127 pH meter and a sensION5 conductivity meter, respectively. 20g air-dry soil was massed into a beaker and mixed into 40mL distilled water. The resulting mixture was stirred for five minutes, allowed to settle to 30 minutes, stirred again, and measured for pH. The mixture was then again allowed to settle and the supernatant was measured for EC.

Soil ions were determined from the extract of a saturated soil paste. The paste was prepared by adding to 100g soil small amounts of distilled water until the paste glistens and just falls from the spatula. The paste was then vacuum-filtered. The extract obtained was tested for hardness, sodium, carbonate/bicarbonate, and chlorides. The divalent cations Ca^{+2} and Mg^{+2} as hardness were determined by the versenate titration method, while carbonates (CO_3^{-2}) and bicarbonates (HCO_3^-) were determined by dilute sulfuric acid titration. Sodium was determined by flame photometry. Chloride (Cl^-) concentrations were determined from Mohr’s titration. Exact methods are given in the Indian Agricultural Research Institute (IARI) Methods manual (Singh et al., 1999).

Soil texture was determined by the international pipette method. Organic carbon was determined by the Walkley and Black method as set forth in the IARI Methods manual (Singh et al., 1999).

Total metals were determined by digestion with hydrofluoric acid based on the method set forth in Methods of Soil Analysis: Part 2 (2nd Ed.) (Page, 1982). Ten mL HF was added to 1g soil inside a closed 250mL bottle of known mass. The bottle was heated at 100C (to speed reaction) until the sample turned clear (1-2 hr), indicating dissolution. After cooling, 100mL saturated boric acid (H_3BO_3) was added. The bottle was then again massed to determine sample volume. Samples were transferred to 250mL nalgene bottles to await AAS analysis.

Metal fractions were determined by Tessier's method (Tessier et al., 1979) as set forth by Chlopecka et al. (1996). The method relies on several sequential chemical washes to extract metals by type of chemical bond, providing improved quantification of metal availability and transport risk over single-wash extractions such as the Mehlich approach. Metals were sequentially extracted into five fractions: exchangeable (EF), carbonate-bound (CF), reducible (RedF), organic-bound (OF), and residual (ResF).

One g dry soil was initially extracted with 8mL 1.0 M magnesium chloride at pH 7 to determine EF. The mixture was agitated at room temperature on a shaker table for one hour before being centrifuged. Eight mL pH 5 1.0 M sodium acetate was then added to the residual wet soil and shaken for 5 hours before being centrifuged to gather the CF sample. The RedF sample was gathered by heating 20mL 0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid for 5 hours in a 96degC hot water bath. Following centrifuging and RedF sample collection, the residue was extracted for the OF. Two mL 0.02 M nitric acid and 5mL 30% hydrogen peroxide (adjusted to pH 2 with nitric acid) were added to the residue and heated to 85degC on the hot water bath. After two hours, three additional mL of the adjusted hydrogen peroxide solution were added and the sample heated for another three hours. After cooling, 5 mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added and the sample diluted to 20mL. After 30 minutes of shaking, the solution was again centrifuged and the extract poured off. The RF was determined from the remaining residue. The residue was placed in a platinum crucible with 2mL perchloric acid and 10mL HF. The mixture was heated until almost dry in a hood, whereupon an additional 1mL percholoric and 10mL HF were added and again heated until almost dry. A final 1 mL of perchloric acid was added and the mixture again heated until the presence of white fumes. The residue was dissolved in concentrated HCl and diluted to 25 mL. As set forth in Chlopecka et al.'s procedure, each wash centrifuged for 30 minutes before being rinsed with 8 mL DI water and again centrifuged.

4.1.3.2 Water Sample Analysis

Water sample pH and EC were determined by LiCor 127 pH meters and sensION 5 conductivity meters, respectively. Hardness, sodium, carbonates/bicarbonates, and chlorides were tested by the methods used for the soil paste (Singh et al., 1999).

Water samples were digested with a 50/50 concentrated nitric/perchloric diacid for total metals. Twenty mL water sample was added to 100 mL nitric/perchloric diacid and heated on a hot plate to near dryness. The residue was diluted with DI water to 20.0 mL.

4.1.3.3 Plant Sample Analysis

Samples were stored in plastic bags from the field to the CSSRI laboratory. Samples were rinsed with distilled water and then with a weak acid solution to remove any dust on foliage surfaces as well as the waxy cuticle. The acid solution was rinsed off with distilled water and samples were air-dried on newspaper for 48 hours. Samples were then stored in lightweight paper bags.

Samples were prepared for digestion by oven-drying at 60°C for 24 hours. Oven-dried samples were ground in a blender. The entire sample was ground and mixed thoroughly and then replaced in the oven for 24 hours to achieve a consistent dryness. The samples were again stored in lightweight paper bags until digestion with di-acid, whereupon the acid solution was stored at ambient temperature until metal determination via flame AAS.

4.2 Toxic Metals Removal by Amendments

Amendments were chosen based on low cost and ready availability in India. The amendments chosen to be tested include three biomass-based amendments, a mineral-based amendment, and activated carbon as a standard for water purification. The biomass amendments included sugarcane bagasse (SB), ground rice husk (GRH), and generic sawdust (SD) from a nearby sawmill. The mineral-based amendment was gypsum (G). Powdered activated carbon (PAC) was used as a standard for comparison. The materials are prepared and stored in the CSSRI laboratory as shown in Figure 4.

Figure 4. Sorbents prepared for column packing. Note (from back right): ground rice husk, sawdust, sugarcane bagasse, and gypsum. Powdered activated carbon not pictured as it is packaged commercially.

Amendments were characterized by sorption kinetics and isotherms. A constant-head column-PFR arrangement was used to test sorption capacity and toxic metals breakthrough.

4.2.1 Native Wastewater

In what appears to be somewhat unique in the literature, native wastewater was used to determine the efficacy of amendments. Wastewater was gathered from the same wastewater irrigation source used to irrigate sites 1-7. The wastewater was collected in a 5000L steel tank, as shown in Figure 5, and stored at CSSRI for the duration of these experiments, about 6 weeks.

Figure 5. Steel storage tank for native wastewater collected from the wastewater stream near Site 1.

Wastewater for the experiments was siphoned through a cheesecloth into a 200L plastic barrel. The cheesecloth removed some solids from the wastewater, to give consistency and avoid plugging the packed columns. The wastewater in the barrel was spiked with additional Cd, Ni, and Cr to bring effluent concentration up to more easily detectable levels. A concentrated Cd, Ni, and Cr solution was prepared and mixed into the 200L barrel to achieve a 20 ppm metal solution as shown in Figure 6. The addition of Pb was attempted but proved inadvisable due to incompatible salts settling metals out of solution.

Figure 6. Dr. Khan preparing concentrated metal solution to spike filtered wastewater. Note the vibrant colors of the metals in solution, and potential as dyes.

4.2.2 Sorption Kinetics

Sorption studies were performed with native wastewater spiked to 20ppm of Cd, Ni, and Cr. The low but pervasive background toxic metal levels challenge removal according to sorption theory - the low concentration limits the rate of adsorption, while also slowing any absorption occurring. The higher initial concentrations were also chosen to allow some resolution in the ending concentrations.

Amendments were tested on an equivalent-volume basis. Equal volumes of each amendment were utilized in each column to remove as much variability from the flow regimes as possible. To give meaningful results based on the columns, kinetic tests were performed on an equal volume basis to provide relevant supporting data.

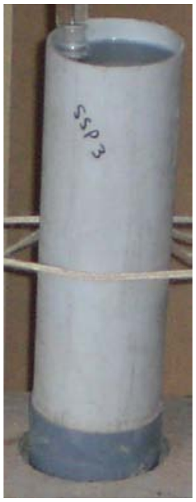
The unpacked density of each amendment was determined. The values were normalized to give the equivalent volume occupied by 5g gypsum. Twenty mL spiked wastewater was combined with the volume-equivalent amounts of amendment in a 50-mL flask. Flasks were shaken for 5 minutes to achieve thorough mixing then allowed to sit for the duration of the experiment. Amendments were tested for 1, 6, 12, 24, and 48-hr durations. At the end of those times, the flasks were again shaken for five minutes and then filtered through Whatman No.1 filter paper. The filtrate was stored in 100-mL nalgene bottles for later metal analysis (see **4.3 Metals Determination**). The storage temperature was room temperature for summer in northern India – approximately 35°C. The first kinetics experiment had three replicates, and the second experiment two.

4.2.3 Adsorption Isotherms

Adsorption isotherms are a standard method to determine and compare the affinity of sorbents (amendments) and sorbates (toxic metals). Amendments were again tested using equivalent-volume amounts of amendment. The 20ppm spiked wastewater was used as a base stock to prepare 2, 5, 10, 15, and 20-ppm spiked wastewater solutions. Twenty mL of each solution was combined with the volume-equivalent amounts of amendment in a flask. The flasks were shaken for 5 minutes, allowed to sit for 24 hours, again shaken for 5 minutes, and then filtered through Whatman No.1 filter paper. The filtrate was stored in 100-mL nalgene bottles at 35°C for later metal analysis. The 24-hr isotherm experiment had three replicates.

4.2.4 Column Plug Flow Reactor (PFR) Design

A small constant-head column was designed to test amendment sorption capacity and the breakthrough curve. The column consisted of a 10x40cm PVC pipe capped on the bottom end. The cap was drilled to accept small hose barb. The column was filled with the amendment to act as a packed-bed PFR. A column design schematic is shown in Figure 7 below.



Freeboard	10cm
CaCO3	5cm
Sand	5cm
Packed Material	10cm
Sand	5cm
CaCO3	5cm
TOTAL:	40cm

Figure 7. Column packing schematic. Note felt was used at every material interface except between the freeboard-CaCO3 interface.

A bottom layer of sand and marble ($CaCO_3$) chips was included to prevent the amendment from washing out and plugging the hose barb. A 10-cm depth of amendment was packed into the middle of the column. A top layer of sand and marble chips prevented the amendment from floating up, maintaining the packed bed. Layers of heavy felt were used to separate layers of material. The volume-equivalent masses packed into each column are shown in Table 4.

Table 4. Column packing masses of amendments.

Amendment	Unpacked Density (g/L)	Volume-equivalent masses (g)
G	1950	5.0
SB	829	2.1
GRH	700	1.8
SD	368	0.9
PAC	448	1.2

A custom frame was designed and built to hold volumetric flasks upside-down above the columns. The airlock formed by setting the lip of the volumetric flask at the surface of the column water allowed for a constant-head on the water passing through the packed bed of amendment. The configuration is shown below in Figure 8.

Figure 8. Constant-head flask arrangement designed for our experiment by Dr. Khajanchi Lal.

The valve at the bottom of the column was designed to control flow. By restricting flow the solution would be forced to saturate the column and all sorptive surfaces contained within, limiting preferential flow paths. Due to the packing process, flow limitation via the valves was not required, as the material retarded the flow of water to the point achieving a 1 L/d flow rate became difficult for activated carbon and gypsum.

4.2.5 Column Operating Protocol

Six columns were prepared for each amendment: three for spiked wastewater and three for a DI water control. For each amendment, columns 1-3 were used for DI water control and columns 4-6 indicated wastewater. Four additional columns with no amendment and only sand and marble chips were prepared as a second control. Two columns were used for spiked wastewater and two for DI water.

With the valves closed, the columns were filled until saturated (water remaining in the 1L volumetric flask). The columns were allowed to sit in this state for 48 hours before beginning to pass water through.

After 48 hours, the valves were opened to allow water to pass through. A 1000mL graduated cylinder was used to catch column effluent. When full, samples were taken by pouring off approximately one-third of the graduated cylinder, then swirling the remainder and decanting 100mL into the sample bottle. Thus, the samples are not ‘after’ each 1L of water but an aggregate sample across the 1L passing through the column. Samples were stored in the lab at 35°C. As just-in-time metals analysis was not available, DI columns were operated for 15L while wastewater columns were operated up to 20L of collected effluent as much as lab time constraints allowed.

The valves were adjusted as well as possible to a flow rate of approximately 1 L/day. The time of each 1L volumetric flask addition to the top of the column was recorded, as was the time of each sample from the 1L graduated cylinder. Adjustment of the valves continued throughout the study in an effort to achieve a 1L/day rate. Attempts were also made to adjust and standardize flow rate based on drops per minute. This effort was stymied by non-uniform glass geometry at the tip of the valve barbette, causing nonstandard droplet size, and the effort was eventually abandoned. Instead, the columns were checked on roughly 6-hr intervals to empty filled effluent graduated cylinders and refill emptied volumetric flasks.

4.2.6 Effluent Analysis

Column effluent samples were stored in nalgene bottles at 35°C in the CSSRI lab until testing could be arranged. Effluent samples were analyzed without further filtering or other manipulation.

4.3 Metals Determination

Metals determinations were made at the end of experiments. Flame AAS analysis was performed by the research team. Some samples with trace concentrations were sent to a UIUC microanalysis lab with lower detection limits.

4.3.1 Flame AAS

4.3.1.1 Instrument

The instrument used was a Hitachi Z-5000 Polarized Zeeman flame AAS. The Hitachi Z-5000 is a double-beam AAS, which provides a more accurate relative absorption measurement instead of an absolute one.

4.3.1.2 Standards

Stock standards of 0.5, 1, 2, 4, and 10 ppm were prepared for Cd, Ni, and Cr. The standards were prepared with double-distilled water and stored separately from samples to be analyzed.

4.3.1.3 Operating Protocol

The absorbance of each standard was measured, and then samples were processed through the AAS, with care to rinse the aspirator tube with DI water between each sample. Where sample absorbance readings were greater than the 10ppm reading for an element, samples were diluted. Samples were tested in order of Cd, then Ni, then Cr – from expected lowest concentration to expected highest concentration – to prevent dilutions from pushing the observed concentration below the detectable limits. At the end of a run, the standards were tested against their initial readings to ensure validity across the run. A best-fit polynomial curve between the absorbance reading and concentrations was generated for each run. Sample concentrations were calculated from the best-fit curve.

4.3.2 MS-ICP for Trace Concentrations

Soil metal samples were sent to a UIUC microanalysis lab with lower detection limits than flame AAS. The lab used indium and gallium for interference comparison. Results were reported back in parts per billion (ppb) and back-calculated to mg metal/kg soil.

4.4 Repeat Metal Sorption Experiments

Due to broad scatter in metal results from the initial batch of metal sorption lab experiments, repeat experiments were performed for removal kinetics, isotherms, and column studies. The repeat kinetics and isotherm experiments utilized 10g of amendment in 60 mL of wastewater spiked to 20ppm of each metal (Cr, Cd, and Ni). The columns were operated for further volumes of water passing through.

Errors in the analysis of the initial samples were attributed to the combination of the utilization of native wastewater and long storage time, allowing residual organics to form colloids and precipitate metals from solution, preventing them from being detected in the AAS experiments.

4.5 Modeling

Kinetics and sorption models were used to generate standard comparisons between sorbents. These models are process-based in nature.

4.5.1 Kinetics Modeling

Both linear and nonlinear models were fitted to the data based on concepts from Kumar and Sivanesan (2005). 48-hour concentrations were assumed to be equilibrium values.

4.5.1.1 PseudoFirst-Order Model

The model used was a linearized form based on the pseudofirst-order Lagergren kinetics (Lagergren, 1898),

$$\ln(q_e - q) = \ln(q_e - K_1 t) \tag{1}$$

where q (mg/g) is the amount of metal ion sorbed to the surface of the sorbent at any time t (hr) , q_e (mg/g) is the amount at equilibrium, and K_1 (mg/g-hr) is the sorption rate constant.

4.5.1.2 PseudoSecond-Order Model

The plotted concentrations were fitted to a pseudosecond-order kinetic model from Ho and McKay (1998) as used by Guo et. al. (2008) for rice husk sorption modeling,

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where K_2 (g/mg-s) is the sorption rate constant.

4.5.1.3 Statistical Validity Testing for Kinetics

Using simple r^2 values is a weak comparison technique for the determination of goodness-of-fit. Adjusted-r^2 for these models will be identical to r^2, as both models are linearized for parameter determination. These non-nested models further forestall the use of the t- and F-tests for statistical comparison.

The models may be compared for goodness-of-fit using Akaike's Information Criterion (AIC) and Bayesian Information Criterion (BIC). Despite low *n*-values causing possible bias, both models use identical sets of observations to formulate the model. This suggests AIC and BIC may provide a more informed goodness-of-fit than simple r^2.

AIC may be calculated from the following equation, adjusted for small sample set bias as unadjusted AIC tends to overfit models:

$$AIC = n * \ln\left(\frac{RSS}{n}\right) + 2K + \frac{2K(K+1)}{n-K-1} \tag{3}$$

where *RSS* is the residual sum of squares, *n* is the number of observations (5), and *K* is the number of parameters in the model (2 for the linearized forms). A superior model will have a lower AIC than other models.

BIC is calculated very similarly:

$$BIC = n * \ln\left(\frac{RSS}{n}\right) + K \ln(n) \tag{4}$$

with a built-in adjustment for sample size. As for AIC, a lower BIC value suggests less error is present in the model.

4.5.2 Adsorption Isotherms

The two common sorption isotherms are described below. Both isotherms assume monolayer adsorption onto active soil surfaces.

4.5.2.1 Freundlich Isotherm

The Freundlich equation is given as

$$q = K_f C^n \tag{5}$$

Where q (mg/g) is the mass adsorbed per mass adsorbate, C (mg/L) is the liquid concentration, and K_f (mg/g) and n are constants. The equation can be linearized to

$$\log(q) = \log(K_f) + n \log(C) \tag{6}$$

4.5.2.2 Langmuir Isotherm

The Langmuir equation is given as

$$q = \frac{q_e K_a C}{1 + K_a C} \tag{7}$$

Where q_e (mg/g) is the equilibrium mass adsorbed per mass adsorbate and K_a (L/mg) is a constant. The equation can be linearized to

$$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{K_a q_e C} \tag{8}$$

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Toxic Metals in Agricultural Lands

5.1.1 Toxic Metals in the Soil

Soils metal data was ascertained through total soil metal measurements and further sequential fractional extractions via Tessier's method.

5.1.1.1 Total Soil Metals

Twelve sites were identified and sampled for metals. The twelve sites were split between wastewater (W), conjunctive (C), and tube-well (T) sourced irrigation water. The sites were sampled at 0-15, 15-30, 30-60, and 60-90cm depths. The results for Cd, Cr, and Ni detections are shown in Figures 9, 10, and 11 respectively. The bar charts show the total amount of metals determined to be in the soil via acid digestion, arranged by site and further divided by depth.

Figure 9 shows the cadmium concentrations by site and sample depth. The high spikes seen in sites 2C, 3W, and 11T suggest sample contamination, possibly due to the metal-type soil auger used to collect samples.

The general trend seems to indicate that soil Cd concentrations decrease or remain relatively constant with depth, suggesting Cd applied via irrigation are saturating upper layers first and only then moving further down into the soil profile. This would suggest that leaching to groundwater would be of relatively low concern, given the relatively lower groundwater tables (>15m) and vast amount of sorptive surface to be saturated before reaching groundwater.

Contradicting that theory is the observation that a break seems to exist around 0.25 mg Cd/kg soil, with tube-well irrigated sites falling above that break and wastewater and conjunctively irrigated sites falling below that line. Some recent evidence (Aulakh et al., 2009) has suggested that Indian groundwaters are laden with heavy metals, particularly those located near industrial areas. This finding was most unexpected.

A possible recommendation is to utilize conjunctive irrigation, giving cropping benefits as well as reducing metal load in fields from possibly contaminated groundwater sources.

Sites 1C and 8C show extremely low levels of metals compared to other sites; site 2C does show higher levels than other sites but the validity of those data must be called into question given the extremely high readings found for the site. It is unfortunate that for sites 1C and 8C the 30-60 and 60-90cm samples were lost in transport, as they could provide insight into the validity of the effectiveness of conjunctive irrigation for reducing metal loading in field irrigation.

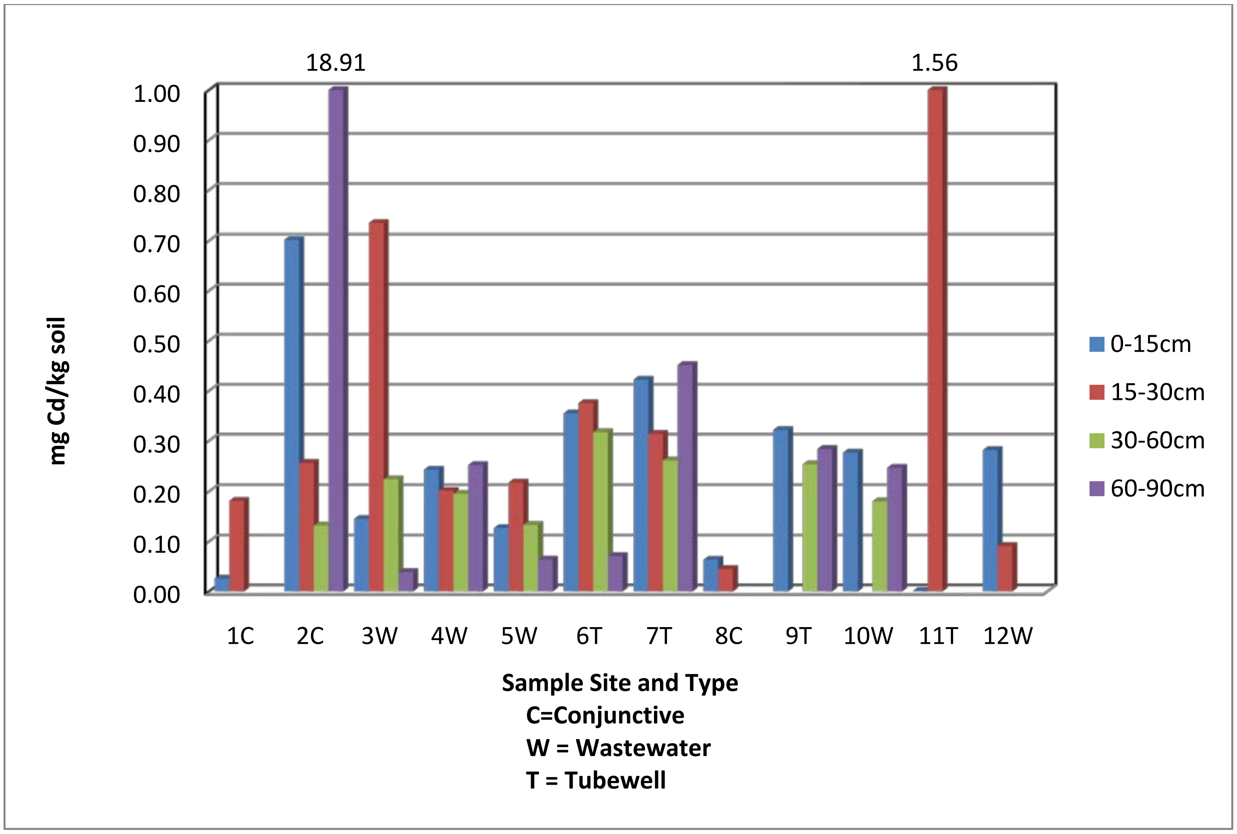


Figure 9. Total Cd concentration by sample depth and sample site and irrigation type.

Total chromium in soil samples for the 12 sites is shown below in Figure 10. Chromium is present at much higher concentrations than Cd, ranging from some 5-65 mg/kg soil as compared to Cd’s 0.02-0.7 mg/kg soil.

Whereas Cd concentrations tended to be highest in the surface sample, Cr concentrations tend to peak around the 30-60cm depth before falling off into the 60-90cm depth. However, concentrations were much more uniform across both sample depth and soil type than were Cd concentrations. These results favor a theory that Cr leaching to groundwater may not be an issue.

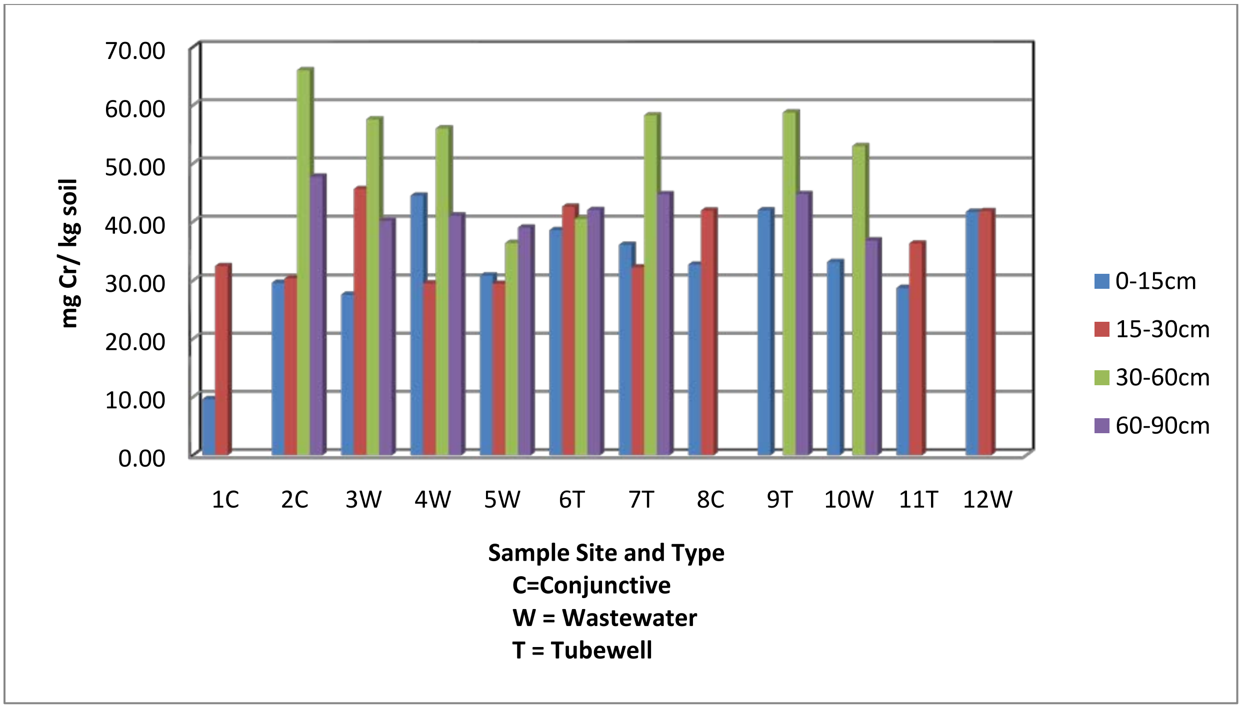


Figure 10. Total Cr concentrations by sample depth and sample site and irrigation type.

Total soil nickel concentrations are shown in Figure 11. Concentrations were generally lower than Cr, ranging from 5-25 mg/kg soil. As with Cd, a spike for site 2C is observed for Ni, further suggesting the soil sample may be contaminated.

Ni samples seem to follow a hybrid of the Cd and Cr trends, with high sample values in the surface 0-15 and lower 30-60cm sample depths, and skipping over the 15-30cm depth. No clear differences appear between different irrigation types.

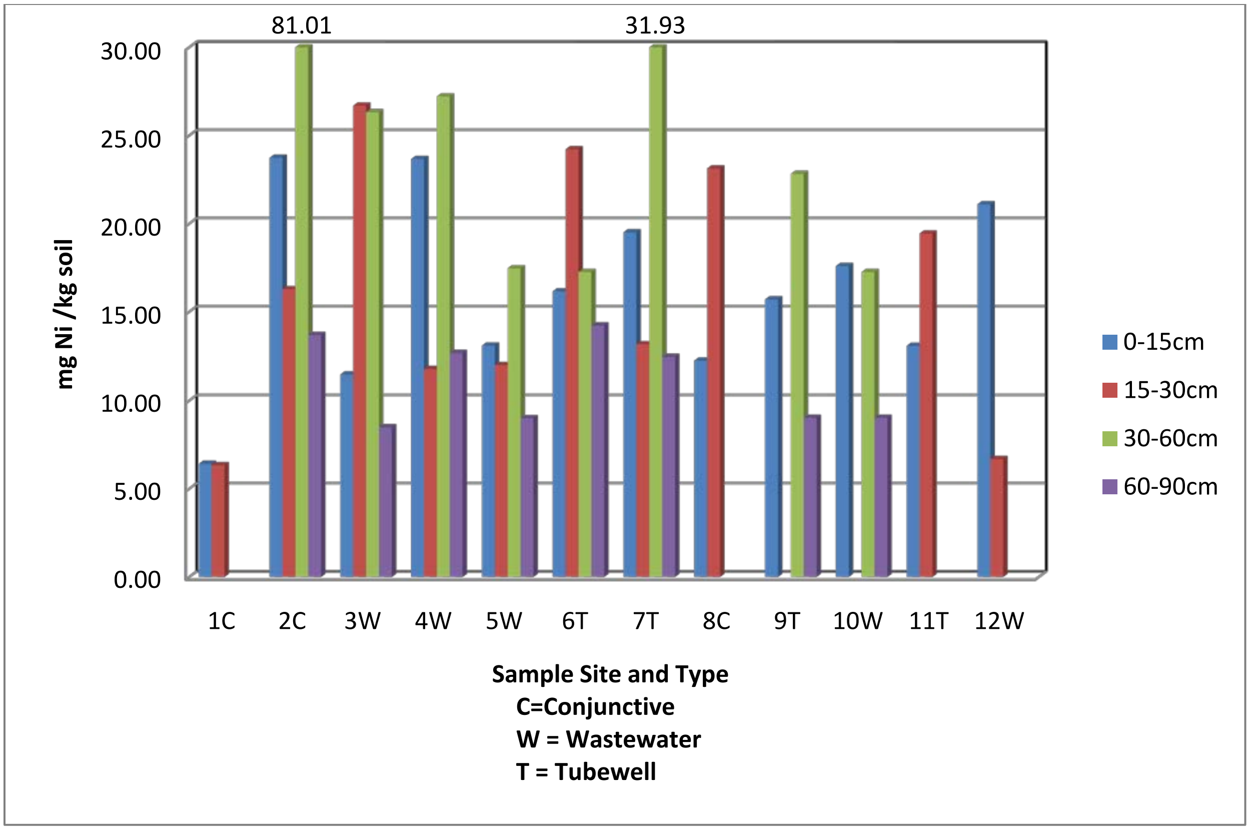


Figure 11. Total Ni concentration for by sample depth and soil sample site and irrigation type.

Other collected soil data, including pH, EC, and ions, are listed in Appendix A.

5.1.1.2 Metals in Soil Chemical Fractions

Sufficient funds were available to analyze soil samples collected only from the top two depth layers, 0-15 cm (A) and 15-30cm (B) for the exchangeable fraction (EF), carbonate fraction (CF), reducible fraction (RF), and organic fraction (OF). The residual fraction (ResF) was not analyzed, nor were the C and D depth layers (30-60 and 60-90cm).

While chromium and nickel were present in sufficient concentrations to be detectable, the UIUC MSICP lab could not resolve cadmium from background noise. It is likely a modified version of the metal extraction procedure could be used to detect cadmium, either increasing the quantity of soil used for the extraction and/or distilling the sample down to a more concentrated volume for analysis.

Some samples were not analyzed due to volume loss through several months of storage and freight from India to the USA. The affected samples are shown below as yellow blocks in Table 5.

Table 5. Fraction samples with insufficient volume for analysis.

	Chromium				**Nickel**			
Site & Depth	**EF mg/kg**	**CF mg/kg**	**RF mg/kg**	**OF mg/kg**	**EF mg/kg**	**CF mg/kg**	**RF mg/kg**	**OF mg/kg**
1A	🟨	1.04	6.2	4.2	🟨	0.08	4.8	2.6
1B	0.12	1.84	5.2	6.2	2.00	2.24	3.6	3.2
2A	0.15	0.49	8.2	3.6	1.92	0.72	13.4	2.8
2B	🟨	4.08	7.2	8.2	🟨	3.44	5.4	3.2
3A	0.07	0.88	18.4	2.6	0.69	0.96	28.0	1.0
3B	0.15	1.68	4.8	3.8	4.24	1.12	2.0	1.7
4A	🟨	0.47	6.6	4.2	🟨	0.76	13.2	3.4
4B	0.08	1.68	5.4	4.4	0.48	2.48	3.8	2.6
5A	🟨	0.41	10.0	8.6	🟨	0.93	11.6	3.2
5B	0.07	1.92	5.6	3.2	0.23	2.64	3.2	1.3
6A	0.10	0.88	10.2	5.0	1.28	0.46	11.2	3.2
6B	0.01	2.00	6.2	3.0	0.08	2.40	4.0	1.0
7A	0.12	🟨	7.6	5.8	0.88	🟨	9.8	2.4
7B	0.08	1.44	7.6	3.2	2.64	1.28	6.4	1.5
8A	🟨	0.73	5.4	6.4	🟨	0.08	5.4	6.4
8B	0.18	2.08	5.8	7.2	3.84	2.80	3.8	3.8
9A	0.26	0.64	5.6	4.2	8.80	0.24	4.8	2.0
9B	🟨	0.69	7.2	4.2	🟨	0.08	5.0	1.7
10A	0.08	0.30	6.6	7.0	0.88	0.45	11.0	5.6
10B	0.12	0.57	6.6	3.0	1.60	0.08	8.2	1.8
11A	0.10	0.80	5.2	42.0	0.08	0.08	4.4	4.0
11B	0.11	🟨	5.8	5.0	2.48	🟨	7.0	2.2
12A	0.07	0.54	5.2	6.8	0.88	0.25	6.0	5.4
12B	0.12	🟨	6.2	4.6	0.72	🟨	5.4	3.2

The results for chromium and nickel are shown in Figures 12 through 15. Chromium was found primarily in the reducible and organic fractions, with the carbonate fraction containing much less Cr and the exchangeable fraction containing only incidental amounts. While the overall trend remains the same, some EF and CF detections were unavailable for some sites (see Table 6).

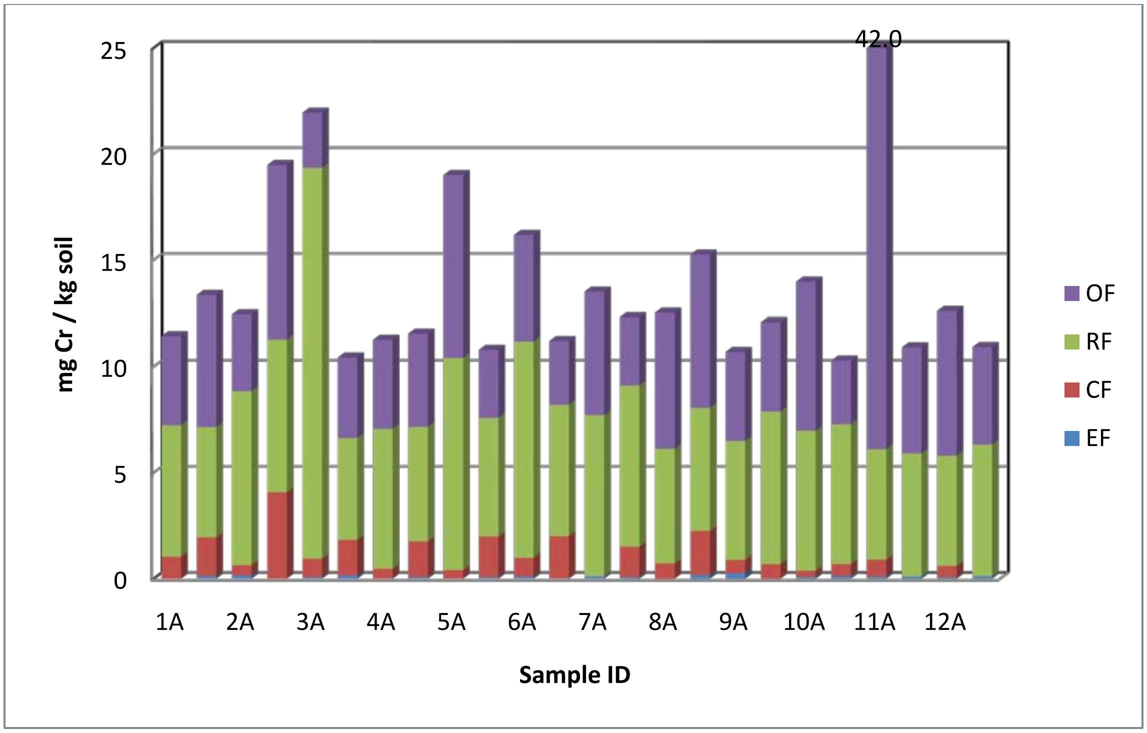


Figure 12. Chromium content (mg/kg) by soil fraction.

Excluding that sample, chromium is present within the organic fraction from 2.6-8.6 mg/kg soil, excluding the spike at site 11A indicating likely OF sample contamination. While it may be rationalized that the high CEC of the organic fraction would retain a significant amount of metals, the fractionation method is designed to remove those metals in the exchangeable fraction, leaving those metals detected in the organic fraction chemically integral within soil biomass. At the overall average OC percent for the A and B depth layers of 0.33%, and using a 1%OC= 1.6%OM ratio would suggest metals accumulate within soil biomass at levels of 492-1630 mg/kg soil organic matter.

Chromium is present within the soil reducible fraction at levels from 4.8-18.4 mg/kg soil – nearly double those of chromium within the soil organic fraction. Perhaps more significantly, while the soil organic material remains relatively constant, the periodic saturation and drying of the soil under flood irrigation practices changes soil redox potential through the crop year, suggesting these metals may be more mobile than the load present within the soil organic complex.

Figure 13 below shows the relation between the total soil metals found by acid deconstruction and the four soil fractions analyzed. The differences may be attributed to irreversibly bound soil metals (ResF), experimental errors, and differences between the two soil samples analyzed. Sites with missing fraction detections (see Table 6) are not included.

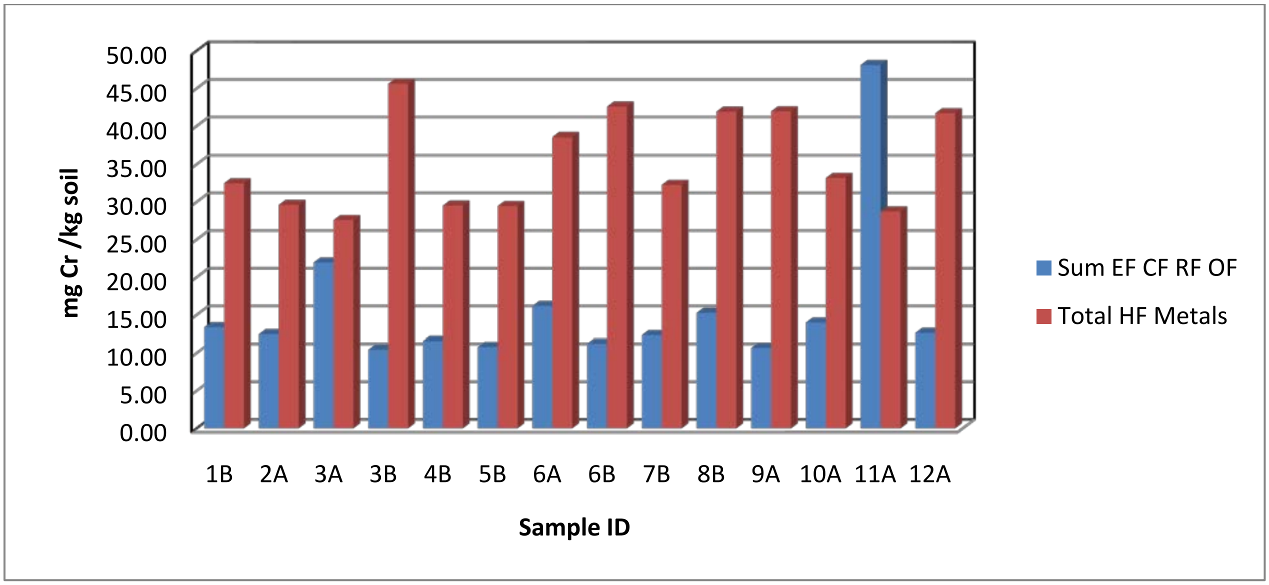


Figure 13. Chromium fraction recovery by selected site.

This graph suggests that generally over 50% of metals observed through HF deconstruction are irreversibly bound within the soil matrix, posing no threat to human consumption. Analysis of the prepared RF samples could validate this finding. Further, the graph validates the expected contamination error for the sample 11A OF detection.

Although some EF samples are notably absent, the general trend of Cr presence is ResF > RF > OF > CF > EF, where the residual metal concentrations are imputed. These findings compare favorably to those of Lucho-Constantino et al. (2005) – the only authors found to have published using Tessier’s method in soil wastewater irrigation applications. Lucho-Constantino et al. similarly found the residual fraction by far to hold the plurality of metals for soil Cr. Remaining Cr was primarily bound to the organic fraction and then the reducible fraction, with trace amounts in the other fractions.

Figure 14 below shows Ni present within soil fractions. Ni is dominantly present in the reducible fraction, but is also notably present in the EF, CF, and OF fractions. As shown in Table 6 above, some EF and CF fractions are not shown.

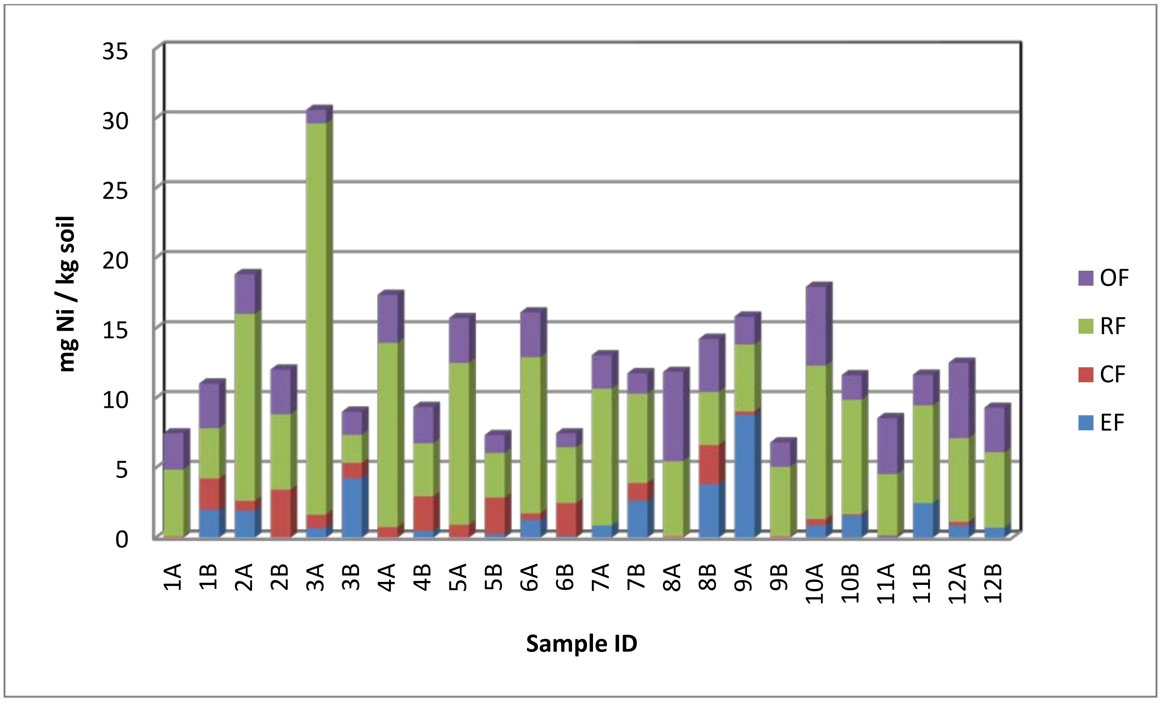


Figure 14. Ni content (mg/kg) by soil fraction.

Nickel is present on the RF from a range of 2-28 mg/kg soil, much greater than the ranges for EF, CF, and OF. As with Cr above, this suggests the flood irrigation pattern resulting in changing redox potential could pose a mobility risk. Nickel is also present on the exchangeable fraction from trace concentrations up to 8.80 mg/kg soil for those samples represented in the above graph (see Table 6), suggesting plant uptake of nickel may be probable.

Fraction recovery is compared to HF deconstruction in Figure 15 below. As for chromium above, the sites selected included those in which all fraction samples had sufficient quantity for analysis after freight to the USA. In eight of the selected sites, fraction recovery exceeds the total Ni detected by HF deconstruction, from 126-324%. This suggests that the fractionation process may have introduced Ni contamination, or that the latency between the initial HF deconstruction and sample testing again introduced errors.

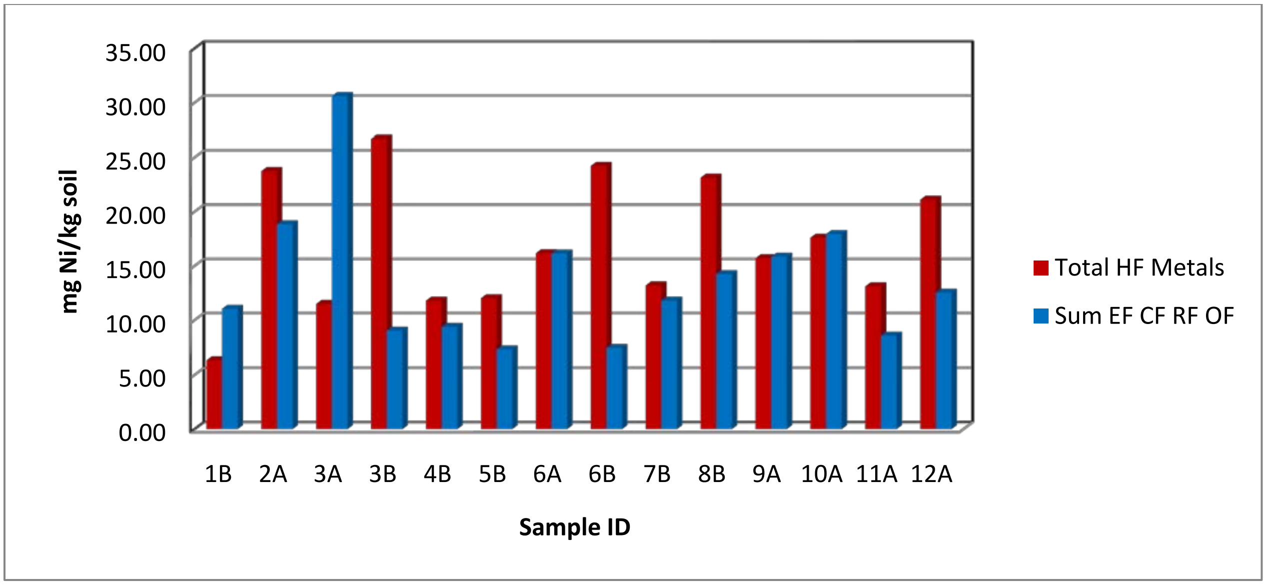


Figure 15. Ni Fraction recovery by selected site.

Given the unexpected high recoveries, a meaningful residual fraction trend cannot be imputed. For the fractions analyzed, nickel is detected RF > OF > EF > CF. Were all EF and CF fractions analyzed, it is likely EF could overtake OF as the fraction in which the second-highest Ni detections were found.

5.2 Toxic Metals Removal by Sorbents

Removals were tested by sorption kinetics, adsorption isotherms, and column modeling. The raw data from the initial rounds of testing are shown in Appendix B. Results from the repeated experiments are shown in Figures 16-31. As can be seen in Appendix B, the data shows wide fluctuations. Samples from the initial round of experiments awaited analysis for up to 6 weeks. The wait time is believed to have allowed settling of suspended organics present in the native wastewater, reducing aqueous sorbed metals. The settled organics and metals would not have been aspirated by the AAS feed tube, leading to inaccurate representations of metal contents, and is one possible explanation for the inexplicably low concentration results of the initial experiments.

5.2.1 Sorption Kinetics

The sorption kinetics data and results are displayed in several forms for Cr and Ni in the following section. Cadmium in samples was unable to be resolved from background levels using flame AAS. It is likely that Cd may have a higher sorption affinity than either Cr or Ni, and is thus scavenged to lower concentrations during preferential sorption.

5.2.1.1 Chromium Kinetics

Transforming the concentration data to show the percent of chromium adsorbed, Figure 17 shows the effect of sorbent contact time on chromium. The immediate (1-hr) 100% removal of Cr by carbon suggests the sorption sites were not saturated, rendering the carbon experiment invalid for complete comparison to the other sorbents. However, the other sorbents did not reach 100% saturation, allowing for comparison between them.

Gypsum was nearly completely ineffective at precipitating Cr. Sawdust led both rice husk and bagasse in performance for Cr removal, eventually removing over 80% of the Cr. Sawdust, bagasse, and rice husk shared similar trends in adsorbance. While the rate of removal slowed with time, removal slowly continued throughout the 48 hours. This suggests that additional sorption sites became available throughout the experiment, possibly through decay and exposure to additional surfaces. It is possible that more finely processing the material would result in improved removal through exposure to more active surfaces.

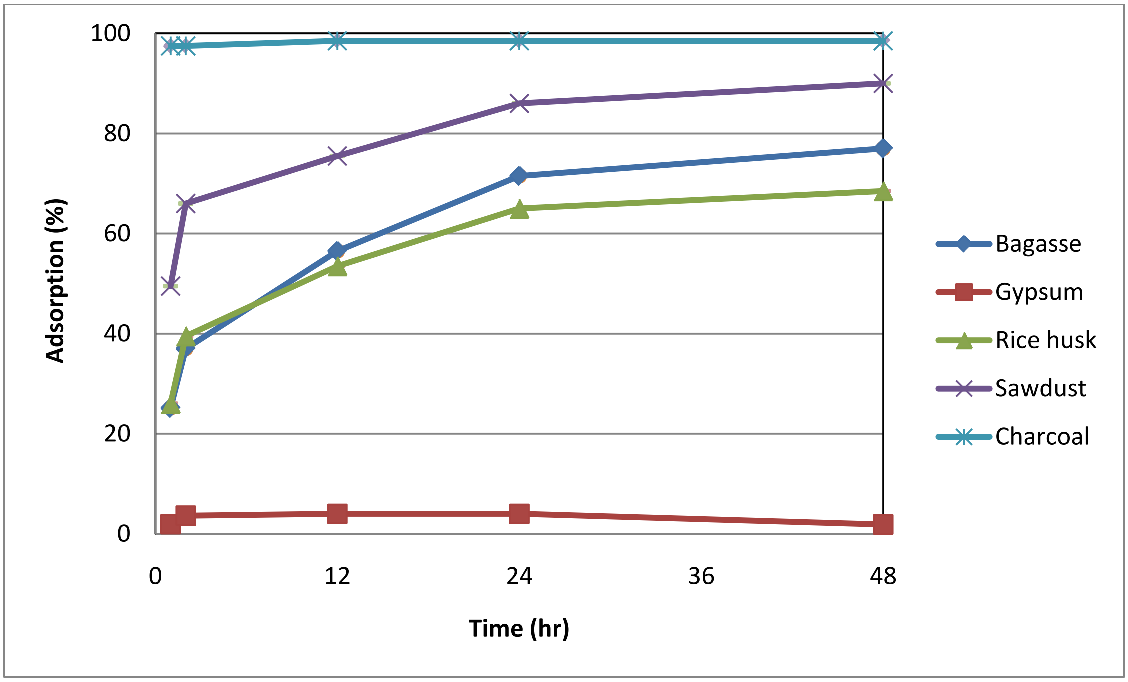


Figure 16. Plot of % adsorption vs. contact time for chromium.

At the low initial concentration of 20 ppm, chromium achieved a maximum 48-hr loading capacity of 0.90, 0.78, and 0.68 mg Cr/mg of sawdust, bagasse, and rice husk sorbents, respectively. In general, the loading rates achieved are expected to be far below the maximum rates found in the literature. The relatively dilute nature of the solution, combined with the relatively low amount of solution placed into contact with the sorbent, would not suggest otherwise. It is possible that a repeat experiment would place a much smaller amount of sorbent in contact with the solution to achieve higher loading rates. However, such a repeat experiment would not mimic the realistic conditions of low environmental metal concentrations as the performed experiment attempts.

From the plot it is apparent the activated carbon nears 100% Cr removal within the first hour – the sorption is rapid. Without any data points in the first hour, and without saturating the sorption sites, an accurate sorption model for carbon cannot be accurately fit. The opposite is true for gypsum – minimal removal is accomplished throughout the 48-hr test period. However, for bagasse, ground rice husk, and sawdust sufficient resolution appears present to fit sorption models. By assuming the 48-hr concentration to be the equilibrium concentration and linearizing the Lagergren equation, pseudo-first and pseudo-second order models were fitted to the data. Figures 17 and 18 below show the linearized plots for the pseudo 1^{st}- and 2^{nd}-order models.

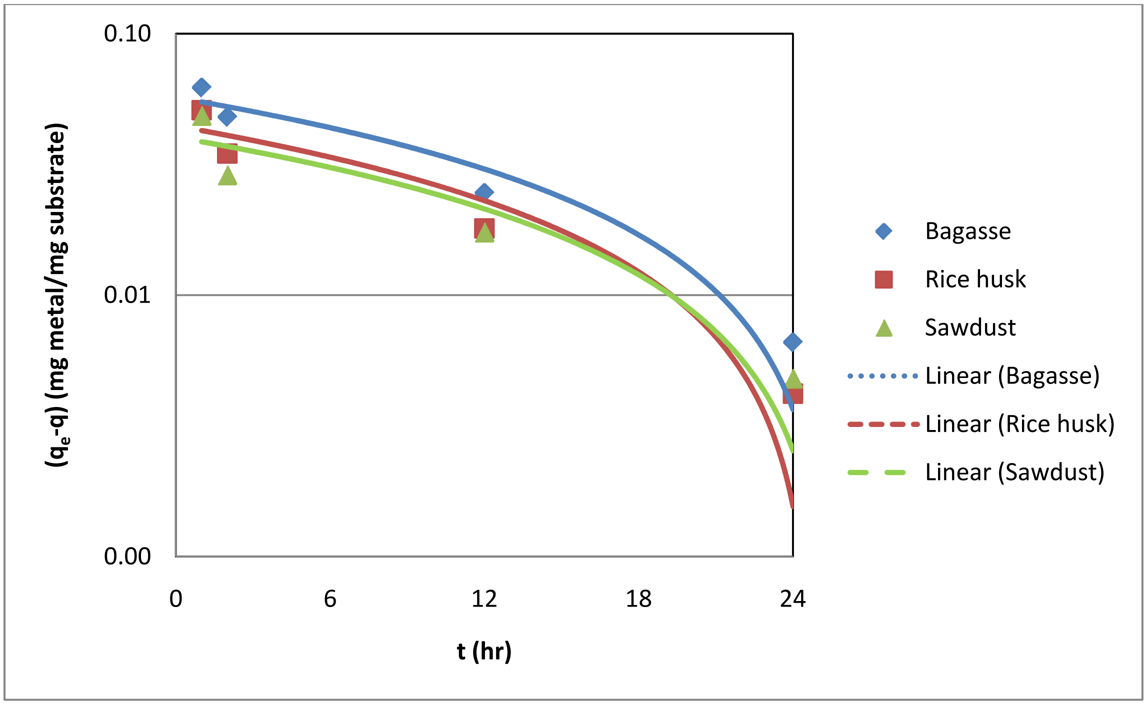


Figure 17. Lagergren 1st-order plots for Cr.

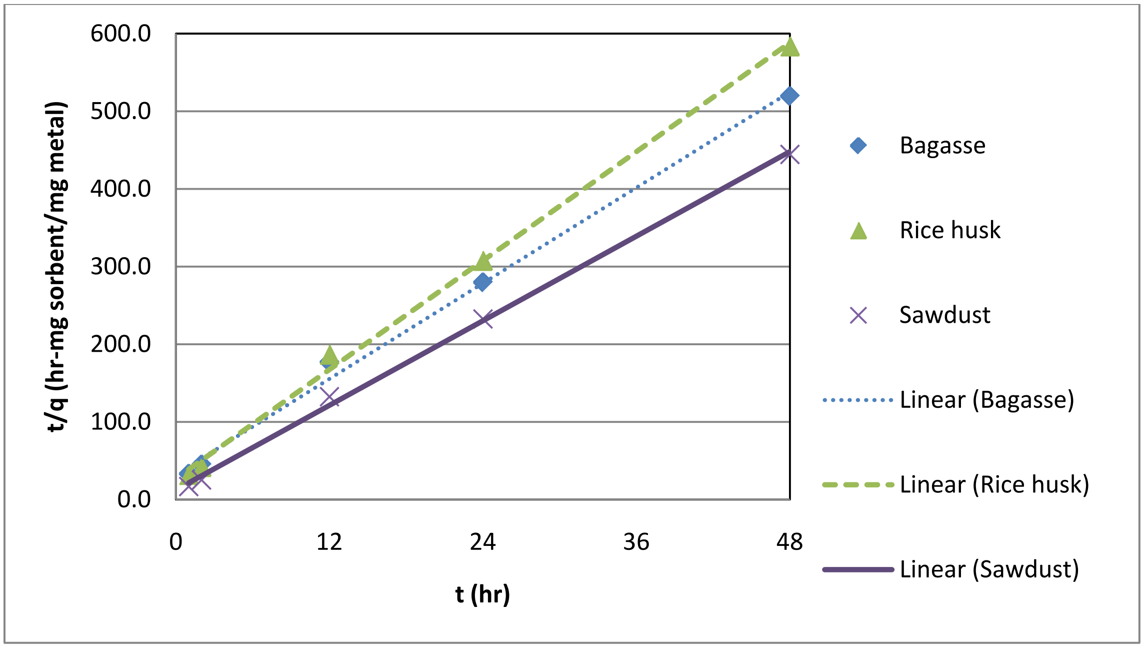


Figure 18. Pseudo- 2nd-order plots for Cr.

With linear best-fit lines applied to the data, the r^2 and coefficient values for the three sorbents responsive to the metal loading are given in Table 7 below.

Table 6. Chromium kinetic model constants and correlation values for Eqs. 1 and 2.

Chromium Sorbent	1st-order			2nd-order		
	q_e	K_1	r^2	q_e	K_2	r^2
Bagasse	-0.093	-2.7285	0.9868	0.0974	3.26	0.9960
Rice husk	-0.1014	-2.9673	0.9788	0.0855	5.04	0.9975
Sawdust	-0.0906	-3.1068	0.9590	0.1102	6.67	0.9985

While criticism of linearizing such models exists in the literature (McCuen and Surbeck, 2008; Kumar and Sivanesan, 2006), in particular suggesting linearization overstates the accuracy of said models, the standard method for reporting results has been via linearization of pseudo-first and pseudo-second order models (Kumar and Sivanesan, 2006; Guo et al., 2008; Ho and McKay, 1999; Kumar and Bandyopadhyay, 2005).

The information-based AIC and BIC criteria for the chromium kinetic models are shown below in Table 7. Lower values indicate models more closely represent the observed data. For chromium, contrary to r^2 values, the first-order model appears superior to the linearized second-order model.

Table 7. Chromium kinetics AIC and BIC values.

Chromium Sorbent	AIC 1st-order	AIC 2nd-order	BIC 1st-order	BIC 2nd-order
Bagasse	-23.6	5.5	-33.6	-1.3
Rice husk	-52.7	7.0	-62.7	0.2
Sawdust	-25.9	6.9	-35.9	0.1

It is also appropriate to recognize that the range over which these kinetics have been fit is on the high end of the literature. These experiments test kinetic results over a 48-hr period, similar to that of Mohan and Singh (2002) and Celik and Demirbas (2005), as opposed to the shorter 1-6 hour periods in the literature (Kumar and Bandyopadhyay, 2005; Wong et al., 2005). It is interesting to note that removals continued up through 24 hours, as opposed to more typical equilibrium times of some 1-2 hours found in the literature.

The relative paucity of equilibrium points does also bring into question whether the 48-hr value does accurately represent the equilibrium (q_e) value for kinetics modeling purposes. The 24-hr data points would suggest the 48-hr points to be approaching equilibrium; it appears however somewhat risky to consider the value at the outside of the data range to be a typical equilibrium value.

5.2.1.2 Nickel Kinetics

Figure 19 shows percent adsorption of Ni in solution onto sorbent materials. While activated carbon scavenged all Cr from the solution within the first hour, the efficacy for Ni was much less. Conversely, whereas gypsum was ineffective for Cr, it performed nearly as well as rice husk for Ni removal. .

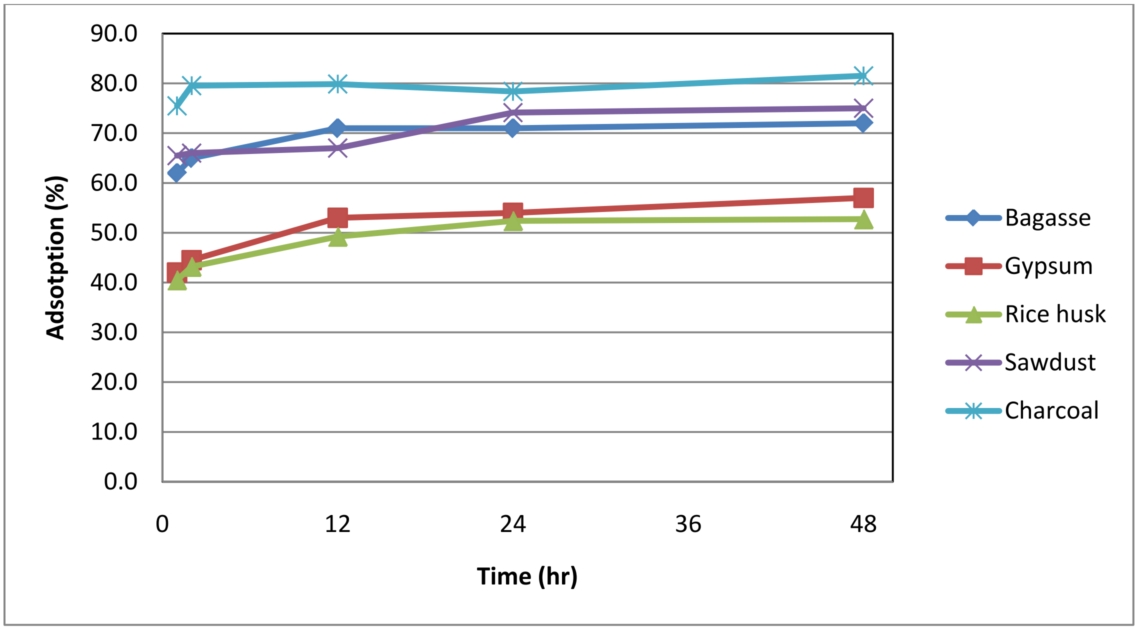


Figure 19. Percent Ni adsorption plotted against time.

Overall, the adsorbents are less responsive to Ni adsorption than Cr adsorption. Activated carbon remains the superior treatment, but sawdust and sugarcane bagasse, responding similarly to Ni adsorption, perform to within 85% of activated carbon's sorption capacity. Nickel is sorbed at a capacity of 0.98, 0.90, 0.86, 0.69, and 0.64 mg/mg of activated carbon, sawdust, bagasse, gypsum, and rice husk sorbents, respectively.

The Lagergren 1-st order kinetics and a pseudo-second order kinetic model were fit to the nickel sorption capacity data for all sorbents but activated carbon, which reaches saturation levels at one hour. The results are shown below in Figures 20 and 21.

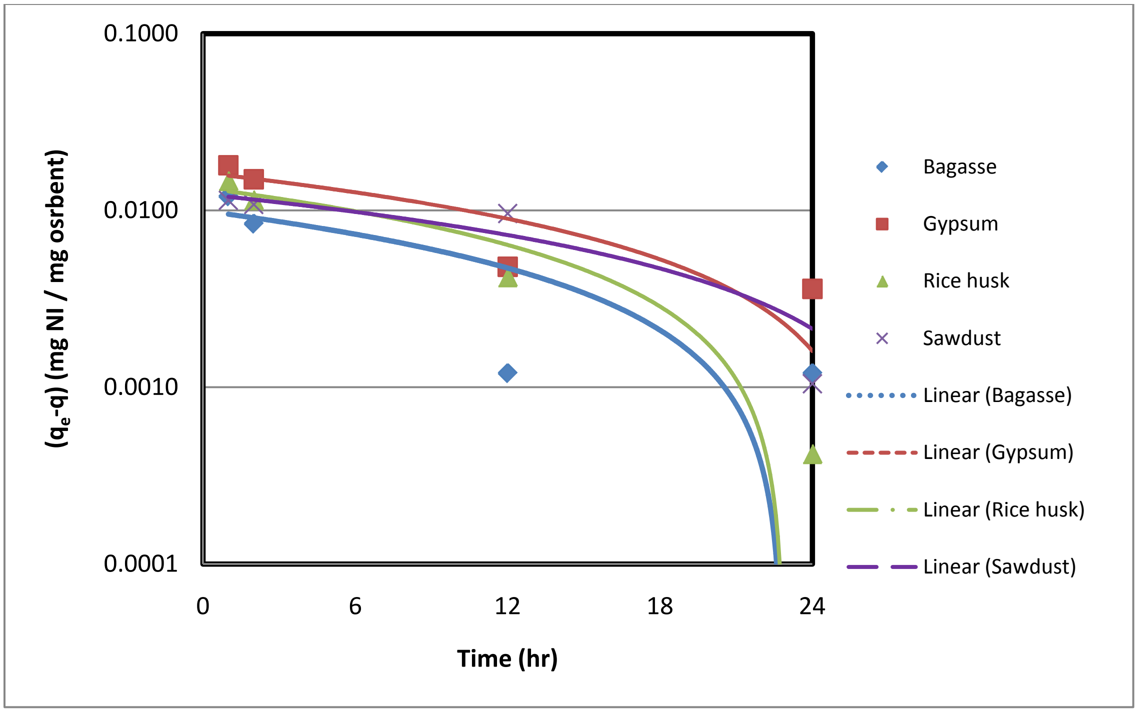


Figure 20. Lagergren first-order kinetics for Nickel.

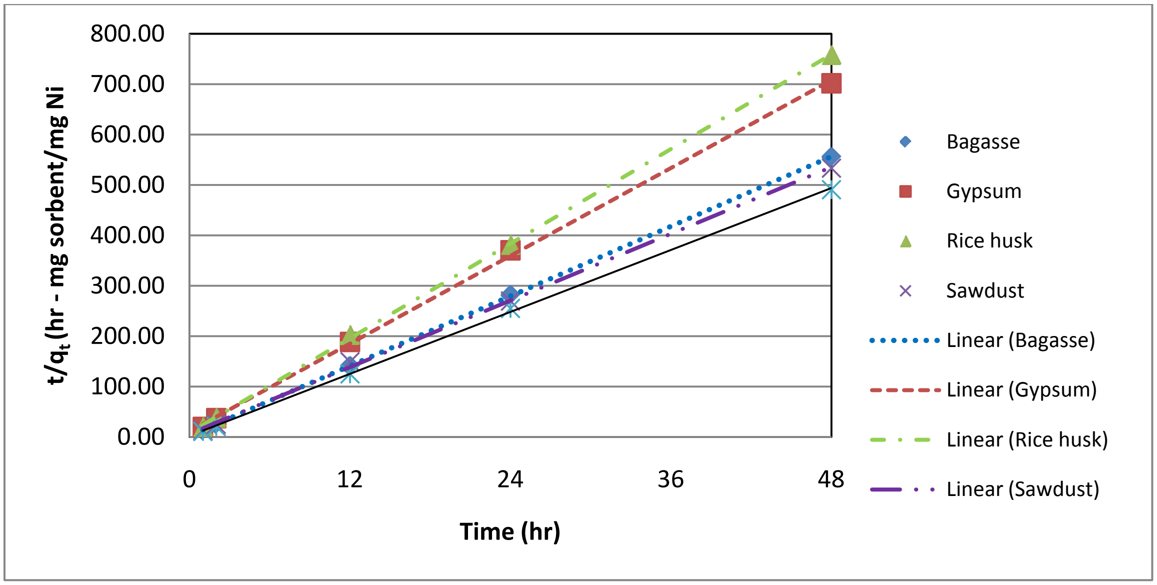


Figure 21. Lagergren 2nd-order plot for Nickel.

Table 8 below shows the r^2 and constant values for the two kinetic models, while table 9 shows AIC and BIC values. While simple r^2 would suggest the linearized second-order model to be superior, AIC and BIC indicate the first-order model most closely represents the observed data for all sorbents. The goodness-of-fit value for bagasse pseudo-second order sorption illustrates the concerns of using model linearization techniques.

Table 8. Nickel kinetics model constants and correlation values for Eqs. 1 and 2.

Nickel Sorbent	1-st order q_e	K_1	r^2	2nd-order q_e	K_2	r^2
Bagasse	-0.102	-4.67	0.7867	0.087	50.00	1.0000
Gypsum	-0.071	-4.10	0.8939	0.069	19.14	0.9993
Rice husk	-0.150	-4.03	0.9785	0.064	29.35	0.9998
Sawdust	-0.099	-4.17	0.8325	0.091	19.19	0.9992

Table 9. Nickel kinetics AIC and BIC values.

Nickel Sorbent	AIC 1st-order	AIC 2nd-order	BIC 1st-order	BIC 2nd-order
Bagasse	-40.7	8.4	-47.5	1.7
Gypsum	-35.6	7.7	-42.4	0.9
Rice Husk	-38.1	8.1	-44.9	1.3
Sawdust	-38.4	7.7	-45.2	0.9
Charcoal	-45.8	8.3	-52.6	1.5

5.2.2 Equilibrium Isotherms

Results for the 12-hour isotherms are presented in the following section. While twelve hours is a different period of time than the 48-hr equilibrium concentrations used for kinetics modeling, the kinetics show overall the 12- and 48-hr ending concentrations are substantially the same in comparison to the initial concentrations.

5.2.2.1 Chromium

Figures 22 and 23 below show the 12-hr Freundlich and Langmuir isotherm plots for chromium.

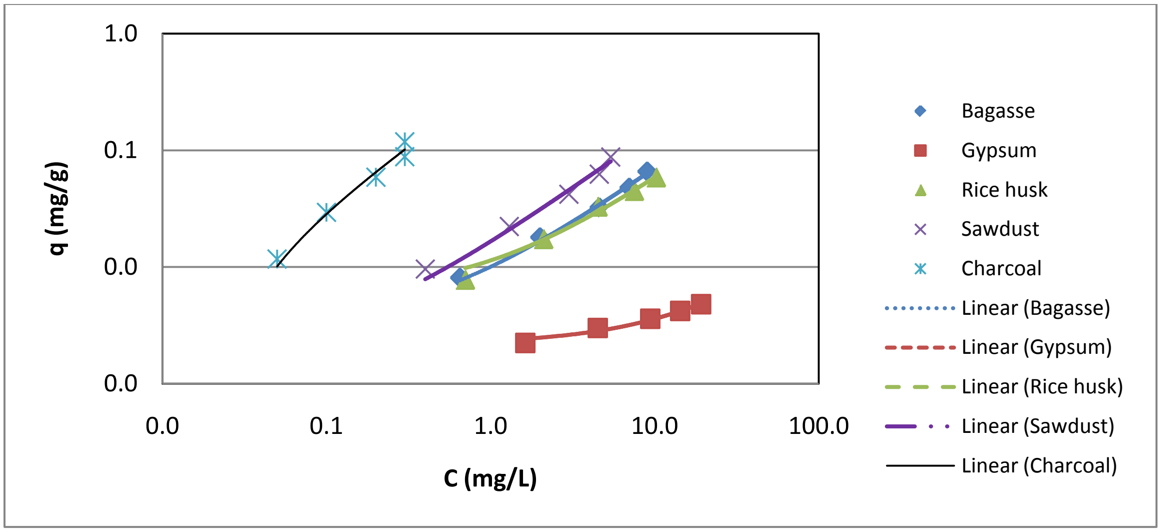


Figure 22. 12-hr Freundlich isotherm for Cr.

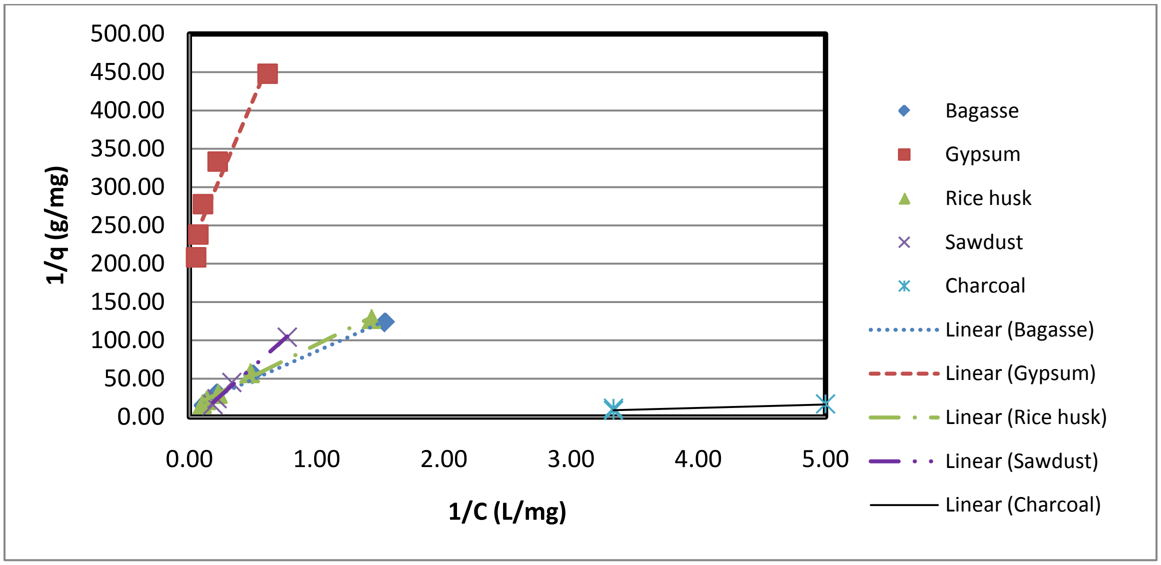


Figure 23. 12-hr Langmuir isotherm for Cr.

The fit constants, K_f and n for Freundlich and K_a for Langmuir isotherms, respectively, are shown in the Table 9 below, along with the r^2 value from the linear best fit line from which the constants were derived.

Table 10. Chromium isotherm model constants and correlation values for Eqs. 5 and 7.

Chromium	Freundlich			Langmuir		
	K_f	n	r^2	q_e	K_a	r^2
Bagasse	0.010842	0.7763	0.9922	0.081553	0.16676	0.9892
Gypsum	0.001906	0.3007	0.9919	0.004593	0.556032	0.9385
Rice husk	0.010172	0.7531	0.9987	0.082129	0.147778	0.9939
Sawdust	0.01905	0.8123	0.9856	-0.12151	-0.05581	0.9943
Charcoal	0.42228	1.1874	0.9848	-0.16219	-1.37294	0.992

From the table, it appears that, generally, the chromium isotherms fit very well and are very closely grouped in goodness of fit with the exception of the Langmuir isotherm for gypsum. While the goodness-of-fit may seem high, similar r^2 values (>0.95) have been achieved by many authors for metal sorption onto these alternative sorbents, including Cd, Zn, Pb, Ni, and Cr (Mohan and Singh, 2002; Krishnani et al., 2008; Guo et al., 2008; Kumar and Bandyopadhyay, 2006).

5.2.2.2 Nickel

Figures 24 and 25 below show the Freundlich and Langmuir isotherms for Ni sorption.

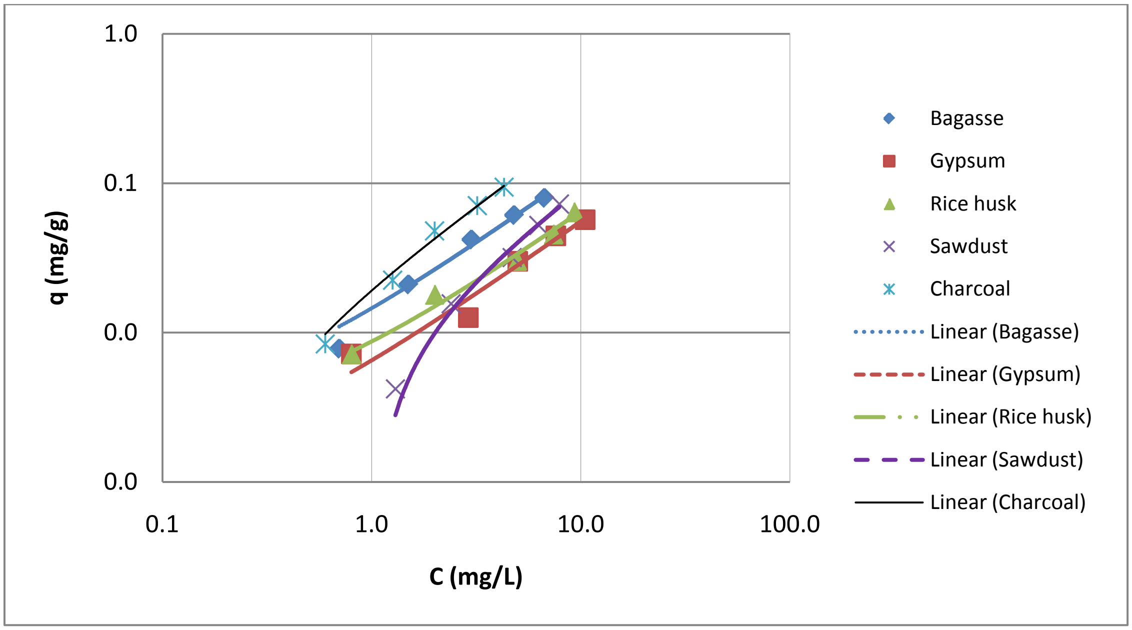


Figure 24. Freundlich isotherm for Ni.

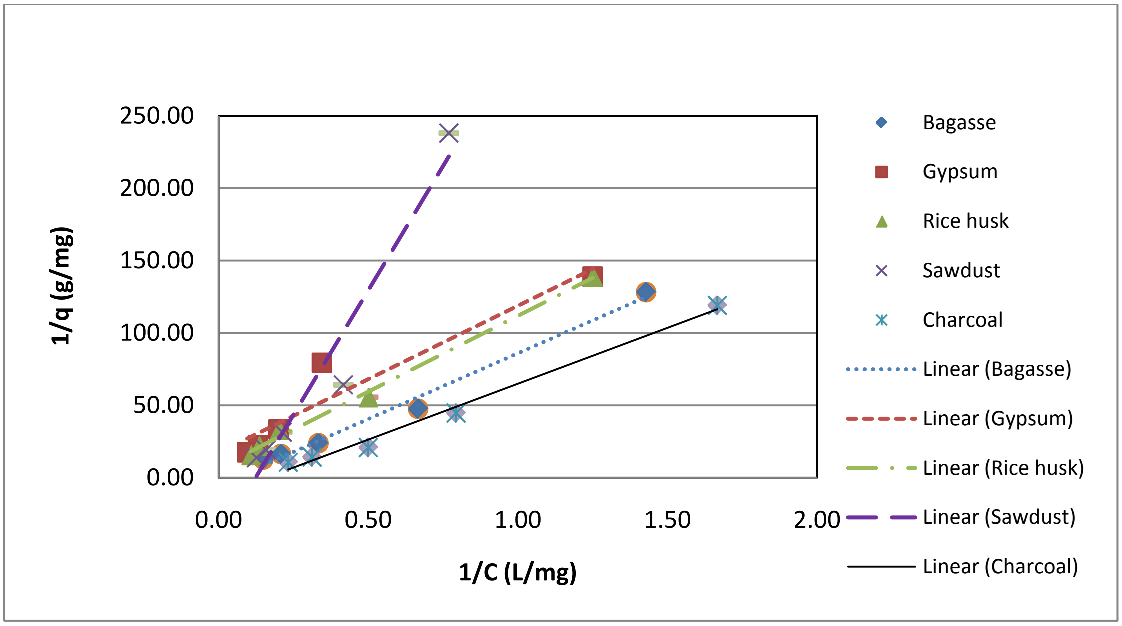


Figure 25. Langmuir isotherm for Ni.

The fit constants, K_f and n for Freundlich and K_a for Langmuir isotherms, respectively, are shown in the Table 10 below, along with the r^2 value from the linear best fit line from which the constants were derived. As discussed above, such high r^2 values have been widely achieved throughout the literature. In contrast to chromium above, the Freundlich isotherm appears to describe the behavior of nickel sorption onto these treatments marginally better than the Langmuir isotherm. However, all treatments have r^2 values > 0.90, suggesting the trends and assumptions inherent in the Langmuir and Freundlich isotherms are reasonable for these removal approaches.

Table 11. Nickel isotherm model constants and correlation values for Eqs. 5 and 7.

Nickel	**Freundlich**			**Langmuir**		
	K_f	**n**	**r^2**	**q_e**	**K_a**	**r^2**
Bagasse	0.01245	1.0223	0.9890	-0.204	0.054	0.9893
Gypsum	0.00743	0.8376	0.9436	0.058	0.171	0.9111
Rice husk	0.00898	0.8377	0.9855	0.143	0.067	0.9953
Saw dust	0.00325	1.5159	0.9837	-0.024	0.124	0.9488
Charcoal	0.01692	1.2432	0.9878	-0.081	0.159	0.9894

5.2.3 Column Studies

The column studies were expected to provide the most realistic and applicable results of any of the modeling experiments performed in this work. It is unfortunate that the packing process slowed hydraulic conductivity to the point that it was not possible to collect the desired amount of leachate in the experimental time available. As discussed in the methods section, a top limit of 25L was selected for leachate collection as just-in-time analysis was not available to detect metal breakthrough. Those samples were later discarded due to sample testing latency, and subsequent quantities of water were passed through the columns.

The repeat column experiment for nickel were operated through 16, 12, 11, 9, and 5 liters of effluent for the sugarcane bagasse and control, gypsum, rice husk, sawdust, and charcoal treatments, respectively. As these figures highlight, the packing process was extremely effective in achieving complete saturation of the treatment media. Equivalent packing efforts resulted in notable differences in flow rate through the columns. Finer-sized media, such as the powdered activated carbon, was packed to very low flow rates, while coarser particles such as gypsum, ground rice husk, and sawdust had higher conductivities. The highest flow rate was observed for the coarsely ground and spongy sugarcane bagasse media.

Although the columns were not subject to any appreciable head pressures (<10cm H_2O), this does suggest standard approaches used to force water through activated carbon PFR's would have to be modified for head pressure, packing density, and/or depth to achieve equivalent contact times, beyond any modifications which may be desirable to achieve longer contact times due to media less activated than PAC.

The results are presented in the following sections in terms of volumetric concentration breakthrough curves. As with the kinetic and isotherm results, cadmium was unable to be resolved from column effluent.

5.2.3.1 Nickel

The nickel breakthrough curves are presented below in Figure 30. The initial wastewater spiked 20ppm Ni concentrations fall to below 3ppm for the first liter of effluent, before rising to as high as 6ppm. No columns appear to have reached total breakthrough – not even the control columns.

The DI water control treatments have an average 0.94ppm concentration, with a 0.33ppm standard deviation. While this might suggest all detections are 1ppm too high, the 5 liters of effluent passed through activated carbon all have lower detections than the control, suggesting either some link in the $CaCO_3$/sand/felt chain is contaminated with pervasive low Ni concentrations or that the DI control water source is contaminated.

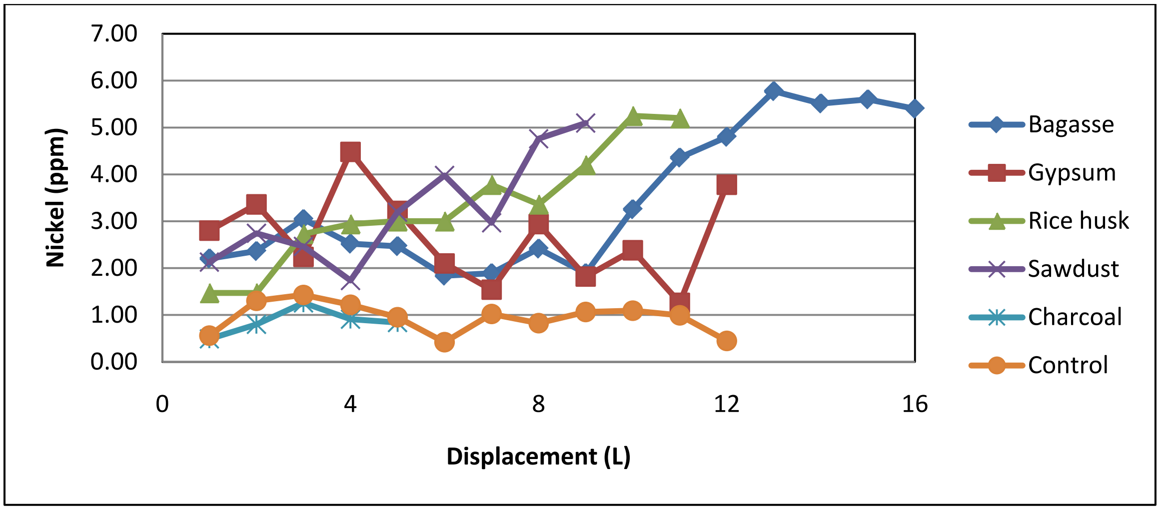


Figure 26. Ni breakthrough curves.

The bagasse, gypsum, and sawdust treatments exhibit a trend where a local concentration maximum exists between 3-6 liters of effluent. The nonlinear trend appears to continue for the control and bagasse treatments. Rice husk and sawdust treatments were not operated through sufficient effluent volumes to determine if the trend continues.

Bagasse, rice husk, and sawdust treatment exhibited a positive overall trend. Although breakthrough is not a linear process, this suggests the three treatments are headed towards breakthrough. The slightly negative trend for gypsum is consistent with the gypsum metal removal mechanism, which is chemical precipitation via pH modification. This trend might be expected to continue until all gypsum was dissolved into the passing effluent stream.

5.2.3.2 Chromium

Chromium breakthrough curves are presented below in Figure 31. Contrary to the nickel breakthroughs shown above, three distinct breakthrough patterns are apparent for Cr. Gypsum is completely ineffective at Cr removal, closely tracking the spiked control effluent concentrations. Bagasse, rice husk, and sawdust perform consistently with each other, leaving 4-7ppm Cr in the effluent. Activated carbon scavenges all Cr present down to trace levels. These findings reinforce the sorbent-Cr sorption trends discussed above.

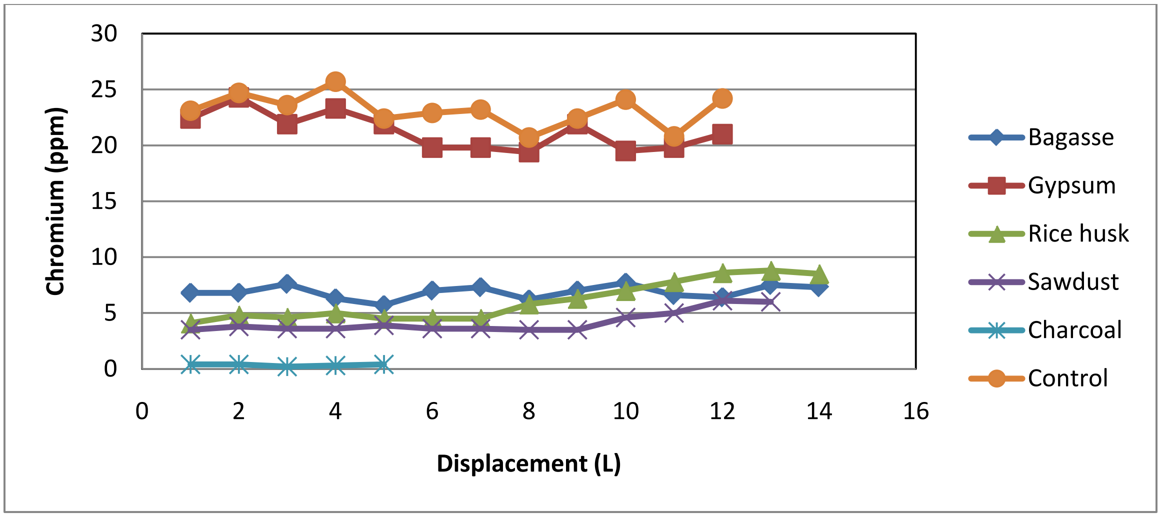


Figure 27. Cr breakthrough curves.

CHAPTER 6: CONCLUSIONS

This research utilized a variety of novel concepts to characterize cadmium, nickel, and chromium in the plant-soil-water system near Panipat, India and assess the effectiveness of sugarcane bagasse, sawdust, gypsum, and ground rice husk to remove metals from environmental wastewaters.

Plant and soil samples were gathered from fields representing the spectrum of irrigation choices: exclusive use of industrially-contaminated surface water or groundwater as well as the conjunctive use of both. Water samples were gathered from groundwater sources as well as the conjunction of the industrial effluent pipe and irrigation stream. It is unfortunate that the flame AAS detection method was unable to yield distinguishable levels of plant and water metal contamination in the samples tested. A more accurate detection method is expected to determine trace metal concentrations, allowing BCF's and total soil metal loadings to be estimated.

Soils were not only sampled 90cm deep into the soil profile but also fractionated into five distinct chemical pools. A simple test for total metals indicated the concentrations of Cr > Ni > Cd, with soil metal concentrations in the upper 90cm of soils ranging from 5-65, 5-25, and 0.02-0.7 mg/kg soil, respectively. Cadmium concentrations tended to fall with depth, while Cr concentrations peaked from 30-60m mg/kg soil and Ni showed a trend of double peaks in the 0-15 and 30-60cm sampling layers. The evidence suggests metals may be more prevalent in groundwater irrigated fields as opposed to surfacewater-irrigated fields, possibly due to contaminated groundwaters. This finding is most unexpected based on the literature and anecdotal evidence of local scientists.

For the top two soil layers (0-15 and 15-30cm), total soil Cr and Ni were further characterized by chemical binding mechanism into suspected soil pools via Tessier's method. Nickel was bound to soil fractions RF > OF > EF > CF. Chromium was bound onto the soil fractions RF > OF > CF > EF. Higher concentrations on the soil reducible fractions suggest metals may become available during redox changes, such as occur when a rice paddy is flooded. Increased mobility during rice nutrient uptake would be a direct pathway to human consumption, increasing metal toxicity and cancer risks.

With an eye towards reducing soil metal loading, the inexpensive sorbents sugarcane bagasse, sawdust, ground rice husk, and gypsum were compared to powdered activated carbon for sorption capacity and speed, and metal scavenging ability. Bagasse, ground rice husk, and sawdust all trended similarly for Cr removal,, while gypsum was an ineffective treatment. For Ni removal, gypsum and rice husk performed similarly, as did sawdust and bagasse, with the latter scavenging metals to lower concentration than the former. Cadmium concentrations were too low to be identified from background noise. The processes employed competitive sorption, wherein all metals were present in solution simultaneously. Cadmium may have outcompeted Cr and Ni for sorption sites on sorbent materials.

In an effort to standardize comparisons, the sorbents were fit to linearized first- and second-order kinetic models and Langmuir and Freundlich isotherms. High r2 values were achieved for linearized kinetics fits, particularly for the second-order equations. Conventional F- and t-tests are not suitable to test these non-nested models for statistical validity. However, the information-theoretic based approaches of AIC and BIC indicated that first-order sorption kinetics were a better fit for all sorbents than the linearized pseudo-second order sorption model.

Both Langmuir and Freundlich isotherms described the observed data. The low number of sample points may have contributed to the high r2 values (> 0.95), although other authors have achieved similar values. This suggests the assumptions inherent in the Langmuir and Freundlich isotherms, i.e. monolayer absorption, are appropriate for these sorbents.

Sorbents were used to fill constant-head packed-bed column reactors (PFR’s) to mimic actual field-use situations. Breakthrough curves were inconclusive, likely due to the relatively dilute and low volumes of wastewater passed through them. Further investigation along this vein appears warranted to generate the realistic data required to successfully engineer and implement alternative sorbent-based PFR’s.

These overall results indicate possible treatment methods and materials for industrial wastewater that can be used for irrigation or used as supplemental irrigation in Indian conditions. Locally available low-cost materials show great promise to be used as metal removal media. Further investigation with small plots and field scales would be necessary to confirm the benefit of results found in this study to make a realistic impact on Indian agriculture.

CHAPTER 7: FUTURE WORK RECOMMENDATIONS

Time, equipment, and financial resources constrained some elements of this research. The literature suggests some other metals,notably lead (Yadav et al., 2002), may be present at levels of concern in northern Indian soils. While extensive work has been performed, none has been published using Tessier's method in the northern Indian wastewater irrigation context. Total metal samples indicating the presence of metals deep in the soil profile (>30cm) suggest further sample preparation via Tessier's method may also prove rewarding.

Further soil characteristic comparison may prove of interest to soil scientists. Singh et al. (2006) used a method of multiple statistical regression to compare effects of soil metals and measured soil parameters. In particular, CEC and CaCO3 determination may provide valuable parameters against which to compare soil metal EF and CF concentrations.

Analysis of plant and water samples via MS-ICP or graphite furnace AAS would provide bioconcentration data, as well as providing baseline data for surface water and groundwater metal concentrations.

Operating the comparative column study to breakthrough to determine realistic sorbent metal capacity (mg/kg) would provide a valuable comparison of different materials under similar lab conditions. This would be an initial step towards quantifying the necessary relationships to use amendments in common practice.

REFERENCES

Ahmad, I., S. Hayat, and J. Pichtel. 2005. *Heavy Metal Contamination of Soil: Problems and Remedies*. Enfield, USA: Science Publishers, Inc.

Aulakh, M. S., M.P.S. Khurana, and D. Singh. 2009. Water Polluted Related to Agricultural, Industrial, and Urban Activities, and its Effects on the Food Chain: Case Studies from Punjab. *Journal of New Seeds* 10 (2): 112-137.

Babel, S., and T.A. Kurniawan. 2003. Low-cost adsorbents for heavy metal uptake from contaminated water: a review. *Journal of Hazardous Materials* B97: 219-243.

Bahmanyar, M. A. 2008. Cadmium, Nickel, Chromium, and Lead Levels in Soils and Vegetables under Long-Term Irrigation with Industrial Wastewater. *Communication s in Soil Science and Plant Analysis* 39: 2068-2079.

Bailey, S. E., T.J. Olin, R.M. Bricka, and D.D. Adrian. 1998. A review of potentially low-cost sorbents for heavy metals. *Water Resources* 33(11): 2469-2479.

Chlopecka, A., J.R. Bacon, M.J. Wilson, and J. Kay. 1996. Heavy Metals in the Environment. *Journal of Environmental Quality* 25: 69-79.

Celik, A., and A. Demirbas. 2005. Removal of Heavy Metal Ions from Aqueous Solutions via Adsorption onto Modified Lignin from Pulping Wastes. *Energy Sources* 27: 1167-1177.

Duffus, J. H. 2002. “Heavy Metals” – A Meaningless Term? *Pure Appl. Chem.* 74(5): 793-807.

Guo, X., S. Zhang, and X. Shan. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials* 151: 134-142.

Ho, Y.S., and G. McKay. 1998. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Trans. Inst. Chem.* 76B: 332-340.

Jain, C. K. 2004. Metal fractionation study on bed sediments of River Yamuna, India. *Water Research* 38(3): 569-579.

Jain, H. G., and G.J. Chakrapani. 2008. Enrichment and fractionation of heavy metals in bed sediments of River Narmada, India. *Environmental Monitoring and Assessment* 141(1-3): 35-48.

Kabata-Pendias, A. 1993. Behavioral properties of trace metals in soils. *Applied Geochemistry* 2: 3-9.

Krishna, A. K., and P.K. Govil. 2004. Heavy metal contamination of soil around Pali Industrial Area, Rajasthan, India. *Environmental Geology* 47: 38-44.

Krishnani, K. K., X. Meng, C. Christodoulatos, and V.M. Boddu. 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *Journal of Hazardous Materials* 153: 1222-1234.

Kumar, U., and M. Bandyopadhyay. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology* 97: 104-109.

Kumar, V. K., and S. Sivanesan. 2005. Selection of optimum sorption kinetics: Comparison of linear and non-linear method. *Journal of Hazardous Materials* B134: 277-279.

Lagergren, S. 1898. Zur theorie der sogenannten adsorption gelster stoffe. *Kungliga*
Svenska Vetenskapsakademiens. Handlingar 24(4): 1-39.
Translation: 'About the theory of so-called adsorption of soluble substances'

Lucho-Constantino, C., F. Prieto-Garcia, L.M. Del Razo, R. Rodriguez-Vazquez, and H.M. Poggi-Varaldo. 2005. Chemical fractionation of boron and heavy metals in soils irrigated with wastewater in central Mexico. *Agriculture, Ecosystems & Environment* 108(1): 57-71.

McCuen, R., and C. Surbeck. 2008. An alternative to specious linearization of environmental models. *Water Research* 42(15): 4033-4040.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis* 15(12): 1409-1416.

Minceva, M., R. Fajgar, L. Markovska, and V. Meshko. 2008. Comparative Study of Zn2+, Cd2+, and Pb2+ Removal From Water Solution Using Natural Clinoptilotitic Zeolite and Commercial Granulated Activated Carbon. Equilibrium of Adsorption. *Separation Science and Technology* 43: 2117-2143.

Mohan, D., and K.P. Singh. 2002. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste. *Water Research* 36: 2304-2318.

NIH. 2005. Report on Carcinogens, Eleventh Edition; U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program.

American Society for Agronomy and Soil Science Society of America. 1982. *Methods of Soil Analysis Part 2. Chemical and Biological Properties.* 2nd ed. Edited by Page.

Sharma, R. K., M. Agrawal, and F. Marsall. 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotoxicology and Environmental Safety* 66: 258-266.

Singh, D., P.K. Chhonkar, and R.N. Pandey. 1999. *Soil Plant Water Analysis: A Methods Manual.* Indian Agricultural Research Institute, New Delhi.

Singh, K. P., D. Mohan, V.K. Singh, and A. Malik. 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. *Journal of Hydrology* 312 (1-4): 14-27.

Singh, K. P., A. Malik, V.K. Singh, and S. Sinha. 2006. Multi-way analysis of soils irrigated with wastewater—A case study. *Chemometrics & Intelligent Laboratory Systems* 83(1): 1-12.

Standard Methods for the Examination of Water & Wastewater. 2005. Centennial Edition. A.P.H.A, Washington.

Terdkiatburana, T., and S. Wang. 2008. Competition and complexation of heavy metal ions and humic acid on zeolitic MCM-22 and activated carbon. *Chemical Engineering Journal* 139 (3): 437-444.

Tessier, A., P.G.C. Cambell, and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844-851.

United States Environmental Protection Agency. 2000a. Cadmium Compounds Hazard Summary. Available at: http://www.epa.gov/ttn/atw/hlthef/cadmium.html. Accessed 29 July 2009.

United States Environmental Protection Agency. 2000b. Nickel Compounds Hazard Summary. Available at: http://www.epa.gov/ttn/atw/hlthef/nickel.html. Accessed 25 August 2009.

United States Environmental Protection Agency. 2006. Consumer Factsheet on: CADMIUM. Available at: http://www.epa.gov/safewater/pdfs/factsheets/ioc/cadmium.pdf. Accessed 29 July 2009.

United States Environmental Protection Agency. 2009a. Technical Factsheet on: CADMIUM. Available at: http://www.epa.gov/safewater/pdfs/factsheets/ioc/tech/cadmium.pdf. Accessed 29 July 2009.

United States Environmental Protection Agency. 2009b. Technical Factsheet on: CHROMIUM. Available at: http://www.epa.gov/safewater/pdfs/factsheets/ioc/tech/chromium.pdf. Accessed 29 July 2009.

United States Environmental Protection Agency. 2009c. Technical Factsheet on: NICKEL. Available at: http://www.epa.gov/safewater/pdfs/factsheets/ioc/tech/nickel.pdf. Accessed 29 July 2009.

Wong, K., C. Lee, K. Low, and M. Haron. 2005. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere* 50: 23-28.

Yadav, R. K., B. Goyal, S.K. Sharma, S.K. Dubey, and P.S. Minhas. 2002. Post-irrigation impact of domestic sewage effluent on composition of soils, crops, and ground water—A case study. *Environment International* 28(6): 481-486.

APPENDIX A: MEASURED SOIL PARAMETERS

Table A1. Soil sample measured parameters.

Sample	pH	EC	Soil Ions				Texture				OC	Total		
	--	(dS/m)	$[Ca^{2+}/Mg^{2+}]$ (me/L)	$[CO_3^{2-}]$ (me/L)	$[HCO_3^-]$ (me/L)	$[Cl^-]$ (me/L)	Sand (%)	Silt (%)	Clay (%)	Soil Type --	(%)	^{114}Cd (mg/g)	^{52}Cr (mg/g)	^{58}Ni (mg/g)
1.1A	8.2	0.12	5.15	0.00	7.48	5.81	58	22	19	Sandy Clay Loam	0.41	1.10	46.4	37.2
1.1B	7.9	0.10	5.39	0.00	9.92	6.12	58	21	22		0.21	0.23	43.7	18.2
1.1C	8.0	0.08	4.04	0.00	7.80	4.43	63	15	20			0.39	71.6	38.1
1.1D	8.1	0.09					65	15	20			0.20	48.7	20.7
1.2A	7.9	0.07	5.72	0.00	9.76	4.28					0.46	0.56	60.8	25.5
1.2B	7.7	0.09	5.72	0.00	8.46	5.66					0.28	0.66	56.3	30.5
1.2C	7.7	0.06	3.70	0.00	5.85	5.66						0.51	66.5	24.9
1.2D	7.8	0.06										0.44	52.8	28.0
1.3A	7.7	0.19	6.06	0.00	8.46	10.09	58	21	25	Sandy Clay Loam	0.41	0.44	52.2	28.0
1.3B	7.5	0.19	6.06	0.00	12.68	9.48	55	21	23		0.21	1.24	76.9	45.0
1.3C	7.9	0.12	5.39	0.00	8.13	9.79	58	3	24			0.34	49.8	19.9
1.3D	7.6	0.13					53	21	29			0.37	50.0	20.4
1.4A	7.8	0.17	8.75	0.00	12.68	9.63					0.44	0.64	72.6	41.3
1.4B	7.8	0.21	8.75	0.00	9.76	10.09					0.28	0.54	55.5	22.7
1.4C	8.0	0.18	10.77	0.00	5.20	12.54						0.30	69.6	39.8
1.4D	8.3	0.22										0.88	70.6	18.1
1.5A	8.0	0.11	5.39	0.00	9.43	6.27					0.30	0.21	105.1	129.0
1.5B	8.2	0.09	4.04	0.00	8.13	5.66					0.22	0.35	89.9	41.1
1.5C	8.1	0.10	3.70	0.00	6.83	18.81						0.31	88.9	43.2
1.5D	8.4	0.08										0.21	57.4	27.6
1.6A	7.7	0.08	5.39	0.00	7.48	3.52					0.35	0.50	63.8	27.2
1.6B	7.8	0.10	5.39	0.00	6.18	5.05					0.18	0.41	91.6	50.2
1.6C	7.9	0.10	3.03	0.00	4.55	4.13						0.40	92.9	36.1

Table A1 (cont.)

Sample	pH	EC	Soil Ions				Texture				OC	Total		
			$[Ca^{2+}/Mg^{2+}]$	$[CO_3^{2-}]$	$[HCO_3^-]$	$[Cl^-]$	Sand	Silt	Clay	Soil Type		^{114}Cd	^{52}Cr	^{58}Ni
	--	(dS/m)	(me/L)	(me/L)	(me/L)	(me/L)	(%)	(%)	(%)	--	(%)	(mg/g)	(mg/g)	(mg/g)
1.6D	8.0	0.10										0.28	82.3	26.8
1.7A	7.6	0.09	7.41	0.00	8.13	6.42	58	24	24	Sandy Clay Loam	0.41	29.20	73.7	21.2
1.7B	7.7	0.11	5.39	0.00	8.46	8.56	55	21	22		0.21	0.06	61.5	13.0
1.7C	7.9	0.10	4.38	0.00	8.13	1.07	48	24	24			0.39	63.7	19.7
1.7D	8.2	0.11					48	22	24			0.10	61.0	14.1
2.1A	8.25	0.42	4.04	0.00	9.76	6.42					0.62	0.11	65.4	22.2
2.1B	8.48	0.39	3.70	0.00	8.78	8.26					0.25	0.72	71.3	19.9
2.1C	8.49	0.41	4.04	0.00	7.80	10.24						0.44	69.4	14.0
2.1D	8.46	0.42										0.39	58.3	14.3
2.2A	8.29	0.16	5.72	0.00	8.46	2.60					0.28	0.04	15.0	10.0
2.2B	8.48	0.14	6.06	0.00	6.50	1.99					0.12	0.11	56.8	21.3
2.2C	8.5	0.09	3.70	0.00	6.18	2.60						0.002	46.9	21.4
2.2D	8.49	0.16										0.44	65.2	33.0
2.3A	8.24	0.42	4.38	0.00	8.13	4.13					0.65	0.28	50.2	9.8
2.3B	8.5	0.42	5.05	0.00	8.13	5.05					0.30	0.07	65.4	36.1
2.3C	8.51	0.40	3.70	0.00	5.85	4.59						2.37	55.2	29.6
2.3D	8.48	0.47										0.14	64.4	10.3
2.4A	8.51	0.16	4.38	0.00	6.18	3.21					0.40	0.36	82.8	62.0
2.4B	8.74	0.16	3.70	0.00	6.50	2.60					0.19	0.32	51.8	8.8
2.4C	8.75	0.13	4.38	0.00	5.85	6.27						0.24	61.9	24.1
2.4D	8.69	0.11										0.54	68.6	11.7
2.5A	8.13	0.32	5.39	0.00	8.46	5.35					0.52	0.42	54.2	10.4
2.5B	8.43	0.43	4.71	0.00	9.43	5.05					0.31	0.83	76.9	27.2
2.5C	8.51	0.55	5.72	0.00	8.13	9.79						0.31	53.6	17.2
2.5D	8.53	0.42										6.84	67.4	11.8

APPENDIX B: INITIAL SORBENT STUDY RESULTS

(Note 0.00 values imply metals below detectable limits.)

C = carbon
Cont = control column effluent
G = gypsum column effluent
HMSD = heavy metal soil digestion (one of Tessier's fractions)
I = isotherm
K1 = 1st kinetics
K2 = 2nd kinetics
P = plant diacid digest
PM = press mud (sugarcane bagasse) column effluent
RH = rice husk column effluent
SD = sawdust column effluent

The letters in the second column indicate the liters of effluent collected (A=1, B=2, …)

Table B1. First-round sorbent study sample results.

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
C1	C	0.00	0.00	0.13
C1	D	0.00	0.00	0.04
C1	E	0.00	0.00	0.04
C1	F	0.00	0.00	0.05
C1	G	0.00	0.00	0.05
C1	H	0.00	0.00	0.04
C1	I	0.00	0.00	0.04
C2	C	0.00	0.00	0.06
C5	C	0.00	0.00	0.05
C5	D	0.00	0.00	0.04
C6	B	0.00	0.00	0.05
C6	C	0.00	0.00	0.04
CONT1	C	0.00	0.00	0.01
cont1	D	0.00	0.00	0.03
cont1	E	0.00	0.00	0.03
cont1	F	0.00	0.00	0.04
cont1	G	0.00	0.00	0.03
cont1	H	0.00	0.00	0.03
cont1	I	0.00	0.00	0.03
cont1	J	0.00	0.00	0.06
cont1	K	0.00	0.00	0.03
cont1	L	0.00	0.00	0.17
CONT2	C	0.00	0.00	0.00
CONT3	C	0.87	1.30	2.56
cont3	D	9.42	4.35	0.02
cont3	E	6.30	3.41	2.48
cont3	F	1.46	1.77	2.09
cont3	G	1.86	1.87	3.51
cont3	H	3.69	2.79	3.80
cont3	I	3.78	3.15	3.99
cont3	J	2.84	2.95	3.80
cont3	K	2.16	2.95	3.70
CONT4	A	2.38	0.00	3.33
CONT4	C	1.18	1.35	3.15
G1	C	0.00	0.00	0.02
G1	D	0.00	0.00	0.05

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
G1	E	0.00	0.00	0.05
G1	F	0.00	0.00	0.05
G1	G	0.00	0.00	0.04
G1	H	0.00	0.00	0.05
G1	I	0.00	0.00	0.06
G1	J	0.00	0.00	0.05
G1	K	0.00	0.00	0.23
G2	C	0.00	0.00	0.01
G3	C	0.00	0.00	0.01
G4	A	0.00	0.00	1.94
G4	C	0.00	0.00	2.48
G4	D	0.00	0.00	0.48
G4	E	0.00	0.00	0.07
G4	F	0.00	0.00	0.00
G4	G	0.00	0.00	3.70
G4	H	0.00	0.00	0.00
G4	I	0.00	0.00	3.51
G4	J	0.00	0.00	2.89
G4	K	0.00	0.00	3.61
G5	A	0.00	0.00	1.45
G5	C	-2.00	0.00	2.32
G5	D	0.00	0.00	2.72
G5	E	0.00	0.00	2.64
G5	F	0.00	0.00	2.56
G5	G	0.00	0.00	2.72
G5	H	0.00	0.00	2.89
G5	I	0.00	0.00	3.06
G6	C	0.00	0.00	2.16
HMSD	1	0.00	0.00	0.02
HMSD	2	0.00	0.00	0.04
HMSD	3	0.00	0.00	0.02
HMSD	4	0.00	0.00	0.03
HMSD	5	0.00	0.00	0.03
HMSD	6	0.00	0.00	0.03
HMSD	7	0.00	0.00	0.03
HMSD	8	0.00	0.00	0.02
HMSD	9	0.00	0.00	0.04
HMSD	10	0.00	0.00	0.03

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
HMSD	11	0.00	0.00	0.03
HMSD	12	0.00	0.00	0.03
HMSD	13	0.00	0.00	0.06
HMSD	14	0.00	0.00	0.03
HMSD	15	0.00	0.00	0.04
HMSD	16	0.00	0.00	0.04
HMSD	17	0.00	0.00	0.05
HMSD	18	0.00	0.00	0.04
HMSD	19	0.00	0.00	0.05
HMSD	20	0.00	0.00	0.06
HMSD	21	0.00	0.00	0.03
HMSD	22	0.00	0.00	0.03
HMSD	23	0.00	0.00	0.03
HMSD	24	0.00	0.00	0.03
HMSD	25	0.16	0.00	0.03
HMSD	26	0.00	0.00	0.05
HMSD	27	0.00	0.00	0.05
HMSD	28	0.00	0.00	0.46
HMSD	29	0.00	0.00	0.05
HMSD	30	0.00	0.00	0.05
HMSD	31	0.00	0.00	0.05
HMSD	32	0.00	0.00	0.03
HMSD	33	0.00	0.00	0.03
HMSD	34	0.00	0.00	0.03
HMSD	35	0.00	0.00	0.03
HMSD	36	0.00	0.00	0.02
HMSD	37	0.00	0.00	0.03
HMSD	38	0.00	0.00	0.03
HMSD	39	0.00	0.00	0.02
HMSD	40	0.00	0.00	0.04
HMSD	41	0.00	0.00	0.04
HMSD	42	0.00	0.00	0.03
HMSD	43	0.00	0.00	0.03
HMSD	44	0.00	0.00	0.00
HMSD	45	0.00	0.00	0.04
HMSD	46	0.00	0.00	0.03
HMSD	47	0.00	0.00	0.03
HMSD	48	0.00	0.00	0.04

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
I	1	-2.00	-2.00	-2.00
I	2	0.17	0.29	0.03
I	3	0.17	0.29	0.03
I	4	0.21	0.62	0.17
I	5	0.22	0.62	0.09
I	6	0.14	0.59	0.06
I	7	0.36	0.87	0.57
I	8	0.38	0.87	0.08
I	9	0.42	0.87	0.43
I	10	0.58	1.51	3.93
I	11	0.65	1.56	5.65
I	12	0.56	1.45	4.54
I	13	0.63	1.61	8.37
I	14	0.66	1.66	1.72
I	15	0.60	1.53	0.99
I	16	0.00	0.34	1.31
I	17	0.00	0.39	1.38
I	18	0.00	0.32	1.25
I	19	0.00	0.62	4.23
I	20	0.00	0.57	4.33
I	21	0.00	0.54	4.23
I	22	0.00	0.59	1.12
I	23	0.00	0.57	1.65
I	24	0.00	0.69	1.58
I	25	0.00	2.26	2.72
I	26	0.11	1.95	2.89
I	27	0.00	1.25	2.98
I	28	0.00	1.48	4.72
I	29	0.11	1.17	3.70
I	30	0.12	1.17	4.30
I	31	-2.00	-2.00	-2.00
I	32	0.15	1.15	0.75
I	33	0.16	1.15	0.77
I	34	0.11	2.74	2.00
I	35	0.11	2.74	1.80
I	36	0.09	4.19	1.87
I	37	1.69	3.83	4.13
I	38	1.67	3.86	4.23

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
I	39	1.72	3.86	4.65
I	40	2.85	7.42	2.56
I	41	2.86	7.27	1.87
I	42	3.44	7.42	2.40
I	43	5.04	8.71	2.32
I	44	5.55	8.71	3.80
I	45	5.49	8.40	2.98
I	46	0.65	0.29	0.37
I	47	0.45	0.29	0.31
I	48	0.31	0.59	0.49
I	49	0.70	0.62	1.12
I	50	0.59	0.72	0.75
I	51	0.80	0.67	1.45
I	52	1.17	0.87	2.58
I	53	1.32	0.94	3.27
I	54	1.20	0.87	2.33
I	55	1.67	1.33	5.30
I	56	1.65	1.30	4.33
I	57	1.79	1.34	5.42
I	58	2.79	1.48	9.88
I	59	-2.00	-2.00	-2.00
I	60	2.88	1.51	6.37
I	61	0.00	0.00	0.31
I	62	0.00	0.00	0.52
I	63	0.00	0.00	0.75
I	64	0.00	0.00	2.83
I	65	0.00	0.00	2.10
I	66	0.00	0.00	2.26
I	67	0.00	0.00	5.19
I	68	0.00	0.00	6.00
I	69	0.00	0.00	4.75
I	70	0.08	0.28	1.45
I	71	0.08	0.36	0.03
I	72	0.15	0.52	1.31
I	73	0.19	0.45	1.79
I	74	0.22	0.51	1.87
I	75	0.35	0.49	1.25
K1	1	0.30	NIL	2.64

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
K1	2	0.33	1.62	2.89
K1	3	0.34	1.67	2.81
K1	4	0.32	1.43	9.97
K1	5	0.33	1.45	10.02
K1	6	0.30	1.43	9.33
K1	7	0.30	1.38	8.70
K1	8	0.30	1.43	6.83
K1	9	0.32	1.43	6.70
K1	10	0.38	1.35	2.83
K1	11	0.30	1.21	2.72
K1	12	0.32	1.21	4.12
K1	13	0.33	1.11	1.28
K1	14	0.33	1.11	1.37
K1	15	0.31	1.23	1.03
K1	16	0.00	5.70	2.81
K1	17	NIL	NIL	3.06
K1	18	0.00	1.55	NIL
K1	19	NIL	NIL	NIL
K1	20	NIL	NIL	NIL
K1	21	0.00	2.31	2.72
K1	22	NIL	NIL	NIL
K1	23	0.10	1.65	NIL
K1	24	0.15	0.75	2.64
K1	25	0.17	1.38	2.32
K1	26	0.14	0.94	1.72
K1	27	0.18	1.01	2.56
K1	28	0.13	0.75	2.48
K1	29	0.12	0.80	2.56
K1	30	0.14	0.73	3.24
K1	31	0.63	0.00	2.89
K1	32	0.70	0.00	2.72
K1	33	0.53	0.00	2.64
K1	34	0.64	0.00	1.87
K1	35	0.80	0.00	2.09
K1	36	0.82	0.00	2.01
K1	37	0.87	5.90	1.72
K1	38	0.79	5.18	2.16
K1	39	0.68	5.90	2.09

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
K1	40	1.15	4.75	1.65
K1	41	0.09	6.45	0.75
K1	42	0.40	6.29	9.85
K1	43	0.49	6.09	6.71
K1	44	1.94	5.73	7.35
K1	45	1.73	5.59	6.31
K1	46	0.75	0.99	2.32
K1	47	0.73	0.97	2.09
K1	48	0.64	0.00	1.87
K1	49	1.39	0.00	10.17
K1	50	1.47	0.00	2.01
K1	51	0.78	1.01	9.66
K1	52	1.08	0.99	8.87
K1	53	1.07	0.99	8.58
K1	54	1.01	0.97	7.44
K1	55	0.90	0.92	4.22
K1	56	1.06	0.99	4.76
K1	57	0.69	0.81	0.82
K1	58	0.72	0.87	1.17
K1	59	1.02	0.94	2.42
K1	60	0.47	0.97	2.67
K1	61	0.14	0.47	7.37
K1	62	0.09	0.44	8.04
K1	63	0.20	0.49	8.40
K1	64	0.00	0.38	9.20
K1	65	0.00	0.35	8.86
K1	66	0.00	0.00	8.43
K1	67	0.00	0.28	7.63
K1	68	0.00	0.30	7.31
K1	69	0.00	0.24	8.20
K1	70	0.00	0.92	9.94
K1	71	0.00	0.23	9.44
K1	72	0.00	0.26	NIL
K1	73	0.07	0.00	9.95
K1	74	0.00	0.00	8.86
K1	75	0.16	0.33	8.47
K1	control	8.50	0.70	2.89
K2	1	0.09	0.44	0.00

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
K2	2	0.11	0.42	0.06
K2	3	0.24	0.76	0.33
K2	4	0.23	0.79	0.50
K2	5	0.39	1.36	1.38
K2	6	0.39	1.34	0.88
K2	7	0.40	1.55	2.42
K2	8	0.39	1.58	2.72
K2	9	0.47	2.39	7.19
K2	10	0.00	2.11	4.10
K2	11	0.00	0.46	0.79
K2	12	0.11	0.48	0.77
K2	13	0.15	0.71	1.94
K2	14	0.24	0.92	1.96
K2	15	0.22	0.92	4.59
K2	16	0.22	1.95	5.04
K2	17	0.30	1.92	9.48
K2	18	0.53	1.95	9.32
K2	19	0.54	2.69	2.60
K2	20	0.41	4.16	2.61
K2	21	0.34	1.31	0.67
K2	22	0.33	1.36	0.56
K2	23	0.78	2.39	1.82
K2	24	0.85	1.98	1.66
K2	25	1.65	4.72	5.33
K2	26	1.25	4.28	5.04
K2	27	1.42	6.11	8.95
K2	28	1.71	7.07	9.67
K2	29	2.58	9.81	2.35
K2	30	2.58	9.74	2.23
K2	31	0.24	0.35	0.36
K2	32	0.24	0.25	0.21
K2	33	0.54	0.48	0.56
K2	34	0.52	0.48	0.79
K2	35	0.75	0.79	1.74
K2	36	0.98	1.00	2.71
K2	37	1.00	1.07	2.89
K2	38	1.39	1.44	5.55
K2	39	1.48	1.58	5.95

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
K2	40	1.46	1.58	6.38
K2	41	0.00	0.00	0.24
K2	42	0.00	0.00	0.06
K2	43	0.00	0.00	0.40
K2	44	0.00	0.00	0.54
K2	45	0.00	0.27	1.63
K2	46	0.00	0.28	1.28
K2	47	0.21	0.47	1.90
K2	48	0.21	0.48	2.54
K2	49	0.36	1.00	5.08
K2	50	0.35	0.92	4.91
K2 10ppm spike		9.36	2.22	7.12
K2 15ppm spike D(1:5)		2.46	3.33	1.89
K2 20ppm spike D(1:5)		3.19	4.54	2.85
K2 2ppm spike		2.08	2.72	1.18
K2 5ppm spike		5.98	6.48	2.98
NIL	NIL	-2.00	-2.00	-2.00
NIL	NIL	-2.00	-2.00	-2.00
NIL	NIL	-2.00	-2.00	-2.00
NIL	NIL	-2.00	-2.00	-2.00
P	1	0.00	0.00	0.25
P	2	0.00	0.00	0.11
P	3	0.00	0.00	0.08
P	4	0.00	0.00	0.11
P	5	0.00	0.00	0.10
P	6	0.00	0.00	0.20
P	7	0.00	0.00	0.10
P	8	0.00	0.00	0.12
P	9	0.00	0.00	0.13
P	10	0.00	0.00	0.13
P	11	0.00	0.00	1.52
P	12	0.00	0.00	0.05
P	13	0.00	0.00	0.46
P	14	0.00	0.00	0.24
P	16	0.00	0.00	0.10
P	17	0.00	0.00	0.17
P	18	0.00	0.00	0.07

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
P	19	0.00	0.00	0.06
P	20	0.00	0.00	0.11
P	21	0.00	0.00	0.11
PM1	B	0.00	0.00	0.01
PM1	C	0.00	0.00	0.01
PM1	D	0.00	0.00	0.08
PM1	E	0.00	0.00	0.08
PM1	F	0.00	0.00	0.05
PM1	G	0.00	0.00	0.04
PM1	H	0.00	0.00	0.08
PM1	I	0.00	0.00	0.05
PM1	J	0.00	0.00	0.06
PM1	K	0.00	0.00	0.05
PM1	L	0.00	0.00	0.06
PM2	B	0.00	0.00	0.01
PM2	C	0.00	0.00	0.00
PM3	B	0.00	0.00	0.02
PM3	C	0.00	0.00	0.01
PM4	A	0.25	0.00	1.56
PM4	B	1.01	0.00	0.06
PM4	C	0.29	0.40	0.03
PM4	D	0.53	0.51	0.08
PM4	E	0.35	0.38	0.09
PM4	F	1.23	1.45	0.09
PM4	G	1.46	1.72	0.21
PM4	H	1.73	2.19	0.29
PM4	I	1.60	1.87	0.27
PM4	J	0.79	1.11	0.21
PM4	K	0.32	0.54	0.15
PM4	L	0.32	0.40	0.14
PM4	M	0.19	0.33	0.16
PM4	N	0.24	0.31	0.15
PM4	O	0.25	0.30	0.12
PM4	P	0.39	0.63	0.41
PM4	Q	0.93	4.43	719.08
PM5	B	1.30	1.35	2.08
PM5	B	0.20	0.52	0.04
PM5	C	0.00	0.00	0.03

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
PM5	D	0.33	0.26	0.08
PM5	E	0.25	0.31	0.06
PM5	F	0.51	0.46	0.08
PM5	G	1.19	0.91	0.16
PM5	H	1.32	1.06	0.21
PM5	I	1.18	0.00	0.21
PM5	J	0.87	0.82	0.53
PM5	K	0.17	0.00	0.12
PM6	B	0.00	0.00	0.03
PM6	C	0.12	0.27	0.03
PP3A		0.00	0.00	0.03
PP3B		0.60	0.80	1.25
PSW4		0.00	0.00	0.02
RH1	B	0.00	0.00	0.01
RH1	C	0.00	0.00	0.01
RH1	D	0.00	0.37	0.03
RH1	E	0.00	0.00	0.05
RH1	F	0.00	0.00	0.03
RH1	G	0.00	0.00	0.05
RH1	H	0.00	0.00	0.02
RH1	I	0.00	0.00	0.03
RH1	J	0.00	0.00	0.04
RH1	K	0.00	0.00	0.03
RH1	L	0.00	0.00	0.06
RH1	M	0.00	0.00	0.11
RH2	B	0.00	0.00	0.00
RH2	C	0.00	0.00	0.00
RH3	B	0.00	0.00	0.02
RH3	C	0.00	0.00	0.05
RH4	A	0.00	0.00	1.62
RH4	B	0.00	0.00	0.46
RH4	C	0.00	0.00	0.24
RH4	D	0.32	0.00	0.40
RH4	E	1.36	0.00	0.46
RH4	F	2.84	0.00	0.66
RH4	G	1.30	0.00	0.43
RH4	H	0.24	0.00	0.17
RH4	I	0.00	0.00	0.18

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
RH4	J	0.00	0.00	0.16
RH4	K	0.00	0.00	0.16
RH4	L	0.00	0.00	0.19
RH4	M	0.00	0.00	0.18
RH5	A	0.08	0.00	4.18
RH5	C	0.12	0.25	0.47
RH5	D	0.08	0.00	0.42
RH5	E	0.58	0.00	0.45
RH5	F	0.37	0.00	0.29
RH5	G	0.00	0.00	0.28
RH5	H	0.31	0.00	0.24
RH5	I	0.12	0.00	0.15
RH5	J	0.00	0.00	0.14
RH5	K	0.00	0.00	0.19
RH6	A	0.09	0.00	3.18
RH6	C	0.00	0.00	0.30
SD1	B	0.00	0.00	0.01
SD1	C	0.00	0.00	0.05
SD1	D	0.00	0.00	0.04
SD1	E	0.00	0.00	0.05
SD1	F	0.00	0.00	0.04
SD1	G	0.00	0.00	0.04
SD1	H	0.00	0.00	0.05
SD1	I	0.00	0.00	0.05
SD1	J	0.00	0.00	0.05
SD1	K	0.00	0.00	0.04
SD1	L	0.00	0.00	0.04
SD1	M	0.00	0.00	0.05
SD2	B	0.00	0.00	0.01
SD2	C	0.00	0.00	0.01
SD3	B	0.00	0.00	0.02
SD3	C	0.00	0.00	0.03
SD4	A	0.11	0.00	1.75
SD4	B	0.49	1.27	2.33
SD4	C	11.74	0.84	0.56
SD4	D	5.69	0.00	0.05
SD4	E	6.62	0.00	0.69
SD4	F	6.06	0.00	0.66

Table B1 (cont.)

Sample ID		[Cd] (ppm)	[Ni] (ppm)	[Cr] (ppm)
SD4	G	0.00	0.00	0.55
SD4	H	1.36	0.27	0.19
SD4	I	0.14	0.00	0.09
SD4	I	0.10	0.00	0.08
SD4		0.00	0.00	0.03
SD5	A	0.20	0.00	3.68
SD5	B	0.40	1.02	1.60
SD5	C	12.80	1.46	1.08
SD5	D	4.41	1.57	0.65
SD5	E	3.13	1.89	0.60
SD5	F	3.10	1.99	0.57
SD5	G	1.34	1.23	0.32
SD5	H	0.12	0.47	0.35
SD6	A	0.00	0.00	1.34
SD6	B	0.00	0.00	3.36
SD6	C	13.15	2.32	8.58