UTILIZATION OF UNIVERSITY OF FLORIDA FLUX METER FOR ESTIMATING
ARSENIC CONTAMINATION IN GROUNDWATER

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL
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Groundwater contamination is a major problem in today's environment. In Florida, the ground water standards are equivalent to the drinking water standards according to the Florida Department of Environmental Protection (FDEP). Among the various contaminants, organic, inorganic, microbial pathogens and radioactive contaminant, inorganic contaminants are of high interest because most of these contaminants are readily soluble in water, and have a high potential to contaminate groundwater. The present research focused on the groundwater contamination due to arsenic. The maximum permissible concentration of arsenic in drinking water in United States is $10\mu g\ l^{-1}$ or 10 ppb as recommended by United States Environmental Protection Agency. The purpose of the research was to evaluate the use of the University of Florida flux meter for estimating arsenic contamination in the groundwater. The flux meters were placed in three wells located perpendicular to the flow lines in the center of model aquifer. The internal adsorbent chosen was activated alumina due to its high efficiency in removal of arsenic. Adsorption of arsenic on activated alumina showed a linear trend with a K_d value of

1.844 L kg^{-1}. The procedure for extracting arsenic adsorbed by activated alumina was evaluated and it was found that extraction efficiency of acid (88%) is comparatively more than that of base (84%). Flux meter tests were conducted for arsenic concentration of 12 ppm at a flow rate of 0.84 cm/hr. The flux meter in the central well estimated 99% of the actual arsenic concentration in aquifer Therefore this provides an efficient and cost effective way to estimate arsenic flux in the field.

CHAPTER 1
INTRODUCTION

General

Groundwater contamination is a major problem in today's environment since

groundwater constitutes major portion of potable water in Florida. In Florida, the ground

water standards are equivalent to the drinking water standards, as stated by Florida

Department of Environmental Protection (FDEP). Groundwater can be contaminated by

disease-producing pathogens, leachate from landfills and septic systems, careless disposal

of hazardous household products, agricultural chemicals, and leaking underground

storage tanks (Ginn et al., 2002; Day et al., 2001; Leeuwen, 2000). There are four basic

types of contaminants that include organic, inorganic, radioactive elements, and

microbial pathogens (Salas and Ayora 2004; Jones and Huang, 2003; Barry et al., 2002;

Ginn et al., 2002). Among the various contaminants, inorganic contaminants are of high

interest because most of these contaminants are readily soluble in water, and have a high

potential to contaminate groundwater.

Relative to other oxyanion forming minerals, arsenic is problematic because of its

mobility in most of its oxidations states and at almost all pH values. During 2001,

roughly 96% of the arsenic imported into the United States was in the form of arsenic tri-

oxide (Solo-Gabriele et al., 2002). Most of this arsenic trioxide was used for the

production of arsenic acid used for wood preservation. Arsenic is brought into the State

of Florida for the production of chromated copper arsenate (CCA) treated wood (Chirenje

et al., 2003 and Solo-Gabriele and Townsend, 1999). CCA is composed of three major

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elemental constituents, copper (Cu), chromium (Cr), and arsenic (As), among which arsenic is the most hazardous. The present research focused on the soil and groundwater contamination due to arsenic. Arsenic is a semi-metal element, found in environment combined with other elements such as oxygen, chlorine, and sulfur to form inorganic arsenic compounds. It also combines with carbon and hydrogen to form organic compounds. It most often exists in organic form as monomethyl arsonic acid (MMA) and dimethyl arsonic acid (DMA). Arsenic exists in the environment most often in two oxidation states: arsenite, As (III), and arsenate, As (V), respectively (Singh and Pant 2003; Meng et al., 2002). Under oxidation conditions (and aerobic environments) arsenates are stable species (as oxyanions H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$ or AsO_4^{-3}) and are strongly sorbed onto clays, iron, and manganese oxides and hydroxides, and organic matters. However, under most reducing conditions (and anaerobic environment) arsenites (H_3AsO_3, $H_2AsO_3^{-1}$, $HAsO_3^{-2}$) are the predominant arsenic compounds (Chakravarty et al., 2002).

According to Kayajanian (2003), studies on Utah cancer mortality as a function of lifetime arsenic exposure indicated that for concentration range of 1-25 ppb, there are 2.682 cancers per 100 people and in the 5 years following initial arsenic medication, around 6.45 deaths are expected. The maximum permissible concentration of arsenic in drinking water in United States is $10\mu g\ L^{-1}$ or 10 ppb as recommended by United States Environmental Protection Agency, USEPA (2001). In addition to the arsenic contamination in water sources, dietary intake of arsenic through the food chain via uptake from contaminated soils may adversely affect human health (Alam et al., 2003). The current soils clean up goals set by the Florida department of environmental

protection for arsenic in residential and industrial soils are 0.8 mg/kg and 3.6 mg/kg respectively (Solo-Gabriele et al., 2002).

Various scientists and organizations have made an attempt to identify the source of contaminant and degree of contamination in groundwater using different field monitoring techniques (Montas et al., 2000; Brusseau and Srivastava, 1997). This research discusses a new devise named Flux meter that allows to simultaneously measuring cumulative dissolved solute fluxes when placed within a flow field. The Flux meters have been tested for most of the organic contaminant analysis both in lab as well as field for contaminant flux, groundwater flow and flow direction (Hatfield et al., 2003; Klammler 2001).

Purpose and Objectives

The purpose of this research was to evaluate the use of flux meter for estimating arsenic contamination in the groundwater. Before bench scale flux meter tests are performed, information regarding the type of adsorbents and its interaction with arsenic should be understood very well. Hence, the objectives of this research were 1) review of adsorption and extraction characteristics of arsenic to different materials and 2) to evaluate the applicability of these materials as flux meter sorbent media for arsenic flux measurement, 3) to simulate the arsenic contamination for various Florida soil types. This thesis seeks to give the basic understanding of the solute transport and theoretical contemplation of flux meter for estimating fluid and contaminant flux, arsenic contamination and need of flux meter for estimating fluid flow and contaminant flux in the groundwater.

CHAPTER 2
THEORETICAL BACKGROUND

Advective-Dispersive Transport of Reactive Solutes

In non-ideal condition found in the environment, a reactive solute interacts with the

solid matrix during flow. The solute is, therefore distributed between the fluid and the

sorbed phases. If a primary anisotropic system is assumed, for the steady water flow,

under saturated or uniformly unsaturated conditions, the solute transport equation for a

homogeneous media can be represented by (Domenico and Schwartz, 1990)

$$\theta_w \frac{\partial C_w}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \theta_w D_w \frac{\partial^2 C_w}{\partial x^2} - q_w \frac{\partial C_w}{\partial t} \qquad (2.1)$$

where
θ_w= volumetric water content
C_w= solute concentration in water (μg L^{-1})
ρ_b= bulk density of sorbing media (g/cm^3)
S= sorbed solute concentration (mg/kg)
D_w = dispersion coeffecient (cm^2/hr)
q_w = advective mass flux (cm/hr)

Three most commonly known isotherms that define the adsorption characteristics of

any adsorbent are linear isotherm, Freundlich isotherm and Langmuir isotherm (Zheng

and Bennett 2002, Charbeneau 2000). Freundlich and Langmuir isotherms can be used to

represent both linear and non-linear isotherms.

Linear Isotherm

When the sorbed phase solute concentration is linearly proportional to the solute

concentration in the solution phase, the sorption isotherm is linear isotherm, and is

represented by S = K_d.C_w. Therefore, the equation 2.1 is transformed to

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$$\frac{\partial C_w}{\partial t}[1+\frac{\rho_b K_d}{\theta_w}] = D_w \frac{\partial^2 C_w}{\partial x^2} - v\frac{\partial C_w}{\partial t}$$
(2.2)

The transport velocity (cm/hr) is represented by v. The adsorption coefficient (K_d) is a measure of how tightly the solute binds or sticks to soil particles. The greater the K_d value, the less likely a chemical will leach or contribute to runoff.

The retardation factor, $R = (1 + \rho K_d/\theta_w)$, expresses how much slower a contaminant moves than does the water itself. Equation 2.2 is therefore transformed to

$$\frac{\partial C_w}{\partial t} = D^* . \frac{\partial^2 C_w}{\partial x^2} - v^* \frac{\partial C_w}{\partial t}$$
(2.3)

where $D^* = \dfrac{D}{R}$ and $v^* = \dfrac{v}{R}$

When $K_d = 0$, it implies that $R = 1$ and hence $D^* = D$ and $v^* = v$, which reverts the equation (equation 2.3) back to the non-reactive ideal solutes. Hence the equations below show the effect of retardation factor on the solute transport. As K_d and R increases, the distance to solute peak decreases. The distance to solute peak (x^*) is given by

$$x^* = [v^*t] = \frac{vt}{R}$$
(2.4)

The time of arrival of solute peak (t^*) is delayed and is given by

$$t^* = [L/v^*] = \frac{LR}{v}$$
(2.5)

Non-linear (Freundlich isotherm)

In this type of isotherm the solute mass is proportional to the concentration raise to N.

$$S = K \, C_w^N, \quad N \neq 1$$
(2.6)

Hence, retardation factor $R = [1 + \dfrac{\rho K N C_w^{N-1}}{\theta_w}]$

It is evident from the above equation that R is not a constant but is a function of C_w.

N<1, R (C_w) decreases as C_w increases for C_w >1

N>1, R (C_w) increases as C_w increases for C_w >1

N = 1, R is independent of C_w and hence leads to the linear isotherm.

Non-linear (Langmuir Isotherm)

Langmuir isotherm is the most common type non-linear isotherm and in this

isotherm

$$S = \frac{S_{max}kC_w}{1 + kC_w} \qquad\qquad (2.7)$$

Hence, retardation factor for Langmuir isotherm is $R(C_w) = [1 + \dfrac{\rho S_{max} k}{\theta_w (1 + kC_w)^2}]$

In non-ideal environmental conditions, it is very difficult to obtain the accurate

values of various parameters and hence accurate flux measurement is difficult. There is a

need for accurate and easy to use equipment for the calculation of groundwater flux and

contaminant flux. A new method utilizing flux meter has been developed at the

University of Florida and laboratory tested for measuring both contaminant and

groundwater fluxes at hazardous waste site.

University of Florida Flux Meter

The University of Florida flux meter measures cumulative dissolved solute fluxes

with directions simultaneously when placed within a flow field (Hatfield et al., 2003).

The device consists of a self-contained permeable unit that intercepts the groundwater

flow without retaining it. A matrix of hydrophobic and hydrophilic sorbents in the device

sorbs dissolved organic and inorganic solutes present in the water intercepting the unit, thus indicating the amount of contaminant carried by the groundwater. The sorbent matrix is also impregnated with known amount of one or more fluid soluble "resident tracers" that leaches from the sorbent at the rate proportional to the fluid flux (Hatfield et al. 2003) and provides an estimate for the fluid flow. The flux meter has been validated and used for estimating fluid flow and contaminant flux for various organic contaminants. This research seeks to explore the use of flux meter for measuring arsenic contamination. .

Estimating Fluid Flux

Fluid flow can be estimated by placing flux meter device in a monitoring well perpendicularly intercepting the groundwater flow. The amount of tracer leaching out of the device gives the measure of fluid flux. It is assumed that a) the various tracers used do not mutually affect their partitioning properties; b) tracers partition isotherm is linear and, c) tracer transport due to dispersion is negligible (Hatfield et al., 2003). Therefore the distance that the tracer is pushed away by the water can be calculated as

$$\Delta x = v_{tr}\Delta t = \frac{v\Delta t}{R} \qquad (2.8)$$

where v_{tr} = tracer transport velocity.

If the water flows through the meter at the rate $v_{tr} = v/R$, the remaining amount of the tracer with respect to the initial tracer amount (represented by m_R) gives the measure of how much water has passed the unit. The rate of v_{tr} is measured by $v_{tr} = v/R$. Given the cross sectional area of the unit, one can relate this concentration to the area still occupied by the tracer as

$$A = 2r^2 \sin^{-1}(\frac{a}{r}) - a\Delta x \qquad (2.9)$$

$$m_R = \frac{A}{\pi r^2} \qquad (2.10)$$

$$\Delta x = \frac{q\Delta t}{R\theta} = 2r \ [v = \frac{q}{\theta}] \qquad (2.11)$$

where

$$a = \sqrt{[r^2 - (\frac{\Delta x}{2})^2]} \qquad (2.12)$$

r = radius of the device

If ξ, is the dimensionless cumulative volume of fluid conveyed through the device, then equation 2.10 can also be stated as

$$m_R = \frac{2}{\pi}[\sin^{-1}\sqrt{(1-\xi^2)} - \xi\sqrt{1-\xi^2}] \qquad (2.13)$$

$$\xi = \frac{q\Delta t}{2\theta Rr} \qquad (2.14)$$

However, due to the circular cross section only at the very beginning is the tracer present over the whole width of the device (2r). As the tracer is desorbed, some water will pass the device without leaching out any of the tracer. The distance "a" from the center, this is equal to the radius of the section at the beginning. This also decreases with growing Δx and the water passing the device at distances greater than "a" from the center does not leach out tracer any more. Therefore, equation 2.13 must be used to describe the relation between the relative remaining tracer mass m_R and the dimensionless cumulative volume ξ. To simplify equation 2.13, Klammler (2001) performed regression analysis for the variation of ξ with m_R and observed that regression equation is almost linear for ξ less

than equal to 0.6, which corresponds to the m_R equal to 0.3. The regression equation obtained was

$$m_R = -1.2\ \xi + 1.0 \qquad\qquad\qquad (2.15)$$

After keeping the flux meter in the groundwater for a determined amount of time, the amount of tracer left in the sorbent media (m_R) is extracted. The dimensionless cumulative volume of water, ξ, intercepted by the flux meter at a specified depth can be obtained using equation 2.15. The specific discharge, q, can then be calculated using the equation 2.14. The specific discharge calculated using equation 2.14 is the discharge through the flux meter. Because the material used in the aquifer can be different from that used in flux meter, the permeability (or hydraulic conductivity) of flux meter can be different from permeability of the surrounding aquifer. The specific discharge in the well and surrounding aquifer can be related as (Hatfield et al., 2003)

$$\frac{q}{q_o} = \frac{2k}{k + k_o} \qquad\qquad\qquad (2.16)$$

Where, q and q_o are the specific discharge through the flux meter and surrounding aquifer respectively. k is the hydraulic conductivity of flux meter and k_o is the hydraulic conductivity of aquifer.

Estimating Solute Mass Flux

The dotted area shown in Figure 2-1 is where the contaminant is sorbed in to the device. The respective retardation factor of the contaminant (R_{cont}) quantifies the fraction of the cross sectional area of the device that is actually occupied by the sorbed contaminant (Klammler 2001). Hence the actual concentration of contaminant in aqueous phase is given by

$$C = \frac{M_{cont}}{r^2 \pi L (1 - m_{R,cont}) R_{cont} \theta} \qquad (2.17)$$

where
M_{cont} = mass of contaminant sorbed (mg)
r = radius of the flux meter cylinder (cm)
L = length of sorbent matrix (cm)
$m_{R,cont}$ = relative mass of hypothetical resident tracer retained after time period t.
R_{cont} = retardation of sorbent (contaminant) on matrix (L g^{-1})
θ = water content in the device.
To calculate the amount of tracer retained in the flux meter ($m_{R,cont}$) that is required

for contaminant flux calculations (equation 2.17), an imaginary tracer is assumed in the

flux meter that has the same leaching properties as that of contaminant (i.e. the tracer and

contaminant have the same retardation factor). Equation 2.13 and 2.14 can then be used

for calculating $m_{R,cont}$ using the parameters of sorbent matrix.
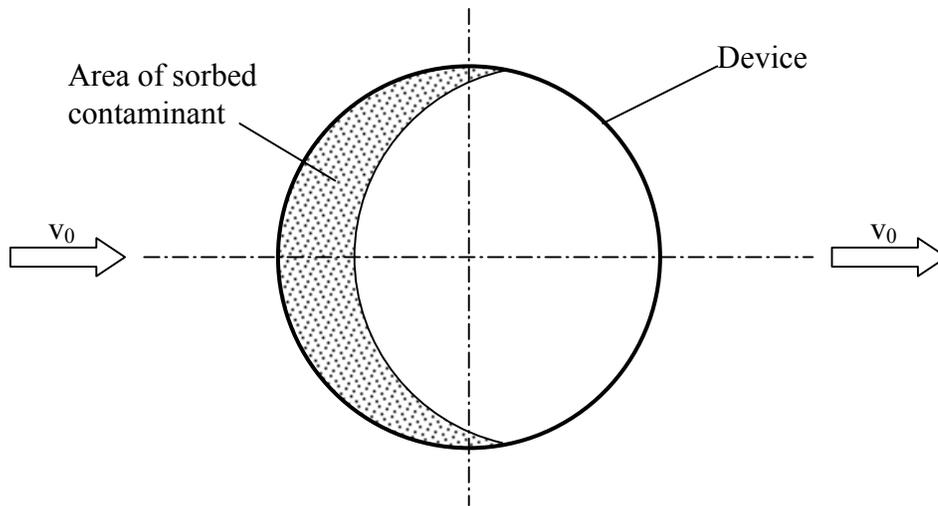
Figure 2-1 Contaminant sorbed by the sorbing matrix

Since the calculated concentration is same in the aqueous phase of the aquifer and

aqueous phase of the device, it can be directly used to calculate the contaminant flux

using

$$J = q_o \cdot C \qquad (2.20)$$

Like any other process, flux meter also has a disadvantage in it. This method only works for plume constituents that are actually retained by the sorbing matrix of the device. For plume constituents that are not retained by the sorbing matrix, the contaminant flux is not measured. Hence the prior knowledge of type of contaminant in the area of interest is very important. Evaluating flux meter for monitoring arsenic concentration and the various parameters needed to be considered while simulating field conditions in lab are discussed in next chapter. Also, this method has not been validated for wide scale use for measuring inorganic solutes.

CHAPTER 3
LITERATURE REVIEW

Arsenic predominantly exists in two oxidation states, As (III) and As (V). USEPA

2001 and FDEP 2004 have revised their maximum contamination level limits from 50µg

l^{-1} to 10µg l^{-1} starting from 2006 and 2005, respectively. In this study, arsenic

contamination due to chromated copper arsenate (CCA) leaching from construction and

demolition landfills is considered. Various factors that can affect the sorbed concentration

of arsenic are discussed and affect of varying soil types is also initiated.

Occurrence of Arsenic

Occurrence of arsenic can be both anthropogenic including mining and industrial

waste, and geogenic such as volcanic eruption and weathering, in nature. High

concentration of arsenic in ground water can occur in some areas as a result of inputs

from geothermal sources. Nimick et al. (1998) found up to 370µg l^{-1} arsenic in Madison

River water as a result of geothermal inputs from the yellow-stone geothermal system.

Smedley and Kinniburgh (1996) noted high arsenic concentrations (around 200-300µg l^{-1}

^{1}) in surface waters affected by Sn and Au mining activities. Azcue and Nriagu (1995)

conducted experiments for arsenic concentrations in Moira lake of Canada throughout the

year and showed the significant seasonal difference with an average concentration of 62

µg l^{-1} during summers and 22 µg l^{-1} during winters, they attributed this difference to the

depleted oxygen levels in the bottom lake waters as a result of biological productivity

during summers.

Arsenic is widely used in making wood preservatives like CCA, insecticides and pesticides and for various other agricultural and industrial purposes. Due to its widespread use in agriculture, industry, and medicine, it has gained attention of lot of scientists and researchers for its health effects and required remediation procedures. Arsenic is brought into the State of Florida primarily for the production of CCA-treated wood (Chirenje et al., 2003 and Solo-Gabriele and Townsend, 1999). Upon disposal, the majority of CCA-treated wood is may be disposed in unlined construction and demolition (C&D) landfills, or recycled as mulch or wood fuel. As a result, a considerable amount of arsenic can be potentially released into the Florida environment. Townsend et al. (2000) estimated that, in Florida, CCA-treated decks impact ~ 10 000 ha or 10^8 m^2 of soil, and the amount of CCA-treated utility poles in use is $7x10^5$ m^3. Arsenic is predominant in +5 oxidation state in CCA, though as the pH changes the stable oxidation state for arsenic varies (Solo Gabriele et al., 2002 Bull, 2000).

Fate and Transport of Arsenic

Relative to other oxyanion forming minerals, arsenic is problematic because it is mobile in most of the oxidations states and at almost all pH values, whereas other oxyanion like selenium are mobile as selenate (SeO_4^{-2}) under oxidizing conditions but are immobile under reducing conditions either due to the stronger adsorption of its reduced form, selenite (SeO_3^{-2}), or due to its reduction to metal (Smedley and Kinniburgh, 1996). Chen et al. (2002) collected over 448 samples to determine arsenic distribution in soils of Florida. The soil order described by Chen et al. (1999) is used to classify different types of soils including Alfisols (14%), Entisols (22%), Histosols (10%), Mollisols (4%), Inseptisols (3%), Spodisols (28%) and Ultisols (19%). Clark et al. (2004) grouped these soil types into three classes, class 1, 2, and 3 of arsenic retention indices. Class 1 includes

Marls and Histosols; these soils have the greatest retention and minimal leaching capability of arsenic. Class 2 includes Entisols, Alfisols and Ultisols. These soils found to have moderate retention with moderate potential for leaching. Class 3 have the least retention and greatest risk for leaching and it include Spodosols. Chen et al. (2002) observed the decrease in arsenic concentration with following trend in soil order: Histosols> Inceptisols> Mollisols> Ultisols> Entisols, Alfisols> Spodosols. A cumulative probability curve for Arsenic concentration in Florida surface soils was developed as shown in Figure 3-1 (Chen et al., 2002), where x-axis plots a histogram of the data categories and y-axis plots the frequency of the data in percentage. Numbers in parentheses are sample sizes of individual soil orders.
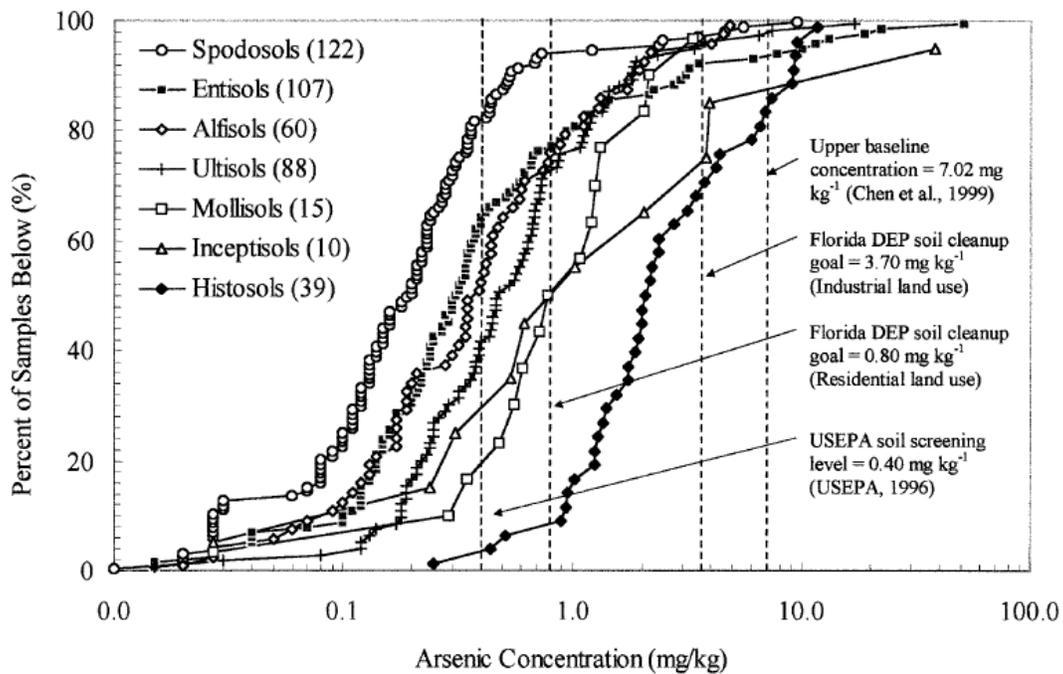
Figure 3-1: Cumulative probability curve for "As" in Florida surface soils
(Chen et al. 2002)

Adsorption Characteristics of Arsenic

Redox potential (E_h), and pH are most often the controlling factors in mobility of arsenic in the environment. Under oxidizing conditions, $H_2AsO_4^-$ is dominant, at low pH (pH of 2 to 6); while at high pH (6 to 12), $HAsO_4^{-2}$ becomes dominant (Smedley and Kinniburgh, 2002). The E_h-pH diagram for arsenic is given in Figure 3-2. Solubility of arsenic in natural systems is strongly influenced by its capacity to be adsorbed by different minerals present in soils. The interaction of arsenic with different minerals is represented in the Table 3-1.
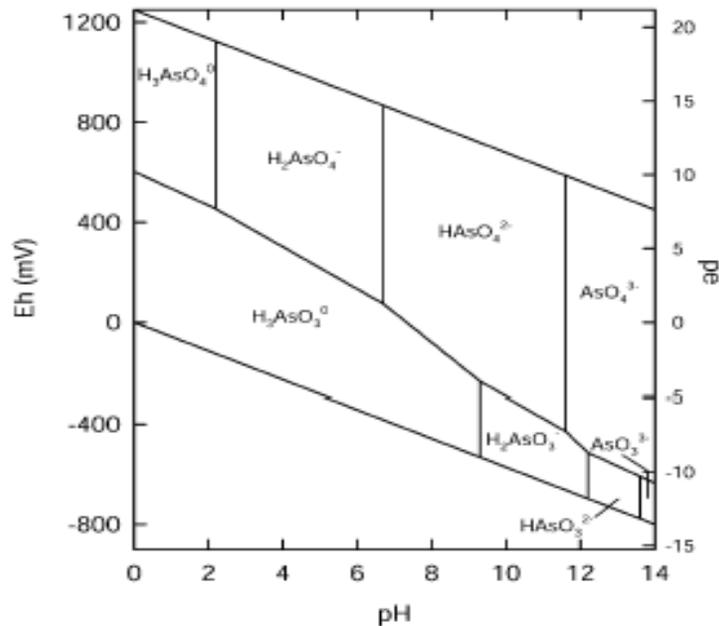
Figure 3-2: Eh-pH diagram for inorganic arsenic compounds
(Smedley and Kinniburgh, 2002)

Among the treatment processes appropriate for removal of arsenic, activated alumina adsorption is considered to be in-expensive and more versatile (Wang et al., 2000). Activated alumina (AA) has high efficiency to adsorb arsenic in both of its oxidation states. However, ionic strength, pH, competing ions, and temperature can significantly change adsorption characteristics of activated alumina for arsenic (Deliyanni

et al., 2003; Meng et al., 2002; Lin and Wu, 2000; Wang et al., 2000; Halter and Pfiefer 2001). Lin and Wu (2000) found that arsenite uptake on activated alumina is much less than arsenate uptake at almost all pH conditions. The uptake of arsenite was found to increase with the increasing pH until pH $\sim$ 7, and then decrease as pH increases. This was attributed to surface charge of AA, which is positive until pH $<$ pH_{zpc} (point of zero charge). Deliyanni et al. (2003) observed the effect of ionic strength of solution on the sorption process of arsenate ions on alkaganeite by varying the concentrations of (0-0.1M KNO_3). Observations indicated that as the concentration of KNO_3 is increased, the removal of arsenic is improved until saturation, when varying the amount of sorbent. This improvement was attributed to certain depression of negative solid surfaces charges in the alkaline region, caused by the presence of inorganic electrolyte, which enhanced the interaction between surface sites and arsenic oxyanions. These adsorption characteristics of arsenic highly differ in presence of intersecting minerals like phosphorous. British Geological Survey (BGS 2001) calculated sorption of As (V) and As (III) by Hydrous Ferric Oxide (HFO) as a function of arsenic concentrations and pH in 0.01M NaCl background electrolytes. Observations were made in the absence and presence of an equilibrium dissolved phosphate-P concentration of 1 mg l^{-1}. Results indicated that over the pH range of 6 to 8, As (III) sorbs more strongly than As (V), the reverse was seen in the absence of phosphate. Meng et al. (2002) investigated the combined effect of phosphate, silicate and bicarbonate on the adsorption of arsenic by iron hydroxides. The apparent adsorption constants indicated that the affinity of the anions for iron hydroxide sites decreased in the order as arsenate $>$ phosphate $>$ arsenite $>$ silicate $>$ bicarbonate.

Table 3-1: Behavior of arsenic with different minerals

Mineral	Comment	Reference
Akaganeit (β-FeO(OH))	The maximum load capacity was found to be about about 100-120 mg As(V) per g of Akaganeite when .5g l^{-1} used. The amount of arsenate adsorption increases by lowering the pH, increasing the amount of sorbent and ionic strength of the system.	*Deliyanni et. al. (2003)*
Clay mineral	An increased Arsenic content has been noted with the increasing clay content of the contaminated soils.	*Galba and Polacek, (1973)*
Hametite & Feldspar	The effect of solute concentration, detention time, pH temperature, and agitation rate of the adsorbent like Hematite and Felspar. The maximum removal was found to be 100% and 97% with hematite and felspar respectively at optimum conditions.	*Singh et. al. (1996)*
Orange Juice Residue (OJR)	Found that for iron-loaded phosphorylated OJR, maximum adsorption capacity for As(V) and As(III) was 0.94 and 0.91 mol/kg at their optimum pH values 3.1 And 10.0, respectively	*Ghimire et. al. (2002)*
Activated Alumina (AA)	Uptake of arsenite is much less than that of arsenate for AA in most pH conditions. Pore diffusion coefficients And tortuosity factors of arsenate and arsenite were interpreted for AA grains with different grain size and different pH.	*Lin and Wu (2000)*
HFO	Discussed kinetics and pH dependence of As(V) and As(III) adsorption on HFO . Found very high As(V) and As(III) loadings (up to 4–5 mol As kg^{-1}) at the highest concentrations.	*Raven et al. (1998)*
HFO	Sorption of As(V) and As(III) on HFO at As concentration of environmental significance (low micromolar range) and pH 4–9. SO$_4$ decreased adsorption Of As(V) and As(III), especially at low pH, while Ca Increased As(V) adsorption at high pH. 1mM bicarbonate did not act on either As(V) or As(III) adsorption greatly	*Wilkie and Hering (1996)*

Phosphate, silicate and bicarbonate decrease the removal of As (III) even at relatively low concentrations and low surface site coverage (Meng et al., 2002). Effect of temperature as discussed by Pattanayak et al. (2000) showed that higher temperatures could lead to lower metal uptakes.

Another easily available adsorbent considered by researchers for arsenic adsorption is activated carbon. Lorenzen et al., (1995) and Pattanayak et al., (2000) used activated carbon and its derivatives with different ash contents for arsenic adsorption. Lorenzen et al. (2002) used peat-based carbon with 5-6% ash content and coconut shell carbon with 3% ash content for arsenic adsorption. Peat based carbon was found to perform better that coconut shell carbon, implying that carbon with higher ash content can perform better. Activated Carbon was found to be less effective and efficient for removal of Arsenic than other adsorbents like activated alumina and iron hydroxide.

Laboratory Analysis

The two adsorbents considered in this research for use of flux meter were activated alumina and activated carbon. These two adsorbents were chosen because activated alumina has a very high efficiency for arsenic adsorption and activated carbon is one of the most commonly used adsorbent for most of the adsorption based remediation procedures.

Adsorption Isotherms

Adsorption isotherms define the effectiveness of adsorbents (activated alumina and activated carbon) for the adsorption of arsenic. In this research batch experiments were performed for adsorption isotherm. Most of these adsorption experiments were performed at constant temperature and controlled pH.

Extraction and Analysis:

Arsenic extraction can be achieved by using strong acidic or alkaline solutions. Lorenzen et al., (1995) used copper pretreated peat based carbon with a 100-ppm arsenic solution for 24 hrs at a pH of 6 and checked the elution with distilled water, acids and alkalis of different pH at different temperatures and flow rates. The acidic solutions were found to be more effective than the alkaline solutions based on results seen in this research. Singh et al., 1996 observed the effect of effluent flow rate on elution and found that the faster flow rate resulted in lower peak and lower arsenic concentrations at low number of bed volumes and there was a beneficial effect of a higher flow rate towards the end of an elution run. Once arsenic is extracted, it can be analyzed using Graphite Furnace Atomic Adsorption Spectrometer (GFAAS) techniques for concentration range of 5-100 μg l^{-1}using EPA method 7060 A, Inductively Coupled Argon Plasma Spectroscopy (ICP) for concentrations above 100 μg l^{-1} using EPA method 3010A and 6010 B, and Spectrophotometer (Bran+Luebbe GmbH) using industrial method 26-71E for concentration range 0.4-20 ppm. GFAAS can also analyze the solid samples directly, though often digestion is performed on solid samples for analysis (Sahuquillo et al. 2003). The advantages of this technique are its low detection limits, the minimum sample manipulation, its relative simplicity and the short time required to obtain the results.

Flux Meter Analysis

Various scientists and organizations have made an attempt to identify the source of contaminant and degree of contamination in groundwater using different field monitoring techniques (Brusseau and Srivastava 1997, Montas et al., 2000). Brusseau and Srivastava (1997) collected a dense, 3 dimensional array of sampling points to obtain time-series data and spatial distribution which was used to determine the zeroth, first and second

spatial moments of the plume. Montas et al. (2000) presented a methodology for designing groundwater quality monitoring well network in space and time, and to evaluate the performance of the resulting network. However, the two techniques are often time consuming and include various assumptions in the contaminant flux calculations and large number of wells are drilled for correct measurement of contaminant (Montas et al., 2000). Zhang et al. (2002) performed experimental investigation of contaminant transport in coastal groundwater. The experiments were performed in a flow tank and glass beads were used as the homogeneous porous media. The salt water and fresh water intrusion was taken into consideration by incorporating the vertical/horizontal ratio of the sloping seaward boundary keeping freshwater and saltwater at the high and low elevation respectively. In this thesis, University of Florida flux meter are discussed for their use for measuring contaminant flux in groundwater. Flux meter has been validated for most of the organic contaminant analysis both in lab as well as field for contaminant flux, groundwater flow and flow direction. In this research, use of flux meter for inorganic contaminant like arsenic was analyzed.

Computer Model Simulation

A numerical model simulation is performed using MODFLOW MT3DMS for arsenic contamination in various soil types. Soil classification described in earlier section is used because various scientists working on arsenic contamination and its concentrations in soils of Florida prefer this classification for research (Chen et al., 1999; Clark et al., 2004). The advantages of using MODFLOW include numerous facilities for data preparation, easy exchange of data in standard form, extended worldwide experience, continuous development, availability of source code, and relatively low price (McDonald and Harbaugh, 1988).

Partition coefficients were calculated for different soil types based on arsenic concentration of 48 ppm. The K_d values were calculated using solution to solid ratio of 1:5. They range from 0.2 to 0.8, highest in marls and histosols (soil and water department, University of Florida). Bulk density values were based on the ranges from USDA county soil classification.

Porosity calculations are done on the basis of linear relation between porosity and bulk density developed by NASA staff science 2003.

CHAPTER 4
MATERIALS AND METHODS

Various adsorption, extraction and analysis methods were performed for arsenic

adsorption onto activated carbon and activated alumina. The adsorption experiments were

performed as batch experiments for different time periods with respect to different

adsorbents because equilibrium time for each adsorbent is different. Extraction was

performed using strong acidic as well as alkaline solution of nitric acid and sodium

hydroxide respectively. Simple digestion process explained by EPA method 3010A for

extraction of arsenic from soils was used for extracting arsenic from activated alumina

using acid. For extraction using strong bases, standard procedure described by water

chemicals codex (1982) was used. Analysis was performed using GFAAS (Graphite

Furnace Atomic Adsorption Spectrometer) for all concentrations since it can measure

concentrations as low as 5 ppb ($\mu g \ l^{-1}$). For higher concentrations, samples were diluted

to bring them within the detection range of 5 − 100 ppb. Typical flux meter set up is then

discussed and various boundary conditions and assumptions involved with the method

are described.

Adsorption Isotherms

Experimental quantities vary significantly for adsorption on activated carbon and

activated alumina because of their different efficiencies to adsorb arsenic. Activated

Alumina acts as a strong adsorbent whereas activated carbon is a weak adsorbent. In this

research, trace metal grade arsenic (Fisher Scientific) was used for analysis. Granular

activated alumina and activated carbon used in this research is commercially available

(Fisher Scientific). Adsorption experiments of arsenic on activated alumina were conducted using 40 ml glass vials fitted with a Teflon-lined septa screw-top cap. In each experiment .02-.20 g of activated alumina grains were placed into the vial (Lin and Puls, 2000) and 30 ml solution prepared at a predetermined arsenic concentration using de-ion water. The temperature of the system was kept constant, and the reciprocating speed was kept at 70 rpm for all experiments. System was kept on rotator for 48 hrs, for adsorption to come into equilibrium (Lin and Puls, 2000). In adsorption experiment for activated carbon, 40 ml vials and varying amount of activated carbon (1 - 5 grams) were used (Pattanayak et al., 2000). The reciprocating speed was kept at 70 rpm and system was kept for 72 hrs for adsorption to come into equilibrium (Pattanayak et al., 2000). After rotating at their respective times, activated carbon/aluminum was allowed to settle for 12 hrs. Solution was then filtered for analysis using GFAAS. Since the initial concentration of arsenic in the solution was known and arsenic left in the solution were analyzed, respective calculations for sorbed concentration was performed.

Extraction Method

Arsenic extraction from activated alumina was performed using strong acid and alkaline solutions using techniques described by EPA method 3010A and water chemical codex respectively.

For extraction using acid, a known volume of well-mixed sample was transferred to a 250 ml Griffin beaker, 2 ml of 30% H_2O_2 and sufficient concentrated HNO_3 was added to get an acid concentration of 1% (v/v). It was allowed to digest at 105^oC for 2 hrs. The solution was then filtered and injected into the furnace for analysis.

For extraction using base, first the extraction solution was prepared by adding 100 ml of 0.1 M potassium hydrogen phthalate to 47 ml of 0.1 N sodium hydroxide. Solution

was then diluted to 200 ml using de-ionized water. 0.1 g of sample was taken into a 250 ml beaker and 50 ml of extraction solution was added to completely digest activated alumina samples. A drop of non-ionic surfactant (Brij 97) was then added and solution was agitated with a magnetic stirrer for 1 hour. This solution was then filtered and analyzed using GFAAS.

Analysis Method

As discussed above, arsenic analysis was performed using EPA method 7060 A. the detection limit for this method is 1 µg/l (1ppb). Samples were analyzed by GFAAS on a Perkin Elmer SIMAA 6000 THGA. The details of parameters used are:

Wavelength= 193.7nm
Injection size = 20 µl
Matrix Modifier = 7 µl of 700 ppm $Pd(NO_3)_2$

These parameters were used on the basis of the guidelines provided by the manufacturer. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters were periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. 20 micro liter aliquot of sample was injected into the furnace and atomized. If the concentration was found to be greater than the highest standard (100 ppb), the sample were diluted in the acid matrix (suggested by EPA method 7060A) and reanalyzed.

Flux Meter

Before conducting bench scale flux meter experiments for estimating contaminant flux, the basic instrument was set up for simulating true field conditions. Hence this

section is divided into two, one containing information on set-up of the flux meter and second on running the experiment.

Flux Meter Set-up

The test aquifer was set up in a box of approximately 46 cm length and 30 cm width. Well casing and screen are constituted by a 3.2 cm inner diameter PVC tube that is slotted over the entire height of the aquifer and that was glued to the bottom of the box to keep it in position. A metal grid was placed 3.8 centimeters from the box walls where the water enters and leaves to avoid intrusion of the aquifer material into glass beads. Glass beads possesses a very high permeability compared to aquifer, which serves to establish a vertical plane of constant head over the entire cross sections where the water enters and leaves the aquifer. The aquifer consists of 20-30 mesh Ottawa sand (hydraulic conductivity, 4.45 cm/min and porosity 0.3) that reaches up to a height of 11.5 cm in the box.

The filling of box was performed by adding water simultaneously with the sand in order to obtain a saturated aquifer from the beginning. The boundary conditions of uniform flow field have to be approximated by the bench-scale aquifer. These conditions are constant head at infinity on two opposite sides of the well and straight streamlines going parallel to the other sides of the infinity. To achieve these conditions, the distance from the well screen to the box walls on one side and to the gravel pack on the other side were considered big enough in relation to the well diameter to assume the boundary conditions for a uniform flow field as valid.

The water supply of the aquifer was established using a Kimax brand aspirator bottle with tubulation, which was used as a water reservoir that keeps the head at a constant level. As illustrated in Figure 4-1, this was achieved by placing a tube into the

closed container that maintains atmospheric pressure at its bottom. In order to guaranty

constant head conditions in the aquifer, the bottom of this tube was elevated to the level

of the top part of the aquifer. A constant flow pump on the other side of the aquifer was

used to convey a known constant flow through the aquifer, which was then collected in

another container to allow control of the actual flow over a certain time. A typical setup

of the flux meter is shown in Figure 4.1 (Klammler 2001).

Running Experiment

Before the experiment can be started, the device has to be prepared. As stated in the

previous section, it has to consist of a self-contained permeable unit that intercepts the

groundwater flow without retaining it. In this case, 8-14 mesh activated alumina

(hydraulic conductivity, 4.82 cm/min, porosity 0.382, particle density of 2.45 kg/l, and

bulk density is1.5 kg/l) was used for the permeable media, which took the role of the

sorbent for arsenic contamination. The sorbents (activated alumina) in the device sorbs

dissolved inorganic solutes (arsenic) present in the water intercepting the unit, thus

indicating the amount of contaminant carried by the groundwater. The device was placed

in the well, and pump was set to the required flow rate and started. In this case, flow rate

was approximately 4.83 mL/min, which result in specific discharges of 0.84 cm/hr for the

uniform flow field (cross sectional area A = 420 cm^2).

The running times was aimed to be 7 hrs hours, thus conveying a total volume of

about 1500 mL to 2000 mL of water through the aquifer per run. A control volume at the

end of the process is used to quantify the total volume conveyed through the aquifer in

order to compute the actual average flow rate over the running time.

p_o

$p < p_o$

Sorbent media

Aquifer surface

$p = p_0$

$p = p_0$

O_0

O_0

Valve

Valve

Constant head

Constant flow
pump

Well Screen

Glass Beads

Control
volume

Ottawa Sand

q_0

q_0

α

Q_0

Q_0
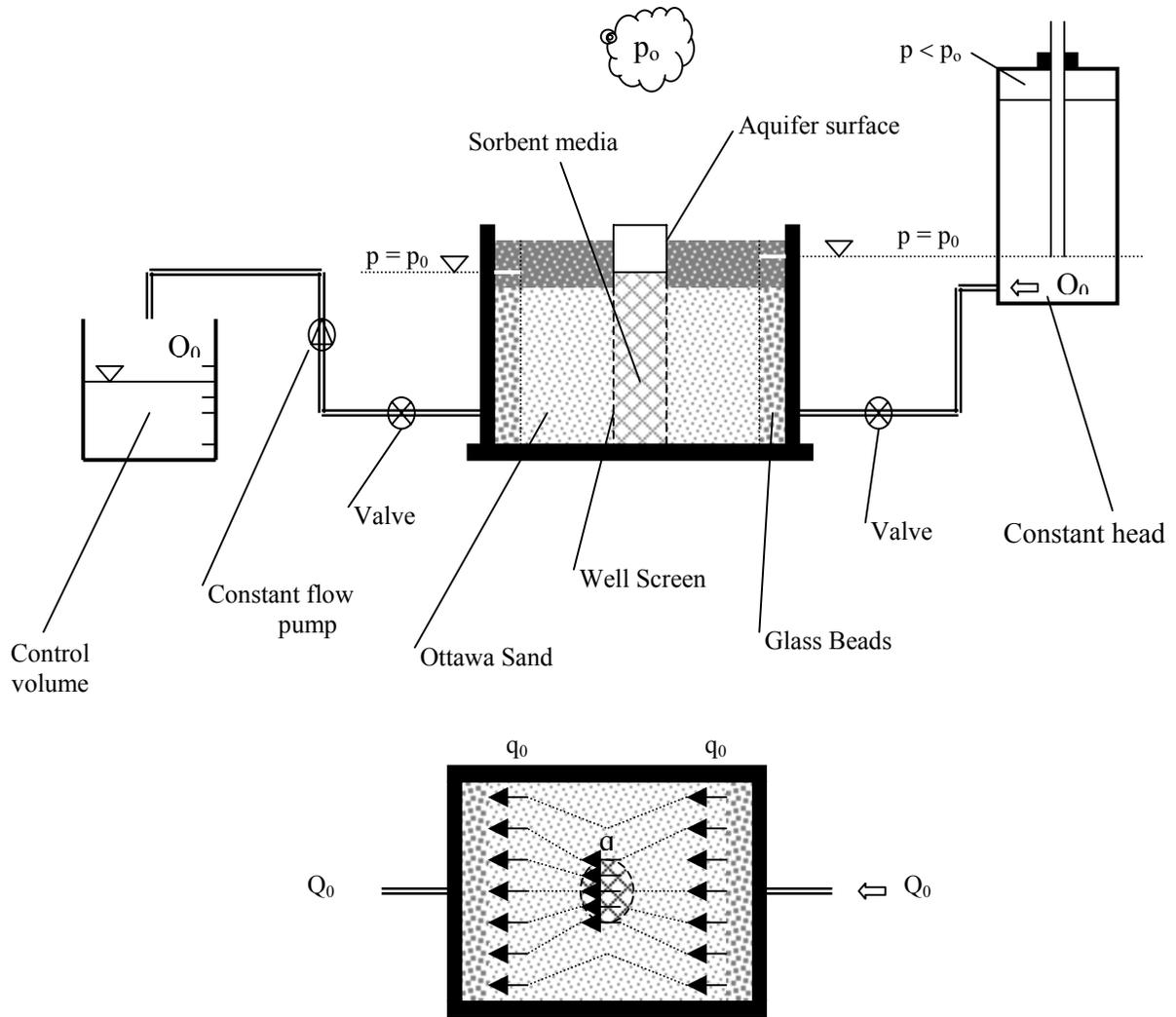
Figure4-1 Bench Scale set-up of flux meter (Klammler, 2001)

3.2cm

3 in

Well L

3 in

12 in

Well C

3 in

Well R

3 in

1.5 in

15 in
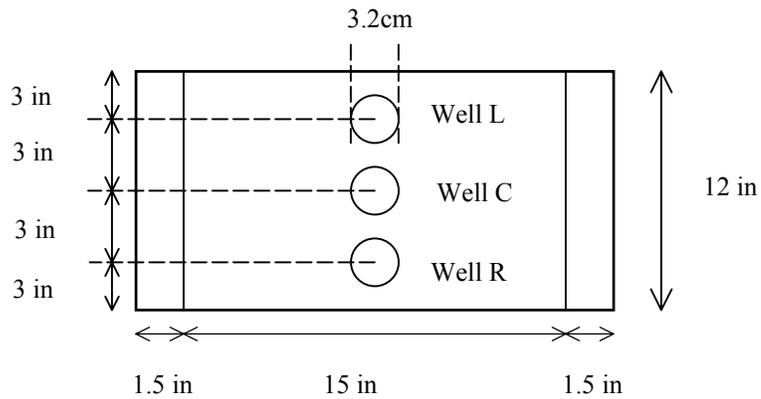
1.5 in

Figure 4-2 Cross sectional dimensions of flux meter

Since the hydraulic head at the beginning of the aquifer was set to a certain value by the constant head reservoir and the flow rate was determined by the setting of the pump, the hydraulic head at the end of the aquifer changes with changing flow rates.

CHAPTER 5
RESULTS AND DISCUSSION

Batch experiments for measuring adsorption coefficient for arsenic adsorption onto activated carbon and activated aluminum were conducted at predetermined arsenic concentrations. Strong acid and base extracts were analyzed for extraction efficiency, and GFAAS was used for analysis. Flux meter tests were performed at a flow rate of 0.69 cm/hr to simulate horizontal flow lines and steady state in the box.

Adsorption Experiments

Batch experiments measuring adsorption coefficient for arsenic adsorption on activated carbon and activated alumina were conducted for constant concentrations of 36 ppb and 17.4 ppm respectively (Pattanayak et al., 2000; Lin and Wu, 2000). These values were used based on experiments conducted at different concentrations used for adsorption of arsenic (Lin and Wu, 2000; Lorenzen et al., 1995). It was observed that activated carbon is a weak adsorbent for arsenic contamination whereas activated aluminum is a strong adsorbent for arsenic contaminant. Hence higher concentrations were used for activated aluminum over activated carbon. Adsorption experiments for arsenic adsorption on activated carbon indicated that activated carbon is not an adequate sorbent for arsenic, therefore, it was not examined for extraction and flux meter experiments. The results obtained from adsorption experiments for arsenic on activated aluminum are shown in Table 5-1. Activated alumina was allowed to adsorb 30 ml of 17.4-ppm arsenic solution for 48 hrs and final concentration of arsenic left in the solution was measured, which is indicated as solution concentration (C) in Table 5-1. The total

mass sorbed by activated alumina (total mass – mass lest) was calculated. Mass sorbed

was then normalized with respect to mass of activated alumina to give sorbed

concentration (S).

Table 5-1 Adsorption of arsenic on activated alumina

Solution Concentration(C)	Total Mass	Mass Left	Mass Sorbed	Sorbed Concentration (S)
ppm(mg/l)	(mg)	(mg)	(mg)	per unit AA mass (mg/g)
8.09	0.52	0.24	0.28	13.89
2.91	0.52	0.09	0.43	7.18
1.58	0.52	0.05	0.47	4.68
1.76	0.52	0.05	0.47	3.41
1.36	0.52	0.04	0.48	2.68
1.33	0.52	0.04	0.48	2.21

The adsorption isotherm (the curve of sorbed concentration Vs concentration in the

solution) was analyzed and for the lower range of activated alumina as in this case (0.02g

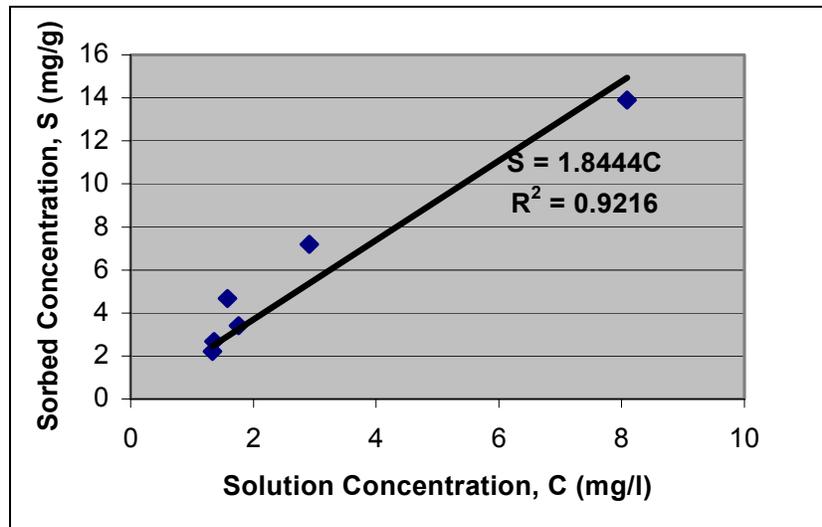to .2g), a linear isotherm is obtained (Figure 5-1).

Figure 5-1: Adsorption isotherm of arsenic on activated alumina

The adsorption isotherm (Figure 5-1) is linear with K_d value of 1.844 L/g. The

adsorption isotherm obtained by (Lin and Wu 2000; Singh and Pant 2003) was found to

follow non-linear trend. The difference can be attributed to lower range of solution concentrations used in the analysis which lie on the lower end of the range used by Lin and Wu 2000, and Singh and Pant 2003. However from the data it is evident that activated alumina has a very high efficiency for arsenic and at lower concentrations of arsenic, it can adsorb almost all of arsenic present in the solution.

Extraction Experiments

Since activated carbon was not found to be a promising adsorbent for arsenic, only extraction of arsenic from activated alumina was considered for the analysis. Extraction using acid and base was analyzed using EPA method 3010A and water chemical codex (Glaze et al., 1982) prescribed method (from materials and methods section). Extraction efficiency was calculated at the ratio of amount of arsenic extracted per unit amount of arsenic sorbed. Extractions performed using strong base, sodium hydroxide and strong acid, nitric acid were compared and it was observed that acidic extraction is more efficient for extracting arsenic from activated alumina.

Nitric acid was used for extraction and the results obtained are shown in Table 5-2. A graph of actual amount of arsenic on activated alumina with amount of arsenic extracted using acid is shown in Figure 5-2.

Table 5-2 Arsenic extracted using nitric acid

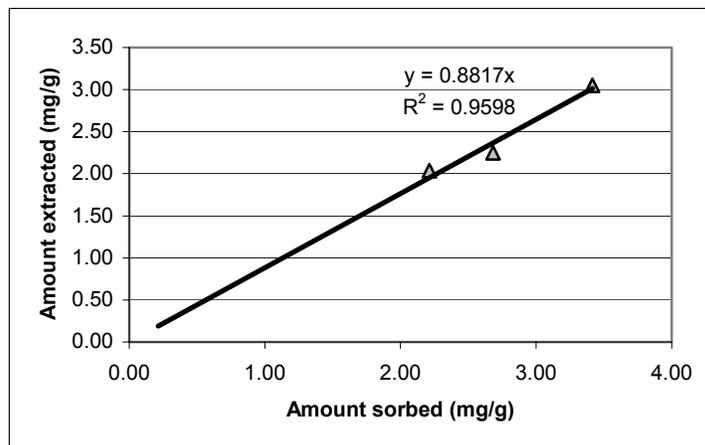| Conc. of As in extracted solution (mg/l)	Mass of AA (g)	Volume of extraction solution (l)	As per unit mass of AA	
			Extracted (mg/g)	Actual (mg/g)
6.20	0.1016	0.05	3.0512	3.4148
6.19	0.1378	0.05	2.2460	2.6838
6.60	0.1622	0.05	2.0345	2.2125

Figure 5-2 Amount extracted using acid vs. initial concentration

Graph of amount extracted with respect to actual amount on activated alumina

(Figure 5-2) indicated that extraction efficiency of nitric acid is around 88%. Extractions

were also performed using strong base, sodium hydroxide.

Table 5-3 Arsenic extracted using sodium hydroxide

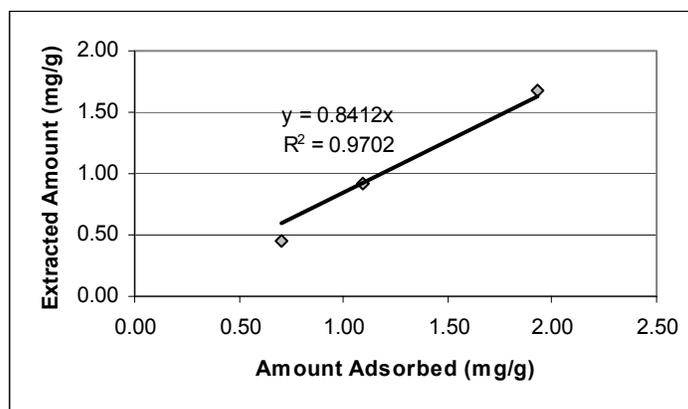| Conc. Of As in extracted solution (mg/l)	Mass of AA (g)	Volume of extraction solution (l)	As per unit mass of AA	
			Extracted (mg/g)	Actual (mg/g)
3.54	0.1055	0.0500	1.6777	1.9301
1.96	0.1072	0.0500	0.9142	1.0924
0.96	0.1059	0.0500	0.4514	0.7043

Figure 5-3 Amount extracted using base vs. initial concentration

The results obtained from extraction using base are shown in Table 5-3. The graph of actual amount of arsenic on activated alumina with amount of arsenic extracted using base (sodium hydroxide) is shown in Figure 5-3.

Figure 5-3 indicates that extraction efficiency of sodium hydroxide to extract arsenic is around 84%. However, the results obtained for both types of extraction were similar i.e. efficiency of 85-90%.

Flux Meter Bench Scale Experiments

The UF flux meter was tested in the lab for its ability to determine arsenic contaminant flux. Dimensionless cumulative mass (ξ) for activated alumina was calculated (equation 2.15) from given parameters (section of materials and methods) to be 0.59. Since this is less than 0.6, the linear relation developed by Klammler (2001) was used to calculate mass of imaginary tracer retained in the flux meter (equation 2.15) as

$$1 - m_{R,cont} = 1.2\xi = \frac{1.2q\Delta t}{2\theta R_{cont} r} \tag{5.1}$$

Since the hydraulic conductivity of activated alumina (4.82 cm/min) is more than the hydraulic conductivity of Ottawa sand (4.45 cm/min), the specific discharge through flux meter was different from that through the surrounding aquifer. Therefore, to calculate specific discharge in flux meter, q_o was multiplied with a factor of 1.04 (equation 2.16). Also, from the extraction experiment the amount of arsenic sorbed per unit mass of activated alumina was obtained. If this sorbed mass is denoted by m_{cont}, then the concentration of arsenic in the solution as indicated by flux meter can be calculated as (using equation 2.14, 2.15 and 2.17)

$$C = \frac{m_{cont}\rho r}{0.6q\Delta t} \tag{5.2}$$

where $m_{cont} = \dfrac{M_{cont}}{\rho L \pi r^2}$ (5.3)

Arsenic was extracted using acid based on EPA method 6010A. Mean and standard deviation of calculated concentration using actual and corrected mass (88% extraction efficiency) was calculated. Results obtained from the flux meter analysis are shown in Table 5-4. From statistical t-test, 95% confidence intervals ($\mu \pm \dfrac{t_{0.025} * s}{\sqrt{n}}$, where μ is the sample mean, $t_{0.025}$ is the t-test parameter, s is the sample standard deviation and n is the number of samples takes) for actual and corrected concentrations are 9.79 ± 1.79 and 10.97 ± 2.24 respectively. Arsenic concentration used in the influent solution in flux meter set up was 12ppm, which lies within the 95% confidence interval obtained from the concentration calculations using corrected mass. However, because the degree of freedom for the analysis was low (df = 2, which results in high value of parameter $t_{0.025}$) confidence interval provides a wide range for concentrations.

Table 5-4 Concentrations measured from flux meter tests

Well Location	Extracted mass m_{cont}		Concentration Calculated Using $= \dfrac{m_{cont}\,\rho^{*}}{0.6q\,\Delta t}$	
	Actual	Corrected	Actual mass	Corrected mass
	(µg/g)	(µg/g)	(mg/l)	(mg/l)
Well L	14.25	15.96	9.36	10.48
Well C	16.17	18.11	10.62	11.89
Well R	14.29	16.01	9.73	10.89
		Mean	9.79	10.97
		Std Dev	0.72	0.81

Since well L and well R are the peripheral wells (Figure 4-2), and due to possible convergence of flow lines; flow through well L and well R might have been lower when compared to the center well. Similarly, the total mass of arsenic passing through the well on sides might have been less than expected, which in turn would result in lower estimated flux concentration. From Table 5-4, calculated concentrations in well L and

well R (Figure 4-2) are less than the concentration calculated in well C. Well C provides

a good estimate (estimated value = 11.89ppm) of the actual concentration (12ppm) of

arsenic in the solution. This implies that flux meter is a promising tool to assess arsenic

contamination in groundwater.

Computer Simulation Results

Arsenic concentration is plotted with respects to time for varying soil types. The

parameters used for the analysis were taken from research through various journals and

documents as well as from data collected by University of Florida, soil and water

department.

Table 5-5: Soil properties

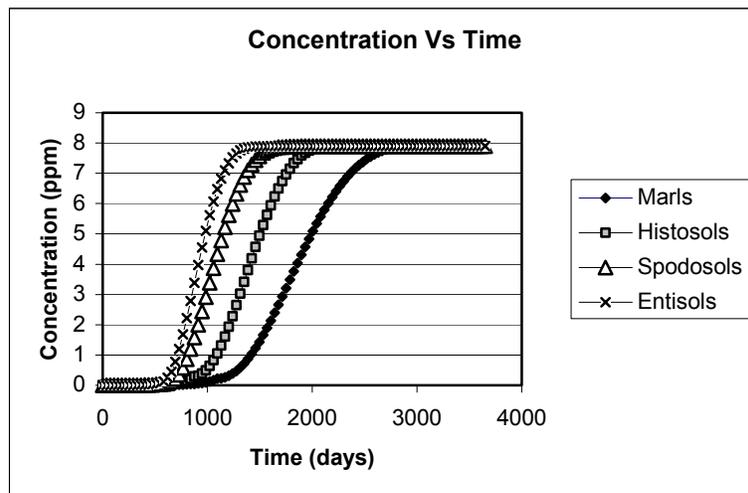| Soil Type	Silt+Clay Content	Bulk Density	K_d	Porosity
Marls	95	1000	0.8	0.62
Histosols	90	600	0.7	0.76
Spodosols	13.7	1300	0.3	0.51
Entisols	3.85	1300	0.2	0.51

Figure 5-4: Concentration of arsenic vs. time for varying soil type.

The data used is described in the literature review section of the thesis. Most of this

data is obtained from findings of University of Florida, soil and water science department

or from the research conducted by Clark et al. (2004). As can be seen from the data,

marls and histosols have comparatively high silt and clay content. There high clay content values reflect that higher values of bulk density should be expected. Conversely, marls and histosols were found to have low bulk densities, and this is due to their higher particle fraction. These fractions are mostly organics or limestone particles and are not clay.

Marls are clayey soils and therefore, have a higher efficiency to retain arsenic, which results in minimal leaching. From Marls to Entisols, the soil characteristics change from higher composition of clay to lower composition of clay (and higher composition of sand). From Figure 5-4, one can see that time taken by arsenic to reach maximum concentration decreases with increasing sand content (or decreasing clay content) and decreasing K_d values, hence decrease in dispersion from clayey soil to sandy soil (Marls to Entisols) can be observed. Therefore, break through for entisols was achieved the first, spodosols the second, histosols the third and marls the fourth.

CHAPTER 6
CONCLUSIONS

The purpose of this research was to evaluate the use of flux meter for estimating arsenic contamination in groundwater. The primary objective was to evaluate the capability of activated alumina as a flux meter sorption media for arsenic. Activated alumina was chosen as the potential sorbents because it has a high efficiency for arsenic (Lin and Wu, 2000).

From the batch experiments, it was observed that for constant initial arsenic concentration of 17.4 ppm, with varying amount of activated alumina, a linearly increasing isotherm with K_d value of 1.84 L/g is obtained. This showed that with higher concentrations of arsenic in the aqueous phase, higher concentrations were sorbed onto the solid phase.

Evaluation for determining a suitable technique for extracting arsenic from activated alumina was explored. Both acid as well as base solutions were used. It was observed that acid has relatively higher efficiency to extract arsenic from activated alumina than a base. It was determined that extraction methods, acid and base, extract around 85-90% of arsenic from activated alumina. The acid and base considered in the research were nitric acid and sodium hydroxide respectively. The acid was used for extracting arsenic from flux meter samples.

Bench scale experiments were conducted for evaluating the use of flux meter for estimating arsenic concentration. A continuous flow of 12 ppm aqueous arsenic concentration was maintained through the model aquifer at specific discharge of 0.84

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cm/hr. The flux meters were placed in three wells located perpendicular to the flow lines in the center of model aquifer, and arsenic adsorbed by activated alumina in each flux meter was measured. Concentrations calculated based on the mass sorbed by activated alumina were compared with the aqueous concentration used in the aquifer (12ppm). The statistically estimated range of aqueous concentration, calculated on the based of arsenic extracted from flux meter, provided the 95% confidence interval of 10.97± 2.24 ppm. The flux meter in central well estimated 99% of the actual concentration in aquifer.

The results obtained from flux meter proved it to be a promising device for assessing arsenic contamination in groundwater. Potential applications for this method are measuring arsenic fluxes for quantifying risk to human from arsenic leaching through hazardous waste sites, or from source zones before and after remedial efforts.

Future research can be conducted to evaluate compatibility of various available tracers with activated alumina for fluid flow determination.

LIST OF REFERENCES

Alam M. G. M., Snow E. T. and Tanaka A. 2003. Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. The Science of The Total Environment. 308: 83-96.

Azcue, J. M. and Nriagu, J. O. 1995. Impact of abandoned mine tailing on the arsenic concentrations in Moira Lake, Ontario. Journal of Geochemical Exploration. 52: 81-89.

Barry D. A., Prommer H., Miller C. T., Engesgaard P., Brun A. and Zheng C. 2002. Modeling the fate of oxidisable organic contaminants in groundwater. Advances in Water Resources. 25: 945-983.

British Geological Survey (BGS) 2001. Groundwater studies for arsenic contamination. Report WC/00/19. Volumes 1-10.

Brusseau, M., Srivastava R. 1997. Nonideal transport of reactive solutes in heterogeneous porous media: 2. Quantitative analysis of the borden natural-gradient field experiment. Journal of Contaminant Hydrology. 28(1-2): 115-155.

Bull D. C. 2000. The chemistry of chromated copper arsenate, characteristics of timber treatment plant chemical sludge. Wood Science and Technology. 34:367-376.

Chakravarty S., Dureja V., Bhattacharyya G., Maity S. and Bhattacharjee S. 2002. Removal of arsenic from groundwater using low cost ferruginous manganese ore. Water Research. 36:625-632.

Charbeneau R. J. 2000. Groundwater hydraulics and pollutant transport. Prentice Hall, Inc. Upper Saddle River. NJ.

Chen M., Ma L. Q. and Harris W. G. 2002. Arsenic concentrations in Florida surface soils: influence of soil type and properties. Soil Science Society of American Journals. 66:632–640.

Chen, M., Ma, L.Q. and Harris, W.G. 1999. Baseline concentrations of 15 trace elements in Florida surface soils. Journal of Environmental Quality. 28:1173-1181.

Chirenje T., Ma L. Q., Clark C. and Reeves M. 2003. Cu, Cr and As distribution in soils adjacent to pressure-treated decks, fences and poles. Environmental Pollution. 124:407-417.

Singh T. S. and Pant K. K. 2003. Equilibrium, kinetics and thermodynamic studies for adsorption of As (III) on activated alumina. Separation Purification Technology. 36:139:147.

Smedley P. L. and Kinniburg D. G. 2002. A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry. 17: 517-168.

Smedley P. L and Kinniburgh D. G. 1996. Arsenic contamination of groundwater in bangladesh, Sorption and Transport. British Geological Survey Report WC/00/19. Volume 1.

Solo-Gabriele H., Townsend T.G. 1999. Disposal practices and management alternatives for CCA-treated wood waste. West Manage. Residential. 17:378-389.

Solo-Gabriele H. M., Townsend T. G. and Stook B. 2002. Characteristics of chromated copper arsenate-treated wood ash. Journal of Hazardous Materials. B89: 213–232

Townsend T., Stook K., Tolaymat T., Song J.K., Solo-Gabriele H., Hosein N., and Khan B. 2000. New lines of CCA-treated wood reasch: in-service and disposal issues. Florida Center for Hazardous Waste. Technical Report.

United States Environmental Protection Agency (USEPA) 2001. National primary drinking water regulations arsenic and clarification to contaminants monitoring. DOCID:fr22ja01-29. 66:6975-7066.

Wang L., A. Chen and Fields K. 2000. Arsenic removal from drinking water by ion exchange and activated alumina plant. EPA Publication EPA/600/R-00/088.

Glaze W. H., Buescher C. A. and Mahon H. J.1982. Water chemical codex. Activated alumina. National Academy press. Washington D. C. pp 57-58.

Wilkie, J. A. and Hering J. G. 1996. Adstion of arsenic onto hydrous ferric oxide: effect of adsorbate/adsorbent ratios and co-occuring solutes. Colloidal Surfaces. 107:97-110.

Zhang, W., Cai Y., Tu C., and Ma. L.Q. 2002. Arsenic speciation and distribution in an arsenic hyper accumulating plant. Scie of Total Environment. 300:167-177.

Zheng, C. and Bennett, G.D. 2002. Applied contaminant transport modeling; John Wiley and Sons, Inc., New York City. New York.

BIOGRAPHICAL SKETCH

Prachee Gupta was born in 1980 in Rajasthan, India. She received a Bachelor of Technology (B.Tech) from the Indian Institute of Technology (IIT), Mumbai, in 2002. In the fall of 2002, Prachee joined the University of Florida for a Master of Science in the Department of Civil and Coastal Engineering under the tutelage of her major professor, Dr. Clayton J. Clark, II.