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SORPTION AND TRANSPORT OF POLAR ORGANIC COMPOUNDS IN GROUNDWATER

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ปัจจุบันนี้ได้มีการค้นพบยาหลายชนิดปะปนอยู่ในแหล่งน้ำต่างๆ เช่น แม่น้ำ ทะเลสาบ และน้ำใต้ดินจึงทำให้เกิดการดื้นตัวในการศึกษาการดูดซับและการเคลื่อนที่ของยาในสิ่งแวดล้อมใต้ดิน ในครั้งนี้ได้ทำการศึกษาการดูดซับของยาสี่ชนิดที่มีคุณสมบัติต่างๆกัน ได้แก่ อะซิดาไมโนเฟน (ยาแก้ปวด), 17แอลฟา-เอทินิล เอสทราไดอัล (ฮอร์โมนสังเคราะห์), นาลิดิซิก แอซิด(ยาปฏิชีวนะ) นอฟลอกซาซิน (ยาปฏิชีวนะ) กับซิลิกา อลูมินา และพอราแพค พี นอกจากนี้ยังได้ทำการศึกษาการดูดซับภายใต้การเปลี่ยนแปลงความเป็นกรด-ด่าง ในช่วง pH 4 ถึง pH 9 ดังนั้นการถูกดูดซับของยาเหล่านี้ได้ถูกศึกษาอย่างเป็นระบบ อีกทั้งความรู้พื้นฐานนี้ได้ถูกนำไปขยายต่อ ในการศึกษาการดูดซับและการเคลื่อนที่ของยาในคอลัมภ์ โดยใช้ดะกอนจากชั้นน้ำใต้ดินระดับตื้นในภาคกลางของประเทศไทย จากการทดลองพบว่าลักษณะการเคลื่อนที่ผ่านคอลัมภ์ ของนาลิดิซิก แอซิด และ 17แอลฟา-เอทินิล เอสทราไดอัล นั้นมีลักษณะที่เด่นชัดคือเป็นแบบการเคลื่อนที่แบบไม่อยู่ในภาวะสมดุลอันเกิดจากการดูดซับ โมเดล UFBTC ซึ่งเป็นแบบจำลองการเคลื่อนที่ของสารชนิดหนึ่งมิติได้ถูกนำมาใช้ประกอบกับข้อมูลที่ได้จากการศึกษาการดูดซับขั้นต้นทำให้ได้ค่าความหน่วงต่อการไหล และได้ทำการเปรียบเทียบค่าความหน่วงต่อการไหลของสารในคอลัมภ์ กับค่าความหน่วงต่อการไหลที่ได้จากการประเมินโดยใช้ข้อมูลที่ได้จากการศึกษาการดูดซับแบบแบช ในท้ายสุดได้ทำการศึกษาการดูดซับของยากับดะกอนใต้ดินที่ได้จากหลุมเจาะสำรวจ 3 แห่งในพื้นที่ต้นน้ำบาดาลบริเวณภาคกลางของประเทศไทย โดยดะกอนที่ใช้ในการศึกษามีคุณสมบัติของพื้นผิว (การแลกเปลี่ยนประจุ) และปริมาณคาร์บอนจากสารอินทรีย์ที่แตกต่างกัน ผลจากการศึกษาได้นำมาเปรียบเทียบกับยาฆ่าแมลงซึ่งเป็นสารปนเปื้อนที่รู้จักกันเป็นอย่างดี

สหสาขาวิชาการจัดการสิ่งแวดล้อม
สาขาวิชาการจัดการสิ่งแวดล้อม
ปีการศึกษา 2548

ลายมือชื่อนิสิต.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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KEY WORD: SORPTION/SILICA/ALUMINA/ACETAMINOPHEN/
17α-ETHYNYL ESTRADIOL/NALIDIXIC ACID/ NORFOXACIN/
PHARMACEUTICALS

ORANUJ LORPHENSRI: SORPTION AND TRANSPORT OF POLAR ORGANIC COMPOUNDS IN GROUNDWATER. THESIS ADVISOR: PROF. DAVID A. SABATINI, PH.D., THESIS CO-ADVISORS: KHEMARATH OSATHAPHAN, PH.D. AND ASSOC. PROF. CHINTANA SAIWAN, PH.D. 196 pp. ISBN 974-53-2388-8

Currently, pharmaceutical compounds have been widely detected in surface waters and groundwaters, leading to increased interest in the transport of these compounds in the subsurface environment. In this study, the sorption of four pharmaceuticals with various characteristics (non-hydrophobic, hydrophobic, ionizable monoprotic, ionizable amphoteric); acetaminophen (analgesic), 17α-ethynyl estradiol (synthetic hormone), nalidixic acid (antibiotic) and norfloxacin (antibiotic), were evaluated with silica, alumina, and Porapak P (hydrophobic medium). The pH dependent sorption of nalidixic acid and norfloxacin to silica and alumina were studied at pH4 to pH9. The fundamental sorption characteristics were revealed from this study and were extended to sorption and column transport of these pharmaceuticals to natural aquifer media from shallow aquifer, in Central Thailand. The column breakthrough curves of 17α-ethynyl estradiol and nalidixic acid showed sorption-related nonequilibrium characteristics. The UFBTC, one dimensional finite different transport model was used to model the column experiment data. The comparisons of Retardation Factor from column transport studies and predicted from batch studies were presented. Finally, the subsurface sediments (clayey silts and sands) with varying surface property (i.e., AEC, CEC) and organic carbon contents from three boreholes in groundwater recharge area, Central Thailand were studied for sorption affinity and compared to the more common pollutant (i.e., pesticide mobility scale).

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ABBREVIATIONS

ACE	Acetaminophen
AEC	Anion Exchange Capacity
C	Concentration [M/L^3]
C_e	Equilibrium concentration in the aqueous phase [M/L^3]
CEC	Cation Exchange Capacity
D	Hydrodynamic dispersion [L^2/T]
DGR	Department of Groundwater Resources
EDCs	Endocrine disrupting chemicals
EE2	17α-ethynylestradiol
F	Fraction of instantaneous sorption domains
HIOC	Hydrophobic ionizable organic compound
HOCs	Hydrophobic organic chemicals
k_1	First-order sorption rate constant
k_2	First-order desorption rate constant
K_d	Linear distribution coefficient.
K_d^{eff}	Linear isotherm centered about the specified concentration
K_f	Freundlich sorption constant
K_{ow}	Hydrophobicity
L	Column length
N	Freundlich exponent
NAL	Nalidixic acid
NISs	Nonionic surfactants
NOR	Norfloxacin
NZP	Normalized zeta potential
P	Peclet number
PPCPs	Pharmaceuticals and personal care products
PZC	Point of zero charge
q_e	Equilibrium mass of chemical sorbed per unit mass or per unit surface area of the sorbent
QSAR	Quantitative structure activity relationship

CHAPTER I

INTRODUCTION

1.1 Background

During the past three decades, the environmental concerns regarding the chemical pollution has concentrated on "priority pollutants". Those are toxic and carcinogenic pesticides and industrial chemicals which are persistent in the environment. This group of chemicals is just a part of the environmental pollutants. The other bioactive chemicals which are receiving less attentions as potential environmental pollutants include pharmaceuticals and personal care products (PPCPs). However, if we carefully count the amount of uses, the fact is that this type of chemical is used in the same quantities as the agrochemicals (Daughton and Ternes, 1999).

Pharmaceuticals can enter the environment in several pathways (Figure 1.1). Many pharmaceuticals used in human medical care and animal husbandry are not eliminated in the human and animal body. They are excreted by slightly transforms or even unchanged and often conjugate to polar molecules. Theses conjugate are easily cleaved during sewage treatment and discharged almost unchanged into receiving waters (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998; Stan and Heberer, 1997; Ternes, 1998; Wilken et al., 2000). Veterinary pharmaceuticals used in animal feeding operations may be released to the environment with animal wastes through overflow or leakage from storage structures or land application (Meyer et al., 2000). The pharmaceuticals used in aquaculture may also be released to the the environment through the outflow of the operation and may

infiltrate directly to groundwater. In case of recharge conditions, they may also leach from the contaminated surface waters into the groundwater aquifers (Heberer and Reddersen, 2001; Heberer and Stan, 1997).

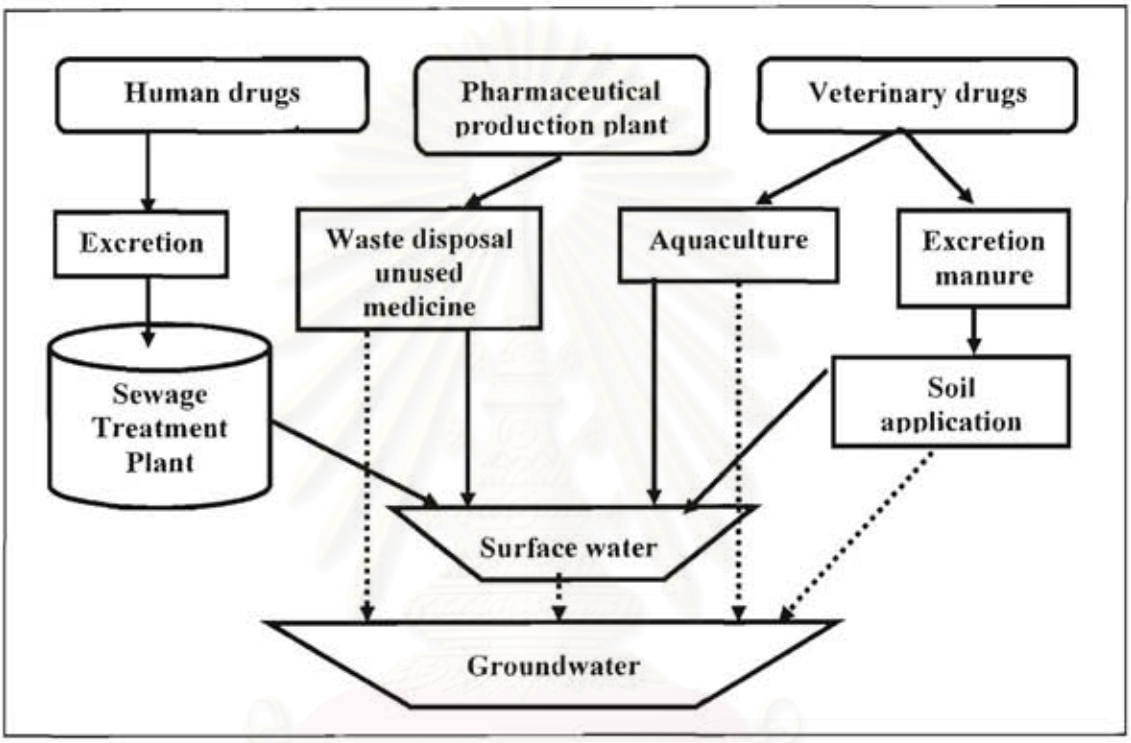


Figure 1.1 Possible sources and pathways for the occurrence of pharmaceuticals residues in the aquatic environment. (modified from Heberer, 2002)

The first evidence of occurrence of pharmaceuticals in aquatic environment was reported by Garrison et al. (1976) and Hignite and Azarnoff (1997), who detected clofibric acid in the lower micrograms per liter range in treated sewage in the United States. And more recently, a wide variety of pharmaceutical compounds has been detected at low concentrations (micrograms per litre and nanograms per liter) in some of the lakes, rivers and ground water in Europe and USA (Buser et al.,

1998; Daughton and Ternes, 1999; Holm et al., 1995; Kolpin et al., 2002; Raloff, 1998). These findings have raised the concern that not only are pharmaceutical compounds present in our water systems but that they may have detrimental effects on ecological and human health. Nowadays, the occurrence and fate of pharmaceuticals in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry (Daughton and Ternes, 1999; Daughton and Jones-Lepp, 2001; Halling-Sørensen et al., 1998; Heberer, 2002; Stan and Heberer, 1997). Reviews from Daughton and Ternes (1999), Halling-Sørensen (1998) and Jørgensen and Halling-Sørensen (2002) summarize most of the literatures in this new emerging field about the environmental relevant of pharmaceuticals. The groups of pharmaceuticals that have received recent public attentions are antibiotics, nonprescription drugs, other prescription drugs and reproductive hormones. Nonprescription drugs were found with the greatest frequency. Antibiotics, other prescription drugs and reproductive hormones were found at relatively similar frequencies of detection (Daughton and Ternes, 1999; Halling-Sørensen et al., 1998; Panter et al., 2000). Table 1.1 summarized the selected pharmaceuticals which were identified in environmental samples or having significant with respect to aquatic life (Daughton and Ternes, 1999).

The human health and environmental concerns regarding antibiotics are the development of antimicrobial drug resistant in livestock. Many antibiotics used for livestock are the same or related to drugs consumed in human, therefore, there is concern that resistant organism may pass from animals to humans through the handling of animal or food derived from animal (Mathews Jr., 2001). In addition, the concerns regarding hormones, which are classified as endocrine disruptors, is the

Table 1.1 Pharmaceutcals in environmental samples-or having significance with respect to aquatic life (Taken from Daughton and Ternes, 1999).

Compound CAS name	CAS RN MW Formula	Use/origin	Environmental occurrence	Trade names, comments, and nontarget species effects.
Acetaminophen N-(4-Hydroxyyphenyl) acetamide: (Paracetamol)	103-92-2 151.17 $C_8H_9NO_2$	Analgesic/anti-inflamatory	Efficiently removed by POTW (Ternes, 1998); POTW max. effluent: 6.0 µg/L; not detected in surface water (Ternes, 1998).	e.g., Tylenol: Daphnia immobilization EC_{50} (0.27-0.90 mM (Lilius et al., 1995)
17α-ethynylestradiol (17α)-19-Norpregna-1,3,5 (10)-trien-20-yne-3,17-diol	57-63-6 296.41 $C_{20}H_{24}O_2$	Oral contraceptive (in combination with progestogens)	Up to 7 ng/L in POWT effluent (Routledge et al., 1998). Not detected in German surface water above 0.5 ng/L (Halling-SØrensen et al., 1998), but found in Dutch Rhine water up to 4.3 ng/L (Belfroid et al., 1999)	Prime synthetic suspect regarding estrogenic effects in fish; the natural estrogen is 17β-estradiol: e.g., Oradiol
Fluoroquinolone Carboxylic acid Large class: e.g. ciprofloxacin	e.g., 85721-33-1 331.35 $C_{17}H_{18}FNO_3O_3$	Antibiotics	As one of only many classes pf pharmaceuticals, antibiotics in general has been investigated for their occurrence in the environment is a leading proposed cause of the rise in resistnace among pathogenic bacteria. Strongly sorbs to soil (Burhenne, Ludwig, Nikoluodis et al., 1997; Burhenne, Ludwig and Spiteller, 1997). Highly active in hospital wastewaters (Hartmann et al., 1998,Hartmann et al., 1999).	Gyrase inhibitors (needed for DNA replication); excreted mainly as parent compound

reproductive disorder. The scientists in the United Kingdom observed endocrine disruption in fish exposed to wastewater effluents. Early studies documented the development of female characteristics, such as the production of vitellogenin, an egg sac protein, when the male fish were exposed to undiluted wastewater effluent (Purdom et al., 1994). Follow-up bioassays, conducted to identify the causative agent for endocrine disruption, implicated estrogenic hormones, such as 17β -estradiol (a natural estrogen present in urine) and ethinyl estradiol (an ingredient of birth control pills) (Desbrow et al., 1998). These findings were complemented by exposure studies demonstrating feminization of male fish at hormone concentrations as low as several parts per trillion (a few nanograms per liter). Although pharmaceuticals have been widely detected, little information exists on their fate and transport in groundwater systems; such knowledge is necessary to properly respond to the presence of pharmaceuticals in the environment.

Therefore, four pharmaceuticals, namely acetaminophen (analgesic drug), nalidixic acid (antibiotic), norfloxacin (antibiotic) and 17α-ethinyl estradiol (synthetic hormone for birth control), are selected for this study regarding environmental occurrences and their interesting chemical properties in relative to water solubility and partition to organic phases (log K_{ow}).

1.2 Objectives of the study

The objective of this study is to determine the fate and transport of pharmaceutical compounds which have partly hydrophilic and partly hydrophobic structure. The chosen pharmaceuticals exhibit an increasing trend of hydrophobicity in water. The study will demonstrate the affect of media properties (charged solid

surface) and groundwater chemical condition (pH) on sorption and transport with pure minerals, hydrophobic medium and subsurface sediments.

1.3 Hypotheses

The hypothesis guiding this research is that the sorption and transport of pharmaceuticals are affected by chemical properties of pharmaceuticals, sorbent properties and groundwater chemical properties. Sorption and transport of ionizable pharmaceuticals depends greatly on solute pH.

1.4 Scopes of the Study

1. To evaluate the batch sorption of selected pharmaceuticals with varying levels of hydrophobicity and charged moieties on two artificial subsurface media (positively and negatively-charged surface), a hydrophobic medium and subsurface sediments. This study extended the earlier study by Intravichit, 2003.

2. To evaluate the transport (mobility) of selected pharmaceuticals in continuous flow column studies to mimic pharmaceuticals transport in the groundwater flow condition.

3. To evaluate pH impacts on sorption and transport.

4. To evaluate the sorption affinity of selected pharmaceuticals with the subsurface sediments obtained from bore holes in major shallow aquifer at recharge area, Central of Thailand.

CHAPTER II

LITERATURE REVIEW

2.1 Theoritical Background

There are two fundamental motivations for sorption based on three elements e.g., solute or sorbate (e.g., pharmaceuticals), solvent (e.g., water) and sorbent (e.g., solid surface). The first motivation for sorption is solvent-motivated sorption. This motivation results from the "dislike" of the organic contaminant for solvent ("hydro phobic"). The second motivation is sorbent-motivated sorption, in which the solid phase has a greater affinity for the solute than does the solvent. This motivation may be active for ionic organic compounds (Palmer et al., 1992).

2.1.1 Sorption Fundamental

One of the major physiochemical processes that can effect the fate and transport of organic contaminants (e.g., pharmaceuticals) in the subsurface is sorption (Palmer and Johnson, 1991). It is the transfer process of chemicals in aqueous state into aquifer matrix (solid phase). Sorption is not always a single simple process, but rather often results from combination of interactions. Sorption is the process that includes adsorption and absorption. Adsorption is the accumulation of a chemical at the interface of two contiguous phases (accumulation of sorbate onto soil solid surface) (Yaron et al., 1996). Absorption is the partitioning between two contiguous phases (accumulation of sorbate into organic carbon) (Weber et al., 1991).

Sorption to natural media may be purely physical, as with van der Waals forcess, or chemical in nature, as with electrostatic interactions. The mechanism of sorption processes include ionic, hydrogen and covalent bonding, charge transfer or electron-donor acceptor mechanisms, van der Waal forces, ligand exchange and partitioning.

- Ionic binding involves ionized, or easily ionizable groups. Carboxylic and phenolic hydroxyl groups of humic substances. For example, pesticides (diquat and paraquat) bind to soil humic substances by ion exchange via their cationic group (Gevao et al., 2000).

- Humic substances, with many oxygen- and hydroxyl-containing functional groups, form H-bonds with complimentary groups on organic molecules. Organic molecules compete with water for these binding sites. H-bonding is suggested to play a major role in the adsorption of several non-ionic polar pesticides (Senesi et al., 1984). Acidic and anionic pesticides (2,4-D and 2,4,5-T,dicamba) can interact with soil organic matter by H-bonding at pH values below their pKa in non-ionized forms through their –COOH, -COOR and identical groups (Carringer et al., 1975; Khan, 1973; Senesi et al., 1984).

- van der Waals force consists of weak short-range dipolar or induced-dipolar attraction that exist, in addition to stronger binding forces, in all adsorbent-adsorbate interactions. Interactions between non-ionic and nonpolar pesticides on suitable humic acid molecules are of particular relevance.

- Adsorption by ligand exchange involves the replacement of relatively weak ligands, e.g., H_2O partially holding polyvalent cations associated with

soil organic matter by suitable adsorbent molecules such as s-triazines and anioic pesticides (Nearpass, 1976; Senesi, 1992).

- Charge-transfer complexes are formed via electron donor-acceptor mechanism, wih pesticides possessing, alternatively, electron donor or electron acceptor properties.

- Hydrophobic partioning assumes that humic substances both in the solid- and dissolved-phase are treated as a non-aqueous solvent into which the organic compounds can partition from water (Chiou et al., 1986). Non-polar and hydrophobic compounds can undergo sequestration during prolonged residence. (Pignatello and Xing, 1996) referred to sequestration as slow sorption.

- The formation of covalent bonds between organic compounds and their metabolites and soil humic substances are often mediated by chemical, photochemical or enzymatic catalysts leading to stable, mostly irreversible incorporation into the soil (Chiou et al., 1983; Chiou and Shoup, 1985). The organic compounds which are most likely to bind covalently to soil humic matter have functionallities similar to the components of humus.

The composition of soil and sediment includes both mineral matter and organic matter as the primary constituents. Naturally-occuring solid phases (e.g., aquifer materials) are not only chemically and physically inhomogeneous, but are normally coated with metal oxides, microorganisms and their excretion products, and humic substances. The soil or sediment, then, is characterized as a dual-function sorbent, in which the mineral matter sorbs the contaminant by adsorption while the SOM sorbs the contaminant by a partition process (Chiou et al., 1983; Chiou and Shoup, 1985). General mechanisms for any organic chemical interaction to any

natural solid are described as follows (Schwarzenbach et al., 2003): 1) partitioning from aqueous phase to natural organic matter especially hydrophobic organic compounds 2) displacing water molecules from the region near a mineral surface by weak intermolecular forces (van der Waals). 3) The ionizable organic chemicals can have further interaction such as attracting to specific surface sites exhibiting the opposite charge, if the sorbate is ionizable in the aqueous solution and 4) Chemically bonding to the solids, if the sorbate and sorbent have mutually reactive moieties (such as carbonyl on the sorbate and an amino group on the sorbent).

2.1.2 Sorption of Nonionic Organic Compounds

Sorption to natural sediments is probably the main factor on transport and fate of organic contaminants in the environment (Morel and Gshwend, 1987). The organic matter and mineral matter in natural sediment distinctly contribute to the sorption of nonionic organic compounds. The soil/sediment organic matter (SOM) acts as a partition medium, and the mineral matter functions act as an adsorbent. For nonionic/nonpolar solutes in sediment-water systems, where a significant SOM content is present (organic carbon content greater than 0.1%), the solute partitioning in SOM dominates over adsorption on mineral matter because of strong suppression by water of solute adsorption on polar mineral surfaces (Chiou et al., 1983; Rutherford and Chiou, 1992). In many sand aquifers, however, the organic carbon content is near or below the limit where the organic matter is considered dominant. Piwoni and Banerjee (1989) suggested the need for sorption studies in sand aquifers in order to refine carbon based estimates.

2.1.3 Sorption of Ionic Organic Compounds

Ionizable organic compounds such as phenol, quinoline, and organic acid can lose or gain proton depending upon the pH. The ionized compounds are much more water soluble and less hydrophobic than uncharged forms (Palmer and Johnson, 1991). Therefore, the ionized forms have much lower K_{oc} than uncharged forms. The main controlling factors for ionizable organic compounds are pH and surface charged condition.

Pharmaceutical compounds may consist of a combination of nonpolar and polar or ionizable functional groups. For pharmaceuticals with single ionizable group (Figure 2.1), the pKa establishes the fraction of neutral or ionized form that exists at a given pH. The pKa of a monoprotic acid is the pH at which half of the functional groups are neutralized and half are ionized.

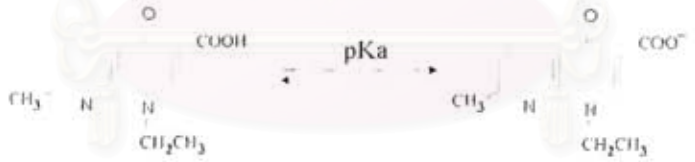


Figure 2.1 Ionization scheme of monoprotic molecule (Takác-Novák and Tam, 2000

At one pH unit lower than the pKa, the functional groups exist predominately (91%) in the neutralized form, while at one pH unit higher than the pKa the functional groups exist predominately in the ionized form, as expressed by the Henderson-Hasselbalch equation (Watson, 1999):

$$\frac{[A-]}{[HA]} = 10^{(pH-pKa)} \qquad (1)$$

For diprotic compounds, dissociation/protonation microconstants (pk) are useful to depict the site-specific ionization of individual functional groups, which can be applied for calculating the pH-dependent distribution of species (microspeciation). For a diprotic amphoteric drug (i.e., norfloxacin) with pKa values of comparable magnitude, the (de)protonation of one group affects the other.).

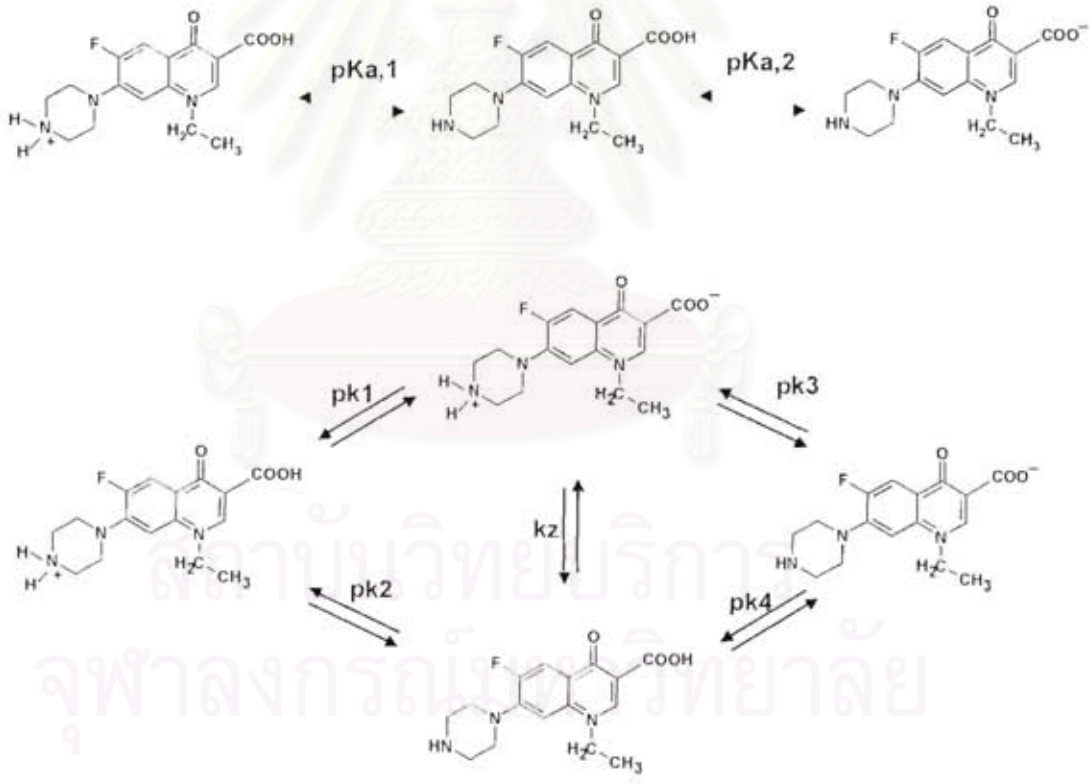


Figure 2.2 Ionization scheme of diprotic amphoteric norfloxacin molecules (Takác-Novák and Tam, 2000).

Depending on the pH values of the media, the two ionizable sites, such as an acidic (-COOH) and a basic (-N) groups, may exist in four different microspecies, namely cation (H_2X^+), zwitterion ($HX\pm$), neutral species (HX^0, chargeless) and anion (X-) which are shown in Figure 2.2. It is generally accepted that the neutral form is more hydrophobic. The pKa values disclose no information about the equilibrium that generates HX^0. On the other hand, the microconstants (pk_1 through pk_4) and the tautomeric ratio (kz) describe the amount of various microforms as a function of pH. These parameters are especially useful in research areas where the ionization state of each functional group plays an important role in the absorption of drug molecules.

Norfloxacin (diprotic amphoteric molecule) has two relevant ionizable functional groups, which means that their acid base chemistry involves two protons. Norfloxacin belongs to the quinolone class, which have a carboxyl group that is normally stronger acid than the ammonium group, and it has an pKa_1 value of 6±1 in water. As a result, pKa_1 value can be associated with the carboxylic acid functional group and pKa_2 value with the ammonium functional group (Ross and Riley, 1992; Takác-Novák and Tam, 2000).

Surface Charge of Alumina and Silica

Alumina and silicon oxides are common constituents of rocks, sediment and soils. They have the advantage of being very simple solids, the simplest that can be found in nature, and of providing possibility to start to understand simple systems before going on to complicated ones. Most of the studies concerning adsorption on alumina and silica surfaces have been done using synthetic oxides, which can have crystalline, amorphous, gel, or colloidal forms. These synthetic forms are preferred to natural ones because of their more reactive surfaces and their higher level of purity. The surface properties having a direct influence on adsorption are the specific surface areas ($m^2.g^{-1}$), the density of reactive surface sites ($site.nm^{-2}$), the surface acidity, the surface charge, and its evolution with pH and ionic strength. All these parameters are important because they indicate if conditions are favorable for the interactions between the surface and the solution (high surface of contact, favorable electrostatics).

The pH where the mineral has an equal number of negatively and positively-charged sites is called the isoelectric point or the point of zero charge (PZC) for the mineral. At pH values lower than the PZC, the net surface charge is positive and anion adsorption is dominant; at pH values higher than the PZC the net charge is negative and cation adsorption occurs. However, it is important to note that while the net surface charge may be predominately negative or positive depending on the pH, some oppositely charged sites will still exist.

Silica and alumina surfaces also differ with their PZC (Point of zero). Surfaces are positively charged for pH lower than Pzc and negatively charged for

higher pH. PZC for the silica surface generally ranges between pH 2–4 and between pH 8–9.5 for alumina. For pH of natural waters, (pH 5–9) (where adsorption of ions occurs, generally), the two surfaces have opposite charges. Alumina and silica surfaces are positive and negative, respectively, in this pH range; thus, the adsorption of anions on the alumina and adsorption of cations on the silica surface are likely, where electrostatic is favorable. For alumina, this results in the tendency to adsorb cations at high pH and to adsorb anions at low pH. In contrast with alumina, silica carries negative surface charge over the entire usually studied pH range (4–10). This creates favorable electrostatic conditions for cation adsorption, while the ability of silica to adsorb anions is limited.

Surface Charge of Natural Aquifer Media

Unlike pure systems, natural soil/sediment contains varying proportions of aluminosilicate clay minerals and noncrystalline inorganic materials, such as oxides of Si, Fe, Al and Mn, and organic matter that have a range of surface properties. Although the clay minerals might be a significant factor in influencing soil physiochemical properties due to their large surface area and their predominance in natural soils, the small fraction of metal-oxides and organic matter may also have a great potential for determining widely variable surface electrochemical properties. Many soil physical and chemical properties are directly or indirectly controlled by nature and amount of surface charge as well as their variation with soil solution characteristics (Barrow, 1987; Barrow, 1996; Greenland and Hayes, 1981). Sources of surface charge in soils include both inorganic and organic components. Soil colloids, which are smaller than 2 μm in size and account for generally less than 10% of soil in

weight, bear more than 70–80% of soil charges (Mattson, 1931). A combination of high charge and very small particle size results in a high charge density and furthermore an actively reactive surface of colloids. Thus, any change of soil colloidal properties can affect a series of contaminant reactions in soil. The main components of soil colloids are layer silicates, oxides of Fe, Al and Mn and organic materials. Larger phyllosilicate mineral grains, i.e., kaolinite montmorillonite and illite, are usually coated to a greater or lesser extent by organic material and smaller amorphous or crystalline inorganic materials, i.e., Fe- and Al-oxides and hydroxides, released from primary mineral weathering or from the deposition of translocated material (Hendershot and Lavkulich, 1983).

2.1.4 Sorption Isotherm

Several conceptual and empirical models have been used to describe equilibrium phase distributions for the sorption of organic compounds in subsurface systems. There are three common types of adsorption models namely; linear, Freundlich and Langmuir model.

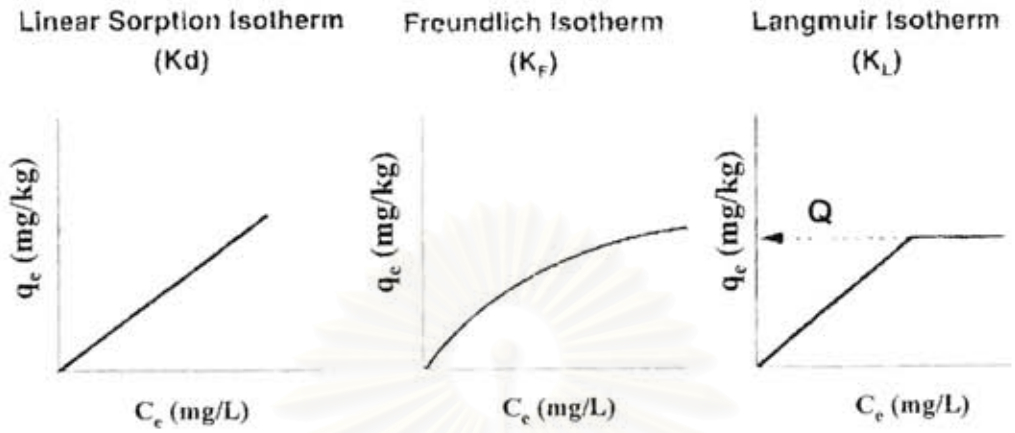


Figure 2.3 Sorption isotherms (a) Linear sorption isotherm (b) Freundlich Isotherm (c) Langmuir Isotherm.

1. Linear model. The linear model is the simplest model in which it is assumed that the sorbed and solution phase concentrations are directly proportion:

$$q_e = K_d C_e \tag{2}$$

where q_e is the amount of solute sorbed by the solid phase at equilibrium, K_d is the distribution coefficient, and C_e is the amount of solute in the aqueous phase at equilibrium. Chiou et al. (1977) indicated that sorption phenomena dominated by partition-based process should be governed by linear isotherms until aqueous-phase solubility is approached, while Karickhoff (1981) has suggested that it the aqueous phase concentration is below 10^{-3} M, or less than one-half the aqueous solubility of the solute, the resulting sorption isotherm will be linear.

Organic Carbon Normalization. Organic carbon normalization is frequently employed to reduce the variability between K_d, solid data of one compound in different soils.

$$K_{oc} = K_d / f_{oc} \tag{3}$$

where f_{oc} is the mass fraction of organic carbon in soil. This approach has been extended to relate solute hydrophobicity to sorptive capacity using empirical correlations of the general form.

$$\log K_{oc} = a \log K_{ow} + b \tag{4}$$

where K_{ow} is the octanol-water partition coefficient of a solute and the coefficient a and b are related to sorbent properties (Schwarzenbach and Westall, 1981). In general, such relationships provide only first-order approximations of sorptive capacity, and then only if an appropriate correlation is chosen. If the soil or sediment differs significantly from those for which a given correlation was developed, order of magnitude differences in the K_{oc} values for specific compound may exist. Such difference can be attributed largely to differences in the properties of soil organic matter, and to a lesser extent to the contributons of other soil materials (e.g., clay minerals) to solute uptake (Weber et al., 1991; Weber et al., 1992)

2. Langmuir model. The Langmuir model, one of the first theoretical treatments of nonlinear sorption, has been successfully applied to a wide range of systems exhibiting limiting or maximum sorption capacities. This model is derived by

equating the rates of adsorption onto bare surfaces and desorption from occupied sites at equilibrium. The details of the development are readily available in the literature (Weber Jr. and Digiano, 1995).

$$q_e = Qb\frac{C_e}{1+bC_e} \tag{5}$$

where q_e is the maximum sorption capacity, and the coefficient b is the ratio of adsorption and desorption rate coefficient ($b=k_s/k_d$). The Langmuir equation reduces to a linear relationship at low concentrations, while the maximum sorption capacity, Q, is attained at the concentrations corresponding to monolayer coverage.

3. Freundlich Model. The energetic of sorption are generally far more complex in practice than implied by the linear and Langmuir models. It is in fact unrealistic to expect that models based on single linear partition mechanism or a limiting sorption capacity will be appropriate for most environmentally relevant sorbate-sorbent systems. In practice, equilibrium sorption data are often best described by models that can accommodate heterogeneous site energies, the most simple of which is the Freundlich model:

$$q_e = K_f C^N{}_e \tag{6}$$

where K_f and n are characteristic parameters. As illustrated in Figure 2.3b, values of N less than 1 results in convex adsorption isotherms, while values of N greater than 1 lead to concave adsorption isotherm; the model reduces to the linear

form given in equation (1) where N equals 1. Values of K_f and N are typically obtained by fitting log-transformed sorption data to the linearized logarithmic form of the Freundlich equation:

$$\log\ q_e = \log K_f + N \log\ C_e \qquad (7)$$

Although more reliable estimates of K_f and N generally obtained by a non-linear regression of untransformed data, the original development of Freundlich model was largely empirical but theoretical justifications of the model for sorption on heterogeneous surfaces subsequently have been presented (Carter et al., 1995). Theoretical analyses reveal that the parameter K_f is a measure of sorption capacity, while the exponent characterizes sorption intensity; more specifically, the cumulative magnitude and the diversity of sorption energies. Values of N reported for the sorption of hydrophobic organic compounds by soil and sediments have been varied from approximately 0.4 to 1.2 (Miller and Weber, 1986; Mingelgrin and Gerstl, 1983). These finding suggested that a broad range of sorbate-sorbent interaction energies were involved in natural systems and that such interaction energies may vary considerably between different solute and solid phases.

2.1.5 Transport of Organic Contaminant Through Porous Media

Major transport processes in porous media include advection and dispersion. In sand and gravel aquifers, the main factor in the movement of contaminant is advection, the process by which solutes are transported by the bulk motion of the groundwater flow. The driving force of groundwater flow is the hydraulic gradient. The average linear velocity at which groundwater flows through a granular medium, such as sand and gravel aquifer, is equal to the product of the

gradient and the capability of the medium to transmit water (ratio of hydraulic conductivity and porosity) (Freeze and Cherry, 1979). Groundwater velocities in such aquifers typically range between 1 m/y and 1000 m/y (Mackay et al., 1985). Dissolved contaminants spread as they move with the groundwater. This process is called dispersion and is caused by two fundamental processes, mechanical mixing and molecular diffusion. Mechanical mixing results from variations in groundwater velocity within the porous aquifer caused by friction forces, variation in pore geometry and variation in local flow directions. The molecular diffusion caused by diffusion of the solute from a zone of higher concentration to a zone of lower concentration.

Some dissolved contaminant may interact with the aquifer media along the flow path through adsorption, partitioning, ion exchange and other processes (Freeze and Cherry, 1979). Sorption causes reduction of concentration in the aqueous phase, and retardation of the movement of the contaminant relative to groundwater flow (Rao and Davidson, 1979). For some contaminants, such as ionic species of certain organic solutes. Many factors control the degree of interactions. These include the concentration and characteristics of the contaminant, the characteristics of the aquifer solids, the pH of the groundwater, and the presence of other dissolved constituents.

Fate and transport of organic compound in groundwater highly depends on sorption to aquifer materials. Approaches for determining the sorption of organic compound range from simple estimation from K_{ow} and semi-empirical equation to batch and column experiment and to field transport experiments. However, using the sorption coefficient from simple estimation should be avoided or used with extreme caution (Stephanatos et al., 1991). Besides the uncertainty inherent

in simple estimation, considerable uncertainty also exists with respect to the applicability of batch-derived sorption estimates to flow system (e.g., Brusseau, 1992).

For sediments having organic carbon content greater than 0.1%, it is generally assumed that the sorption of nonionic hydrophobic organic compounds (HOCs) depends mainly on the soil/sediment organic matter (SOM). In many aquifer sands, however, the organic carbon content is near or below the limit where the organic matter is considered dominant. Piwoni and Banerjee, 1989 suggested the need for sorption studies in aquifer sands in order to refine carbon based estimation.

In addition, specific sorbate-sorbent interactions may be relatively unimportant for the sorption of HOCs since the sorption is generally thought to be driven by a partitioning between the solution and organic matter component of the sorbent (Chiou et al., 1979; Chiou et al., 1983; Karickhoff, 1981; Mackay and Powers, 1987). Thus, chemical nonequilibrium may be ruled out as a probable nonequilibrium mechanism for HOCs (Brusseau et al., 1989). It must be stressed that, while chemical nonequilibrium may be unimportant for nonpolar organic chemicals, it may well be important for other organic chemicals such as pesticides (Brusseau et al., 1989) and pharmaceuticals which have molecular structures in between that of HOCs and amphiphiles and often have one or more functional group(s).

The principle processes governing the solute transport of organic solute in ground water are advection, dispersion, sorption and transformation (Freeze and Cherry, 1979; McCarty et al., 1981). Two assumptions regarding solute transport in groundwater are described as follows;

Local Equilibrium Assumption

The local equilibrium assumption (eq.2) requires the sorption rate to be fast relative to the other rate parameters influencing the solute transport (Benker et al., 1998).

Solute transport through soil/sediment is a significant process for contamination of groundwater. Parameters that influence solute transport through soil/sediment are soil water velocity, adsorption-desorption characteristics, chemical reactions and transformation by microorganisms (Selim et al., 1976).

The contaminant transport with sorption: In the absence of transformation processes, subsurface contaminant transport is described by advection, dispersion and adsorption processes according to the following governing equation (assuming equilibrium sorption) (Freeze and Cherry, 1979):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{8}$$

Linear sorption isotherm

$$R = 1 + \frac{\rho}{\theta} K_d \tag{9}$$

Freundlich nonlinear sorption isotherm

$$R = 1 + \frac{\rho}{\theta} K_f C^{N-1} \tag{10}$$

Langmuir sorption isotherm

$$R = 1 + \frac{\rho}{\theta}\left[\frac{K_L A_m}{(1 + K_L C)^2}\right] \tag{11}$$

where R [dimensionless] is the retardation factor; C [M/L^3] is the solute concentration; t [T] is time; D [L^2/T] is the hydrodynamic dispersion; v [L/T] is the average pore water velocity; ρ [M/L^3] is the bulk density; θ is the effective porosity; K_d is the sorption coefficient; K_f is the Freundlich sorption coefficient; and N is the Freundlich nonlinearity parameter.

Nonequilibrium Assumption

Several processes have been proposed as being responsible for nonequilibrium sorption (rate-limited). Nonequilibrium processes have been grouped into two general classes; transport-related and sorption related (Brusseau et al., 1991a). Transport-related nonequilibrium often refers to physical nonequilibrium, which results from the existence of a heterogeneous flow domain (e.g. aggregates, macropore, stratified media). It should be noted that the transport-related nonequilibrium affects both sorbing and non sorbing solute. The sorption-related nonequilibrium may result from chemical nonequilibrium or from rate-limited diffusive mass transfer (e.g., film diffusion, retarded intraparticle diffusion and intra sorbent diffusion as shown in Figure 2.4) as discussed in Grathwohl, 1998; van Genuchten, 1981; van Genuchten and Wagenet, 1989. Chemical nonequilibrium (e.g. chemisorption) is caused by rate-limited interaction between sorbate and sorbent.

According to two types of nonequilibrium assumptions mentioned above, there are two models describing non-equilibrium conditions; two-region model and two-site model (van Genuchten, 1981; van Genuchten and Wagenet, 1989).

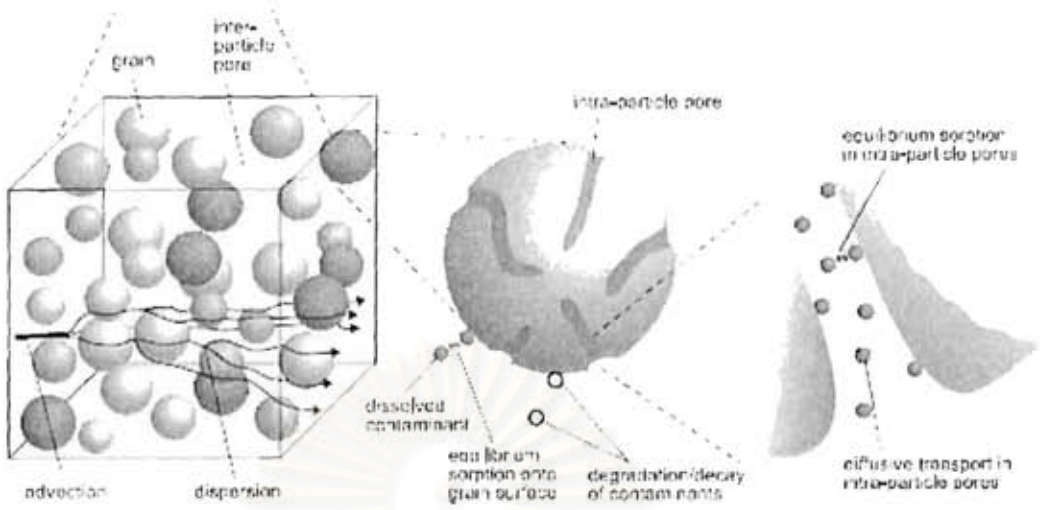


Figure 2.4 Schematic view of the most relevant transport process in a hydraulically and lithologically heterogeneous aquifer (taken from Liedl and Ptak, 2003).

The two-region model (transport-related nonequilibrium) conceptually divides the porous medium into mobile and immobile regions. Van Genuchten (1981) assumed that advective-dispersive transport is restricted to the mobile water region, and the transfer of solute between mobile and immobile regions is diffusion limited (Gaber et al., 1995). The two-site model (sorption-related nonequilibrium) conceptually divides the porous medium into two domains. The first domain assumes sorption is instantaneous. The second domain assumes that sorption is rate-limited. The sorption model based on first-order mass transfer is described as follows (Selim et al., 1976):

$$S_1 = FK_dC \tag{12}$$

$$\frac{dS_2}{dt} = k_1S_1 - k_2S_2 \tag{13}$$

Where S_1 and S_2 $[MM^{-1}]$ are the sorbed-phase concentration in the equilibrium and the rate-limited domain, respectively; K_d $[L^3M^{-1}]$ is the equilibrium sorption coefficient ; F [unitless] is the fraction of sorbent for which sorption is instantaneous and k_1, k_2 $[T^{-1}]$ are first-order sorption and desorption rate constant, respectively. These equations can represent each of three processes (e.g., transport-related nonequilibrium, chemical nonequilibrium and intrasorbent diffusion) (Brusseau, 1992).

Nonequilibrium sorption may result from chemical nonequilibrium or from rate-limited diffusive mass transfer (e.g., film diffusion, retarded intraparticle diffusion and intra organic matter diffusion) as discussed in Brusseau et al., 1991a; Grathwohl, 1998; van Genuchten and Wagenet, 1989. The latter is more common in subsurface systems.

The following dimensionless equations represent the transport of sorbing solutes under one-dimensional, steady water flow in homogeneous porous medium (Brusseau et al., 1991a).

$$\beta R\frac{\partial C^{\bullet}}{\partial T}+(1-\beta)R\frac{\partial S^{\bullet}}{\partial T}=\frac{1}{P}\frac{\partial^2 C^{\bullet}}{\partial^2 X}-\frac{\partial C^{\bullet}}{\partial X} \tag{14}$$

$$(1-\beta)R\frac{\partial S^{\bullet}}{\partial T}=\omega(C^{\bullet}-S^{\bullet}) \tag{15}$$

Where

$$C^{\bullet}=\frac{C}{C_o} \qquad\qquad P=\frac{vL}{D} \tag{16), (17}$$

$$S^* = \frac{S_2}{(1-F)k_d} \qquad R = 1 + \frac{\rho}{\theta}k_d \qquad (18),(19)$$

$$T = \frac{vt}{L} \qquad \beta = \frac{1 + F\frac{\rho}{\theta}k_d}{R} \qquad (20),(21)$$

$$X = \frac{x}{L} \qquad \omega = \frac{k_2(1-\beta)RL}{v} \qquad (23),(24)$$

Where β [dimensionless] is the fraction of instantaneous retardation; T [dimensionless] is relative pore volume; S_2 [MM^{-1}] is the sorbed-phase concentration in the rate-limited domain; P [dimensionless] is the Peclet number which is a ratio of advective flux versus dispersive flux; ω [dimensionless] is the Damkohler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption; β and ω specify the degree of nonequilibrium in the system, which decreases as either of the two parameters increase in magnitude; v [LT^{-1}] is the average pore water velocity; L [L] is the column length; F [dimensionless] is the fraction of sorbent for which sorption is instantaneous; x [L] is the distance, and other parameters are as described above.

The application of these transport equations require a value for the K_d which can be obtained by (1) estimation from f_{oc} and K_{oc} (2) batch tests (3) column test or (4) field test. The application of theses model is to predict the transport (mobility) of the contamination at various chemical concentrations along the groundwater flow path.

2.2 Literature Review

Isenbarger (2002) conducted comparative antibiotic resistance of diarrheaal pathogens from Vietnam and Thailand, 1996-1999. Quinolone (nalidixic acid) resistance remains low in both countries, except among campylobactor and salmonella organisms in Thailand. Nalidixic acid resistance among salmonella has more than doubled since 1995 (to 21%) in Thailand but is not yet documented in Vietnam. Resistance to quinolones is correlated with resistance to azithromycin in both campylobacter and salmonella in Thailand. This study illustrated the growing magnitude of antibiotic resistance and important differences between countries in Southeast Asia.

Karickhoff (1981) presented the approach used for estimation of equilibrium sorption behavior which was a combination of thermodynamic theory and empirical correlation. For neutral hydrophobic solutes (generally water solubilities < 10 -3 M), sorption isotherms in the low loading limit are linear, reversible, and can be characterized by a partition coefficient, K_d. These partition coefficients are highly correlated with the organic carbon content of sediments/soils; referencing sorption to organic carbon gives a partition coefficient to organic carbon, Koc, which is highly sediment/soil independent.

Chiou and Kile (1998) presented sorption data obtained on representative samples of polar compounds (substituted ureas and phenolic compounds) and of nonpolar compounds (e.g., EDB and TCE) on a peat soil and a mineral (Woodburn) soil. At relatively low Ce/ Sw, both the nonpolar and the polar solutes exhibit nonlinear sorption. The sorption nonlinearity approaches apparent

saturation at about Ce/Sw) 0.010-0.015 for the nonpolar solutes and at about Ce/Sw)0.10-0.13 for the polar solutes; above these Ce/Sw regions, the isotherms are practically linear. The nonlinear sorption capacities are greater for polar solutes than for nonpolar solutes.

Banerjee (1985) suggested that in subsurface samples sorbent TOC content is a reasonably good predictor of sorption down to about 0.2% TOC. However, as the K_{oc} values decline with the decrease in hydrophobicity of the sorbates, the imprecision of the K_{oc} estimate increases appreciably, demonstrating an interrelationship between sorbate properties and sorbent characteristics other than TOC. It appeared that for very hydrophobic molecules, TOC content of the sorbent will control sorption down to levels of organic carbon that defy quantitation. Conversely, sorption of less hydrophobic organics will likely be affected by clay mineral surfaces, amorphous metal oxides and perhaps other characteristics in many unsaturated and most saturated subsurface environments where organic carbon content is quite low.

Brownawell (1990) studied the factors that control the extent of adsorption of amphiphilic organic cations on environmental and pristine surfaces. The sorbents were kaolinite, montmorillonite, two aquifer materials, and a soil. The distribution ratio of the dodecylpyridinium was strongly dependent on the nature and concentration of the inorganic cations in solution, but virtually independent of solution pH. The adsorption isotherms were distinctly nonlinear, even at very low surface concentrations of organic cations. Two types of adsorption reactions were found to be significant: exchange of pyridinium with an alkali-metal cation, and adsorption of pyridinium with chloride counterion.

Schwarzenbach (1981) conducted laboratory batch and column experiments to elucidate the sorption behavior of nonpolar organic compounds (e.g., halogenated alkenes and benzenes) in a river water-groundwater infiltration system. For the low concentrations typical of the environment, sorption equilibrium can be described by the equation $S = K_dC$ where S = concentration in the solid phase, K_d = partition coefficient, and C = concentration in the liquid phase. For a variety of sorbents, it was found that the partition coefficient K_d can he estimated from its 1-octanol/ water partition coefficient K_{ow} and from the organic-carbon (OC) content f_{oc} (fraction organic carbon) of the sorbents if f_{oc} is greater than 0.001: $\log K_d = 0.72 \log K_{ow} + \log f_{oc} + 0.49$.

Kasnavia et al. (1999) discussed the importance of fluorescence dye sorption when selecting dyes for tracer studies. The effect of dye and media properties on dye sorption was evaluated using four fluorescent dyes (fluorescein, rhodamine B, rhodamine WT and sulforhodamine B) and two oppositely charged mineral surfaces (alumina and silica). Fluorescein, which had only negative functional groups, sorbed least onto negatively charged silica but most onto positively charged alumina. Since fluorescent dyes were subjected to sorption, then dye selection should be based on their chemical properties, media characteristics, and laboratory batch and column studies.

Sabatini (2000) investigated sorption of two fluorescent dyes: fluorescein which has anionic carboxylic functional group, and sulforhodamine B which has cationic functional group) was evaluated with two oppositely charged, consolidated aquifer materials (sandstone and limestone). Sorption kinetic rates decreased with increasing particle size, which is consistent with diffusion-limited intraparticle sorption. The author demonstrated the important of understanding both

equilibrium and kinetics of dye sorption when designing and interpreting tracer studies.

Karapanagioti et al. (2000) investigated the sorptive properties as well as the composition of organic matter in different subsamples (mainly grain size fraction) of the Canadian River Alluvium. Organic petrography was used as a new tool to describe and characterize the organic matter in the subsamples. Soil subsamples with organic matter present as organic coating around the quartz grains evidenced the lowest K_{oc}, the most linear sorption isotherms and the fastest sorption kinetics while subsamples containing predominately coaly, particulate organic matter showed the highest K_{oc}, the highest nonlinearity of sorption isotherm and the slowest sorption kinetics. The study showed that the identification and quantification of the coaly particles within a sediment/soil was a prerequisite in order to understand or predict sorption behavior of organic pollutions.

Kung and McBride (1991) investigated the mechanism of surface bonding of chlorophenols on metal oxides and determine the relative strength of the oxide-organic bond. Iron and aluminum oxides were chosen as adsorbents since they are the most common metal oxides in soil and aquifer materials. Adsorption of 10 chlorinated phenols including mono-, di- and polychlorophenols was studied from the vapor and/or solution phase. Adsorption of chlorophenols from dilute solution was quantified by isotherms to estimate the surface reactivity.

Hari et al. (2005) examined the adsorption of four pharmaceutical compounds, acetaminophen, carbamazepine, nalidixic acid and norfloxacin, in the presence of a natural aquifer material. Adsorption was studied as a function of pH and in the presence of two surfactants, cetylpyridinium chloride (CPC), a cationic surfactant and Tergitol NP9, and ethoxylated nonionic surfactant. In the absence of

surfactants, the results indicated a 1 to 2 orders of magnitude variation in adsorption affinity with changing pH for nalidixic acid and norfloxacin but no measurable adsorption for carbamazepine or acetaminophen. In the presence of surfactant, adsorption of acetaminophen and carbamazepine was enhanced to extents consistent with compound hydrophobicity, while adsorption of nalidixic acid and norfloxacin was not.

Piwoni and Banerjee (1989) found that sorption isotherms for tetrachloroethene on low-carbon subsurface core samples were linear to equilibrium solution concentrations of 2mg/L. Concentrations above this value produced pronounced curvature in the sorption isotherms. Sorption of tetrachloroethene, benzene, trichloroethene, and 1,2-dichlorobenzene on low-organic-carbon aquifer materials (foc < 0.001) was 2~4 times that predicted based solely on sorbent organic carbon content. Estimates of the mineral surface contribution to sorption and the relationship of this mineral component to sorbate K_{ow} are presented. An approach to predicting organic solvent sorption in low-carbon natural environments is proposed.

Ying et al. (2003) studied the sirption and degradation of five endocrine disrupting chemicals (EDCs) including biphenols (BPA), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), 4-tert-octylphenol (4-t-OP) and 4-n-nonylphenol (4-n-NP) using the aquifer material and groundwater from an aquifer in South Australia. The sorption coefficients (K_F, 1/n) measured on the sediment were in the following order 4-n-NP (195, 0.97) > 4-t-OP (90.9, 1.45) > EE2 (24.2, 0.46)> E2 (21.8, 0.40) > BPA (3.98, 0.85). To estminate the travel time of these species in the aquifer at Bolivar research site, the retardation factor was calculated. The retardation factors for this aquifer were found to be 8, 16, 20, 30, 320 qnd 500.

Bintein and Devillers (1994) proposed a general QSAR model using the physicochemical properties of the molecules (i.e. log K_{ow} and pKa) and some relevant properties of soils or sediments (i.e. pH and %OC) to estimate the sorption behavior of both ionized and non-ionized chemicals. The proposed model for organic compound that capable of forming negatively charged ions,

$$\log K_d = 0.92 \log K_{ow} + 1.09 \log f_{oc} + 0.33 \log \frac{1}{1+10^{pH-pKa}} + 0.3$$

was elaborated from 229 K_d values recorded for 53 chemicals. The model was then tested on 500 other K_d values obtained for 87 chemicals.

Benker et al. (1998) estimated the retardation coefficient of trichloroethene (TCE) for a sand aquifer low in sediment organic carbon, Perth, Australia. They found that carbon-based correlation equations were reported to under-estimated the retardation of nonionic hydrophobic organic compounds in aquifers characterized by low organic carbon contents. Laboratory column studies were accurate in assessing the sorption behavior of TCE in the Spearwood Sands. Column studies also avoided the experiment difficulties experienced with the batch studies and prove to be more cost effective.

Brusseau et al. (1989) introduced a flow-interruption method for investigating sorption nonequilibrium. This technique has a greater sensitivity to nonequilibrium than does traditional column experiments and gives the better capability to investigate nonequilibrium. In some situation, this technique may be used to assist in the delineation of mechanism(s) responsible for sorption nonequilibrium. This sorption nonequilibrium exhibited by 2,4-D in column studies suggested to be a result of intraorganic matter diffusion.

Brusseau et al. (1991b) conducted the experiments designed to identify the process(es) responsible for nonequilibrium sorption of hydrophobic organic chemicals (HOCs) by natural sorbents are reported. The results of experiments performed with natural sorbents were compared to rate data obtained from systems wherein rate-limited sorption was caused by specific sorbate-sorbent interactions. This comparison showed that chemical nonequilibrium associated with specific sorbate-sorbent interactions does not significantly contribute to the rate-limited sorption of HOCs by natural sorbents. Hence, attempts were made to interpret the data in terms of two, sorption-related, diffusive mass-transfer conceptual models: retarded intraparticle diffusion and intraorganic matter diffusion. The analyses provide strong evidence that intraorganic matter diffusion was responsible for the nonequilibrium sorption exhibited by the systems investigated in this study.

Lee et al. (1990) investigated sorbent and solvent characteristics influencing sorption of pentachlorophenol (PCP). Analysis of aqueous sorption data for several sorbents over a broad pH range suggested hydrophobic sorption of neutral PCP predominates at pH <7. At pH > **7,** sorption of the pentachlorophenolate anion (PCP) and the formation and sorption of neutral ion pairs [e.g., metal cation (M^+) + (PCP^-) = $MPCP^O$] was considered. The observed sorption data were described over the entire pH range with knowledge of pH, soil organic carbon content, and PCP's pKa,. Increased sorption of PCP^- was observed with increasing ionic strength for batch sorption studies conducted in aqueous $CaCl_2$ solutions.

Lee et al. (1991) studied sorption nonequilibrium of a series of chlorophenols by fitting a bicontinuum sorption model to breakthrough curves measured by miscible displacement techniques. A single log-log inverse relationship was observed between the desorption rate coefficient (k_2, h^{-1}) and the equilibrium

sorption constant (K_p, mL/g) for all chlorophenols as well as for a series chlohlorobenzenes. This suggests that approach to sorption equilibrium for neutral and ionized chlorophenols is constrained in a manner similar to that for nonpolar hydrophobic organic chemicals. For a series of ionized chlorophenols, the fraction of instantaneous sorption domains (F) increased with increasing solute hydrophobicity.

Brusseau (1991) investigated the relationship between sorbate structure and nonequilibrium sorption. The rate-limited sorption of compounds representing eight classes of organic chemicals was examined by use of a single sorbent (sandy aquifer material) and the miscible displacement technique. The breakthrough curves were analyzed by using a bicontinuum model wherein sorption is assumed instantaneous for a fraction of the sorbent and rate limited for the remainder. Sorbate structure was shown to exert minimal impact on the nature of rate-limited sorption for nonionic, low-polarity compounds comprising relatively simple structures and for ionogenic compounds in neutral form. In contrast, sorbate structure appeared to have a significant impact for compounds comprising more complex structures (i.e., pesticides). First-order reverse rate constants determined for the pesticides were at least 1 order of magnitude smaller than those of the non-pesticides. This difference was attributed to differences in degree of constraint on diffusion within the polymeric structure of organic matter.

Rao and Davidson (1979) studied adsorption of 2,4-D amine, atrazine, terbacil and methyl parathion pesticides on soils at pesticide solution concentrations ranging from zero to the aqueous solubility limit of each pesticide. Measured equilibrium adsorption isotherms for nearly all soil-pesticide combinations were of nonlinear Freundlich type. The influence of the shape of the adsorption isotherm on the movement of 2,4-D amine and atrazine through water-saturated soil columns was

also examined. Pesticide effluent concentrations from soil columns were measured at two input solution concentrations (50 and 5000 μg/mL for 24-D amine; 5 and 50 μg/mL for atrazine). In all cases, pesticide mobility was significantly greater for the higher concentrations.

Fesch et al. (1998) developed general concepts for describing, deterministically, the transport processes of solutes with different adsorption characteristics in such systems. Various sets of batch adsorption and miscible displacement experiments were performed covering a wide range of time scales and other experimental conditions. The breakthrough curves BTCs of the nonlinearly sorbing tracer generally exhibited sharp fronts and excessive tailing, consistent with the Langmuir–Freundlich type adsorption at clays. The effect of nonequilibrium mass transfer was most evident from the tailing of the self-sharpened fronts of the BTCs and from the results of interrupted flow experiments.

Fortin et al. (1997) conducted column flow experiments under saturated conditions to investigate the sorption behavior of simazine on a Tujunga sandy loam. The flow interruption technique was used to test whether rate-limited processes were present. Simazine breakthrough data could be best described by a two-stage, two-rate process, where the first rate is considerably faster than the second. Outflow data of the first simazine breakthrough only could be described well with a one-stage, rate-limited sorption model; flow interruption was necessary to reveal the second sorption stage.

Liedl and Ptak (2003) developed a new reactive transport modelling approach and presented examples of its application were presented, dealing with the impact of sorption/desorption kinetics on the spreading of solutes, e.g. organic contaminants, in groundwater. According to this idea, solute uptake by or release

from the aquifer material is modelled at small scale by a ''slow'' diffusion process where the diffusion coefficient is reduced as compared to the aqueous diffusion coefficient due to (i) the size and shape of intra-particle pores and (ii) retarded transport of solutes within intraparticle pores governed by a nonlinear sorption isotherm. This process-based concept has the advantage of requiring only measurable model parameters, thus avoiding fitting parameters like first order rate coefficients.

Sabatini and Austin (1991) used fluorescent dyes as adsorbing ground-water tracers for conducting solute transport studies for adsorbing organic chemicals (e.g., pesticides). The ability of two fluorescent dye (rhodamine WT and fluorescein) to mimic the adsorptive behavior of two herbicides (atrazine and alachlor) with alluvial aquifer sands was evaluated. The difference in sorptive mechanism of fluorescent dyes and most pesticide raised concerns as to the transferability of the result of this research to other subsurface media.

Palmer et al. (1992) studied sorption of hydrophobic organic compounds (HOCs) and nonionic surfactants (NISs) with subsurface materials. The sorption of NISs exceeded, while HOCs agreed well with predictions based on K_{ow} values. It appeared that the nature of the subsurface organic fraction ("mature" versus "recent") affected the sorption isotherms (linear versus nonlinear) for NISs, and they interacted with the mineral fractions of the media; neither of these were observed for HOCs.

Shiau et al. (1993) conducted laboratory and column studies with two subsurface media and demonstrated that structural isomers of rhodamine WT are responsible for the observed two-step sigmoidal breakthrough curve. A linear isotherm was observed at concentration < 100μg/L and Freundlich isotherm was observed at higher concentrations.

Kasnavia et al. (1999) discussed the importance of fluorescence dye sorption when selecting dyes for tracer studies. The effect of dye and media properties on dye sorption was evaluated using four fluorescent dyes (fluorescein, rhodamine B, rhodamine WT and sulforhodamine B) and two oppositely charged mineral surfaces (alumina and silica). Fluorescein, which had only negative functional groups, sorbed least onto negatively charged silica but most onto positively charged alumina. Since fluorescent dyes were subjected to sorption, then dye selection should be based on their chemical properties, media characteristics, and laboratory batch and column studies.

Sabatini (2000) investigated sorption of two fluorescent dyes (fluorescein which has anionic carboxylic functional group, and sulforhodamine B which has a cationic functional group and two anionic sulfate groups) was evaluated with two oppositely charged, consolidated aquifer materials (sandstone and limestone). Sorption kinetic rates decreased with increasing particle size, which is consistent with diffusion-limited intraparticle sorption. The author demonstrated the important of understanding both equilibrium and kinetics of dye sorption when designing and interpreting tracer studies.

Karapanagioti et al. (2000) investigated the sorptive properties as well as the composition of organic matter in different subsamples (mainly grain size fraction) of the Canadian River Alluvium. Organic petrography was used as a new tool to describe and characterize the organic matter in the subsamples. Soil subsamples with organic matter present as organic coating around the quartz grains evidenced the lowest K_{oc}, the most linear sorption isotherms and the fastest sorption kinetics while subsamples containing predominately coaly, particulate organic matter showed the highest K_{oc}, the highest nonlinearity of sorption isotherm and the slowest

sorption kinetics. The study showed that the identification and quantification of the coaly particles within a sediment/soil was a prerequisite in order to understand or predict sorption behavior of organic pollutions.

Zhao et al. (1996) investigated the sorption of ionizable organic compound, dicamba3,6-dichloro-2-methoxy benzoic acid by organo-clays. Organo-clays with higher organic carbon contents usually resulted in greater dicamba sorption. Solution pH can significantly affect the sorption of dicamba by organo-clays, with proximity to the pKa. More dicamba can be sorbed in molecular form (pH < pKa) than the deprotonated, anionic form. Organic cation in excess of clay CEC may, to some degree, play a role in increasing dicamba due to surface charge reversal. Hydrophobic sorption and ionic attraction can cooperatively contribute to the sorption of dicamba.

Vasudevan et al. (2002) studied sorption-desorption of three ionogenic herbicides, 2,4-D (anionic), quinmarec (zwitterionic) and norflurazon (cationic) at mineral-water interface. 2,4-D sorption to iron oxide-rich soils and pure-phase metal oxides appears to be driven by nonspecific electrostatic attraction, specific electrostatic attraction, and van der Waals interactions being secondary. Both the carboxylate and the heterocyclic N groups may participate in sorption of quinmerec, facilitated by specific and nonspecific electrostatic attraction and surface complexation. The heterocyclic N, amine and carbonyl groups of norflurazon did not appear to interact with soil minerals.

Figueroa et al. (2004) studied sorption interactions of three high-use tetracycline antibiotics with monthmorillonite and kaolinite clays under varied pH and ionic strength conditions. Sorption edges were best described with a model that included cation exchange plus surface complexation of zwitterion forms of these

compounds. Zwitterion sorption was accompanied by proton uptake, was more favorable on acidic clay, and was relatively insensitive to ionic strength effects. The result of study indicated that soil and sediment sorption model for tetracyclines, and other pharmaceuticals with similar chemistry must account for solution speciation and the presence of the other competitor ions in soil or sediment pore water.

Rocha et al. (2002) studied the sorption of the herbicide imazaquin in soils with positively balance of charges. Imazaquin has both an acid and basic ionizable groups, and its sorption depends upon the pH, the electric potential and the oxide and organic carbon contents of the soils. Up to pH 5.8, sorption was higher in subsurface than in surface layer of the acric soil, due to the positive balance of charges resulted from the high Fe and Al oxide and the low organic carbon contents. It favored electrostatic interactions with anionic molecules of imazaquin.

Hyun et al. (2003) investigated the significance of anion exchange in petachrorophenol (PCP) sorption by variable-charge soils. The sorption of ionizable chemicals by variable-charge soils from aqueous solution of $CaCl_2$, $CaSO_4$, $Ca(H_2PO_4)_2$ as a function of pH. Differences in sorption from phosphate and chloride electrolyte solution were attributed to pentachlorophenolate interactions with anion exchange sites. Pentachlorophenol exchange correlated well with the ratio of pH-dependent anion exchange to net surface charge. Results for PCP clearly demonstrated that sorption to anion exchange site in variable-charge soils should be considered in assessing pesticide mobility and that phosphate fertilizer application may increase the mobility of acidic pesticides.

Lai et al. (2000) measured sorption coefficient of river sediments. They found that was nonlinear with sorption constants ranging from 0.57 to 0.83. These

data showed that estrogenic steroids had modest sorption on sediment. The sorption of estrogens correlated with the presence of organic carbon content and also increased with salinity in water. The sorption of estrogen to sediments correlated with total organic carbon content. However, the presence of organic carbon was not a prerequisite for sorption. Iron oxide alone was demonstrated to have a sorption capacity of 40% of that of sediment containing 1.1% total organic carbon.

Ying et al. (2003) studied the sorption and degradation of five endocrine disrupting chemicals (EDCs) including biphenols (BPA), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), 4-tert-octylphenol (4-t-OP) and 4-n-nonylphenol (4-n-NP) using the aquifer material and groundwater from an aquifer in South Australia. The sorption coefficients (K_f, 1/n) measured on the sediment were in the following order 4-n-NP (195, 0.97) > 4-t-OP (90.9, 1.45) > EE2 (24.2, 0.46)> E2 (21.8, 0.40) > BPA (3.98, 0.85). The degradation study showed that the EE2 degraded slowly with an estimated half-life of 81 days in the aquifer material under aerobic conditions. Little or no degradation of the five EDCs except slow degradation for E2 was observed within 70 days under anaerobic conditions in native groundwater.

Hari et al (2005) examined the adsorption of four pharmaceutical compounds, acetaminophen, carbamazepine, nalidixic acid and norfloxacin, in the presence of a natural aquifer material. Adsorption was studied as a function of pH and in the presence of two surfactants, cetylpyridinium chloride (CPC), a cationic surfactant and Tergitol NP9, and ethoxylated nonionic surfactant. In the absence of surfactants, the results indicated a 1-2 orders of magnitude variation in adsorption affinity with changing pH for nalidixic acid and norfloxacin but no measurable adsorption for carbamazepine or acetaminophen. In the presence of surfactant, adsorption of acetaminophen and carbamazepine was enhanced to extents consistent with compound hydrophobicity, while adsorption of nalidixic acid and norfloxacin was not.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Sorbents

Three pure sorbent materials, alumina (γAl_2O_3, PZC ~ 9), silica gel (precipitated silica, PZC ~ 2-4) and Porapak P (nonpolar organic compound), were used in this study. Alumina was obtained from Aldrich Chemical Co, Milwaukee, Wisconsin and has mesh size of 150 and a specific surface area of 155 m^2/g. Silica gel, obtained from Aldrich Chemical Co., has a mesh size of 35 to 60 and a specific surface area of 300 m^2/g. Porapak P is a cross-linked polymer of divinylbenzene/styrene. Porapak P, with mesh size of 80-100 and a specific surface area of 100-200 m^2/g, was purchased from Supelco. The properties of these sorbent materials are listed in Table 3.1.

Table 3.1 The properties of three pure sorbent materials.

Chemical Formula	Point of zero charge(a) (PZC)	Specific Surface Area(b) (m2/g)	Mesh Size (mm)	Cation Exchange Capacity(CEC) (C mol/kg) pH7
γ-Alumina	8.8	155	150 (0.105)	0.7
Silica Gel	2-4	300	35-60 (0.25-0.50)	4.6
Porapak P	N/A*	100-200	80-100 (0.15-0.18)	N/A

References : (a) Kosmulski, 2000, (b) Aldrich Chemical Co.

*N/A-not applicable

Six natutal subsurface sediments were used in this study. They are composed of sand from alluvial deposit in Angthong Province. This sand was used in sorption and transport study. The other five subsurface samples are composed of silts and sands which were collected from drilling operations at three different locations in the northen part of groundwater recharge area in the province of Chainat. The properties of these subsurface sediments were listed in Table 3.2.

Table 3.2 Properties of subsurface sediments used in the study.

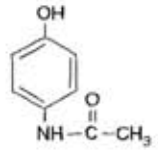
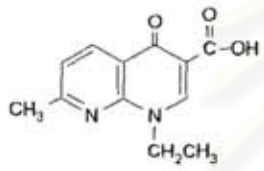
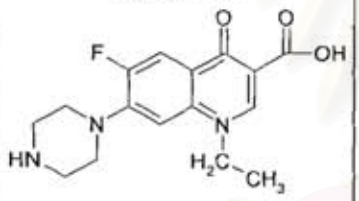
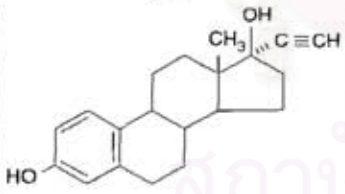
Sample	Location	Province	Type	Depth [m]	AEC [cmol/kg]	CEC [cmol/kg]	OC [%]
Pc03	Wat Phikun Ngam	Chainat	silt	3	2.54	5.50	0.17
Pc10	Wat Phikun Ngam	Chainat	silt	10	2.40	6.00	0.20
Ps17	Wat Phikun Ngam	Chainat	sand	17	1.83	1.10	0.06
Ys11	Wat Yang	Chainat	sand	11	1.76	1.80	0.02
Ks12	Wat Kampaeng	Chainat	sand	12	1.90	2.10	0.02
As10	Pamoke	Angthong	sand	10	2.12	1.20	0.08

3.1.2 Pharmaceutical Compounds

Four pharmaceutical compounds, acetaminophen (analgesic), nalidixic acid (antibiotic), norfloxacin (antibiotic) and 17α-ethynyl estradiol (synthetic hormone for oral contraceptive), were used in this study. These pharmaceuticals were purchased from Aldrich Chemical Co. Table 3.3 lists the properties of these pharmaceuticals.

Acetaminophen (ACE) is the most frequently consumed over-the-counter (OTC) medication in the United States. It is the active ingredient in common

Table 3.3 Physicochemical properties of the four pharmaceuticals studied.

Common name and Molecular Structure	Mol. Formula Mol. Weight	Water Solubility (mg/l)	Log Kow	pKa
Acetaminophen 	$C_8H_9NO_2$ 151.17	12,900[a]	0.46[b]	9.38[c]
Nalidixic Acid 	$C_{12}H_{12}N_2O_3$ 232.24	33[d] (pH 5) 328[d] (pH 7) 27,600[d] (pH9)	0.80[e], 1.54[f] (pH 5) 0.37[e], 0.47[f] (pH 7) -0.60[e], 1.16[f] (pH 9)	5.95[d]
Norfloxacin 	$C_{16}H_{18}FN_3O_3$ 319.33	161,000[d] (pH 5) 400[d] (pH 7) 910[d] (pH 9)	-1.7[f] (pH 5) -1.0[f] (pH 7) -1.63[f] (pH 9)	6.22[d] (pKa_1), 8.51[d] (pKa_2)
17α-ethynyl estradiol 	$C_{20}H_{24}O_2$ 296.41	19.1[g]	3.67[h]	10.4[i]

References : a. Chen et al., 2002, b. Snyder et al., 2003, c. Dasmalchi et al., 1995, d. Ross and Riley, 1990, e.Intravichit, 2003, f. Takács-Novák et al., 1992, g. Yalkowsky, 1999, h. Hansch et al., 1995, I Hurwitz and Liu, 1977

generic drugs such as Paracetamol, Tylenol, Panadol and Excedrin. Since its approval as an OTC medication in 1960, acetaminophen has risen in popularity above all other non-steroidal anti-inflamatory drugs (NSAID's), such as aspirin and ibuprofen, for a number of reasons: One, it is an effective mild analgesic (pain reducer) and

antipyretic (temperature reducer), but does not have the blood thinning effects of aspirin or ibuprophen. Two, it is preferred for pain relief in infants, children, and adults because of its compatibility with many symptoms. Three, normal and healthy patients taking acetaminophen at the appropriate therapeutic dosages have relatively few side effects, none of them serious. (www.home.uchicago.edu/~wardw/-Acetaminophen%20Information.htm). Acetaminophen has been reported to be present in sewage treatment plant effluents up to a concentration of 6 μg/L (Daughton and Ternes, 1999). Moreover a potential source of environmental release of acetaminophen is its use for the control of brown tree snakes (Johnston et al., 2002). Although no specific indications of its toxicity towards test organisms have been so far documented, on the basis of the precautionary principle its removal should be achieved in all the waters for human use (Andreozzi et al., 2003).

Nalidixic acid (NAL) is a quinolone antibacterial drug which is used in the treatment of urinary tract infections and it is also sometimes given for the prevention of recurrent urinary tract infections. Nalidixic acid is fast acting and usually clears acute outbreaks of infection completely within a few days. While it is effective against almost all species of bacteria that commonly infect the urinary tract, because some organisms rapidly develop resistance, a second course of treatment is less likely to be as effective. Nalidixic acid has chemical name 1-ethyl-1, 4-dihydro-7-methyl-4-oxo-1, 8-naphthyridine-3-carboxylic acid. It a pale yellow, crystalline substance and a very weak organic acid. www.cix.co.uk/~cyberville/medizine/-nalidixi.htm)

Norfloxacin (NFC) is a synthetic, broad-spectrum antibacterial agent for oral administration. Norfloxacin, a fluoroquinolone, is 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolinecarboxylic acid. Norfloxacin is a white to

pale yellow crystalline powder. Norfloxacin, a fluoroquinolone, differs from non-fluorinated quinolones by having a fluorine atom at the 6 position and a piperazine moiety at the 7 position. (www.rxlist.com/cgi/generic3/norfloxacin.htm).

17α-ethynyl estradiol (EE2) is a synthetic steroid hormone, which is classified as endocrine disrupter. This is a powerful synthetic estrogen similar to the natural female sex hormone estradiol and its widest use is in oral contraceptive pill preparations where it is combined with a synthetic progesterone drug (progestogen). Ethinyloestradiol is also used to supplement natural estrogen when the body's production is low - such as during menopause. In these conditions it is often given with progestogen and is occasionally used to control abnormal bleeding from the uterus, and to treat delayed sexual development (hypogonadism) in females. Certain cancers of the prostate respond to this drug and it is sometimes given in high doses for post-coital contraception. In conjunction with cyproterone it is used to treat severe acne in women. (www.cix.co.uk/~cyberville/medizine/ethinylo.htm).

3.1.3 Chemicals

Reagent grade methyl alcohol (MeOH) 99% purity, purchased from Aldrich Chemical Co., was used as a solvent for preparing pharmaceutical stock solutions. Dilution of concentrated hydrochlororic acid (HCl), 12.1 N, was used in acid titrations. Dilution of concentrated sodium hydroxide (NaOH), 50% w/w, was used in basic titrations. Hydrochlororic acid and sodium hydroxide were obtained from Fisher Scientific. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), obtained from Fisher Scientific, was employed for ionic strength control. For the octanol-water

partitioning experiment, ACS Reagent grade 1-octanol, 99+%, was used. The 1-octanol was purchased from Aldrich Chemical Co.

3.2 Methods

3.2.1 Batch experiment

To determine the equilibrium sorption coefficient, the media were weighed into test tubes with Teflon-lined caps. Tube then were filled with the various pharmaceutical solutions which have concentration between 0 mg/l to 10 mg/l. Three replicates were prepared at each concentration generally at a soil solution ratio of 0.1g:10 ml to 3g: 8ml. However, for the series of nalidixic acid and norfloxacin with alumina, a ratio was changed to 0.02 g :10 ml to have proper remaining concentrations. For pH dependent sorption study, pH was controlled by adding 0.02 M of NaOH or HCl in varying amounts in the original sample recipes. The details of batch experiment will be describe in Chapter 4.

3.2.2 Continuous flow experiments

Borosilicate glass columns (i.d. 2.5 cm.; length of 15 cm., Chromaflex) were homogeneously packed with either silica, alumina, or aquifer sand for this research. The pore volume and the amount of sorbent were determined gravimetrically. A peristaltic pump (Masterflex, L/S) was used to establish a constant flow rate through the column, with a three-way switching valve placed in-line to facilitate switching solutions. The volume of effluent was measured and steady flow conditions were maintained during the experiment. A miscible displacement experiment was started by switching to a solution containing 0.01 M $CaCl_2 2H_2O$ and

pharmaceutical which had an initial concentration of 10 mg/l. After completion of pharmaceutical injection, the solute pulse was displaced with electrolyte solution (0.01 M $CaCl_2.2H_20$) until complete pharmaceutical elution was observed and the column was flushed for an additional 24 hours before the tracer pulse was injected. The duration of solute pulse was adjusted to the type of experiment.

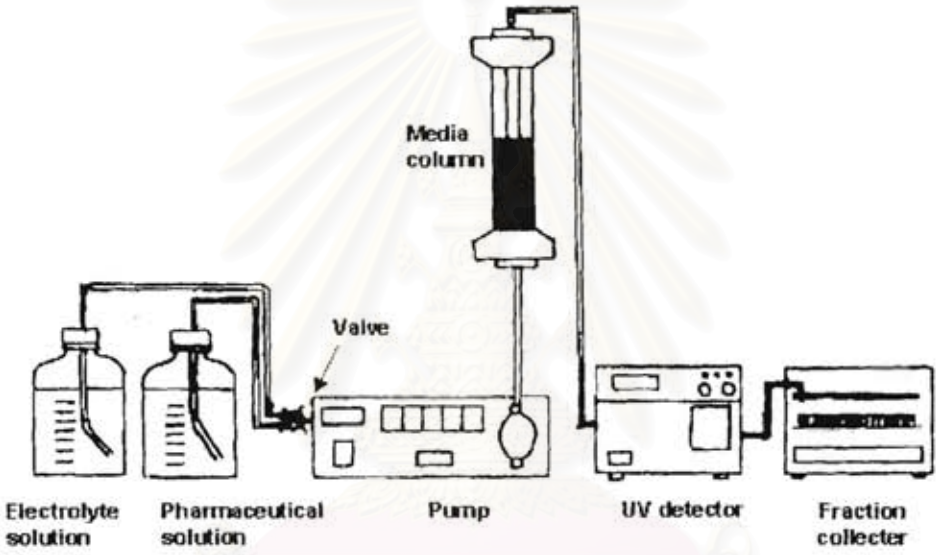


Figure 3.1 Experimental set up for experiment apparatus used for solute displacement study.

3.3 Analytical Instruments

A SHIMADZU UV-1601 spectrophotometer was used to analyze acetaminophen, nalidixic acid and norfloxacin as shown in Table 3.4. A wavelength of 242 nm was used to analyze acetaminophen; a wavelength of 258 nm was used to analyze nalidixic acid; a wavelength of 273 nm was used to analyze norfloxacin. 17α-ethynyl estradiol was analyzed by HP 8452A Diode Array Spectrophotometer

together with 4 cm cell in order to increase the path length and thus improve detection. A wavelength of 280 nm was used to analyze 17α-ethynyl estradiol.

Table 3.4 Wavelength used in the pharmaceutical analysis.

Pharmaceuticals	Wavelength used (nm)
Acetaminophen	242
17α-ethynyl estradiol	280
Nalidixic acid	258
Norfloxacin	273

3.4 Zeta Potential Measurement

Electrophoretic mobility measurements for the pure silica and alumina were carried out in 0.01 M $CaCl_2$ background electrolyte at various pH by electrophoretic light scattering of dilute suspensions placed in an electric field on a zeta meter (ZM3-83, Staunton VA) as shown in Figure 3.2. The unit automatically calculates the electrophoretic mobility of the particles and converts it to zeta potential using the Smoluchowski equation (Alkan et al., 2005). The suspensions were equilibrated for 24 hour before the measurements. The result of zeta potentials in millivolt were plotted along with the pH. The point of zero charge (PZC) , which was the pH at zero zeta potential was estimated.

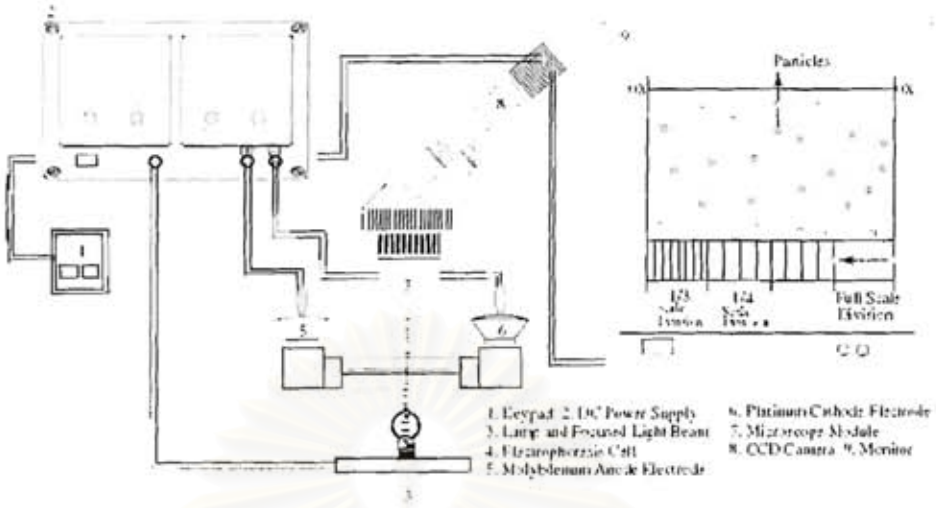


Figure 3.2 Schematic drawing of Zeta meter (Alkan et al., 2005).

3.5 Anion Exchange Capacity and Cation Exchange Capacity

Anion exchange capacity (AEC) was determined at the natural soil pH for all sediments for a subset of soils using NH_4Cl as a saturating solution and KNO_3 as a replacing solution using the unbuffered salt extraction method recommended by Sumner and Miller (1996). The chloride extracted by KNO_3 was used for AEC calculations. Chloride determination was performed by argentometric method. Cation exchange capacity (CEC) was determined by ammonium acetate (pH7) method recommended by the Soil Survey Laboratory Staff (1992).

CHAPTER IV

SORPTION OF ACETAMINOPHEN, 17α-ETHYNYL ESTRADIOL, NALIDIXIC ACID AND NORFLOXACIN WITH SILICA, ALUMINA AND A HYDROPHOBIC MEDIUM

4.1 Theoretical background

Many pharmaceuticals are not completely metabolized in humans or animals, and are eventually discharged into the environment where they may be persistent in aquatic systems (Heberer, 2002). Recently, pharmaceuticals have been detected in the effluent of sewage treatment plants, in surface waters and in groundwaters (Daughton and Ternes, 1999; Golet et al., 2002; Halling-Sørensen et al., 1998; Heberer et al., 2001; Ternes et al., 2002). Pharmaceuticals not only enter the environment from personal uses but also from veterinary and aquaculture uses (Kolpin et al., 2002; Toll, 2001). Pharmaceuticals commonly detected in the environment include antibiotics, endocrine disrupters and non-prescription analgesic drugs. The presence of pharmaceutical and personal care products in aquatic environments is an emerging concern in the environmental community (Boxall et al., 2004; Buser et al., 1998; Drewes et al., 2002). Although pharmaceuticals have been widely detected, little information exists on their fate and transport in groundwater systems; such knowledge is necessary to properly respond to the presence of pharmaceuticals in the environment.

Sorption to solid surfaces is a major process affecting the transport and fate of pharmaceuticals in the environment. Sorption is strongly influenced by media properties such as organic content, surface reactivity and specific surface area (Baily and White, 1970). For soils and sediments which contain significant amounts of

organic matter, the sorption of organic chemicals is often controlled by the organic carbon content of the medium due to the hydrophobicity of organic matter (Chiou et al., 1979; Stevenson, 1976). However, in aquifer sediments (i.e., sand and clay) the level of organic carbon content is typically quiet low, and the adsorption to mineral surfaces can be significant (Banerjee et al., 1985; Brownawell et al., 1990; Hundal et al., 2001; Schwarzenbach et al., 2003; Schwarzenbach and Westall, 1981), especially for organic molecules that contain polar and ionizable functional groups. The factors affecting sorption of pharmaceuticals (i.e.,oxytetracycline, estrogen) to environmental materials and metal oxides have been studied by several researchers (Figueroa and MacKay, 2005; Figueroa et al., 2004; Sithole and Guy, 1987). The sorption and transport of pharmaceuticals in ground water depends on aquifer media properties (e.g., point of zero charge (PZC)), pharmaceutical properties (e.g., pKa and hydrophobicity) and groundwater properties (e.g., pH). While aquifer media are predominantly negatively-charged at neutral pH (e.g., silica sands), minerals which have a net positive charge at neutral pH (e.g., alumina and iron oxides) will often be present in small amounts or as surface coatings and may influence adsorption (Hyun et al., 2003; Kosmulski, 2000). The aqueous charge of mineral surfaces is established by coordination with water which can be protonated or deprotonated depending on the pH, and properties of the underlying minerals (Kasprzyk-Hordern, 2004; Koretsky, 2000; Park and Regalbuto, 1995).

The pH where a mineral has an equal number of negatively and positively-charged sites is called the isoelectric point or the point of zero charge (PZC) for the mineral. At pH values lower than the PZC, the net surface charge is positive and anion adsorption is dominant; at pH values higher than the PZC the net

charge is negative and cation adsorption occurs. However, it is important to note that while the net surface charge may be predominately negative or positive depending on the pH, some oppositely charged sites can still exist.

Pharmaceutical compounds may consist of a combination of nonpolar and polar or ionizable functional groups. For pharmaceuticals with ionizable groups, the pKa establishes the fraction of protonated and deprotonated form that exists at a given pH. The pKa of a monoprotic acid is the pH at which equal concentrations of protonated and deprotonated compound are present. At one pH unit lower than the pKa, the functional groups exist predominately (91%) in the neutralized form, while at one pH unit higher than the pKa the functional groups exist predominately in the ionized form, as expressed by the Henderson-Hasselbalch equation (Watson, 1999):

$$\frac{[A-]}{[HA]} = 10^{(pH-pKa)} \qquad (1)$$

Some pharmaceuticals have multiple functional groups and can both accept and donate protons at a given pH. The result is that these compounds can have cationic, neutral, zwitterionic, and anionic forms as a function of pH (Ross and Riley, 1994).

4.2 Objectives of the Study

The objective of this study is to investigate how properties of the sorbent (i.e., surface charge), pharmaceuticals (i.e., pKa, hydrophobicity or K_{ow}) and the aqueous solution (i.e., pH) affect the sorption of pharmaceuticals. In order to identify the dominate pharmaceutical interactions with charged mineral surfaces at neutral pH, silica and alumina were used as adsorbent materials with net negative and positive charges at neutral pH, respectively. In addition, a synthetic hydrophobic

medium (Porapak P) was used to evaluate the significance of hydrophobic sorption for the pharmaceutical compounds. Furthermore, to better understand the role of adsorbent surface charge and pharmaceutical ionization/protonation, adsorption studies were conducted for pH values ranging from 4 to 11.

4.3 Materials and Methods

Three pure sorbent materials, alumina (γAl_2O_3, PZC ~ 9), silica gel (precipitated silica, PZC ~ 2-4) and Porapak P (nonpolar organic compound) were used in this study. Alumina was obtained from Aldrich Chemical Co, Milwaukee, Wisconsin and has mesh size of 150 and a specific surface area of 155 m^2/g. Silica gel, obtained from Aldrich Chemical Co. has a mesh size of 35 to 60 and a specific surface area of 300 m^2/g. Porapak P is a cross-linked polymer of divinylbenzene/styrene. Porapak P, with mesh size of 80-100 and a specific surface area of 100-200 m^2/g, was purchased from Supelco. The properties of these sorbent materials are listed in Table 3.1 Surface charges of silica and alumina were measured as zeta potential using a zeta meter (ZM3-83, Staunton VA). The electrolyte solution used in the eletrophoresis cell was 0.01 M $CaCl_2$ at various pH.

Four pharmaceuticals were evaluated in this research: acetaminophen (analgesic), 17α-ethynyl estradiol (synthetic hormone), nalidixic acid (antibiotic) and norfloxacin (antibiotic); all were purchased from Aldrich Chemical Co. These pharmaceuticals were selected to represent a range of physiochemical properties and types of pharmaceuticals. The molecular structures and chemical properties of these pharmaceuticals are shown in Table 3.3

Reagent grade methyl alcohol (MeOH) 99% purity, purchased from Aldrich Chemical Co., was used as a solvent for preparing pharmaceutical stock solutions. Dilution of concentrated hydrochlororic acid (HCl), 12.1 N, was used in acid titrations. Dilution of concentrated sodium hydroxide (NaOH), 50% w/w, was used in basic titrations. Hydrochlororic acid and sodium hydroxide were obtained from Fisher Scientific. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), obtained from Fisher Scientific, was employed for ionic strength control. For the octanol-water partitioning experiment, ACS Reagent grade 1-octanol, 99+%, was used. The 1-octanol was purchased from Aldrich Chemical Co.

Acetaminophen was prepared in Nanopure water. Nalidixic acid, norfloxacin and 17α-ethynyl estradiol were prepared in stock solutions of MeOH to aid in dissolution. The amount of MeOH was less than 1% in the final samples and thus had negligible impact on sorption. All batch experiments were conducted at room temperature (~22-25°C). Calcium chloride was added to maintain a constant ionic strength (0.01 M $CaCl_2$) for all tests. Triplicate samples were evaluated for each set of conditions. Pharmaceuticals and media blanks were conducted for each isotherm study to account for losses/gains of pharmaceutical concentration during the experimental procedure, which proved to be negligible. When pH values were not externally altered, they remained in the neutral range.

Most sorption studies were conducted using a constant mass of sorbent to volume of solution ratio of 0.1g:10ml. However, for the series of nalidixic acid and norfloxacin with alumina, a ratio of 0.02g:10ml was used, while for the series of nalidixic acid and norfloxacin with silica, a ratio of 0.2g:10ml was used because nalidixic acid and norfloxacin exhibit less sorption to silica. Sorption isotherms of the

pharmaceuticals were measured using at least five initial solution concentrations in triplicate ranging from 1.0 to 10.0 mg/L. The concentrations used in this study were higher than likely environmental concentrations of pharmaceuticals, except directly near a contamination source (Holm et al., 1995), practical aspects of laboratory measurements necessitated use of the higher concentrations. Although field measurements of pharmaceutical concentrations often involve extraction techniques to concentrate many liters of water for analysis, this approach is difficult to apply to measurement sorption because of the larger sample sizes needed and problems of error propagation (Hari et al., 2005).

Acetaminophen, nalidixic acid, and norfloxacin concentrations were varied in a series of 15 ml vials and shaken until equilibrium was achieved (predetermined to be within 24 hours for alumina and silica in kinetic studies; data not shown), and then the samples were centrifuged at 1350 rpm for 15 minutes. The supernatant from each vial was then transferred into a 15 ml vial for subsequent analysis. The series of 17α-ethynyl estradiol solution concentrations were placed in 30 ml vials and shaken for 72 hours (as evaluated in kinetic studies) and then the samples were centrifuged for 15 minutes. The supernatant of each vial was then transferred into another 30 ml vial by transfer pipette.

The effect of pH on the sorption of nalidixic acid and norfloxacin was evaluated in 15 ml glass vials with Teflon-lined caps. Samples were prepared by adding 8 ml of solution to approx. 0.2 g , 0.02 g, 0.1 g of silica, alumina and Porapak P, respectively. pH was controlled by adding 0.02 M of NaOH or HCl in varying amounts in the original sample recipes.

The octanol-water partitioning coefficient (K_{ow}) was determined for nalidixic acid as a function of pH. All octanol-water studies were conducted in 15 ml

glass vials with teflon lined screw caps. An octanol-water ratio of 1:1 (V/V total volume of 10 ml) was used in studies conducted for pH of 4 to 11. The mixture was shaken by rotary shaker. Dilute solutions of HCl and NaOH (0.1 M 0.01M and 0.001M) were used to adjust the pH. The samples were shaken until the pH remained constant. The water phase was transferred into 15 ml vials using a glass pipettes, and the equilibrium nalidixic acid concentrations were then measured.

A SHIMADZU UV-1601 spectrophotometer was used to analyze acetaminophen, nalidixic acid and norfloxacin. At neutral pH, a wavelength of 242 nm was used to analyze acetaminophen. a wavelength of 258 nm was used to analyze nalidixic acid; a wavelength of 273 nm was used to analyze norfloxacin. 17α-ethynyl estradiol was analyzed by HP 8452A Diode Array Spectrophotometer together with 4 cm cell in order to increase the path length and thus improve detection. A wavelength of 280 nm was used to analyze 17α-ethynyl estradiol. In pH dependent experiments, a wavelength of 258 nm was used to analyze nalidixic acid since the spectra has been shown to be relatively independent of pH (Djurdjević et al., 1995; Park et al., 2000). For norfloxacin, the spectra varies with pH but was found to be fairy constant below pH 5.6 (peak at 276 nm) and above pH 5.8 (peak at 273 nm), therefore two sets of standard solutions were prepared. The wavelength used for acidic samples was 276 nm, while 273 nm was used for the basic samples.

4.4 Data Modeling

In this study, sorption data are fit with the Freundlich equation, which is a widely accepted model for representing sorption (Weber et al., 1995);

$$q_e = K_{fr} C_e^{\ N} \quad (2)$$

where q_e is the equilibrium mass of chemical sorbed per unit mass (mg/g) or per unit surface area of the sorbent (mg/m^2) and C_e is the equilibrium concentration (mg/L) in the aqueous phase, K_{fr} is the Freundlich sorption constant and N is the Freundlich exponent. When N=1 the Freundlich equation simplifies to the linear (Henry's Law) sorption isotherm and K_{fr} is replaced with the linear distribution coefficient K_d. The sorption distribution coefficient K_d can be described by

$$K_d = q_e / C_e \quad (3)$$

At specific concentrations of nonlinear sorption isotherm, an effective K_d value can be described by substituting Eq.2 into Eq.3 as follows

$$K_d^{\ eff} = K_{fr} C_e^{\ N-1} \quad (4)$$

where $K_d^{\ eff}$ defines the linear isotherm centered about the specified concentration.

4.5 Results and Discussion

4.5.1 Sorption Studies

Equilibrium sorption studies were conducted with the four pharmaceutical compounds (acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin) and three sorbents (silica, alumina and Porapak P). The initial experiments were conducted at neutral pH; at this pH value, nalidixic acid and norfloxacin existed mainly in ionized form and neutral form at small amount while

acetaminophen and 17α-ethynyl estradiol existed mainly in their neutral form. The sorption isotherms in Figures 4.1 to 4.4, are plotted with error bars which represent 95% confidence intervals of triplicate samples; at times the error bars are on the order of or smaller than the data symbol and may thus be unnoticeable on the graph.

The sorption isotherms of 17α-ethynyl estradiol to Porapak P, alumina, and silica are shown in Figure 4.1. While linear sorption was observed between 17α-ethynyl estradiol and Porapak P, no significant sorption was observed onto silica or alumina. The linear sorption coefficient to Porapak P was 4.4×10^{-3} L/m^2 (Table 4.1). Due to its pKa of 10.4, 17α-ethynyl estradiol exists in neutral form at neutral pH and is thus highly hydrophobic (log K_{ow} of 3.67). Thus, the dominant sorption mechanism at neutral pH is expected to be hydrophobic interaction between the molecule and the organic fraction of the surface.

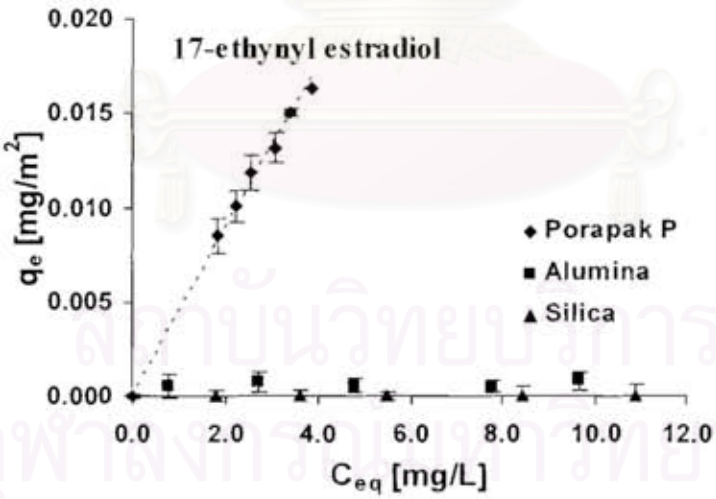


Figure 4.1 Sorption isotherms of 17α-ethynyl estradiol to Porapak P (pH 7.34±0.17), alumina (pH 7.42±0.01), and silica (pH 6.71±0.02).

Table 4.1 Summary of the sorption coefficients of 17α-ethynyl estradiol, acetaminophen, nalidixic acid, and norfloxacin to alumina, silica, and Porapak P. The sorption coefficients are normalized by specific surface area of sorbents.

Pharmaceuticals	Sorbent	pH	K_d[L/m^2]	R^2
17α-ethynyl estradiol	Alumina	7.42 ± 0.01	n/s[a]	-
	Silica	6.71 ± 0.02	n/s	-
	Porapak P	7.34 ± 0.17	4.4×10^{-3}	0.97
Acetaminophen	Alumina	7.40 ± 0.04	n/s	-
	Silica	6.81 ± 0.11	n/s	-
	Porapak P	7.21 ± 0.09	n/s	-
Nalidixic acid	Alumina	7.31 ± 0.05	2.7×10^{-2}	0.99
	Silica	6.64 ± 0.03	4.3×10^{-5} [b]	0.99
	Porapak P	6.70 ± 0.02	2.0×10^{-4}	0.99
Norfloxacin	Alumina	6.81 ± 0.12	7.8×10^{-3} [c]	0.99
	Silica	6.64 ± 0.04	2.0×10^{-4}	0.97
	Porapak P	6.05 ± 0.10	7.0×10^{-5}	0.93

[a] n/s - not significant,

[b] K_d^{eff} (5 mg/L) = 4.3×10^{-5} L/m^2 calculated from C_e= 5 mg/l, K_{fr} = 8.3×10^{-5} and N = 0.59

[c] K_d^{eff} (5 mg/L) = 7.8×10^{-3} L/m^2 calculated from C_e= 5 mg/l, K_{fr} = 1.2×10^{-2} and N = 0.73

The sorption isotherms of acetaminophen to silica, alumina, and Porapak P, are shown in Figure 4.2. With a pKa of 9.4, acetaminophen exists almost entirely in the neutral form at neutral pH. Thus, hydrophobic interaction was expected as the main sorption mechanism. However, unlike 17α-ethynyl estradiol, acetaminophen is not very hydrophobic, as demonstrated by its log K_{ow} of 0.46 versus 3.67 for 17α-ethynyl estradiol. The low hydrophobicity of the neutral form of acetaminophen helps explain the negligible sorption to Porapak P. The fact that acetaminophen existed almost entirely in the neutral form explained the low adsorption to alumina and silica. Thus, low sorption was observed for all three media.

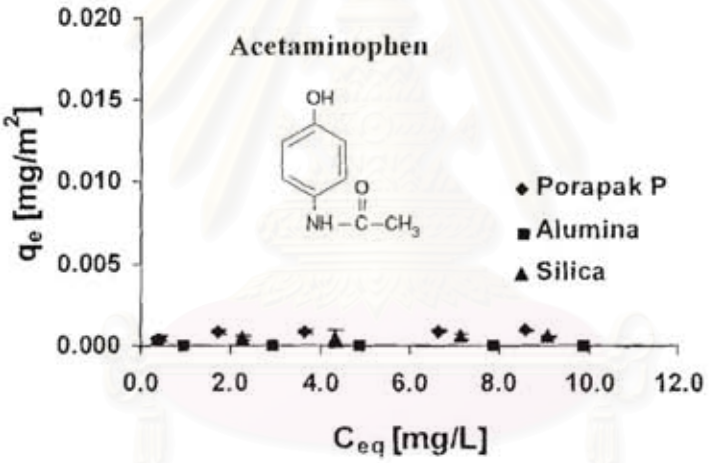


Figure 4.2 Sorption isotherms of acetaminophen to Porapak P (pH 7.21±0.09), alumina (pH 7.40±0.04), and silica (pH 6.81±0.11).

The sorption isotherms of nalidixic acid with alumina, Porapak P, and silica are shown in Figure 4.3. The nalidixic acid sorption coefficient with alumina was 2.7×10^{-2} L/m^2 (pH 7.31 ± 0.05), with Porapak P was 2.0×10^{-4} (pH 6.70 ± 0.02) L/m^2, and with silica was 4.3×10^{-5} (K_d^{eff} at C_e = 5 mg/L, pH 6.64 ± 0.03) L/m^2. Nalidixic acid sorption to negatively-charged silica and Porapak P was much less than to alumina, as expected. The sorption isotherm of nalidixic acid was linear for alumina and Porapak P but nonlinear for silica. Since the neutral pH of the isotherms (pH of 6.64-7.31) is close to the pKa of the nalidixic acid (pH~6), nalidixic acid was present in both neutral and negatively-charged forms (see Figure 4.5 for speciation as a function of pH). Therefore based on this speciation, both electrostatic and hydrophobic sorption mechanisms could be anticipated, although it was not possible to distinguish between the two mechanisms in this work. However, while the sorption onto silica here is very low, it is consistent with results of previous research (Hari et al., 2005; Schwarzenbach and Westall, 1981) The sorption to positively-charged alumina was roughly two orders of magnitude higher than for the hydrophobic Porapak P (Table 4.1). This shows that the electrostatic attraction had a greater influence on the sorption than did hydrophobic interaction.

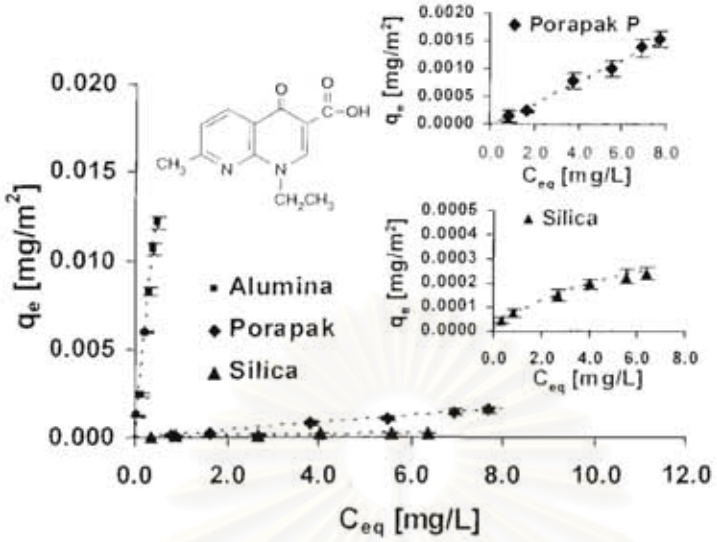


Figure 4.3 Sorption isotherms of nalidixic acid to alumina (pH 7.31±0.05), Porapak P (pH 6.70±0.02), and silica (pH 6.64±0.03).

The sorption isotherms of norfloxacin to alumina, silica and, Porapak P are shown in Figure 4.4. The sorption coefficient of norfloxacin to alumina was 7.8×10^{-3} L/m^2 (K_d^{eff} at C_e = 5 mg/L, pH 6.81 ± 0.12), to silica is 2.0×10^{-4} L/m^2 (pH 6.64 ± 0.04) and to Porapak P was 7.0×10^{-5} L/m^2 (pH 6.05 ± 0.10). The norfloxacin isotherm was linear for silica and Porapak P. Norfloxacin has two proton-binding sites (carboxyl and piperazinyl group) with reported pKa values of 6.22 and 8.51, respectively, and has an isoelectric point of 7.4. With these two pKa values, norfloxacin can exist in four forms (neutral, zwitterionic, anionic and cationic). As can be seen from the speciation (shows in Figure 4.6), at low pH (pH < 6.2) the cationic form predominates, at intermediate pH (pH 6.2-8.5) the zwitterionic form dominates, and at higher pH (pH > 8.5) the anionic form dominates. Thus, at neutral pH, the zwitterionic form dominates and adsorption to alumina and silica is expected to dominate over the Porapak P, as observed. However, interestingly, the adsorption

alumina was significantly greater than to silica, suggesting that the anionic functional group of the zwitterionic norfloxacin has a greater affinity for the alumina than does the cationic functional group for the silica. The exact reasons for this are not clear and should be further evaluated in future research. In addition, our research focuses on hydrophobic and electrostatic interactions for explaining sorption of pharmaceuticals; future research should also consider surface complexation with carboxylic groups.

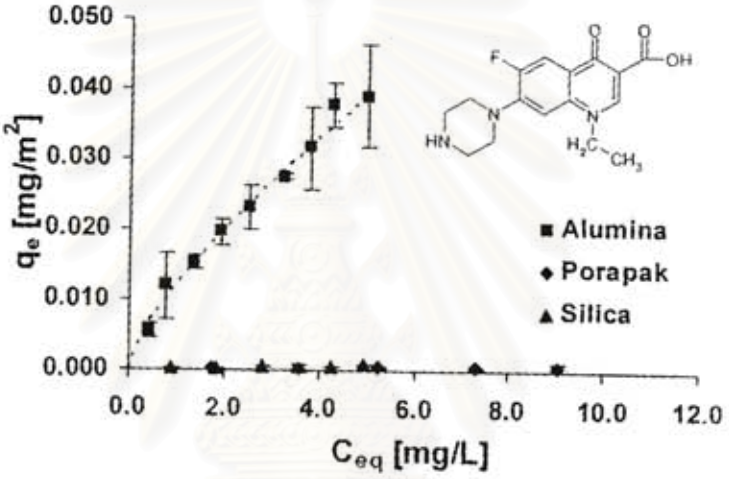


Figure 4.4 Sorption isotherms of norfloxacin to alumina (pH 6.81±0.12), Porapak P (pH 6.05±0.10), and silica (pH 6.64±0.10).

4.5.2 Influence of pH on Nalidixic acid and Norfloxacin Adsorption to Alumina and Silica

To evaluate the influence of pH on adsorption, adsorption studies of nalidixic acid and norfloxacin to alumina and silica were conducted for pH ranging from 4 to 11. Single-point adsorption experiments were used to determine K_d values ($K_d=q_e/C_e$), using an initial concentration of 10 mg/L. Although this analysis implies, a linear isotherm, it was determined that use of single-point measurement was warranted as it would allow the greatest range of experiment to be conducted,

providing a considerable quantity of information about the behavior of pharmaceutical compounds under varying conditions, despite the nonlinearity in the isotherm. This approach is also consistent with previous research (Hari et al., 2005; James et al., 2005; Karapanagioti et al., 2000).

The highest adsorption of nalidixic acid to alumina occurred at a pH of about 6 which was near the pKa value of nalidixic acid (Figure 4.5). At this pKa, the carboxyl functional group was roughly half ionized (i.e., half negatively-charged and half neutral molecules). At higher pH, although a greater fraction of nalidixic acid was ionized, the alumina surface was becoming less cationic as it approached its PZC (pH~9). Thus, the maximum adsorption occurred when the combination of positive surface sites and concentration of the anionic form of nalidixic acid was the highest. Below pH 6, very little of the nalidixic acid was ionized, and the adsorption decreased (Figure 4.5). At pH above 9, the adsorption of nalidixic acid on alumina decreased to its minimum as the alumina became negative above its PZC.

Adsorption of nalidixic acid to silica, which was negatively-charged above its PZC (reportedly 2-4), was maximum at low pH (3-4) and then gradually decreased as pH increased. Thus, as the nalidixic acid and the silica became more neutral at lower pH, the adsorption on silica became maximum, albeit three orders of magnitude less than to alumina; this same trend was observed for K_{ow} (i.e. higher values at lower pH for the more neutral nalidixic acid).

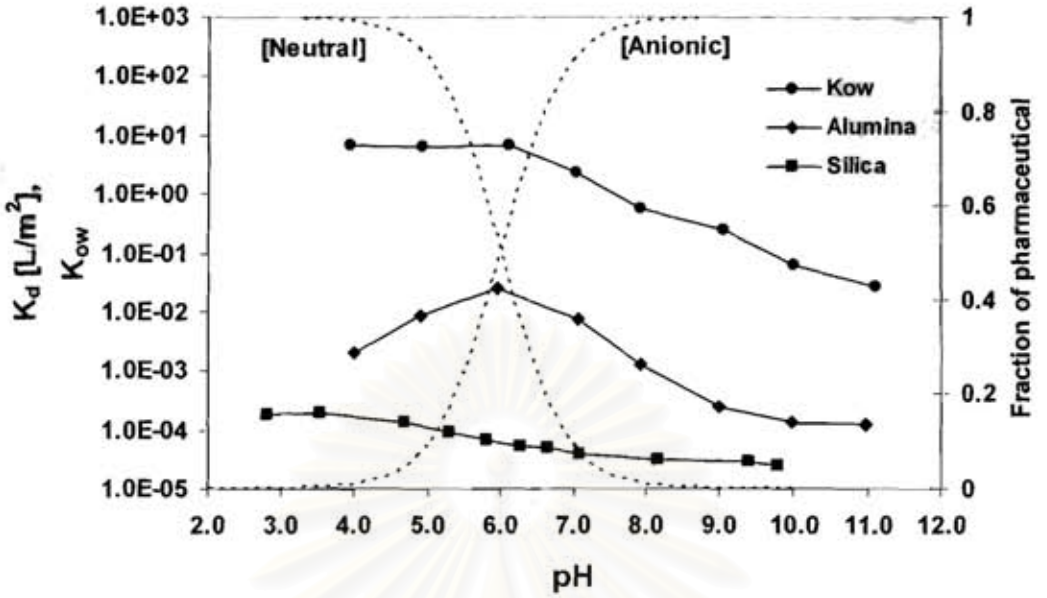


Figure 4.5 pH-sorption profiles of nalidixic acid to alumina and silica are shown along with the fraction of neutral and anionic forms of nalidixic acid and the pH-dependent octanol-water partition coefficient.

For norfloxacin, at pH below 6.2 the positively-charged form of the molecule was dominant (Figure 4.6). At pH between 6.2 and 8.5, the four forms existed with the zwitterionic form being dominant. At pH higher than 8.5, the negatively-charged form of norfloxacin dominated. The maximum adsorption to alumina corresponded to the zwitterionic region (pH 5-10) with the maximum adsorption at pH~6.8, as shown in Figure 4.6. The adsorption to alumina started to increase at pH 4.5, the same point at which the zwitterionic form started to appear in the solution. The adsorption increased to the maximum point around pH 7, near the peak of the zwitterionic form, then declined to its minimum at pH around 10, which was in the area where the alumina became negatively-charged. The adsorption of norfloxacin to silica also occurred in the zwitterionic region, but at pH greater than for alumina, and to a much lower extent than for alumina (Figure 4.6). The adsorption

of norfloxacin on silica reached its maximum at pH 8.2 (close to pKa_2) and then declined to approach minimum adsorption at pH 10, where the zwitterionic form was depleted and most of the norfloxacin was negatively-charged.

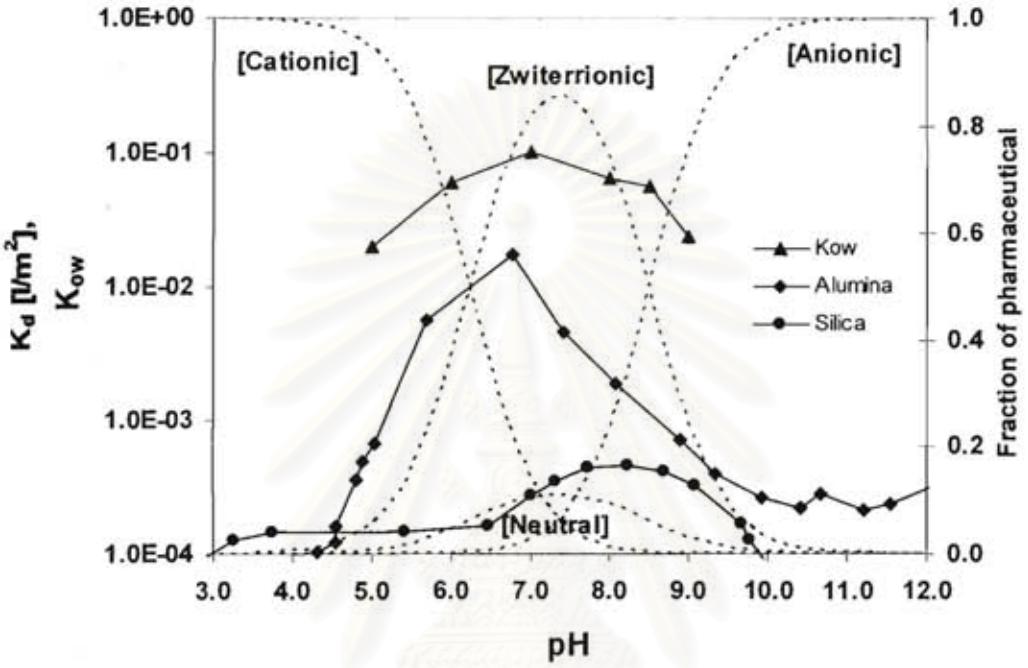


Figure 4.6 pH-sorption profiles of norfloxacin to alumina and silica are shown along with the fraction of anionic, zwitterionic, neutral and anionic forms, and octanol-water partition coefficient. The fractions of pharmaceutical were calculated by using data from Takác-Novák et al., 1990 and Ross and Riley, 1994.

In order to clarify the nature of adsorption of norfloxacin to silica and alumina as a function of pH, the predicted speciation of the four forms of norfloxacin (cationic, zwitterionic, neutal, and anionic) are shown along with the zeta potential (the measurement of surface potential) of silica and alumina (Figure 4.7). Since it is assumed that the adsorption of norfloxacin occurred by electrical attraction of counter-charged norfloxacin and sorbents, a combined factor was introduced which accounts for the combination of surface charge potential of sorbents and form

fraction. The measured zeta potentials were normalized by full scale of measurement and then multiplied by the fraction of each form (zwitterionic, cationic, and anionic). The combined factors for norfloxacin sorption to silica are presented in Figure 4.8. The combined factors of zwitterionic form (black triangle) were plotted along with combined factors of cationic form (blank triangle). Addition of these two factors showed a curve nearly the same shape as the adsorption of norfloxacin to silica (square). The same concept applied for alumina where the fraction of the anionic form was considered for the cationic surface (see Figure 4.9). Since, alumina has a negatively charged surface potential at pH values greater than its PZC (~9), the sorption of anionic form to negatively charged alumina beyond PZC will be negligible. Thus only the zwitterionic form can contribute to adsorption, however, at this pH region the fraction of zwitterionic form is at its minimum and the overall adsorption is thus negligible. The addition of combined factor of zwitterionic and anionic form showed the curve nearly the same shape as the adsorption of norfloxacin to alumina. Thus, this coupling of surface charge and pharmaceutical form as a function of pH helped clarify and confirmed the assumption that adsorption occurred by the electrostatic attraction between counter charges of norfloxacin and counter charges on silica and alumina.

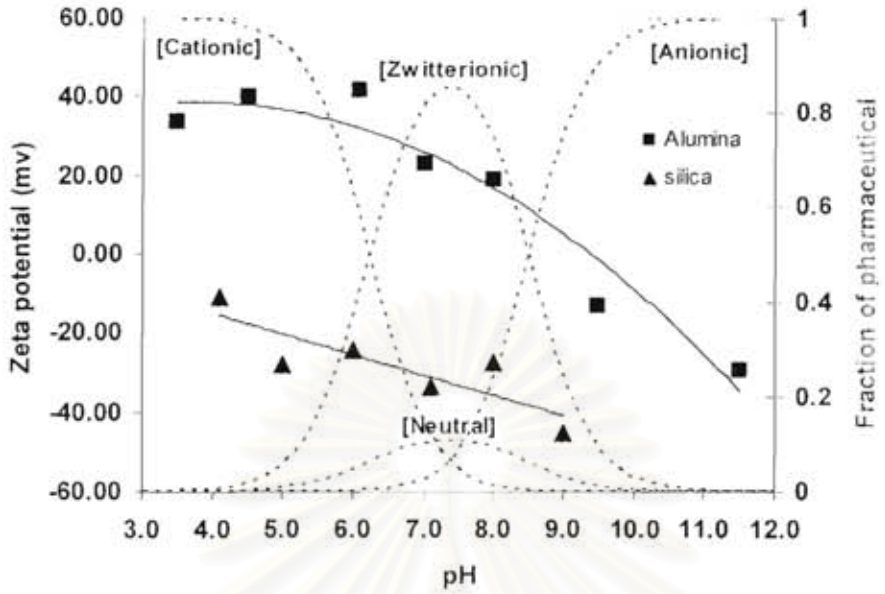


Figure 4.7 Plot of zeta potential of silica and alumina along with fraction of anionic, zwitterionic, neutral and anionic forms of norfloxacin.

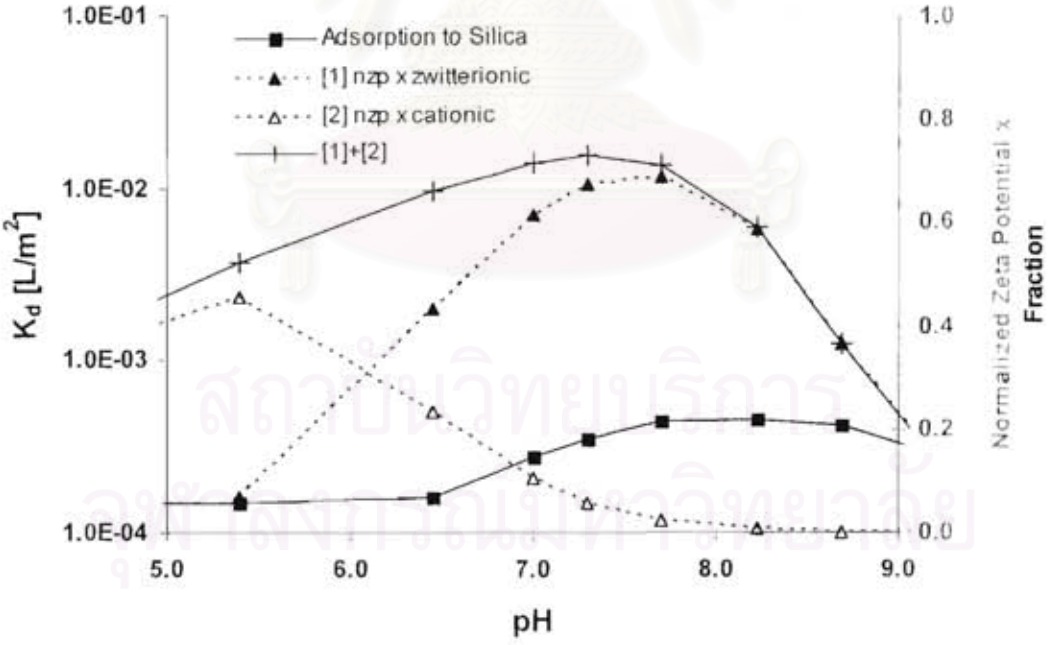


Figure 4.8 The resulting adsorption of norfloxacin to silica is shown with the multiplication of normalized zeta potential (nzp) and fractions of norfloxacin (zwitterionic and cationic forms).

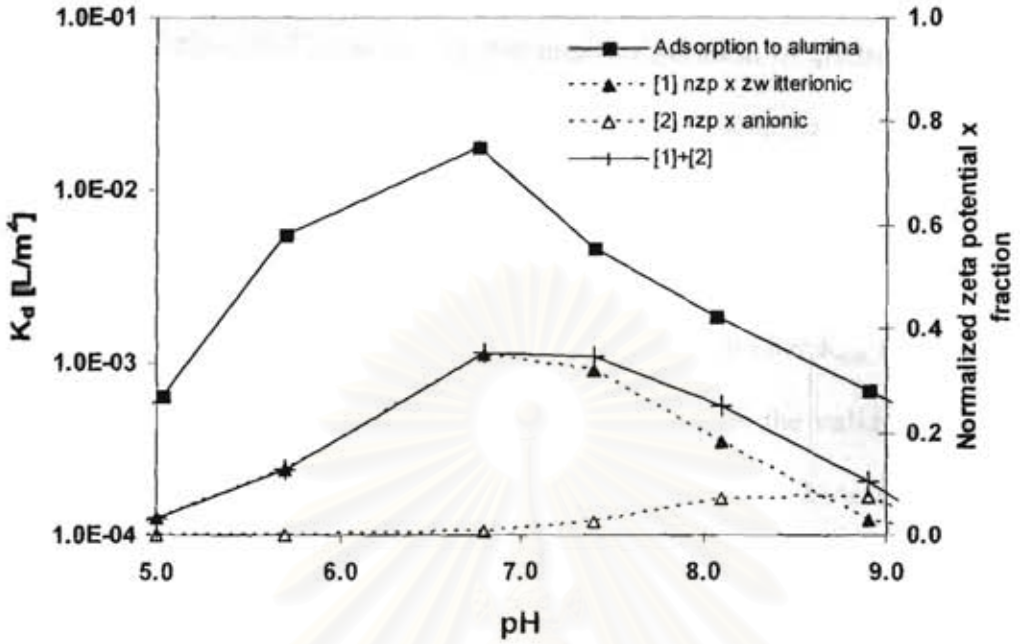


Figure 4.9 The resulting adsorption of norfloxacin to alumina is shown with the multiplication of normalized zeta potential (nzp) and fractions of norfloxacin (zwitterionic and anionic forms).

4.5.3 Influence of pH on Partitioning of Nalidixic Acid and Norfloxacin to Octanol

Having considered the pH-dependent electrostatic interactions between the nalidixic acid, norfloxacin and charged media, we now evaluated the interactions with a neutral organic medium. The pH studies here focused on partitioning into the organic phase octanol as a surrogate for organic matter in aquifer media; this proved more viable than studying pH dependent adsorption to Porapak P because this large pH range significantly altered the Porapak P material (i.e. the organic coating separated from the matrix).

The octanol-water partition coefficients of nalidixic acid as a function of pH were measured to assess its potential for sorption by hydrophobic interaction (i.e., expulsion of neutral organic molecules from the polar water phase (Figure 4.5)). As the pH decreased, the increasing H^+ concentration neutralized the anionic nalidixic functional groups, thereby rendering the nalidixic acid less water soluble and more susceptible to hydrophobic partitioning (e.g. results in higher K_{ow} values). As the pH level increased, the decreasing H^+ concentration causes the nalidixic acid carboxyl group to dissociate in water, thus rendering the nalidixic acid less hydrophobic and more soluble in the water phase (e.g. resulting in a lower K_{ow} values). The pH partitioning of nalidixic acid was maximum at pH of 4 to 6 (nalidixic acid exists largely in neutral form) and gradually declined with increasing pH (as nalidixic acid became increasingly ionized).

The octanol-water partition coefficient of norfloxacin determined at different pH between 5 and 9 are shown in Figure 4.6 (Takács-Novák et al., 1992). The K_{ow} profile of this compound has a bell shape which reflects the maximum hydrophobicity of the compound at its isoelectric point. On comparing the curves for the pH-partition behavior and the fraction of microspeciation of norfloxacin, it became evident that plot of the concentration of zwitterionic and neutral forms as a function of pH showed similar shapes within the intermediate pH range. However, the fraction of zwitterionic form was much greater than the neutral form. Among these two forms, the partition of neutral form into organic phase was expected. Therefore, the sorption to mineral surface, which are charged surfaces in this pH region, will likely be due to electrostatic attraction rather than hydrophobic interactions.

4.6 Conclusions

In an attempt to understand the sorption characteristics of pharmaceuticals in groundwater system, four pharmaceuticals (i.e., ionizable and nonionizable at neutral pH) were selected to investigate how properties of the sorbents (i.e. surface charge), pharmaceuticals (i.e., pKa, hydrophobicity) and aqueous solution affected the sorption of pharmaceuticals. At neutral pH 17α-ethynyl estradiol, hydrophobic and nonionize pharmaceutical, strongly sorbed to the hydrophobic medium. Acetaminophen, nonhydrophobic pharmaceutical, showed no sorption to any media. Nalidixic acid and norfloxacin (monoprotic acid and zwitterionic compound) adsorbed strongly to positively-charge surface and nalidixic acid has higher sorption capacity. The pH sorption profile of nalidixic acid and alumina showed maximum sorption at pH near pKa while norfloxacin with alumina showed maximum sorption capacity at pH in the region of norfloxacin's zwitterionic form. It is reported that quinolone antibiotics can form complexes with divalent cations (Park et al., 2000; Timmer and Sternglanz, 1978). Thus, while this research used a constant calcium chloride concentration of 0.01 M, future research should evaluate the role of varying electrolyte concentration.

This research demonstrates that the adsorption of ionizable pharmaceuticals is strongly dependent on the system pH, the pharmaceuticals properties (pKa), and the nature of the surface charge (point of zero charge). For pharmaceuticals that are uncharged at the environmentally relevant pH ranges, the main sorption factor is their solubility or hydrophobicity; for charged forms, ion exchange appeared to be an important adsorption mechanism.

This study has clearly demonstrated that in the neutral pH range anionic and zwitterionic pharmaceuticals have significantly greater adsorption affinity to positively-charged surfaces as compared to negatively-charged surface. Even though aquifer materials are often dominated by negatively charged silica grains, trace minerals and/or surface coatings (i.e., iron oxides) can contribute small amounts of positively-charged sites. Therefore, it is anticipated that even small amounts of positively-charged surfaces can significantly affect the sorption behavior of these pharmaceuticals. This research thus demonstrates that failure to account for the pH dependence of surface and pharmaceuticals properties, and thus their interactions, can lead to significant errors in assessing the transport of these pharmaceuticals in subsurface systems.

CHAPTER V

SORPTION AND TRANSPORT OF ACETAMINOPHEN, 17α –ETHYNYL ESTRADIOL AND NALIDIXIC ACID WITH AQUIFER SAND

5.1 Theoritical Backgrounds

Recently a number of pharmaceuticals have been identified in rivers, lakes and groundwater (Alder et al., 2000; Daughton and Ternes, 1999; Golet et al., 2002; Halling-Sørensen et al., 1998; Heberer, 2002; Ternes et al., 2002) Classes of pharmaceutical compounds commonly detected in the environment include antibiotics, endocrine disrupters and other non-prescriptive analgesic drugs.

5.1.1 Sorption

Sorption is the major process affecting the fate and transport of chemicals in groundwater. Important media and pharmaceutical properties affecting sorption include point of zero charge (PZC), pKa, K_{ow}, etc. as discussed in Chapter 4. In short, if the pH, pKa, and PZC are such that the pharmaceutical and media are oppositely charged then adsorption will occur by ion exchange; if the pH and pKa are such that the pharmaceuticals is neutral then sorption will occur predominantly by hydrophobic partitioning to the soil organic content. While batch experiments are often used to quantify sorption, certain phenomena are best elucidated in column studies. The column experiment has almost the same solid to solution ratio as observed in aquifer systems; the influent solution can be adjusted and maintained at the desired conditions, and the potential for non-equilibrium process can be

evaluated. In this study aquifer sand was used to evaluate the transport characteristics of pharmaceuticals compound in a natural groundwater media.

5.1.2 Transport

In the absence of transformation processes, subsurface contaminant transport is described by advection, dispersion and adsorption processes according to the following governing equation (assuming equilibrium sorption) (Freeze and Cherry, 1979):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \quad (1)$$

$$R = 1 + \frac{\rho}{\theta}K_d \text{ , linear sorption isotherm} \quad (2)$$

$$R = 1 + \frac{\rho}{\theta}K_f C_o^{N-1} \text{, Freundlich nonlinear sorption isotherm} \quad (3)$$

where R [dimensionless] is the retardation factor; $C[M/L^3]$ is the concentration; t[T] is time; $D[L^2/T]$ is hydrodynamic dispersion; v[L/T] is the average pore water velocity; $\rho[M/L^3]$ is bulk density; θ is effective porosity; K_d is the sorption coefficient; K_f is the Freundlich sorption coefficient; and N is the Freundlich nonlinearity parameter.

Non-equilibrium sorption may result from chemical non-equilibrium or from rate-limited diffusive mass transfer (e.g., film diffusion, retarded intraparticle diffusion, and intra sorbent diffusion) (van Genuchten, 1981; van Genuchten and Wagenet, 1989). The following dimensionless equations represent the nonequilibrium

transport of sorbing solutes under one-dimensional, steady water flow in homogeneous porous medium (Brusseau et al., 1991).

$$\beta R\frac{\partial C^*}{\partial T}+(1-\beta)R\frac{\partial S^*}{\partial T}=\frac{1}{P}\frac{\partial^2 C^*}{\partial^2 X}-\frac{\partial C^*}{\partial X} \tag{4}$$

$$(1-\beta)R\frac{\partial S^*}{\partial T}=\omega(C^*-S^*) \tag{5}$$

Where

$$C^*=\frac{C}{C_o} \qquad ,P=\frac{vL}{D} \tag{6),(7}$$

$$S^*=\frac{S_2}{(1-F)K_d} \qquad ,R=1+\frac{\rho}{\theta}K_d \tag{8),(9}$$

$$T=\frac{vt}{L} \qquad ,\beta=\frac{1+F\frac{\rho}{\theta}K_d}{R} \tag{10),(11}$$

$$X=\frac{x}{L} \qquad ,\omega=\frac{k_2(1-\beta)RL}{v} \tag{12),(13}$$

Where β [dimensionless] is the fraction of instantaneous retardation; R [dimensionless] is the retardation factor which represents the effect of sorption on transport; C [M/L^3] is the input concentration; T [dimensionless] is relative pore volume; S_2 [MM^{-1}] is the sorbed-phase concentration in the rate-limited domain; P [dimensionless] is Peclet number which is a ratio of advective flux versus dispersive flux; ω [dimensionless] is the Damkohler number, which is a ratio of hydrodynamic residence time to characteristic time for sorption; β and ω specify the degree of non-equilibrium in the system, which decreases as either of the two parameters increase in magnitude; v [LT^{-1}] is the average pore water velocity; L [L] is column length; D [L^2T^{-1}] is dispersion coefficient; F [dimensionless] is the fraction of sorbent for which

sorption is instantaneous; K_d [L^3M^{-1}]is the sorption coefficient; T [dimensionless] is relative pore volume; ρ is bulk density [ML^{-3}] ; θ [dimensionless] is porosity; and x [L] is distance.

5.2 Objective of the Study

In previous research we evaluated the sorption of select pharmaceuticals on a range of media surfaces using batch studies. The objective of this research is to build on our previous work by evaluating select pharmaceuticals in continuous flow column studies, thereby allowing us to confirm sorption mechanism identified in the batch studies and to evaluate the kinetics of sorption in column systems. In addition, this work extends previous research which used pure mineral surfaces and organic media to an aquifer sand to evaluate adsorption processes for a heterogeneous natural medium. Moreover, to better understand the role of adsorbent surface charge and pharmaceutical ionization/protonation, column studies were conducted for a range of pH values (ranging from 4 to 9) as was previously done in batch studies.

5.3 Materials and Methods

5.3.1 Materials

Two pure sorbent materials, alumina (γAl_2O_3, PZC ~ 9), silica gel (precipitated silica, PZC ~ 2-4) and aquifer sand were used in this study. Alumina was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin and has a mesh size of 150, a specific surface area of 155 m^2/g. Silica gel, obtained from Aldrich Chemical Co. has a mesh size of 35 to 60, a specific surface area of 300 m^2/g. Porapak P, with a mesh size of 80-100 and specific surface area of 100-200 m^2/g was purchased from Aldrich Chemical Co. While it was evaluated in previous batch studies, Porapak P was not studied in column study because of its characteristic as a gas chromatography column packing media which rendered it unamenable to flow studies in column systems.

The aquifer sand (As10), which is composed mostly of quartz (SiO_2) with minor content of albite ($NaAlSi_3O_8$), biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$), and muscovite $KAl_3Si_3O_{10}(OH)_2$, was collected from shallow alluvial aquifer in Pamok district, Angthong province, central of Thailand. It was sieved through a size 40-80 mesh prior to use. The organic carbon content is ~ 0.08 %. The properties of this sand are listed in Table 3.2.

Three pharmaceuticals were evaluated in this research; acetaminophen (analgesic), 17α–ethynyl estradiol (synthetic hormone), and nalidixic acid (antibiotic). These pharmaceuticals have been identified in the environment and have fundamental properties of interest to this work and our prior batch studies. These pharmaceutical

compounds were purchased from Aldrich Chemical Co. Their molecular structures and chemical properties are shown in Table 3.3.

Reagent grade methyl alcohol (MeOH) 99% purity, purchased from Aldrich Chemical Co., was used as a solvent for preparing pharmaceutical stock solutions. Dilute solutions of concentrated hydrochlororic acid (HCl), 12.1 N, were used in acid titration. Dilution of concentrated sodium hydroxide (NaOH), 50% w/w, was used in a basic titrations. Hydrochlororic acid and sodium hydroxide were obtained from Fisher Scientific. Calcium chloride dihydrate ($CaCl_2 2H_2O$), obtained from Fisher Scientific, was employed for ionic strength control.

While acetaminophen was prepared in Nanopure water, due to lower solubility nalidixic acid, and 17α–ethynyl estradiol were prepared in stock solutions with MeOH; the amount of MeOH was less than 1% in the actual samples and thus had negligible impact on sorption. All column experiments were conducted at room temperature (25°C), and the pH was observed to be near neutral (7.0 ± 0.5) except when the column study was adjusted to pH about 4 and 9. Calcium chloride was added to maintain a constant ionic strength (0.01 M $CaCl_2 2H_2O$) for all tests.

A UV spectrometer was used for measuring pharmaceuticals at mg/L concentrations. A SHIMADZU UV-1601 spectrophotometer was used to analyze acetaminophen and nalidixic acid. A wavelength of 242 nm was used to analyze acetaminophen; a wavelength of 258 nm was used to analyze nalidixic acid; A wavelength of 280 nm was used to analyze 17α–ethynyl estradiol (SHIMADZU-10AV-UV-Vis detector).

In addition to the organic solutes, sodium chloride and sodium nitrate were used in solute displacement experiments to characterize the flow of water through the sorbent column. Chloride was analyzed using an Orion Chloride electrode

(model 94-35A) and sodium nitrate was analyzed by inline UV spectrophotometer using a 300 nm wavelength.

5.3.2 Batch Experiments

For aquifer sand, most sorption studies were conducted using a constant mass of 3g with 8 mL of solution. Acetaminophen, nalidixic acid, and 17α – ethynyl estradiol concentrations were varied in a series of 15 mL glass vials with Teflon-lined caps and shaken until equilibrium was achieved (pre-determined to be within 24 hours in kinetic studies; and then the samples were centrifuged at 1500 rpm for 30 minutes. The supernatant from each vial was then transferred into a 15 mL vial for subsequent analysis. The effect of pH on the sorption of nalidixic acid was evaluated. pH was controlled by adding 0.02 M of NaOH or HCl in varying amounts in the original sample recipes. The sorption characteristics of pharmaceuticals with silica and alumina were reported in Chapter 4.

5.3.3 Continuous Flow Experiments

A borosilicate glass column (i.d. 2.5 cm.; length of 15 cm., Chromaflex) was homogeneously packed with either silica, alumina, or aquifer sand for this research. A 20 μm porosity HDPE bed support served as a media support at the bottom of the column. Silicone tubing was utilized in the pump head and Teflon tubing elsewhere in an effort to eliminate adsorptive losses to the tubing.

The pore volume and the amount of sorbent were determined gravimetrically. A peristaltic pump (Masterflex, L/S) was used to establish a constant flow rate through the column, with a three-way switching valve placed in-line to

facilitate switching solutions. The volume of effluent was measured and steady flow conditions were maintained during the experiment. The set up of experiment apparatus is shown in Figure 5.1.

To minimize gas entrapment, a degassed electrolyte solution (0.01M $CaCl_2.2H_20$) was injected from bottom to top, and purged until the pH of effluent and influent was equal. A miscible displacement experiment was started by switching to a solution containing 0.01 M $CaCl_22H_2O$ and pharmaceutical which had an initial concentration of 10 mg/l. After completion of pharmaceutical injection, the solute pulse was displaced with electrolyte solution (0.01 M $CaCl_2.2H_20$) until complete pharmaceutical breakthrough was observed and the column was flushed for an additional 24 hours before the tracer pulse was injected. The duration of solute pulse was adjusted to the type of experiment. Generally, a pulse of two pore volumes was chosen for conservative tracer. The effluent solution was connected to an inline-UV spectrophotometer (DW-10-D Star Instrument) or automatic fraction collector (Pharmacia Biotech, model RediFrac). Flow rates of ~ 0.5 ml/min were used for the experiment, which corresponds to pore-water velocities of ~ 10 to ~ 20 cm/h. The column runs were operated at room temperature (25°C) with the flow maintaining a relatively neutral pH (7.0 ± 0.5) except for pH dependent study which used pH at 4.3, 6.2, and 8.2. The column packing parameter are shown in Table 5.1.

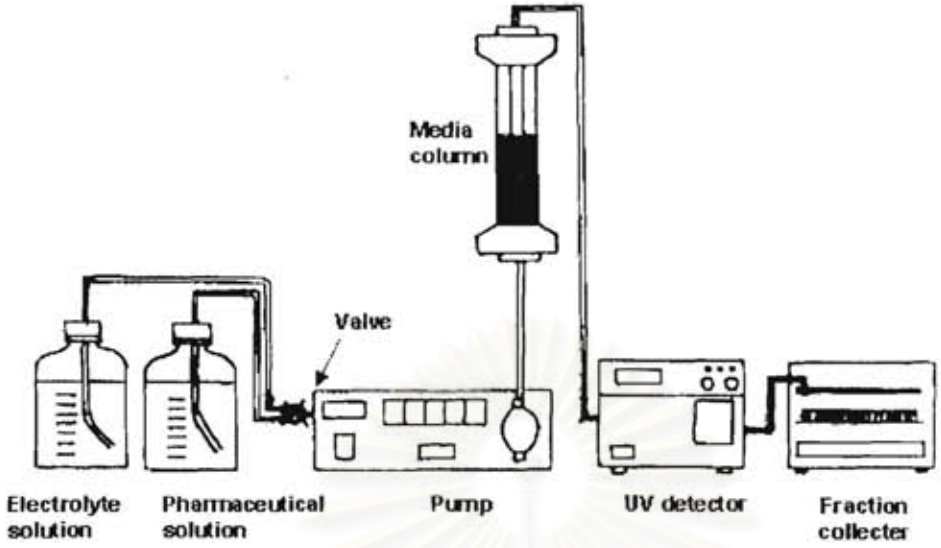


Figure 5.1 Experimental set up for experiment apparatus used for solute displacement study.

Table 5.1 Column packing for the continuous flow experiment.

Pharma-ceuticals	Media	pH	Length [cm]	Bulk Density [g/cm3]	Porosity	Pore velocity [cm/hr]	Dispr. coeff. [cm^2/min]
ACE	Silica	6.7 0.1	4.75	0.43	0.46	14.74	0.038
ACE	Alumina	6.5 0.1	5.10	1.18	0.52	10.49	0.007
ACE	Aq.Sand	6.6 0.1	4.80	1.59	0.43	15.74	0.015
EE2	Silica	6.7 0.1	4.75	0.43	0.40	17.03	0.019
EE2	Alumina	7.6 0.2	5.00	1.2	0.46	11.17	0.026
EE2	Aq Sand	6.5 0.1	10.00	1.53	0.38	18.81	0.024
NAL	Silica	6.6 0.1	4.40	0.46	0.40	17.98	0.010
NAL	Aq Sand	6.2 0.1	10.00	1.48	0.40	18.26	0.025
NAL	Aq Sand	4.3 0.1	4.75	1.61	0.44	12.21	0.004
NAL	Aq Sand	8.2 0.1	5.00	1.53	0.40	13.20	0.010

ACE : Acetaminophen, NAL : Nalidixic acid, EE2 : 17α-Ethynylestradiol
Eq. : Equilibrium model, : Nonequilibrium model

5.3.4 Flow Interruption Experiments

The transport and fate of many contaminants in subsurface systems can be influenced by several rate-limited processes, such as rate-limited sorption, diffusion mass transfer, and transformation reactions. Identification of the controlling process in such system is often difficult, and is confused by additional factor such as nonlinear sorption. Brusseau et al., 1989 introduced the flow interruption technique, which consists of stopping the flow for some period of time before recommencing flow, to identify the shape of organic contaminant breakthrough curves which is influenced by rate-limited sorption, transformation reaction, nonlinear sorption. The flow interruption method has no impact for a system in which nonlinear sorption is the major cause of nonideal transport. Conversely, it can significantly influence systems for which rate-limited sorption is important. For transformation reactions, the concentration will drop for both sorption and desorption front interruptions. This behavior is different than that for systems influenced by rate-limited sorption or physical nonequilibrium, where the concentration drops for sorption front interruption but rises for desorption front interruption. Thus, desorption front interruption are recommended to differentiate between nonequilibrium and transformation processes.

5.4 Results and Discussion

5.4.1 Sorption and Transport of Pharmaceuticals

The column experiments were conducted using silica, alumina and aquifer sand for column packing. The purpose of using pure minerals such as silica and alumina was to compare the result transport characteristics with the batch sorption experiments studied previously. The summary of sorption coefficients for the study was shown in Table 5.2.

Table 5.2 Summary of sorption coefficient (K_d) of 17α-ethynyl estradiol, nalidixic acid to alumina, silica, Porapak P, and aquifer sand. The sorption coefficients were normalized (Intravichit, 2003) by specific surface area of sorbents.

Pharmaceuticals	Sorbent	pH	K_d[L/m^2]	R^2
17α-ethynyl estradiol	Alumina[a]	7.42 ± 0.01	n/s[b]	
	Silica[a]	6.71 ± 0.02	n/s	
	Porapak P[a]	7.34 ± 0.17	4.40×10^{-3}	0.97
	Aq. Sand[c]	6.91 ± 0.14	2.38×10^{-3}	0.96
Nalidixic acid	Alumina[a]	7.31 ± 0.05	3.00×10^{-2}	0.99
	Silica[a]	6.64 ± 0.03	4.30×10^{-5}	0.99
	Porapak P[a]	6.70 ± 0.02	2.00×10^{-4}	0.99
	Aq. Sand[c]	6.65 ± 0.12	1.43×10^{-2}	0.97

[a] Intravichit (2003) · [b] n/s : not significant.
[c] calculated from equation $K_d = KfrCe^{N-1}$ ing Ce=5 mg/l
Acetaminophen sorption was not significant in all cases.

Column breakthrough curves of acetaminophen to all media show ideal breakthrough curve characteristics with the retardation factors (R) of ~ 1.0 (Figure 5.2). The sorption isotherm of acetaminophen to silica, alumina, Porapak P, and aquifer sand are shown in the inset of Figure 5.2. These column breakthrough results are consistent with batch studies from previous research, which showed negligible sorption to all media. Acetaminophen has low hydrophobicity (log K_{ow} 0.46) with a pKa of 9.4 and then exists almost solely in the neutral form at neutral pH range. These explain the low sorption to all charged surface media (i.e., silica, alumina), Porapak P (hydrophobic media). The only mechanism that expected to play major role in sorption of acetaminophen is hydrophobicity. However, both low hydrophobicity of acetaminophen and low organic carbon content of aquifer sand tend to give low sorption which already confirmed by both batch and column experiment.

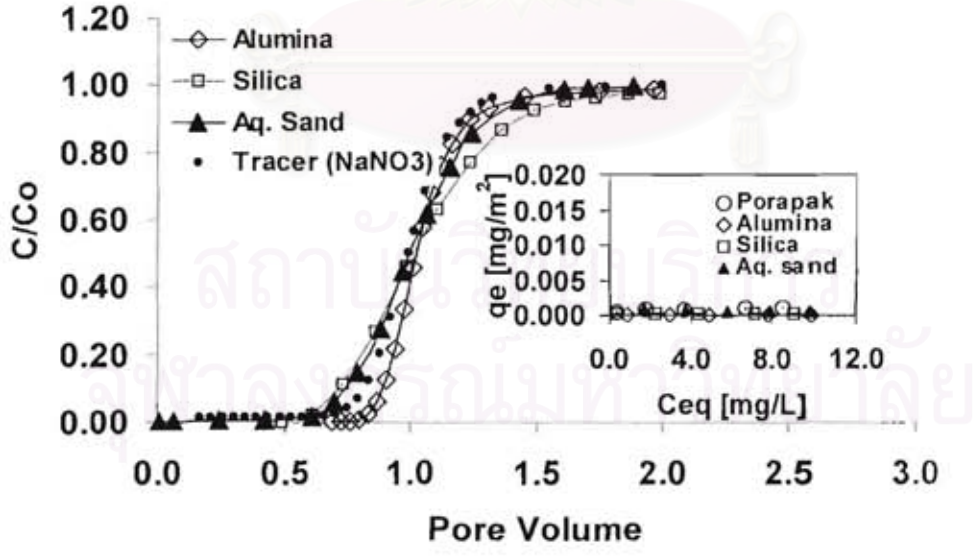


Figure 5.2 Column breakthrough curves of acetaminophen with silica, alumina, and quifer sand which all show retardation factor (R) ~ 1. Batch sorption isotherms of acetaminophen to Porapak P, alumina, silica and aquifer sand are shown in the inset.

Column breakthrough curves of 17α–ethynyl estradiol to silica, alumina and aquifer sand show different characteristics from what was observed with acetaminophen (Figure 5.3). The shape of breakthrough curve displays non-sigmoidal characteristic which are sharpened breakthrough and tailing desorption front. However, the conservative tracer running on these columns display ideal breakthrough, indicating that hydrodynamics are not responsible for this trend. Breakthrough of 17α–ethynyl estradiol with the silica and alumina columns were almost the same (R~ 1.2) whereas the breakthrough with aquifer sand was delayed (R ~ 4.5). The breakthrough in these columns is also consistent with the batch sorption experiment which showed no significant sorption to charged surface of alumina and silica but significant sorption to a hydrophobic medium (see inset to Figure 5.3). 17α –ethynyl estradiol has high hydrophobicity (log K_{ow} ~ 3.67), with a pKa of 10.4. Similar to acetaminophen, it exists predominately in neutral form at the neutral pH range. The sorption isotherms of 17α–ethynyl estradiol to Porapak P (hydrophobic medium), aquifer sand, silica, and alumina are shown inset of Figure 5.3.

The sorption of 17α–ethynyl estradiol to aquifer sand will occur at the organic phase on aquifer media. The high sorption coefficient of 17α –ethynyl estradiol to a hydrophobic medium and aquifer sand is very distinctive from egligible sorption observed for silica and alumina (charged surface). The sorption isotherm of 17α–ethynyl estradiol to aquifer sand is clearly nonlinear. The model fitting for the breakthrough data also shows nonlinear characteristic consistent with the batch study. The aquifer sand is composed mostly of quartz and minor minerals such as feldspar and biotite. The only minor fraction of this media which affects sorption is organic carbon content. While the aquifer sand contains only 0.08 % organic carbon, which is a typical value for this type of sediment, it accounts for the majority of sorption

capacity to the aquifer sand. Therefore, the breakthrough curve through aquifer media shows later breakthrough than pure minerals i.e., silica and alumina.

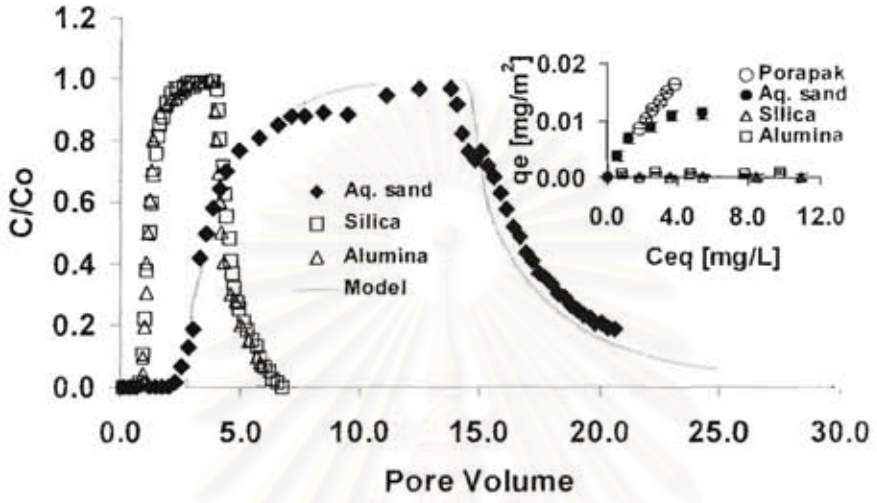


Figure 5.3 Breakthrough curves of 17α-ethynyl estradiol with silica, alumina, and aquifer sand. They all show non-equilibrium characteristic. The model fitting gave the retardation factor (R) ~ 4.5, N ~ 0.6, F ~ 0.49, k_2 ~ 0.1, β ~ 0.6, ω ~ 0.1. Sorption isotherms of acetaminophen to Porapak, alumina, silica and aquifer sand are shown in the inset.

Both breakthrough curves of nalidixic acid with silica and aquifer sand (Figure 5.4 and Figure 5.5) show non-equilibrium characteristic. The conservative tracers running for these columns exhibit ideal breakthrough characteristics. Therefore, the non-ideal transport is sorption related rather than transport related (i.e., due to heterogeneities in the flow field). In order to confirm non-equilibrium condition, a flow-interruption (Brusseau et al., 1997; Brusseau et al., 1989) on column of nalidixic acid and silica at pH 6 was conducted at three points i.e., at both sorption and desorption front and at the plateau C/Co ~ 1 (data not shown). The result of flow interruption confirmed the nonequilibrium transport of nalidixic acid. The breakthrough curves of nalidixic acid with silica and aquifer sand are also nonlinear, as observed by the very long tailing at desorption fronts. The model fitting for these breakthrough data also show nonlinear characteristics corresponding to the result from batch study. The column of nalidixic acid to alumina was not conducted in this study because the result of batch experiment suggests retardation factor is estimated to be 12,000 pore volumes. The sorption isotherms of nalidixic acid with alumina, Porapak P, silica, and aquifer sand are shown inset of Figure 5.4. At neutral pH, nalidixic acid is present in both neutral and anionic forms. Therefore, both hydrophobic and electrostatic sorption mechanisms are expected to be important. However, clearly the electrostatic attraction had a greater influence on the sorption than did hydrophobic partitioning as evidence by high sorption on positively charged alumina but low sorption to hydrophobic medium in batch studies (see inset of Figure 5.4). The sorption isotherm of nalidixic acid was linear for alumina and Porapak P but nonlinear for silica.

The sorption mechanism of nalidixic acid to aquifer sand are expected to be the electrostatic attraction between positively charged mineral surface and negatively charged nalidixic acid, and hydrophobic interaction to organic phase on the surface of sand. Although the main mineral composition is sand (silica), which is normally negative-charged surface, the sorption of nalidixic acid to this sediment is still high. Therefore, the sorption may be contributed by combination effect of the positively charged of mineral oxides (i.e. iron oxide, aluminum oxide) which coexist the silica grains, as evidented by the brown color typical of iron oxide coverage and partition to organic content, even though the amount of organic carbon content is 0.08%. Thus, the resulting retardation factor of nalidixic acid to silica is 8 whereas the aquifer sand exhibits much larger retardation (R~ 150) as shown in Figure 5.4. and Figure 5.5.

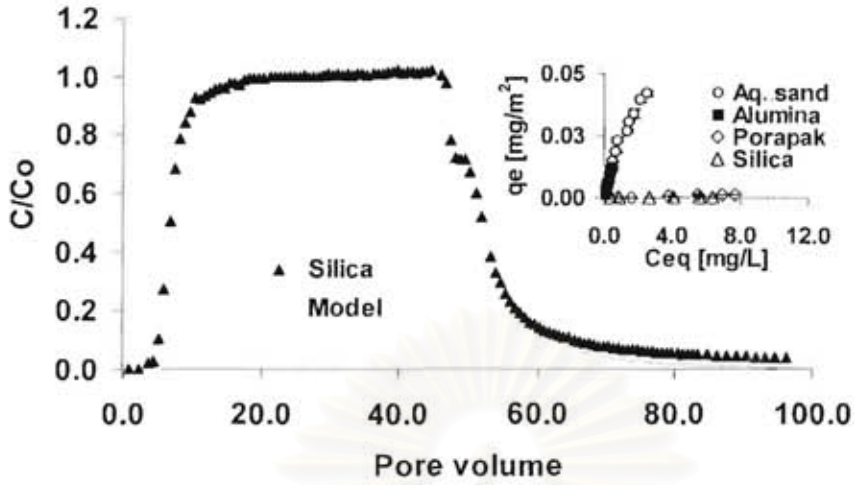


Figure 5.4 Breakthrough curves of nalidixic acid with silica. It shows non-equilibrium characteristic. The model fitting gave the retardation factor (R) 8, N ~ 0.59, F ~ 0.54, k_2 ~1.28, β ~ 0.6, ω ~ 0.1. Sorption isotherms of nalidixic acid to alumina, Porapak,silica, and aquifer sand are shown in the inset.

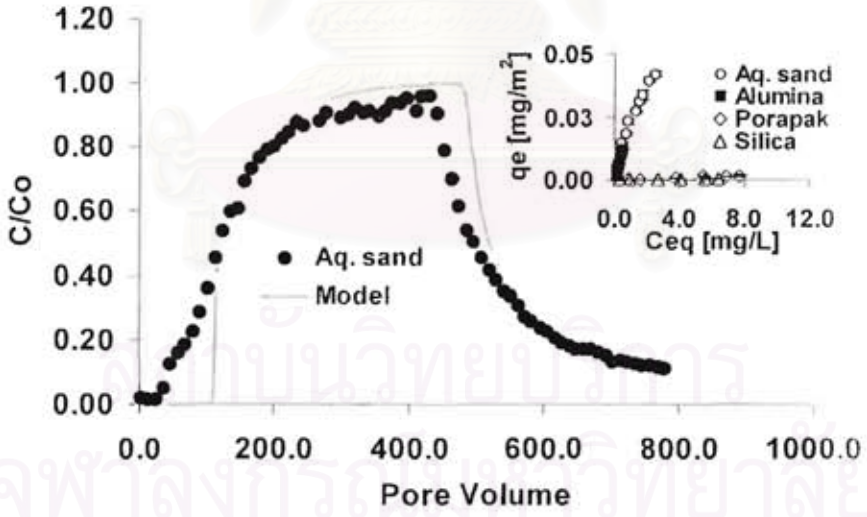


Figure 5.5 Breakthrough curves of nalidixic acid (pH ~ 6.2) with aquifer sand and non-equilibrium nonlinear model. The model fitting gave the retardation factor (R) ~ 150, N ~ 0.5, F ~ 0.6, k_2 ~0.03, β ~ 0.6, ω ~ 0.1. Sorption isotherms of nalidixic acid to alumina, Porapak,silica, and aquifer sand are shown in the inset.

The $\log K_{oc}$ estimation of pharmaceuticals by 1-octanol/water partition coefficient K_{ow} (Karickhoff, 1981) is shown in the Figure 5.6 along with some mono- and poly-aromatic hydrocarbon compounds (i.e., benzene, naphthalene, phenanthrene). This estimation assumes that compounds sorb to natural media by partitioning to organic fraction in the media. The 17α –ethynyl estradiol (EE2) strongly corresponds to this relationship. As mentioned previously this compound is neutralize at neutral pH, hence the sorption would take place by hydrophobic partitioning. While nalidixic acid, which is partially/fully ionized in neutral pH range, shows much larger sorption than the assumption of sorption only by hydrophobicity. The other estimation by (Bintein and Devillers, 1994) which includes the correction factor for ionization process (pKa) is shown in upper straight line over the estimation of Karickhoff, 1981. The estimation better fits for nalidixic acid, however, the real sorption coefficients of nalidixic acid are still greater than the estimation incorporating the correction factor for pKa. Although, at pH about 4 most fraction of nalidixic acid is in neutral form, the sorption coefficient is not consistent with hydrophobic partitioning relationship. The reason of inconsistent is not known.

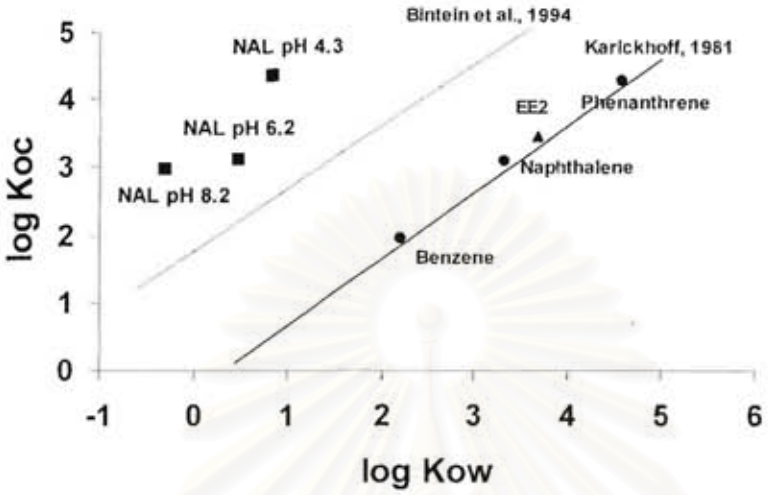


Figure 5.6 The relationship of $\log K_{oc}$ (where $K_{oc}=K_d/f_{oc}$) of aquifer sand and $\log K_{ow}$ from this study were shown along with the $\log K_{oc}$ estimation by 1 octanol/water partition coefficient, $\log K_{ow}$ (lower line, Karickhoff, 1981). The upper line represents the work done by Bintein and Devillers, 1994 which includes correction factor regarding ionization process (pKa). Sorption of acetaminophen is not significant and not shown. NAL, EE2 represent nalidixic acid, and 17α-ethynyl estradiol respectively.

5.4.2 pH Dependent Transport of Nalidixic Acid

Nalidixic acid is a very weak organic acid, with a pKa of 5.95. It suggests that nalidixic presents in both neutral and anionic forms in the neutral pH range and the sorption capacity varies according to pH. In order to investigate the influence of pH to sorption and transport of nalidixic acid on aquifer media, the batch and column experiments in the range of pH 4 to 9 were conducted.

The pH-sorption profiles of nalidixic acid to aquifer sand from batch studies are shown Figure 5.7. The sorption magnitude gradually increases and reaches its maximum at pH ~ 6. The sudden drop of sorption is shown after pH greater than 6 and reaches its minimum at pH~ 7.5-8. It should be noted that the pH at minimum sorption is lower than pH at minimum sorption of alumin at 9 (PZC~9). This may be caused by the iron oxide (i.e., iron oxide having PZC ~ 7-9 (Schwertmann and Cornell, 1991) covering on the sand surface and having lower PZC. According to the concept described above, the breakthrough order of nalidixic acid are pH 4.3, 6.2, 8.2 as shown in Figure 5.8. Among three breakthrough curves the greatest retardation (R~150) can be found in column running with pH 6.2 solute, and the least retardation was found in column of pH 8.2 (R~4.5). At pH 8.2, the shape of breakthrough curve is non-equilibrium and nonlinear as evidenced by long tailing of desorption front. The conservative tracer transport was also performed in these columns showed ideal characteristics. Therefore, if non-equilibrium exists in this system, it is sorption-related and not due to physical/transport processes.

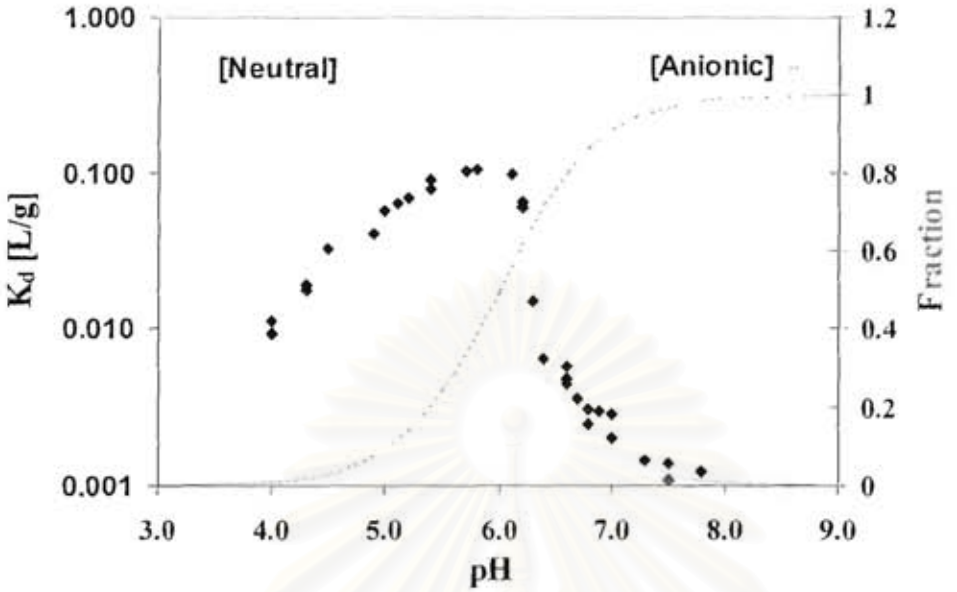


Figure 5.7 pH-sorption profiles of nalidixic acid to aquifer sand is shown along with the fraction of neutral and anionic forms of nalidixic acid.

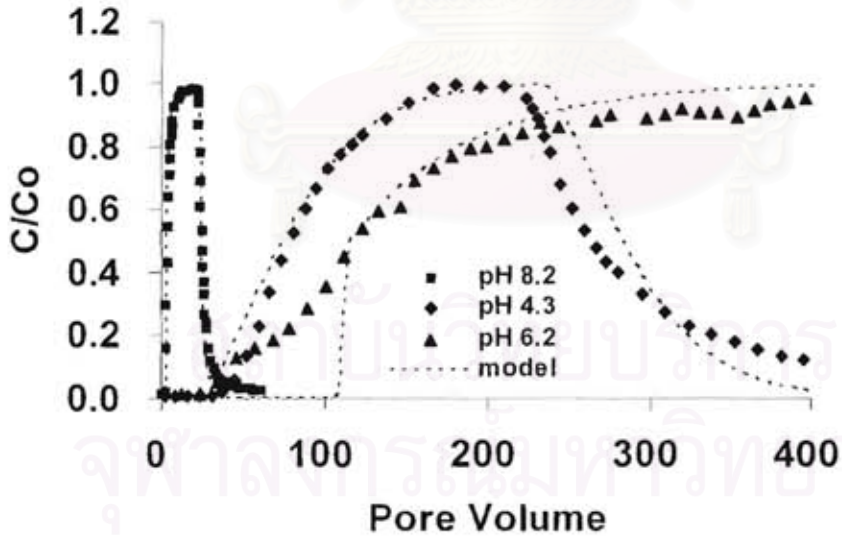


Figure 5.8 Breakthrough curve of nalidixic acid with aquifer sand at different pH. They all show non-equilibrium characteristic. The retardation factors at pH 8.2, 4.3, and 6.2 are 4.5, 83, and 150 respectively.

5.4.3 Flow Interruption

In order to confirm nonequilibrium condition, the flow-interruption on column of nalidixic acid and silica at pH6 was conducted at three points i.e., at both sorption and desorption front and at the plateau (C/Co ~ 1) (Figure 5.9). The interruption period was 8 hours (4.3 PV) while the resident time of the column was (~1.86 hours). The result of flow interruption at the sorption front showed the steps down of the curve. While the desorption front showed a step up. It could be explained that there was further sorption between solute and the media after flow interruption. This meaned the interaction had not reached equilibrium yet. Meanwhile, at the desorption front, the step up concentration after flow interruption meaned further desorption existed. These characteristics followed the work done by Brusseau et al., 1997, which confirmed that the transport process of nalidixic acid to silica at neutral pH was under non-equilibrium condition. The character of breakthrough curve with a simple flow-interruption technique provides more confidence in identifying the process control transport of nalidixic acid. This will help in selecting the appropriate numerical transport model and transport parameters for further contaminant transport modeling.

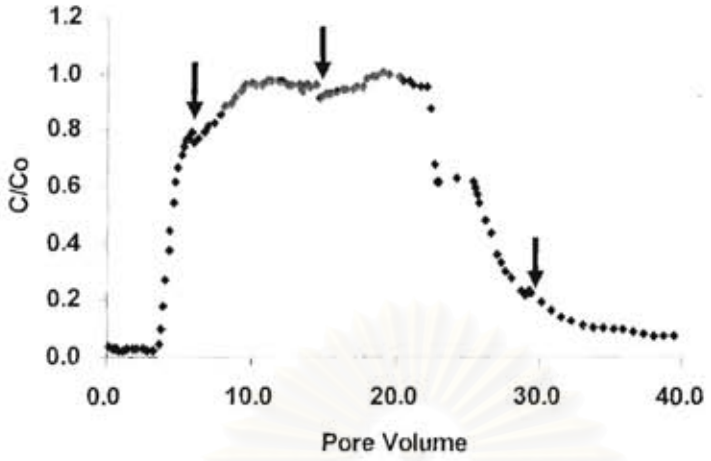


Figure 5.9 Breakthrough curve of nalidixic acid with silica with three 8 hours-flow interruption points.

5.4.4 Modeling

The computer program CXTFIT2 (Toride et al., 1989) was used to simulate the local equilibrium assumption model for tracer and acetaminophen experiment. CXTFIT2 is a non-linear least squares curve fitting computer program that is used to determine dispersion and retardation factor for solute transport of 1-dimensional experiment column data. The hydrodynamic properties (i.e., dispersion coefficient) of the columns packed with the silica, alumina and aquifer sand were inferred from breakthrough curves of the conservative tracers (sodium chloride or sodium nitrate). The shapes of tracer BTCs were highly symmetric with sharp fronts and breakthrough exactly one pore volume. The results also indicate that the flow regime within all column studied was dominated by advection.

The computer program UFBTC, 1989 version 2.0 (University of Florida) was used to simulate non-equilibrium assumption model and/or nonlinear sorption. This program used finite-different numerical techniques to estimate the

relative concentrations at different time. The breakthrough curves for pharmaceuticals were fitted with linear/nonlinear and equilibrium/non-equilibrium model using the calculated average pore water velocity and estimated D obtained from tracer run. The experimental equilibrium adsorption data used for modeling were taken from the previous study. The F and k_2 (Table 5.3) were calculated from the outputs of model fitting parameters (i.e., retardation factor, β, ω).

The two sites model was used to characterize sorption nonequilibrium. It assumes that sorption occurs in two types of domain: an instantaneous equilibrium type and rated-limited type, with the sorption in the latter domain characterized by k_2. The influence of sorption nonequilibrium on organic contaminant transport has been recognized to be important. Brusseau and Rao, 1989 compiled and analyzed extensive sorption kinetic database, revealing the existence of an inverse log-log relationship between desorption rate constants (k_2) and corresponding equilibrium sorption constants (K_d). They noted that the approach toward sorption equilibrium was more constrained for solutes with reactive functional groups (e.g., amino, phenoxyl, and carboxylic acid groups). It was suggested to be the consequence of specific interaction of solute functional groups on the specific charge site on the sorbent. This is reflected by smaller k_2 value for a polar solute when compared with an equally sorptive nonpolar solute.

The log-log plot of k_2 and K_d of ionizable nalidixic acid and 17α–ethynyl estradiol were shown in Figure 5.10. The parameters of nalidixic acid at three difference pH (difference ionization) were shown along with the relationships of hydrophobic and polar/ionizable organic chemicals as compile by Brusseau and Rao, 1989. The low sorption of nalidixic acid agreed very well with the hydrophobic

organic chemicals. While the highest sorption at pH 6.2 (close to pKa ~ 5.9), the point deviated from hydrophobic line towards polar/ionizable organic compounds line.

It was suggested that the most probable potential causes of sorption nonequilibrium of nonhydrophobic (polar/ionizable organic chemicals) were chemical nonequilibrium and intrasorbent diffusion. However, the sorption nonequilibrium for 17α–ethynyl estradiol was unexpected to much different from the hydrophobic relationship. The reason is not known.

A linear relationship of F and ionized fraction of nalidixic were shown in Figure 5.11. It suggested the fraction of instantaneous sorption increased with the amount of ionized fraction of nalidixic acid. At pH 4, the lowest fraction of ionization the F was relatively low, while at higher pH (pH 6.2 and pH 8.2) and higher ionized fraction, F was also relatively high. This may suggested that the more ionized forms exist, the more can reach the instantaneous sorption sites.

The comparison of retardation factor from modeling and calculated from batch studies are shown in Figure 5.12. Generally, there is a good agreement between retardation factors derived from batch experiment and column modeling experiments. However the additional precaution should be concern when using for nalidixic acid. Since the sorption capacity of nalidixic acid varies significantly with pH, especially the pH near its pka. Therefore, the estimation from batch experiment must perform at the same pH condition of column experiment in order to obtain good agreement with column experiment. This finding suggests that using batch sorption data to predict transport in subsurface for ionizable pharmaceuticals must be used with cautions.

Table 5.3 Column packing condition and the result model fitting for the transport experiments.

Pharma-ceuticals	Media	pH	Length [cm]	Bulk Density ρ[g/cm3]	Porosity	Pore velocity [cm/hr]	Dispr. coeff. [cm^2/min]	BTCs Shape	R	N	F	k_2 [1/hr]	β	ω	r^2
ACE	Silica	6.7±0.1	4.75	0.43	0.46	14.74	0.038	Eq.	1.0						0.99
ACE	Alumina	6.5±0.1	5.10	1.18	0.52	10.49	0.007	Eq.	1.1						0.99
ACE	Aq.Sand	6.6±0.1	4.80	1.59	0.43	15.74	0.015	Eq.	1.0						0.99
EE2	Silica	6.7±0.1	4.75	0.43	0.40	17.03	0.019	Non Eq.	1.2	0.60	0.10	1.99	0.85	0.1	0.90
EE2	Alumina	7.6±0.2	5.00	1.2	0.46	11.17	0.026	Non Eq.	1.2	0.60	0.10	1.24	0.85	0.1	0.95
EE2	Aq Sand	6.5±0.1	10.00	1.53	0.38	18.81	0.024	Non Eq.	4.5	0.60	0.49	0.10	0.6	0.1	0.96
NAL	Silica	6.6±0.1	4.40	0.46	0.40	17.98	0.010	Non Eq.	8.0	0.59	0.54	1.28	0.6	1.0	0.97
NAL	Aq Sand	6.2±0.1	10.00	1.48	0.40	18.26	0.025	Non Eq.	150.0	0.50	0.60	0.03	0.6	1.0	0.90
NAL	Aq Sand	4.3±0.1	4.75	1.61	0.44	12.21	0.004	Non Eq.	83.0	1.00	0.39	0.15	0.4	3.0	0.94
NAL	Aq Sand	8.2±0.1	5.00	1.53	0.40	13.20	0.010	Non Eq.	4.5	0.9	0.74	1.47	0.9	0.1	0.97

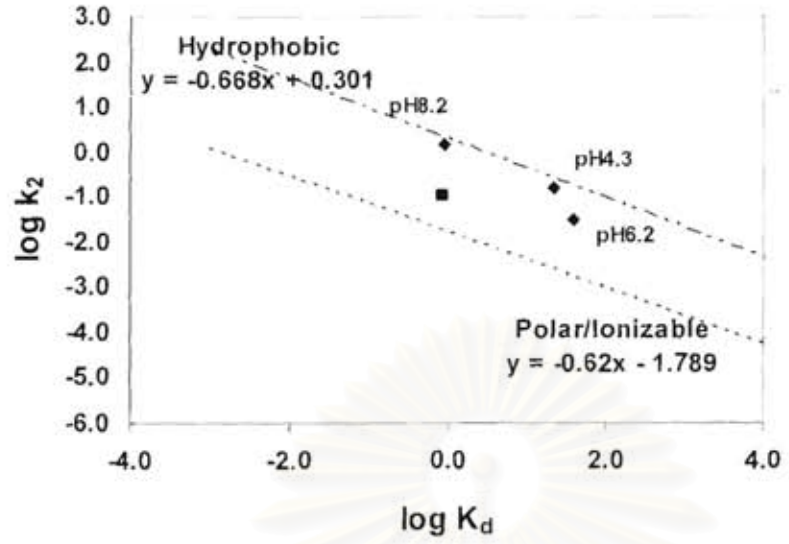


Figure 5.10 The inverse relationship of log K_d and log K_2 of nalidic acid at different pH were plotted along with the relationship of hydrophobic and polar/ionizable organic compounds compiled by Brusseau and Rao 1989. The rectangle represented 17α- ethynyl estradiol.

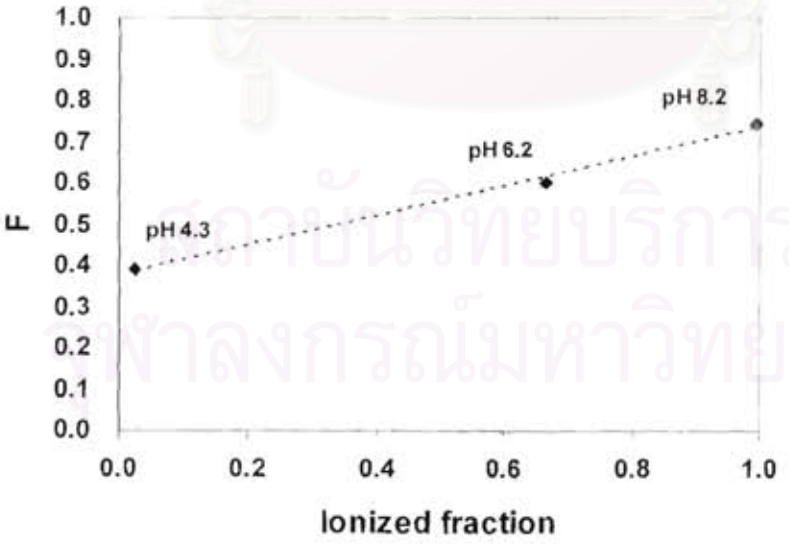


Figure 5.11 The linear relationship of ionized fraction of nalidixic acid at different pH and F.

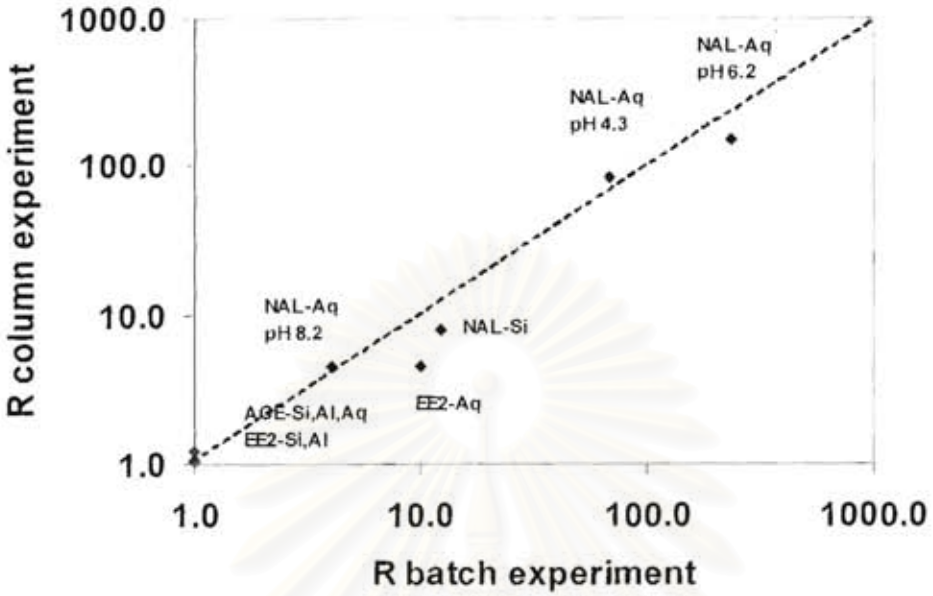


Figure 5.12 Comparison of Retardation factors derived from batch sorption experiment and solute displacement experiment.

5.5 Conclusions

Sorption of acetaminophen, 17α –ethynyl estradiol, and nalidixic acid to pure minerals and a hydrophobic medium was discussed in a previous study. The objective of this research is to build on our previous work by evaluating the sorption and transport of select pharmaceuticals in continuous column flow studies and to assess the role of kinetics in the sorptive transport in column system. The results of column studies with acetaminophen on silica, alumina, and aquifer sand showed ideal breakthrough characteristics with retardation factor near unity, and were thus quiet similar to the conservative tracer. These results are consistent with batch sorption experiments which show not significant sorption to all media. The column transport of 17α–ethynyl estradiol shows nonideal characteristics (nonequilibrium and

nonlinear) for silica, alumina, and aquifer sand. The nonideal breakthrough curves are consistent with the batch sorption experiment, which showed nonlinearity. The aquifer sand, even with low organic carbon content (0.08%), still provided a retardation factor of 4.5. The column transports of nalidixic acid with silica and aquifer sand showed nonideal characteristics (nonequilibrium and nonlinear) and a retardation factor which is strongly pH dependent. The greatest retardation factor of nalidixic acid with aquifer sand (retardation factor of 150) can be found at the pH near its pKa. The lowest retardation factor of nalidixic acid with aquifer sand was found at high pH (~8-9) which is the region where both the mineral surface and the nalidixic acid are negatively charged. Generally, the predictions of retardation factors derived from batch sorption studies give good agreement in prediction of pharmaceuticals transport in column. However, the sorption and transport of ionizable pharmaceutical, such as nalidixic acid, is highly pH dependent and can vary significantly with even small changed in pH near the pKa.

CHAPTER VI

SORPTION OF ACETAMINOPHEN, 17α–ETHYNYL ESTRADIOL, NALIDIXIC ACID, AND NORFLOXACIN WITH SUBSURFACE SEDIMENTS

6.1 Theoritical Background

At present, pharmaceuticals play an important role for human and animal life. Thousand of tons of pharmaceutical products are produced and used each year throughout the world. Pharmaceutical products are commonly used for illness treatment, birth control and stress management (Zuccato et al., 2000). In addition, some pharmaceutical compounds are applied to stimulate a physiological growth in humans, animals and plants. Unfortunately, some pharmaceuticals are not metabolized completely during metabolic processes and they are discharged into water and/or soil environments. Pharmaceuticals can enter in the environment by several pathways, including: sewage treatment plant effluent, aquaculture, waste disposal site, animal wastes and biosolids applied to agriculture fields might run off into nearby surface water or infiltrate through the soil into groundwater (Heberer, 2003).

Recently, the detection of pharmaceuticals in the aquatic environment has become a topic of public interest. Some pharmaceutical compounds are not eliminated in wastewater treatment plants and are not degraded in the environment. They have been detected in surface water, groundwater and drinking water in the ng/L level up to μg/L level (Daughton and Ternes, 1999; Heberer, 2002; Kolpin et al., 2002; Kümmerer, 2001; Zuccato et al., 2000).

Sorption by soil is a major abiotic process controlling the transport and fate of pharmaceuticals in aquifer systems. It is strongly influenced by media properties such as organic content, surface reactivity and specific surface area (Baily and White, 1970). Sorption of nonpolar organic chemicals by subsurface sediments is primarily to the organic content, and quantitative prediction of sorption behavior can be made using sorption coefficients (K_d) normalized to the organic carbon content of soil (K_{oc}) (Lyman et al., 1990).

In a natural water system with many organic contaminants present, adsorption to soil/sediment mineral matter occurs as a consequence of the competition between all species, including water. In the presence of water, the soil/sediment mineral matter prefers to adsorb water because of their similar molecular polarities, while the soil organic matter prefers to adsorb the contaminants (Figure 6.1). This means that the nonionic organic contaminants are not significantly adsorbed to minerals, and that the partition of contaminant is not affected by water or by other contaminants. Therefore, the followiing two processes are at work: (1) the organic contaminants are competitively prevented by water from adhering to the surface of the soil mineral matter, while at the same time (2) the organic contaminants are able to partition independently to soil organic matter (Chiou and Kile, 2000).

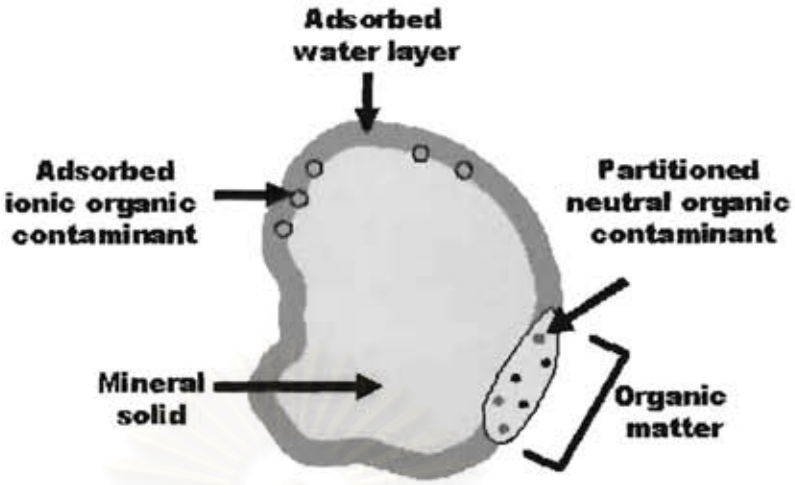


Figure 6.1 Modes of interaction between organic contaminants to natural sediment (modified from Chiou and Kile, 2000).

Pharmaceutical compounds are distinct from nonpolar compound in that they may consist of a combination of nonpolar and/or ionizable functional groups. For pharmaceuticals with ionizable groups, the acid dissociation constant (pKa) establishes the fraction of neutral or ionized form that exists at a given pH. Therefore, using similar models for ionizable organic chemicals has not been succeeded because of the need to consider simultaneously the physical and chemical reactions of the ionized and neutral species as well as changes in the electrostatic properties of the soil surface with changes in parameters such as pH, ionic strength and ionic composition. For organic acids, the use of K_{oc} in conjunction with specification of the organic acid as a function of pH and the pKa has been shown to adequately describe sorption by several soil and sediments (Jafvert, 1990; Lee et al., 1990). In these models sorption was described assuming hydrophobic partitioning onto soil organic matter with the neutral species having a much higher affinity for the soil than the anion. Such a model, however, does not include the interaction of the organic anion to positively

charged sites on the soil surface, which could be significant for variable-charge minerals. Iron and aluminum oxides have pH-dependent charge characteristics that enable the generation of both negatively and positively-charged sites, and are the major minerals responsible for positive charged sites in soils. Evangelou (1998) and Bintein and Devillers (1994) introduced QSAR model including the log K_{ow}, pKa and organic carbon content. This improved the simple semi-empirical models which was used for sorption behavior prediction.

6.2 Objective of the Study

Although analytical methods are available to detect pharmaceuticals, information on the fate and transport of pharmaceuticals when they enter the aquatic environment is still limited. Therefore, this study attempts to evaluate the fate and transport behavior of pharmaceutical compounds. The primary objective of this study is to investigate sorption processes of pharmaceuticals to subsurface sediments vulnerable to contamination in the recharge area, in the central part of Thailand. In this chapter, the pharmaceuticals were selected to represent a range of physiochemical properties and types of pharmaceuticals. Four pharmaceutical compounds from three different classes were evaluated in this research: acetaminophen (analgesic or pain relieving), nalidixic acid (antibiotic), norfloxacin (antibiotic) and 17α-ethynyl estradiol (synthetic hormone which is commonly used contraceptive agent).

6.3 Materials and Methods

6.3.1 Subsurface Sediments

The Department of Groundwater Resources (DGR) 2004 conducted a study on groundwater vulnerability in central Thailand in order to identify areas that should be under precaution of groundwater contamination regarding the geology and the existence of contaminant sources (Figure 6.2). The upper part of the study area, including Chainat, Singburi, Angthong and Suphanburi provinces, has medium to high degree of vulnerability due to the absence of overlying marine clay layer and intensive agriculture activities including large scale animal farming. This area's sedimentation is due to sand/gravel/clay deposits from the river process. In some areas, the sand layers connected to the uppermost layer flood of plain deposits, where surface water can seep through to the shallow groundwater without any protection. Therefore, this area is determined as the recharge area (i.e. natural protection of groundwater in the area is limited due to high possibility of groundwater to be contaminated by polluted surface contaminant sources).

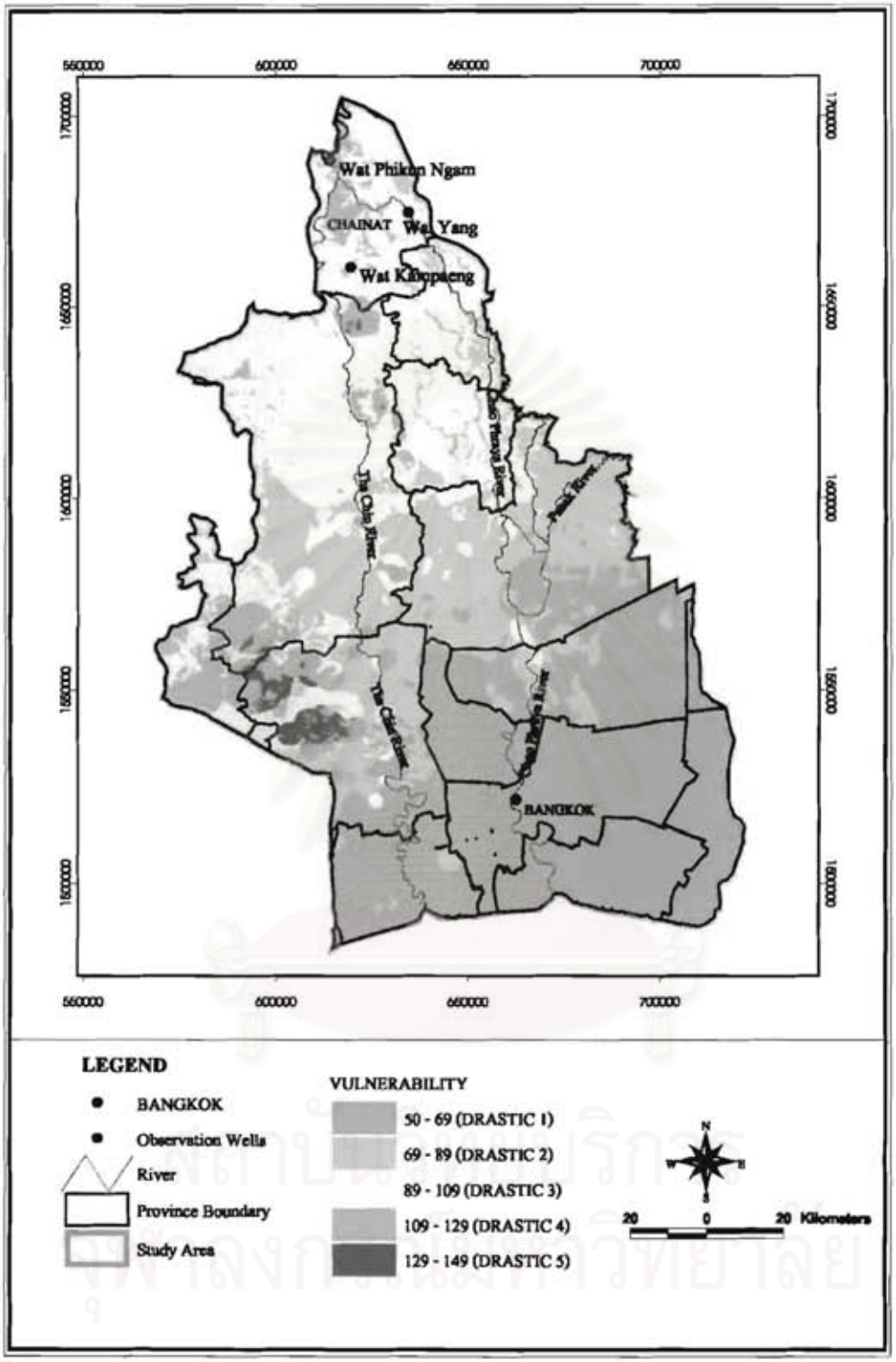


Figure 6.2 Groundwater vulnerability map of central Thailand showing three sample locations (Department of Groundwater Resources, 2004).

Five sediment samples were obtained from three boreholes drilled in the recharge area in Chainat. The samples locations are shown on the groundwater vulnerability map (Figure 6.2). The drilling method used air as a medium for carrying the subsurface sediments to the ground surface. (Figure 6.3). This prevented contamination of the samples by organic compounds routinely used in drilling fluid. Three of the samples were composed primarily by silts (Pc03: at 0-3 m depth), (Pc10: at 9-10 m depth) and sand (Ps17: at 11-17 m depth) from the same borehole. The other two sand samples (Ys11: at 8-11, Ks12: 12 m depth) were collected from different locations. The samples then were air dried before sieving for specific size, between 0.18-0.42 mm (between mesh #40 and #80). The silts also were sieved. The size of silts used in this study is smaller than 0.07 mm. The properties of these subsurface sediment are listed in Table 6.1 and Table 6.2. The organic matters were determined by wet-oxidation method (Walkley and Black, 1934) and reported in organic carbon content by conversion factor. The sands were characterized using X-ray fluorescence to obtain the percentage of metal oxides in the sediments and quantitative analysis by optical microscope to identify mineral contents of the samples.

Table 6.1 Subsurface sediment properties in this study.

Sample	Location	Province	Type	Depth [m]	AEC [cmol/kg]	CEC [cmol/kg]	OC [%]
Pc03	Wat Phikun Ngam	Chainat	silt	3	2.54	5.50	0.17
Pc10	Wat Phikun Ngam	Chainat	silt	10	2.40	6.00	0.20
Ps17	Wat Phikun Ngam	Chainat	sand	17	1.83	1.10	0.06
Ys11	Wat Yang	Chainat	sand	11	1.76	1.80	0.02
Ks12	Wat Kampaeng	Chainat	sand	12	1.90	2.10	0.02

Table 6.2 Chemical composition of the subsurface sediments analyzed by x-ray fluorescence.

Sample	%SiO2	$\%Al_2O_3$	$\%Fe_2O_3$	$\%K_2O$	%CaO	$\%Na_2O$	%MgO
Pc03	61.75	8.89	2.53	2.66	0.50	0.67	0.50
Pc10	63.55	9.25	2.81	2.48	0.51	0.68	0.57
Ps17	82.70	4.88	1.10	2.68	0.27	0.40	0.10
Ys11	76.63	5.23	1.33	2.52	0.87	0.56	0.19
Ks12	76.22	6.16	0.56	2.88	0.07	0.22	0.08

Figure 6.3 Borehole drilling for samples collection.

6.3.2 Pharmaceuticals and Chemicals

Four pharmaceuticals were evaluated in this research: acetaminophen (analgesic), 17α-ethynyl estradiol (synthetic hormone), nalidixic acid and norfloxacin (antibiotics). All pharmaceuticals were purchased from Aldrich Chemical Co , and used as received. These pharmaceuticals were selected to represent a range of physiochemical properties and types of pharmaceuticals. The molecular structures and chemical properties of four pharmaceuticals are shown in Table 3.3.

Reagent grade methyl alcohol (MeOH) 99% purity, purchased from Aldrich Chemical Co., was used as a solvent for preparing pharmaceutical stock solutions. Calcium chloride dihydrate ($CaCl_2 2H_2O$), obtained from Fisher Scientific, was employed for ionic strength control. Acetaminophen was prepared in Nanopure water. Nalidixic acid, norfloxacin and 17α-ethynyl estradiol were prepared in stock solutions of MeOH to aid in dissolution. The amount of MeOH was normally less than 1% in the final samples and thus had negligible impact on sorption.

6.3.3 Analytical Methods

A SHIMADZU UV-1601 spectrophotometer was used to analyze acetaminophen and nalidixic acid. A wavelength of 242 nm was used to analyze acetaminophen; a wavelength of 258 nm was used to analyze nalidixic acid; 17α-ethynyl estradiol was analyzed by high performance liquid chromatography (HPLC) and UV detection. A water-acetonitrile solution (35:65) was used as mobile phase. The isocratic elution with a constant flow rate of 1 mL/min at 29 °C and a pressure approximately 800 bars was applied. A C-18 reversed-phase column (4.6 x 125 mm with an average grit size of the spherical silica gel of 5 μm. The detection was performed with an UV detector at 280 nm. The injection volume was 50 μL and the retention time was approximately 3 minutes.

6.3.4 Batch Experiments

The batch equilibration method was used to measure sorption of the four pharmaceuticals. All batch experiments were conducted at room temperature (~25°C). Calcium chloride was added to mimic background groundwater ionic

strength and to reduce dispersion of fines (0.01 M $CaCl_2$) for all tests. Triplicate samples were evaluated for each set of conditions. Pharmaceutical and media blanks were conducted for each isotherm study to account for losses/gains of pharmaceutical concentration during the experimental procedure, which proved to be negligible. Most of samples remained in the neutral pH range. Sorption isotherms of the pharmaceuticals were measured using at least five initial solution concentrations in triplicate ranging from 1.0 to 10.0 mg/L for acetaminophen nalidixic acid, norfloxacin and 4.0 to 14.0 mg/L for 17α-ethynyl estradiol. Sorption studies were conducted using mass of sorbent to volume of solution ratio of acetaminophen (3g : 8 mL.), nalidixic acid (0.05 g : 8 mL for silt, 3g : 8 mL for sand), norfloxacin (0.01 g : 8 mL), 17α-ethynyl estradiol (3g : 8 mL) and were varied in a series of 15 mL vials. The samples were equilibrated by rotary shaker for 24 hours and were then centrifuged at 1,500 rpm for 30 minutes. The supernatant from each vial was then transferred into a 15 mL vial for subsequent analysis. While concentrations used in this study were higher than likely environmental concentrations of pharmaceuticals, except directly near a contamination source (Holm et al., 1995), practical aspects of laboratory measurements necessitated use of the higher concentrations. Although field measurements of pharmaceutical concentrations often involve extraction techniques to concentrate many liters of water for analysis, this approach is difficult to apply to measurement sorption because of the larger sample sizes needed and problems of error propagation (Hari et al., 2005). In addition, the processes identified at the higher concentrations evaluated here would also be applicable at lower concentrations.

6.3.5 Anion Exchange Capacity and Cation Exchage Capacity

Anion exchange capacity (AEC) was determined at the natural soil pH for all sediments for a subset of soils using NH_4Cl as a saturating solution and KNO_3 as a replacing solution using the unbuffered salt extraction method recommended by (Sumner and Miller, 1996). The chloride extracted by KNO_3 was used for AEC calculations. Chloride determination was performed by the Argentometric method. Cation exchange capacity was determined by Ammonium Acetate (pH7) method recommended by the (Soil Survey Laboratory Staff, 1992).

6.4 Data Modeling

In this study, sorption data is analyzed using the Freundlich equation, which is a widely accepted model for representing contaminant sorption (Weber et al., 1995);

$$q_e = K_f Ce^N \quad (1)$$

where q_e is the equilibrium mass of chemical sorbed per unit mass (mg/g) or per unit surface area of the sorbent (mg/m^2) and C_e is the equilibrium concentration (mg/L) in the aqueous phase. K_f is the Freundlich sorption constant and N is the Freundlich exponent. When N=1, the Freundlich equation simplifies to the linear (Henry's Law) sorption isotherm and K_f is replaced with the linear sorption coefficient K_d. The sorption coefficient K_d can be described by

$$K_d = q_e / C_e \quad (2)$$

At a specific concentrations of nonlinear sorption isotherm, an effective K_d value can be described by

$$K_d^{eff} = K_f Ce^{N-1} \quad (3)$$

Where K_d^{eff} defines the linear isotherm centered about the specified concentration. In this study, 5 mg/L concentration was used as an index concentration. The organic carbon content normalized sorbtion coefficient is described by

$$K_{oc} = K_d / f_{oc} \quad (4)$$

where f_{oc} is the fraction organic carbon content of the sample.

6.5 Results and Discussion

Equilibrium sorption studies were conducted with the four pharmaceuticals (17α-ethynyl estradiol, acetaminophen, nalidixic acid, and norfloxacin) and five sediment samples (two silt samples and three sand samples). The experiments were conducted at a neutral pH; in this pH range, nalidixic acid existed mainly in ionized form and norfloxacin existed in three forms; mainly in zwitterionic, cationic and neutral forms, while acetaminophen and 17α-ethynyl estradiol remained mostly in their neutral form. The sorption isotherms were plotted with error bars representing 95% confidence intervals of triplicate samples. The summary of sorption parameters for the experiments is shown in Table 6.3.

Table 6.3 Summary of the sorption coefficient of pharmaceuticals to subsurface sediments.

Pharmaceuticals	Sorbent	pH	K_f	N	[a]Kd^{eff} [mL/g]	R^2	[b]Retardation factor
17α-ethynylestradiol	Pc03	6.9 ± 0.1	1.17E-02	0.66	7	0.94	29
	Pc10	6.5 ± 0.1	1.97E-02	0.46	8	0.98	33
	Ps17	7.1 ± 0.1	7.02E-03	0.73	5	0.88	21
	Ys11	7.3 ± 0.1	1.13E-02	0.41	4.4	0.90	19
	Ks12	6.9 ± 0.1	7.84E-03	0.58	4	0.97	17
Acetaminophen	Pc03	6.6 ± 0.1			1	0.90	5
	Pc10	6.2 ± 0.1			4	0.93	18
	Ps17	7.3 ± 0.1			n/s		1
	Ys11	7.2 ± 0.1			n/s		1
	Ks12	7.3 ± 0.2			1	0.85	5
Nalidixic acid	Pc03	6.8 ± 0.3	7.10E-02	0.80	52	0.97	209
	Pc10	6.6 ± 0.2	1.07E-01	0.40	41	0.87	165
	Ps17	6.6 ± 0.5	4.00E-03	0.84	3	0.99	13
	Ys11	7.1 ± 0.4	3.00E-03	0.61	2	0.99	9
	Ks12	7.0 ± 0.4	4.60E-02	0.39	17	0.97	69
Norfloxacin	Pc03	6.1 ± 0.1	9.96E-01	0.56	494	0.97	1977
	Pc10	6.2 ± 0.1	1.04E+00	0.34	360	0.95	1441
	Ps17	6.6 ± 0.1	1.51E-01	0.63	83	0.91	333
	Ys11	7.0 ± 0.1			109	0.99	437
	Ks12	6.5 ± 0.2	4.60E-01	0.50	208	0.98	833

[a] calculated at concentration 5 mg/L, [b] bulk density 1.6 g/cm^3 and porosity 0.4 were used

Sorption isotherms of 17α-ethynyl estradiol to subsurface sediments are shown in Figure 6.4. The sorption between 17α-ethynyl estradiol and sediments with Freundlich exponents (N) of ~ 0.4-0.7. This is consisted with work done by others of (Lai et al., 2000; Ying et al., 2003) which showed sorption of 17α-ethynyl estradiol to limestone sediments and river bed sediments to be nonlinear with the N ~ 0.46 in limestone sediment with organic carbon content ~ 0.5 % and N ~ 0.83 in riverbed sediments with organic carbon content ~ 1-3 %. In this study, the greater sorption occurred in silts with the effective sorption coefficient (at 5 mg/L) from 7 to 8 mL/g. The sorption coefficients of sands ranged from 4 to 5 mL/g. With, a pKa of 10.4, 17α-ethynyl estradiol existed mostly in the neutral from at this pH and is thus highly hydrophobic (log K_{ow} of 3.67). Therefore, the dominant sorption mechanism at neutral pH is expected to be hydrophobic interaction between the molecule and the organic fraction of the sediment. It should be noted that both silts have significantly higher organic carbon content (~ 0.2 %) than sands which have very low organic carbon content (~ 0.02-0.06 %) (see Table 6.1). Although, the organic carbon content of silts were one order of magnitude greater than sands, the variation of sorption coefficients in these sample was slightly, and strongly related to amount of organic carbon content. The sorption magnitude strongly depends on the amount of organic carbon of sediments R^2~0.98 as shown in Figure 6.5.

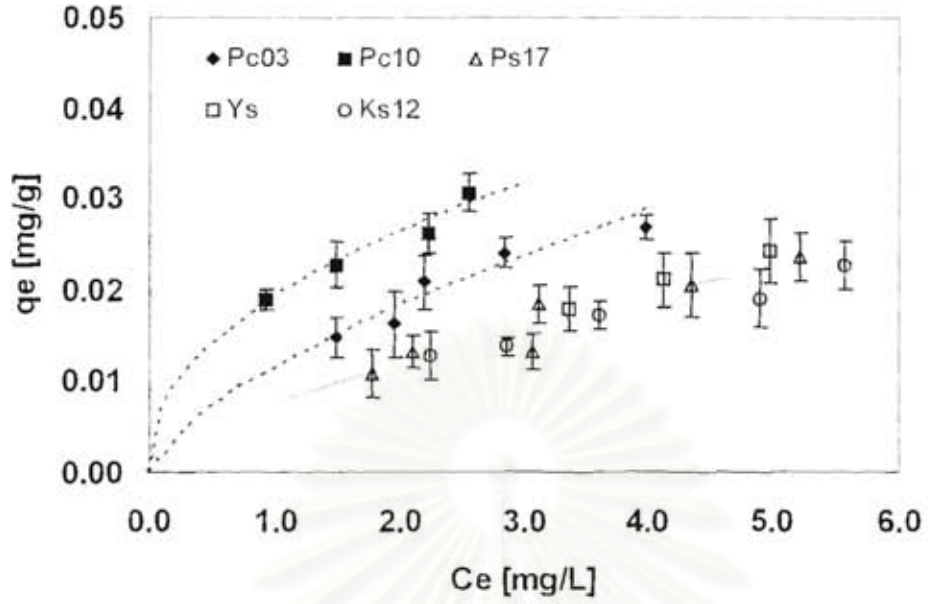


Figure 6.4 Sorption isotherms of 17α-ethynyl estradiol to subsurface sediments.

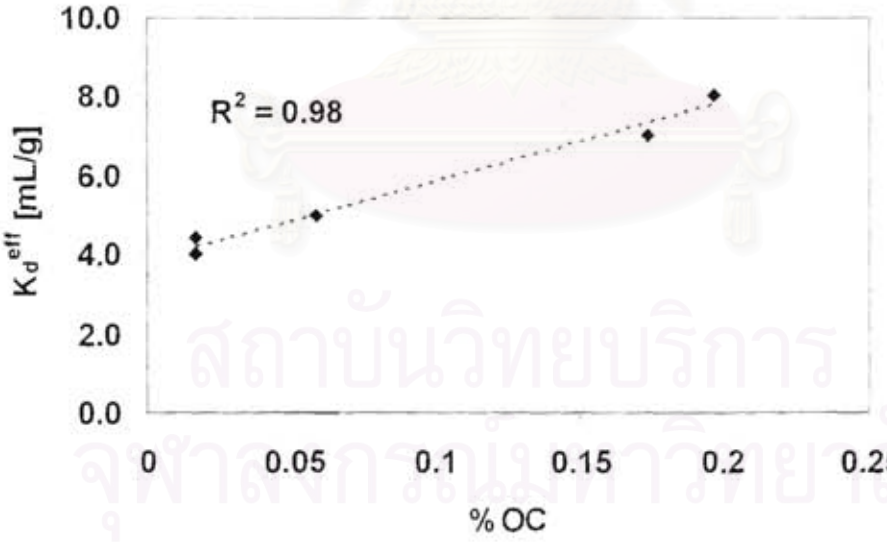


Figure 6.5 The relationship 17α-ethynyl estradiol sorption with organic carbon content of sediment samples.

The sorption isotherms of acetaminophen to subsurface sediments are shown in Figure 6.6. With a low hydrophobicity (log K_{ow} = 0.46) and a pKa = 9.4, acetaminophen exists almost entirely in the neutral form at neutral pH; thus ionic interactions are unlikely. Although acetaminophen exists mainly in the hydrophobic form, sorption of acetaminophen with silica, alumina and hydrophobic medium (Porapak P), as discussed in the Chapter 4, was negligible to charged surface (silica and alumina) as well as hydrophobic medium (Porapak P), consistent with its extremely low K_{ow}.

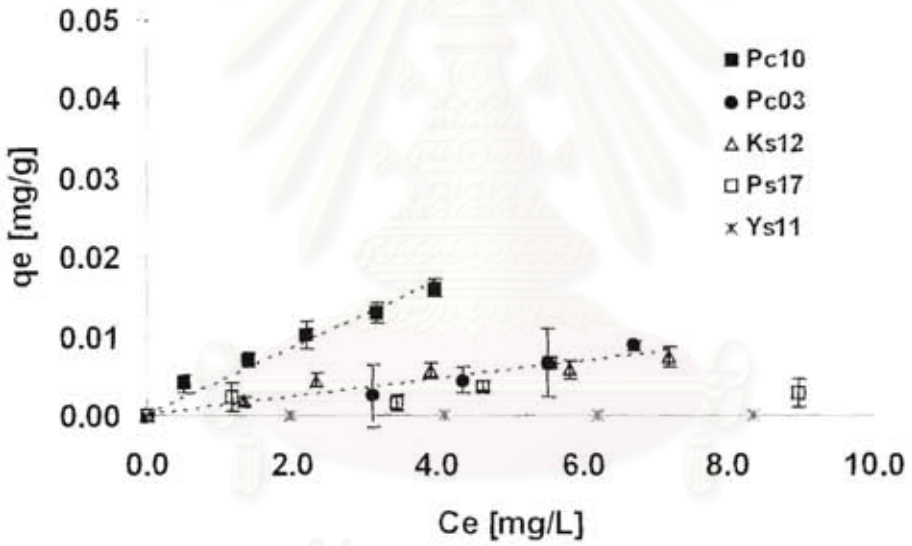


Figure 6.6 Sorption isotherm of acetaminophen to subsurface sediments.

Interestingly enough, the sorption experiments evidenced sorption of acetaminophen to subsurface sediments, especially with silts (K_d^{eff} ~ 1-4 mL/g) and sands (K_d^{eff} ~ 1 mL/g). The relationship of sorption coefficient with organic carbon content is insignificant (R2 ~ 0.36) as shown in Figure 6.7. This result suggests that the sorption influenced by hydrophobicity is not likely. The low hydrophobicity of the

neutral form of acetaminophen can not explain this measurable sorption magnitude. Löffler et al., 2005 found that acetaminophen transformed in the water into volatile transformation products (TPs) within two weeks with the DT_{50} of 3.1 days. In addition, it was suggested from the rapid and extensive binding onto the sediment that acetaminophen, but more likely its TPs, were incorporated into the biomass and may potentially accumulate in sediments. Therefore, from this suggestion, the sorption detected in the subsurface sediments may also caused by the transformation process.

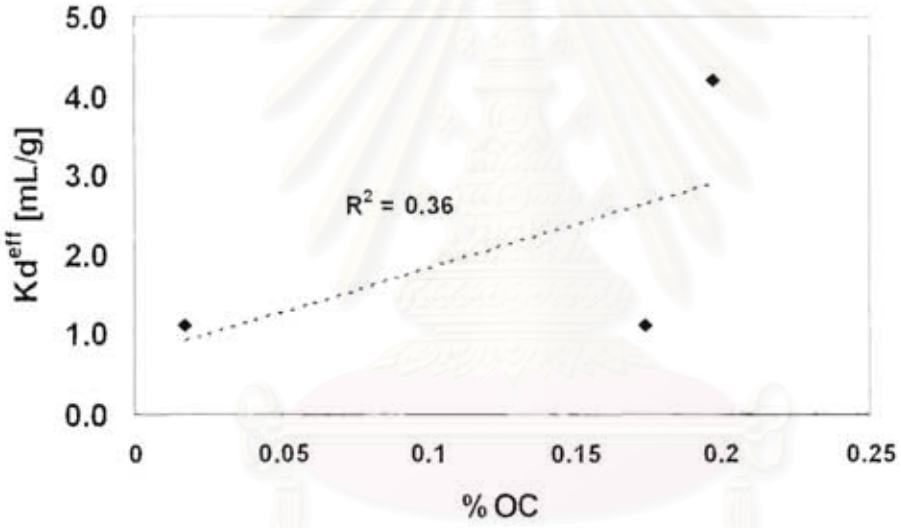


Figure 6.7 The relationship of acetaminophen sorption to organic carbon content.

In order to confirm the relationship of acetaminophen sorption capacity to organic carbon content, the sediments remove the organic matter. The sorption of acetaminophen to organic removed sediments is shown in (Figure 6.8). The organic removed sediments (open symbols) evidenced considerably less to negligible sorption capacity. This result suggested that the organic matters, which have been removed, should influence this sorption. Therefore, detectable sorption to natural subsurface sediments but not significant sorption to hydrophobic medium (Porapak P) may

suggest that the difference nature of organic carbon containing in natural subsurface sediments and synthetic hydrophobic medium.

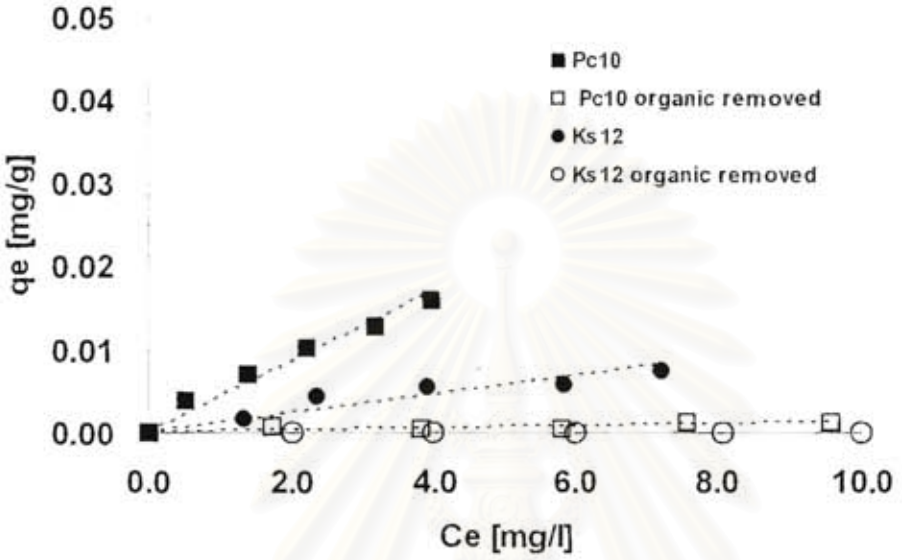


Figure 6.8 Sorption of acetaminophen to Pc10 (% OC 0.197) and Ks12 (% OC 0.0170) and organic removed Pc10 and Ks12.

Under the experimental condition acetaminophen and 17α-ethynyl estradiol were in neutral forms since the pH was still less than their pKa (9.38 for acetaminophen and 10.4 for 17α-ethynyl estradiol). Therefore, It was anticipated that the sorption was driven by hydrophobicity and ionic interactions was considered negligible. Additionally, $\log K_{oc}$ and $\log K_{ow}$ values of acetaminophen and 17α-ethynyl estradiol were plotted and compared with the semi-empirical relationship obtained from Karickhoff, 1981 as shown in Figure 6.9. It was noticeable that acetaminophen, which had very low hydrophobicity ($\log K_{ow} \sim 0.49$) does not comply with this semi-empirical relationship. However, 17α-ethynyl estradiol sorption to silts (%OC > 0.1) were very close with this relationship and sorption to sands which has very little

amount of organic carbon content (< 0.1%) did not agree very well with the semi-empirical relationship. The result of this study suggested that general log K_{oc} and log K_{ow} relationship, which was derived from sorption of hydrophobic organic compound, was able to be used to describe the sorption of neutral and hydrophobic pharmaceutical (e.g. 17α-ethynyl estradiol) to sediments which had high organic carbon content. On the contrary, sorption of neutral pharmaceutical and low hydrophobicity (e.g. acetaminophen) does not agree with this semi-empirical relationship.

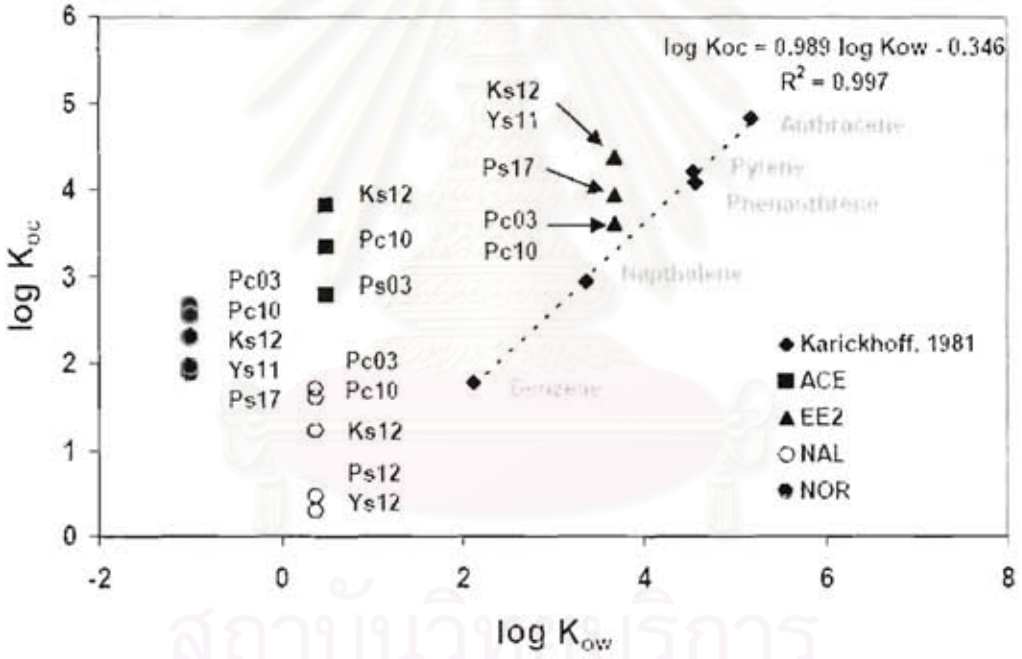


Figure 6.9 Log K_{ow} and log K_{oc} semi-empirical relationship (Karickhoff, 1981) for hydrophobic organic compounds and acetaminophen and 17α-ethynyl estradiol.

The sorption isotherms of nalidixic acid with subsurface sediments are shown in Figure 6.10 and Figure 6.11. The nalidixic acid sorption coefficients with silts ranged from 41 to 52 mL/g (pH 6.6 to 6.8) and to sands ranged from 2 to 17 mL/g (pH 6.6 to 7.1). The corresponding AEC of silts (2.4-2.5 cmol/kg) were greater than AEC of sands (1.76-1.90 cmol/kg). The assessing of sorption of protonated and deprotonated organic compounds should consider the ion exchange capacity, and solution speciation of the compounds in addition to hydrophobic interaction (Figueroa et al., 2004; Hyun et al., 2003)

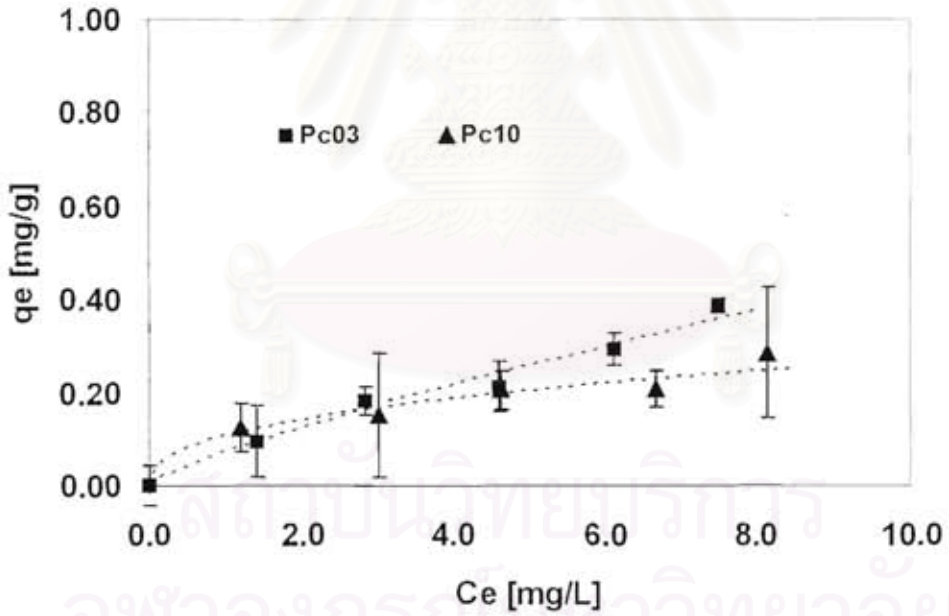


Figure 6.10. Sorption isotherms of nalidixic acid to silts (Pc03 and Pc10).

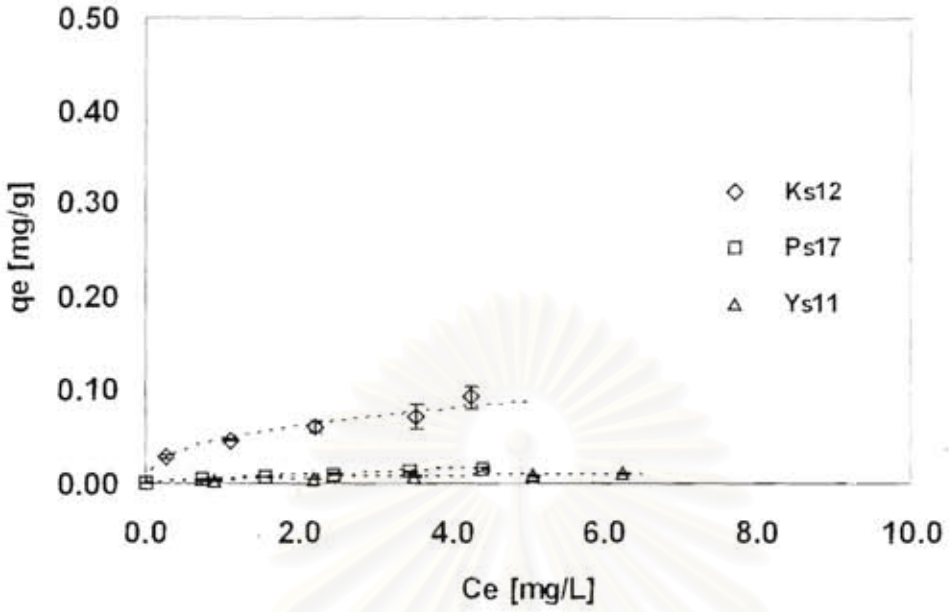


Figure 6.11. Sorption isotherm of nalidixic acid to sands (Ks12, Ps17, Ys11).

The sorption coefficient of Ks12 sand was higher than the other sands, which can be related to the amount of alumina, iron oxide and anion exchange capacity. Since alumina has PZC ~ 8-9 (Kosmulski, 2000) and iron oxide has PZC ~ 7-9 (Schwertmann and Cornell, 1991), then at the experimental pH, both alumina and iron oxide have positively charged surfaces which can give ionic attraction to anionic nalidixic acid. It was noticed that Ks12 sand has AEC and aluminum oxide greater than the others but lowest in iron oxide. It seemed that the sorption of nalidixic acid was greater influenced by amount of aluminum oxide than iron oxide (see Table 6.2). This may result from aluminum oxide and iron oxide having PZC at 8~9 and 7~9 respectively. Then aluminum oxide has the wider range to present in positively-charged surface, while iron oxide has narrower range and then lower amount of positively-charged surfaces.

The sorption isotherms of norfloxacin with subsurface sediments are shown in Figure 6.12. The norfloxacin sorption coefficients with silt were clearly nonlinear and ranged from 360 to 494 mL/g (pH 6.1 to 6.2) and to sands ranged from 83 to 208 mL/g (pH 6.5 to 7.0). It was corresponding to AEC of silts (2.4-2.5 cmol/kg) which were greater than AEC of sands (1.76-1.90 cmol/kg). The sorption coefficient of Ks12 sand had the greatest magnitude than the other sands which were corresponding to the Ks12 having the largest magnitude for both AEC (1.90 cmol/kg) and CEC (2.10 cmol/kg). According to what was found in the earlier study (Chapter 4), at this pH range where the cationic and zwiterrionic norfloxacin dominated over the neutral zwitterionic specie, the sorption of zwitterionic were proved to occur at both negatively and positively-charged surface. However, the sorption affinity occurs more on positively-charged surfaces (alumina) than negatively-charged surfaces (silica) as shown in Figure 4.6.

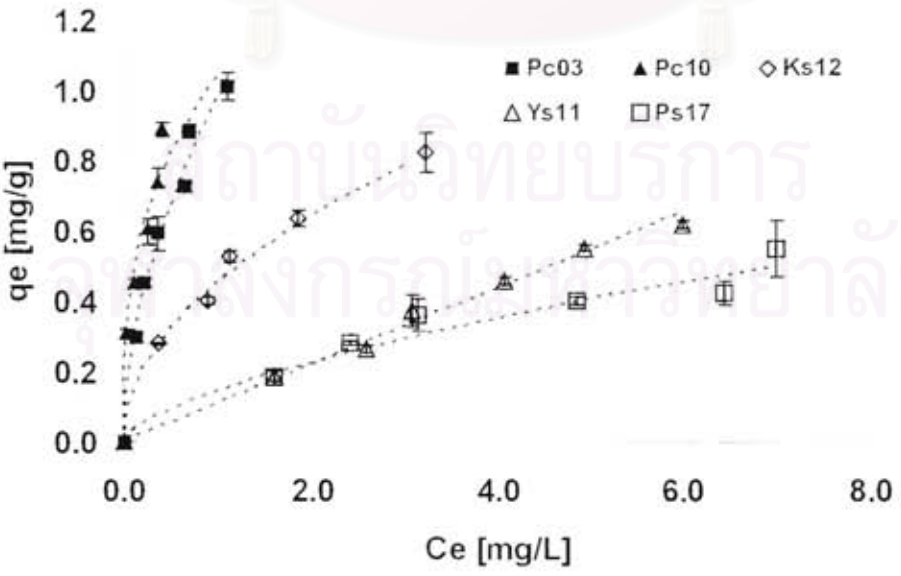


Figure 6.12 Sorption isotherm of norfloxacin to subsurface sediments.

It was anticipated that the amount of aluminum oxide and iron oxide which had positively-charged surface at this pH range played the major role for sorption with the dominant zwitterionic species of norfloxacin. In addition, cationic norfloxacin should sorb to negatively-charged silica. The plots of nalidixic acid and norfloxacin sorption coefficients and AEC are shown in Figure 6.13, Figure 6.14. The correlation coefficient (R^2) of nalidixic (R^2~0.98) to AEC was slightly higher than norfloxacin (R^2~0.95). In addition, the R^2 of norfloxacin to AEC (0.95) and to CEC (0.86) supported the earlier suggestion that the positively-charged mineral surface played a more important role in sorption of the zwitterionic norfloxacin. Furthermore, it was shown that sorption of both nalidixic acid and norfloxacin were more related to alumina oxide than iron oxide.

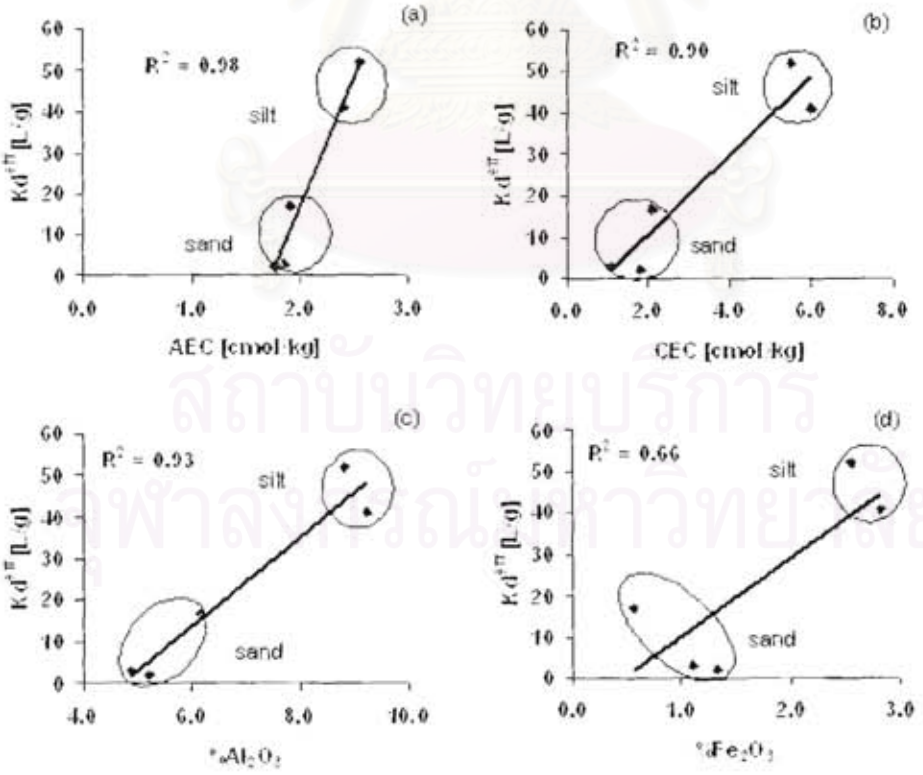


Figure 6.13 The ralationship of AEC, CEC, alumina oxide, iron oxide to the sorption coefficient (at 5 mg/L) of nalidixic acid.

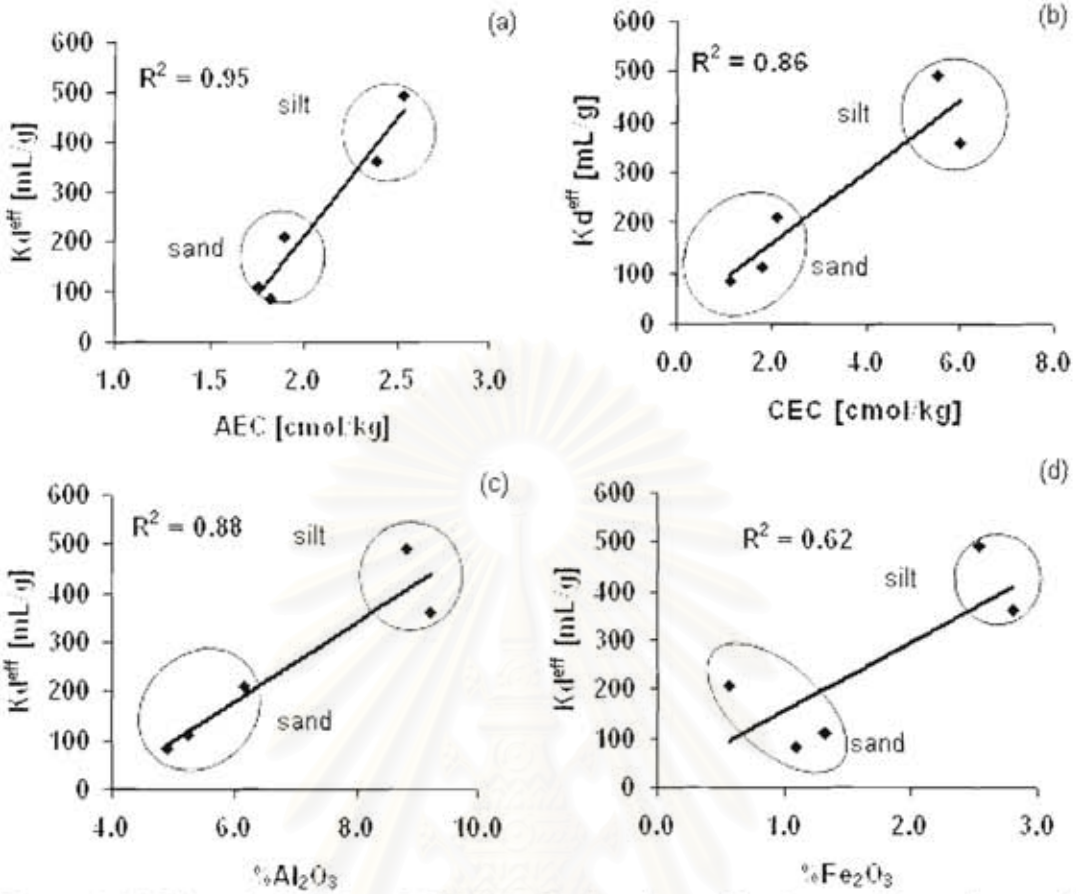


Figure 6.14 The ralationship of AEC, CEC, alumina oxide, iron oxide to the sorption coefficient (at 5 mg/L) of norfloxacin.

Although sorption isotherm of both norfloxacin and nalidixic acid were observed to be nonlinear, the norfloxacin had the greater degree of nonlinearity, with a Freundlich exponent of 0.34-0.63, compare with 0.4-0.84 for nalidixic acid. The nonlinearity of the isotherms likely results from adsorption to heterogeneous sediment surfaces (Weber et al., 1992), and the difference between the nonlinearity of the isotherms was likely due to the difference in the sorption mechanisms which leads to difference sorption affinities for specific surface charge(Hari et al., 2005) . Although norfloxacin is present in cationic, zwitterionic, and uncharged forms at significant fractions at this pH, with the major fraction is zwitterionic form, the bulk of the sorption likely results from charge-charge interactions (Hari et al., 2005) between the zwitterionic forms to both of the positively-charged and negatively-charge surfaces. And cationic forms to negatively-charged surfaces However, it was shown that at this pH (6-7) norfloxacin had affinity approximately two orders of magnitude to positively-charged surface (alumina) higher than to negatively-charged surface (silica) as shown in Figure 4.6.

In contrast, sorption of nalidixic acid at this pH (6-7) is likely the result of adsorption of anionic species (main fraction) to positively-charged surfaces and hydrophobic interactions between the uncharged species (minor fraction) and the organic phases.

Attempting to relate these emerging contaminants (pharmaceuticals in the aqueous environment) to the well known contaminants, this sorption was compared to the pesticide mobility (van Loon and Duffy, 2000) as shown in Figure 6.15. The pharmaceuticals in this study were classified into three different mobility classes (i.e., immobile (K_d > 50 mL/g) , low mobility (K_d between 5 and 50 mL/g) and medium to high mobility (K_d < 5 mL/g). Norfloxacin had the interesting property as being exist in four different forms (cationic at low pH, zwitterionic and uncharged forms at neutral pH and anionic form at high pH), was classified in the same class as immobile pesticides. This agrees with the fact that the major form of norfloxacin at environmentally relevant pH values is zwitterionic, which can have inonic attraction with both positively-charged and negatively-charged sediment surfaces. Moreover, the uncharged form also has the ability to partition into organic matter. Nalidixic acid has both anionic and neutral forms at environmentally pH values. Nalidixic acid shows a wider range of mobility, being classified as immobile in silts and low mobility to sands with high AEC sites and medium mobility to moderately positively-charged surface sands. This wide range of mobility gives complexity in estimation of its fate in the environment. It may result from sorption of nalidixic varies significantly at pH proximity to its pKa (5.9) which was in the experimental pH range as shown in Chapter 4 and 5. 17α-ethynyl estradiol, being highly hydrophobic, was classified as low mobility in silts and medium mobility in all sands. It should be noted that all sands used in this study having low organic carbon contents. However, 17α-ethynyl estradiol still showed significant sorption to these low organic carbon content sediments. Acetaminophen, the least hydrophobic and unionized at this study pH, had the highest mobility and was classified to medium to high mobility as expected.

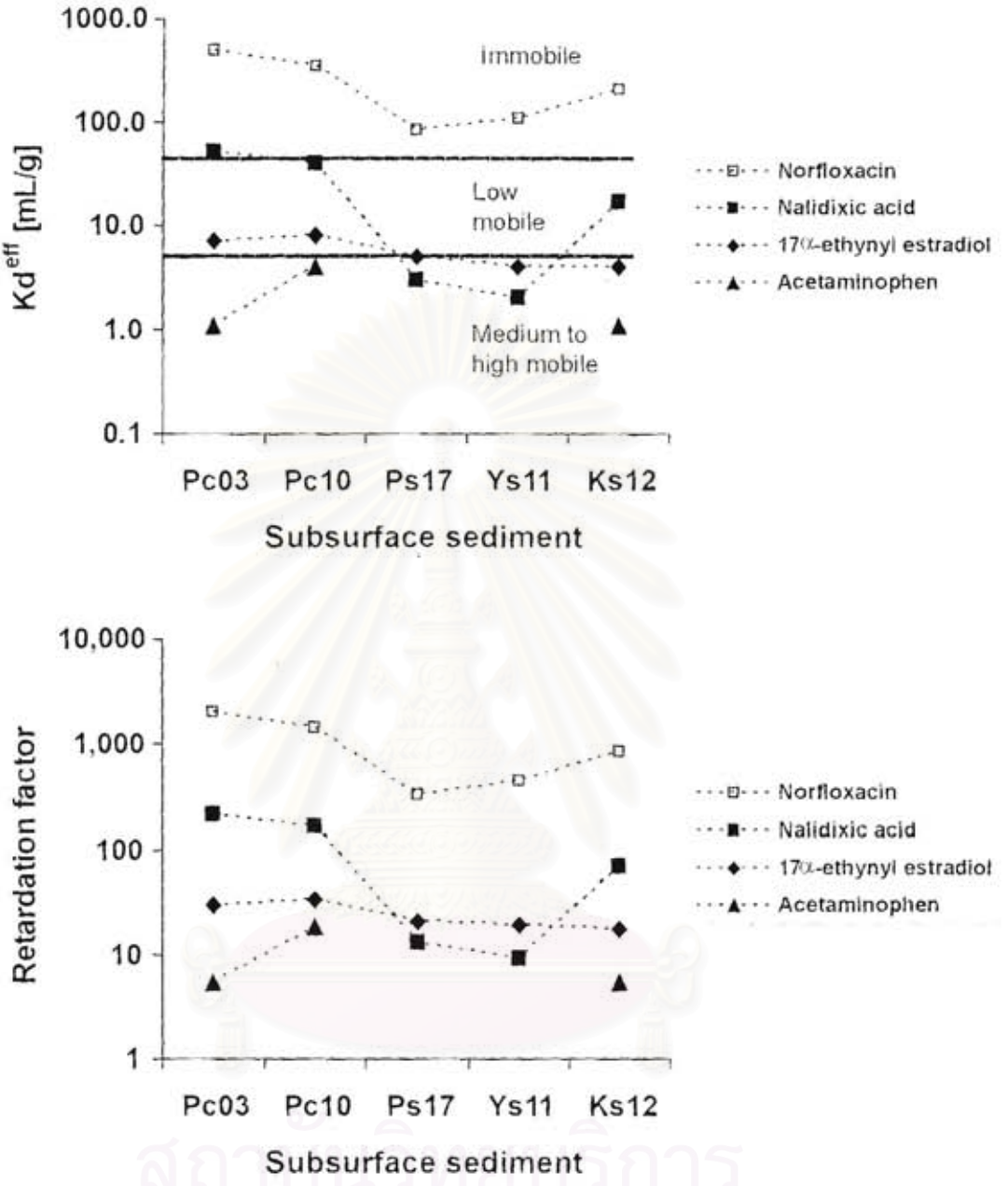


Figure 6.15 Comparison of pharmaceuticals sorption coefficients to the pesticide mobility scale and retardation factor.

To estimate the travel time comparing to the average groundwater flow velocity of these pharmaceutical in the aquifer at this recharge area, the retardation factor, R ($R = 1 + \rho K_d / \theta$) was calculated using the measured K_d^{eff} from different sorption equilibrium concentrations in this study which corresponding to linear isotherms and the measured bulk density of 1.6 g/cm^3 (obtained from Chapter 5) and a porosity of 0.40.

As shown in Table 6.3 and Figure 6.15, the retardation factor of norfloxacin varies from 1441-1977 for silts and 333-833 for sands, the retardation factor of nalidixic acid are 165-209 for silts and 9-69 for sands. It is apparent that the retardation factor of norfloxacin is approximately 10 times greater than the retardation factor of nalidixic acid. This agrees with the earlier study (Hari et al., 2005) with Canadian River Aquifer Sand (CRA), that sorption of norfloxacin is 5 times greater nalidixic acid. The retardation factor of 17α-ethynyl estradiol were 29-33 for silts and 17-21 for sands and the retardation factor of acetaminophen were 5-18 for silts and 1-5 for sands.

It should be mentioned that the pharmaceutical concentrations in environment are several times lower than the concentrations used in this study (Daughton and Ternes, 1999). With the nonlinear sorption behavior of the pharmaceutical in this study, it is concluded that the natural sorption affinity and retardation factor of these pharmaceuticals should be stronger than the sorption affinity in this study. It means that the retardation factors in the environment are greater than values obtain from this study. Hence this study can represent the worst case scenario for prediction of these pharmaceutical existing in groundwater environment.

6.6 Conclusions

In an attempt to understand the sorption characteristics of pharmaceuticals in groundwater system, four pharmaceuticals (i.e., ionizable and nonionizable at neutral pH) were selected to investigate how properties of the sorbents (i.e. AEC), pharmaceuticals (i.e., pKa, hydrophobicity) and aqueous solution (pH) affected the sorption of pharmaceuticals. At neutral pH, the quinolone nalidixic acid and fluoro-quinolone norfloxacin shows strong sorption to silts and sands and were classifed as low and immobile in pesticide mobility scale. Nalidixic acid sorbed strongly to silts and the sands with high anion exchange capacity. The relationship of ionizable nalidixic acid has shown strong relationship with anion exchange capacity which is the parameter corresponding to the abundance of iron oxide and aluminum oxide in these subsurface sediments. While the hydrophobic pharmaceuticals; 17α-ethynyl estradiol was classified as low mobile and acetaminophen had highest mobility in all sediments and classified medium mobile in sands. Although, all sediments used in this study are subsurface sediments which commonly have low organic carbon contents comparing to surface sediments (i.e., river bed sediment), sorption of 17α-ethynyl estradiol still can be observed and less variation among silts and sands.

Comparison between the observed sorption behavior and the hydrophobicity (log K_{ow}) values for three pharmaceuticals (i.e. acetaminophen, nalidixic acid, norfloxcacin) makes it clear that hydrophobicity does not provide the good indicator of the relative sorption of the compounds studied except 17α-ethynyl estradiol which is the neutral and hydrophobic pharmaceutical. Furthermore, to

understand the sorption behavior of ionizable pharmaceuticals to the subsurface sediments the other important factors should be concerned that are pH, ion exchange capacity (AEC, CEC) and PZC of the mineral oxides composing the sediment.

The current risk assessment schemes operate with one single value of K_d (Montforts et al., 1999). However, the majority of reported isotherms are nonlinear such that K_d, decreases with increasing concentration organic compound in the water. Moreover, the organic carbon content should not be the only sediment property considered when assessing the mobility of pharmaceuticals in aquatic environment. Moreover, subsurface sediments usually have low organic content therefore organic carbon normalization only reduced the variation of sorption due to hydrophobic interaction can not explain the variation by the other interactions.

It is important to note that most of sorption isotherms to these pharmaceuticals to subsurface sediments are nonlinear. In addition, the concentrations of pharmaceuticals in aqueous environment are lower than those employed in this study. Therefore, it is likely that K_d values in field sediments are equal or higher than reported in this study. Therefore, the application of what were found in this study, can still apply to estimate the fate and transport of this pharmaceuticals and related organic compounds which have similar properties and sorption behaviors in the worst case scenario prediction of pharmaceuticals existing in groundwater.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Recently, pharmaceutical compounds have been widely detected in surface waters and groundwaters, leading to increased interested in the transport of these compounds in the subsurface environment. Since pharmaceutical compounds have molecular structures in between that of hydrophobic organic compounds (HOCs) and amphiphiles, much needs to be learned about the nature of their interaction with aquifer materials. This research conducted batch sorption and column solute transport studies to pursue the fundamental nature of the interactions of these compounds with pure minerals, hydrophobic medium and subsurface sediments with the goal of better understanding their fate and transport in subsurface environments.

To elucidate the sorption characteristic of pharmaceuticals in groundwater system, two ionizable pharmaceuticals (i.e., nalidixic acid and norfloxacin) and unionizable pharmaceuticals at neutral pH (i.e., acetaminophen and 17α-ethynylestradiol) were selected to investigate how properties of the sorbents (i.e., surface charge), pharmaceuticals (i.e., pKa, hydrophobicity) and aqueous solution affected the sorption of pharmaceuticals. At neutral pH 17α-ethynyl estradiol, strongly sorbed to the hydrophobic medium. Acetaminophen showed little to no sorption sorption to the media. Nalidixic acid and norfloxacin (monoprotic acid and zwitterionic compound) adsorbed strongly to positively-charge surface, with nalidixic acid having the higher sorption capacity. The pH sorption profile of nalidixic acid and

alumina showed maximum sorption at pH near pKa while norfloxacin with alumina showed maximum sorption capacity at pH in the region of norfloxacin's zwitterionic form.

The retardation factor predicted from batch sorption results and from column solute displacement studies were in good agreement. Nonetheless, the prediction of ionizable pharmaceutical such as nalidixic acid under environmental pH relevant should be performed with great precaution because the sorption affinity can significantly vary in small pH range near pKa.

The final part of the research attempt to understand the sorption characteristics of pharmaceuticals to low organic carbon subsurface sediments of three different locations and depths from boreholes in the recharge zone, in the Central of Thailand. This area is classified as vulnerable area to the pollutants due to lack of natural protection and intensive agriculture activities and animal farms. The result of study compared the pharmaceutical sorption affinity to the conventional pollutant mobility (.i.e., pesticide). The overall mobility of pharmaceuticals in subsurface sediments increased from norfloxacin (immobile), nalidixic acid (low mobile-medium mobile), 17α-ethynylestradiol (low mobile), and acetaminophen (medium to high mobile).

Comparison between the observed sorption affinity and the hydrophobicity (log K_{ow}) values for three pharmaceuticals (i.e. acetaminophen, nalidixic acid, norfloxcacin) makes it clear that hydrophobicity does not provide the good indicator of the relative sorption of the compounds studied except 17α-ethynylestradiol which is the neutral and hydrophobic pharmaceutical. Furthermore, to understand the sorption behavior of charged pharmaceuticals to the subsurface

sediments, the other important factors should be concerned that are pH, ion exchange capacity (AEC, CEC).

It is important to note that most of sorption isotherms to these pharmaceuticals to subsurface sediments are nonlinear. In addition, the concentrations of pharmaceuticals in aqueous environment are lower than those employed in this study. Therefore, it is likely that K_d values in field sediments are equal or higher than reported in this study. Therefore, the application of what were found in this study, can still apply to estimate the fate and transport of this pharmaceuticals and related organic compounds which have similar properties and sorption behaviors in the worst case scenario prediction of pharmaceuticals existing in groundwater.

7.2 Recommendations for Future Work

- It is agreed that pharmaceuticals are emerging contaminants. However, currently, there is no survey to explore the environmental existing of the pharmaceuticals in surface water and groundwater in Thailand. Future work should evaluate this aspect.
- The reported concentrations of pharmaceuticals in natural water were generally in microgram per liter except near the source. Therefore, the future research should develop the method to analyze and method of sorption technique as well as analytical technique to overcome the difficulties in the research at this low concentration level.
- The affect of ions existing in the subsurface system should also be studied.
- The geochemical modeling should be explored for modeling fate of the pharmaceuticals.

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APPENDICES

APPENDIX A: BATCH EXPERIMENT DATA

Table A.1 Effect of solution pH on nalidixic acid adsorption by alumina, ratio 0.05g : 25 ml, initial concentration = 10 mg/L.

pH	C_e (mg/L)	Sorbed Conc. (mg/L)	q_e (mg/g)	K_d [L/g]	K_d [L/m^2]
11.0	9.076	0.924	0.178	0.0196	1.26E-04
10.0	9.025	0.975	0.190	0.0211	1.36E-04
9.0	8.418	1.582	0.306	0.0363	2.34E-04
7.9	4.973	5.027	0.989	0.1988	1.28E-03
7.1	1.523	8.477	1.668	1.0953	7.07E-03
5.9	0.492	9.508	1.870	3.7995	2.45E-02
4.9	1.328	8.672	1.722	1.2963	8.36E-03
4.0	3.924	6.076	1.195	0.3046	1.97E-03

Table A.2 Effect of solution pH on nalidixic acid adsorption by alumina, ratio 0.2g : 8 ml, initial concentration = 10 mg/L.

pH	C_e (mg/L)	Sorbed Conc. (mg/L)	q_e (mg/g)	K_d [L/g]	K_d [L/m^2]
2.81	4.189	5.811	0.221	0.0528	1.76E-04
3.53	3.884	6.116	0.222	0.0572	1.91E-04
4.70	4.727	5.273	0.183	0.0388	1.29E-04
5.31	5.650	4.350	0.151	0.0268	8.93E-05
5.83	6.694	3.306	0.126	0.0188	6.27E-05
6.28	7.127	2.873	0.109	0.0154	5.12E-05
6.64	7.408	2.592	0.099	0.0133	4.44E-05
7.08	7.745	2.255	0.082	0.0106	3.53E-05
8.16	8.026	1.974	0.072	0.0089	2.98E-05
9.40	8.186	1.814	0.063	0.0077	2.57E-05
9.80	8.395	1.605	0.056	0.0066	2.22E-05

Table A.3 Effect of solution pH on nalidixic acid adsorption by alumina, ratio 0.02g : 8 ml, initial concentration = 10.26 mg/L.

pH	C_e (mg/L)	Sorbed Conc. (mg/L)	q_e (mg/g)	K_d [L/g]	K_d [L/m^2]
4.2	9.64	0.62	0.214	0.0225	1.4E-04
4.3	9.79	0.47	0.155	0.0159	1.0E-04
4.5	9.71	0.55	0.184	0.0190	1.2E-04
4.5	9.60	0.65	0.239	0.0250	1.6E-04
4.8	8.81	1.45	0.491	0.0558	3.6E-04
4.9	8.50	1.76	0.633	0.0747	4.8E-04
5.0	7.99	2.26	0.803	0.1010	6.5E-04
5.7	3.03	7.23	2.563	0.8539	5.5E-03
6.8	1.15	9.11	3.142	2.7310	1.8E-02
7.4	3.35	6.91	2.377	0.7113	4.6E-03
8.1	5.67	4.58	1.625	0.2867	1.8E-03
8.9	7.87	2.39	0.859	0.1092	7.0E-04
9.3	8.77	1.48	0.543	0.0619	4.0E-04
9.9	9.18	1.08	0.367	0.0407	2.6E-04
10.2	10.03	0.23	0.080	0.0138	8.9E-05
10.4	9.38	0.88	0.318	0.0340	2.2E-04
10.7	9.15	1.11	0.402	0.0440	2.8E-04
11.2	9.38	0.87	0.312	0.0334	2.2E-04
11.5	9.25	1.00	0.336	0.0363	2.3E-04
12.0	9.11	1.15	0.439	0.0483	3.1E-04

Table A.4 Effect of solution pH on nalidixic acid adsorption by alumina, ratio 0.4g : 10 ml, initial concentration = 10 mg/L.

pH	C_e (mg/L)	Sorbed Conc. (mg/L)	q_e (mg/g)	K_d [L/g]	K_d [L/m^2]
2.58	6.41	3.59	0.1419	0.0222	7.38E-05
3.25	5.08	4.92	0.1950	0.0385	1.28E-04
3.74	4.79	5.21	0.2064	0.0441	1.47E-04
5.40	4.74	5.26	0.2069	0.0437	1.46E-04
6.46	4.51	5.49	0.2163	0.0479	1.60E-04
7.08	2.77	7.23	0.2869	0.1039	3.46E-04
7.71	2.32	7.68	0.3027	0.1303	4.34E-04
8.23	2.24	7.76	0.3062	0.1367	4.56E-04
8.69	2.41	7.59	0.2989	0.1241	4.14E-04
9.07	2.94	7.06	0.2797	0.0950	3.17E-04
9.67	4.36	5.64	0.2223	0.0510	1.70E-04
9.78	5.10	4.90	0.1947	0.0382	1.27E-04
9.97	6.07	3.93	0.1563	0.0258	8.60E-05

Table A.5 Norfloxacin adsorption on alumina, ratio 0.01g : 16 ml

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.	Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)		(mg/m2)	
1	0.434	0.425	0.363	0.407	0.039	0.566	0.575	0.637	0.794	0.844	0.926	0.855	0.067	5.52E-03	4.30E-04
2	0.850	0.948	0.567	0.788	0.198	1.150	1.052	1.433	1.769	1.589	2.163	1.840	0.294	1.19E-02	1.90E-03
3	1.364	1.328	1.408	1.367	0.040	1.636	1.672	1.592	2.402	2.410	2.295	2.369	0.064	1.53E-02	4.14E-04
4	1.842	1.957	1.957	1.919	0.066	2.158	2.043	2.043	3.168	2.999	2.945	3.037	0.116	1.96E-02	7.51E-04
5	2.435	2.471	2.657	2.521	0.119	2.565	2.529	2.343	3.664	3.713	3.348	3.575	0.198	2.31E-02	1.28E-03
6	3.277	3.161	3.259	3.232	0.062	2.723	2.839	2.741	4.231	4.285	4.258	4.258	0.027	2.75E-02	1.74E-04
7	3.524	3.826	4.003	3.784	0.242	3.476	3.174	2.997	5.246	4.931	4.524	4.900	0.362	3.16E-02	2.33E-03
8	4.136	4.383	4.304	4.274	0.127	3.864	3.617	3.696	6.062	5.729	5.742	5.844	0.189	3.77E-02	1.22E-03
9	4.977	5.225	4.738	4.980	0.244	4.023	3.775	4.262	6.131	5.542	6.434	6.035	0.454	3.89E-02	2.93E-03

Table A.6 Norfloxacin adsorption on silica, 0.2 g:10 ml

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.	Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)		(mg/m2)	
2.0	0.926	0.978	0.750	0.885	0.120	1.074	1.022	1.250	0.053	0.050	0.061	0.055	0.006	1.83E-04	1.91E-05
4.0	1.808	1.984	1.725	1.839	0.132	2.192	2.016	2.275	0.108	0.100	0.112	0.107	0.006	3.56E-04	2.12E-05
6.0	2.824	2.762	2.917	2.834	0.078	3.176	3.238	3.083	0.157	0.159	0.154	0.157	0.003	5.22E-04	9.66E-06
8.0	4.245	4.255	4.266	4.255	0.010	3.755	3.745	3.734	0.184	0.185	0.185	0.185	0.001	6.16E-04	1.69E-06
10.0	4.981	5.074	4.805	4.953	0.137	5.019	4.926	5.195	0.249	0.245	0.258	0.251	0.007	8.36E-04	2.20E-05

Table A.7 Norfloxacin adsorption on Porapak P, ratio 0.1g:10 ml

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.	Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)		(mg/m2)	
2.0	1.855	1.655	1.781	1.764	0.101	0.145	0.345	0.219	0.014	0.034	0.022	0.023	0.010	1.51E-04	6.48E-05
4.0	3.485	3.306	3.906	3.566	0.308	0.515	0.694	0.094	0.050	0.068	0.009	0.042	0.030	2.74E-04	1.93E-04
6.0	5.389	5.147	5.242	5.259	0.122	0.611	0.853	0.758	0.060	0.084	0.075	0.073	0.012	4.71E-04	7.57E-05
8.0	7.251	7.388	7.251	7.297	0.079	0.749	0.612	0.749	0.074	0.061	0.074	0.070	0.008	4.49E-04	4.86E-05
10.0	9.008	9.439	8.766	9.071	0.341	0.992	0.561	1.234	0.098	0.056	0.123	0.092	0.034	5.94E-04	2.19E-04

Table A.8 Nalidixic acid sorption on As10 , ratio 1.0g: 8 ml, pH6

nitial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
1	0.096	0.065	0.081	0.080	0.016	0.904	0.935	0.919	0.007	0.007	0.0071	0.007	0.0001
2	0.351	0.242	0.250	0.281	0.061	1.649	1.758	1.750	0.012	0.014	0.0134	0.013	0.0010
3	0.494	0.476	0.355	0.442	0.076	2.506	2.524	2.645	0.019	0.020	0.0202	0.020	0.0004
4	0.598	0.831	0.605	0.678	0.133	3.402	3.169	3.395	0.025	0.025	0.0244	0.025	0.0005
5	0.757	0.823	0.791	0.790	0.033	4.243	4.177	4.209	0.031	0.033	0.0317	0.032	0.0013
6	1.276	1.356	1.364	1.332	0.049	4.724	4.644	4.636	0.037	0.036	0.0369	0.037	0.0007
7	1.610	1.574	1.170	1.451	0.244	5.390	5.426	5.830	0.043	0.042	0.0409	0.042	0.0011
8	1.714	1.646	1.792	1.717	0.073	6.286	6.354	6.208	0.044	0.045	0.0490	0.046	0.0027
9	2.137	2.058	1.993	2.063	0.072	6.863	6.942	7.007	0.053	0.053	0.0545	0.054	0.0008
10	2.400	2.381	2.583	2.454	0.111	7.600	7.619	7.417	0.058	0.058	0.0563	0.057	0.0008

Table A.9 Nalidixic acid sorption on As10 . ratio 0.5g: 8 ml, pH4

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
1	0.454	0.403	0.126	0.328	0.177	0.546	0.597	0.874	0.009	0.010	0.014	0.011	0.0028
2	0.948	0.827	0.766	0.847	0.093	1.052	1.173	1.234	0.017	0.019	0.020	0.018	0.0016
3	1.502	1.571	1.355	1.476	0.111	1.498	1.429	1.645	0.023	0.022	0.026	0.024	0.0019
4	2.030	1.978	1.684	1.897	0.187	1.970	2.022	2.316	0.031	0.032	0.037	0.033	0.0029
5	2.506	2.342	2.437	2.428	0.083	2.494	2.658	2.563	0.039	0.041	0.040	0.040	0.0013
6	3.216	3.051	2.740	3.002	0.242	2.784	2.949	3.260	0.044	0.046	0.052	0.047	0.0044
8	3.848	4.004	4.350	4.067	0.257	4.152	3.996	3.650	0.065	0.062	0.058	0.062	0.0035
9	4.636	4.436	4.497	4.523	0.102	4.364	4.564	4.503	0.068	0.072	0.070	0.070	0.0018
10	5.363	4.835	4.887	5.028	0.291	4.637	5.165	5.113	0.074	0.082	0.081	0.079	0.0045

Table A.10 Nalidixic acid sorption on As10 , ratio 0.5g: 8 ml, pH4

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
1	1.071	1.022	0.745	0.946	0.176	-0.071	-0.022	0.255	-0.001	0.000	0.004	0.001	0.0028
2	1.918	1.991	1.877	1.929	0.058	0.082	0.009	0.123	0.001	0.000	0.002	0.001	0.0009
3	2.968	2.919	2.805	2.898	0.084	0.032	0.081	0.195	0.001	0.001	0.003	0.002	0.0013
4	3.888	3.888	3.888	3.888	0.000	0.112	0.112	0.112	0.002	0.002	0.002	0.002	0.0000
5	4.833	4.833	4.865	4.844	0.019	0.167	0.167	0.135	0.003	0.003	0.002	0.002	0.0003
6	5.794	5.826	5.729	5.783	0.050	0.206	0.174	0.271	0.003	0.003	0.004	0.003	0.0008
7	6.885	6.844	6.795	6.841	0.045	0.115	0.156	0.205	0.002	0.002	0.003	0.002	0.0007
8	7.781	8.000	7.935	7.905	0.113	0.219	0.000	0.065	0.003	0.000	0.001	0.001	0.0017
9	9.108	9.059	8.986	9.051	0.061	-0.108	-0.059	0.014	-0.002	-0.001	0.000	-0.001	0.0010
10	10.183	10.215	10.069	10.156	0.077	-0.183	-0.215	-0.069	-0.003	-0.003	-0.001	-0.002	0.0012

Table A.11 Effect of solution pH on nalidixic adsorption on As10 sand, ratio 0.5g : 8ml, initial concentration 10 mg/L

pH	C_e (mg/L)	Sorbed Conc. (mg/L)	q_e (mg/g)	K_d [L/g]	K_d [L/m^2]
4.0	6.285	3.715	0.059	0.0093	6.85E-03
4.0	5.833	4.167	0.066	0.0113	8.34E-03
4.3	4.717	5.283	0.084	0.0178	1.31E-02
4.3	4.529	5.471	0.086	0.0190	1.40E-02
4.5	3.251	6.749	0.105	0.0324	2.39E-02
4.9	2.808	7.192	0.083	0.0402	2.96E-02
5.0	2.177	7.823	0.124	0.0569	4.19E-02
5.0	2.109	7.891	0.126	0.0595	4.38E-02
5.1	2.001	7.999	0.093	0.0632	4.65E-02
5.2	1.623	8.377	0.130	0.0802	5.90E-02
5.2	1.867	8.133	0.094	0.0686	5.05E-02
5.4	1.505	8.495	0.099	0.0896	6.59E-02
5.7	1.244	8.756	0.103	0.1121	8.24E-02
5.7	1.345	8.655	0.101	0.1023	7.52E-02
6.0	1.547	8.453	0.099	0.0871	6.40E-02
6.0	1.539	8.461	0.099	0.0875	6.43E-02
6.0	1.219	8.781	0.103	0.1145	8.42E-02
6.1	5.543	4.457	0.070	0.0127	9.33E-03
6.1	3.727	6.273	0.099	0.0265	1.95E-02
6.1	4.138	5.862	0.092	0.0221	1.63E-02
6.1	1.413	8.587	0.101	0.0969	7.12E-02
6.2	1.959	8.041	0.093	0.0648	4.76E-02
6.2	2.094	7.906	0.091	0.0594	4.36E-02
6.2	1.942	8.058	0.093	0.0653	4.80E-02
6.4	7.111	2.889	0.046	0.0065	4.75E-03
6.6	7.679	2.321	0.037	0.0048	3.51E-03
6.6	7.777	2.223	0.035	0.0045	3.30E-03
6.6	7.265	2.735	0.042	0.0058	4.26E-03
6.7	8.126	1.874	0.029	0.0036	2.61E-03
6.8	8.370	1.630	0.026	0.0031	2.27E-03
6.8	8.646	1.354	0.021	0.0025	1.82E-03
6.9	8.410	1.590	0.025	0.0030	2.18E-03
7.0	8.508	1.492	0.024	0.0028	2.06E-03
7.0	8.865	1.135	0.018	0.0020	1.47E-03
7.3	9.141	0.859	0.013	0.0015	1.08E-03
7.5	9.198	0.802	0.013	0.0014	1.01E-03
7.5	9.344	0.656	0.010	0.0011	8.03E-04
7.8	9.271	0.729	0.012	0.0012	9.17E-04
7.8	9.458	0.542	0.008	0.0009	6.59E-04
7.8	9.483	0.517	0.008	0.0009	6.33E-04
8.0	9.564	0.436	0.007	0.0007	5.28E-04
8.2	9.539	0.461	0.007	0.0008	5.66E-04
8.3	9.539	0.461	0.007	0.0008	5.60E-04

Table A.11 (Continued)

8.5	9.840	0.160	0.003	0.0003	1.89E-04
8.5	9.913	0.087	0.001	0.0001	1.02E-04
8.5	9.816	0.184	0.003	0.0003	2.16E-04
8.7	9.978	0.022	0.000	0.0000	2.51E-05
8.8	9.954	0.046	0.001	0.0001	5.40E-05
8.8	10.011	-0.011	0.000	0.0000	-1.22E-05

Table A.12 Acetaminophen adsorption on As10 sand, ratio 3g:10ml

Initial Conc (mg/L)	C_{eq} no.1	C_{eq} no.2	C_{eq} no.3	Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L) no.1	Ads. Conc. (mg/L) no.2	Ads. Conc. (mg/L) no.3	q (mg/g) no.1	q (mg/g) no.2	q (mg/g) no.3	Ave. q (mg/g)	Stdev.
2	1.687	1.639	1.703	1.676	0.034	0.31	0.36	0.30	0.001	0.001	0.001	0.0011	0.0001
4	3.736	3.655	3.720	3.704	0.043	0.26	0.34	0.28	0.001	0.001	0.001	0.0010	0.0001
6	5.882	5.785	5.688	5.785	0.097	0.12	0.22	0.31	0.000	0.001	0.001	0.0007	0.0003
8	7.818	7.802	8.060	7.893	0.145	0.18	0.20	-0.06	0.001	0.001	0.000	0.0006	0.0005
10	9.786	9.818	9.834	9.813	0.025	0.21	0.18	0.17	0.001	0.001	0.001	0.0006	0.0001

Table A.13 Nalidixic acid adsorption on As10 sand, ratio 1.0g: 8ml, pH6

Initial Conc (mg/L)	C_{eq} no.1	C_{eq} no.2	C_{eq} no.3	Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L) no.1	Ads. Conc. (mg/L) no.2	Ads. Conc. (mg/L) no.3	q (mg/g) no.1	q (mg/g) no.2	q (mg/g) no.3	Ave. q (mg/g)	Stdev.
1	0.096	0.065	0.081	0.080	0.016	0.904	0.935	0.919	0.007	0.007	0.0071	0.007	0.0001
2	0.351	0.242	0.250	0.281	0.061	1.649	1.758	1.750	0.012	0.014	0.0134	0.013	0.0010
3	0.494	0.476	0.355	0.442	0.076	2.506	2.524	2.645	0.019	0.020	0.0202	0.020	0.0004
4	0.598	0.831	0.605	0.678	0.133	3.402	3.169	3.395	0.025	0.025	0.0244	0.025	0.0005
5	0.757	0.823	0.791	0.790	0.033	4.243	4.177	4.209	0.031	0.033	0.0317	0.032	0.0013
6	1.276	1.356	1.364	1.332	0.049	4.724	4.644	4.636	0.037	0.036	0.0369	0.037	0.0007
7	1.610	1.574	1.170	1.451	0.244	5.390	5.426	5.830	0.043	0.042	0.0409	0.042	0.0011
8	1.714	1.646	1.792	1.717	0.073	6.286	6.354	6.208	0.049	0.045	0.0490	0.048	0.0026
9	2.137	2.058	1.993	2.063	0.072	6.863	6.942	7.007	0.053	0.053	0.0545	0.054	0.0008
10	2.400	2.381	2.583	2.454	0.111	7.600	7.619	7.417	0.059	0.058	0.0563	0.058	0.0012

Table A.14 17α-ethynylestradiol adsorption on As10 sand, ratio 3.0g: 8ml

Initial Conc	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.203	0.454	0.855	0.504	0.329	1.80	1.55	1.15	0.006	0.005	0.004	0.0050	0.0011
4	0.793	1.379	1.449	1.207	0.360	3.21	2.62	2.55	0.011	0.009	0.008	0.0093	0.0012
6	2.040	2.460	2.814	2.438	0.388	3.96	3.54	3.19	0.013	0.012	0.011	0.0119	0.0013
8	3.382	3.557	4.054	3.664	0.349	4.62	4.44	3.95	0.015	0.015	0.013	0.0144	0.0012
10	5.138	5.712		5.425	0.406	4.86	4.29		0.016	0.014		0.0152	0.0013

Table A.15 17α -ethynylestradiol adsorption on Pc03 clay, ratio 3.5 g : 10 ml, pH 6.9 ± 0.1

Initial Conc	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
7	1.491	1.834	1.156	1.494	0.339	5.509	5.166	5.844	0.015	0.014	0.0156	0.015	0.0009
8	1.746	1.547	2.563	1.952	0.538	6.254	6.453	5.437	0.017	0.014	0.0172	0.016	0.0014
10	2.153	2.679	1.783	2.205	0.450	7.847	7.321	8.217	0.021	0.020	0.0219	0.021	0.0012
12	2.924	2.776	3.288	2.996	0.264	9.076	9.224	8.712	0.024	0.023	0.0246	0.024	0.0007
14	3.811	4.213	3.935	3.986	0.206	10.189	9.787	10.065	0.027	0.026	0.0268	0.027	0.0005

Table A.16 17α -ethynyl estradiol adsorption on Pc10 clay, ratio 3.5 g : 10 ml, pH 6.5 ± 0.1

Initial Conc	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
6	1.855	1.689	2.453	1.999	0.402	4.145	4.311	3.547	0.011	0.009	0.011	0.011	0.0011
7	2.209	1.803	2.300	2.104	0.265	4.791	5.197	4.700	0.013	0.014	0.013	0.013	0.0007
8	3.026	2.800	3.411	3.079	0.309	4.974	5.200	4.589	0.013	0.014	0.012	0.013	0.0008
10	3.095	3.443	2.840	3.126	0.303	6.905	6.557	7.160	0.018	0.017	0.019	0.018	0.0008
12	4.337	3.827	4.897	4.354	0.535	7.663	8.173	7.103	0.020	0.019	0.022	0.020	0.0014
14	5.178	5.644	4.854	5.225	0.397	8.822	8.356	9.146	0.023	0.022	0.024	0.023	0.0011

Table A.17 17α -ethynylestradiol adsorption on Ps17 sand, ratio 3.5 g : 10 ml, pH 7.1 ± 0.1

Initial Conc	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
6	1.855	1.689	2.453	1.999	0.402	4.145	4.311	3.547	0.011	0.009	0.011	0.011	0.0011
7	2.209	1.803	2.300	2.104	0.265	4.791	5.197	4.700	0.013	0.014	0.013	0.013	0.0007
8	3.026	2.800	3.411	3.079	0.309	4.974	5.200	4.589	0.013	0.014	0.012	0.013	0.0008
10	3.095	3.443	2.840	3.126	0.303	6.905	6.557	7.160	0.018	0.017	0.019	0.018	0.0008
12	4.337	3.827	4.897	4.354	0.535	7.663	8.173	7.103	0.020	0.019	0.022	0.020	0.0014
14	5.178	5.644	4.854	5.225	0.397	8.822	8.356	9.146	0.023	0.022	0.024	0.023	0.0011

Table A.18 17α -ethynylestradiol adsorption on Ys11 sand, ratio 3.5 g : 10 ml, pH 7.3 ± 0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
10	3.398	3.705	2.988	3.364	0.360	6.602	6.295	7.012	0.018	0.017	0.019	0.018	0.0010
12	4.151	3.653	4.553	4.119	0.451	7.849	8.347	7.447	0.021	0.022	0.020	0.021	0.0012
14	4.931	4.469	5.522	4.974	0.528	9.069	9.531	8.478	0.024	0.025	0.023	0.024	0.0014

Table A.19 17α -ethynylestradiol adsorption on Ks12 sand, ratio 3.5 g : 10 ml, pH 6.9 ± 0.1

Initial Conc	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
7	2.221	2.656	1.872	2.250	0.393	4.779	4.344	5.128	0.0127	0.0116	0.0137	0.013	0.0010
8	2.816	2.750	3.013	2.860	0.137	5.184	5.250	4.987	0.0138	0.0140	0.0133	0.014	0.0004
10	3.645	3.367	3.811	3.608	0.224	6.355	6.633	6.189	0.0169	0.0177	0.0165	0.017	0.0006
12	4.888	5.387	4.442	4.906	0.473	7.112	6.613	7.558	0.0190	0.0176	0.0202	0.019	0.0013
14	5.684	5.121	5.890	5.565	0.398	8.316	8.879	8.110	0.0222	0.0237	0.0216	0.022	0.0011

Table A.20 Acetaminophen adsorption on Pc03 clay, ratio 3.0g : 8 ml, pH 6.6±0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.795	0.938	0.573	0.769	0.184	1.205	1.062	1.427	0.003	0.003	0.0038	0.003	0.0005
4	1.288	1.362	1.472	1.374	0.092	2.712	2.638	2.528	0.007	0.007	0.0067	0.007	0.0002
6	1.924	2.258	2.338	2.173	0.219	4.076	3.742	3.662	0.011	0.010	0.0098	0.010	0.0006
8	2.942	2.876	2.723	2.847	0.113	5.058	5.124	5.277	0.013	0.014	0.0141	0.014	0.0003
10	4.135	3.915	4.353	4.135	0.219	5.865	6.085	5.647	0.016	0.016	0.0150	0.016	0.0006

Table A.21 Acetaminophen adsorption on Pc10 clay, ratio 3.0g : 8 ml, pH 6.2±0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.199	0.411	0.213	0.274	0.119	1.801	1.589	1.787	0.005	0.004	0.005	0.005	0.0003
4	1.255	1.198	1.467	1.307	0.142	2.745	2.802	2.533	0.007	0.007	0.007	0.007	0.0004
6	1.439	1.789	1.488	1.572	0.190	4.561	4.211	4.512	0.012	0.011	0.012	0.012	0.0005
8	1.883	1.657	2.098	1.879	0.221	6.117	6.343	5.902	0.016	0.017	0.016	0.016	0.0006
10	2.603	2.992	2.750	2.782	0.197	7.397	7.008	7.250	0.020	0.019	0.019	0.019	0.0005

Table A.22 Acetaminophen adsorption on Ps17 sand, ratio 3.0g : 8 ml, pH 7.3±0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	1.399	0.859	1.225	1.161	0.276	0.601	1.141	0.775	0.002	0.003	0.002	0.002	0.0007
4	3.276	3.445	3.546	3.422	0.136	0.724	0.555	0.454	0.002	0.001	0.001	0.002	0.0004
6	4.532	4.723	4.657	4.638	0.097	1.468	1.277	1.343	0.004	0.003	0.004	0.004	0.0003
8	5.646	5.434	5.556	5.545	0.106	2.354	2.566	2.444	0.006	0.007	0.007	0.007	0.0003
10	8.906	9.248	8.747	8.967	0.256	1.094	0.752	1.253	0.003	0.002	0.003	0.003	0.0007

Table A.23 Acetaminophen adsorption on Ys11 sand, ratio 3.0g : 8 ml, pH 7.2±0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	1.960	1.809	1.876	1.882	0.075	0.040	0.191	0.124	0.000	0.000	0.000	0.000	0.0000
4	4.103	4.205	4.252	4.187	0.076	-0.103	-0.205	-0.252	0.000	0.000	0.000	0.000	0.0000
6	6.215	6.137	6.386	6.246	0.127	-0.215	-0.137	-0.386	-0.001	-0.001	-0.001	-0.001	0.0000
8	8.359	8.069	8.226	8.218	0.145	-0.359	-0.069	-0.226	-0.001	-0.001	-0.001	-0.001	0.0000
10	10.395	8.827	11.082	10.101	1.156	-0.395	1.173	-1.082	-0.001	-0.001	-0.001	-0.001	0.0000

Table A.24 Acetaminophen adsorption on Ks12 sand, ratio 3.0g : 8 ml, pH 7.3±0.2

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	1.320	1.288	1.413	1.340	0.065	0.680	0.712	0.587	0.0018	0.0019	0.0016	0.002	0.0002
4	2.449	2.213	2.348	2.337	0.118	1.551	1.787	1.652	0.0041	0.0048	0.0044	0.004	0.0003
6	3.960	4.018	3.721	3.900	0.157	2.040	1.982	2.279	0.0054	0.0053	0.0061	0.006	0.0004
8	5.948	5.884	5.627	5.820	0.170	2.052	2.116	2.373	0.0054	0.0056	0.0063	0.006	0.0005
10	6.997	7.268	7.363	7.209	0.190	3.003	2.732	2.637	0.0080	0.0073	0.0070	0.007	0.0005

Table A.25 Nalidixic acid adsorption on Pc03 clay, ratio 0.05 g : 8 ml, pH 6.8 ± 0.3

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	1.389	1.189	1.605	1.394	0.208	0.611	0.811	0.395	0.003	0.003	0.0038	0.003	0.0005
4	2.916	2.796	2.796	2.836	0.069	1.084	1.204	1.204	0.007	0.007	0.0067	0.007	0.0002
6	4.596	4.692	4.484	4.590	0.104	1.404	1.308	1.516	0.011	0.010	0.0098	0.010	0.0006
8	6.075	6.235	6.019	6.110	0.112	1.925	1.765	1.981	0.013	0.014	0.0141	0.014	0.0003
10	7.395	7.507	7.539	7.480	0.076	2.605	2.493	2.461	0.016	0.016	0.0150	0.016	0.0006

Table A.26 Nalidixic acid adsorption on Pc10 clay, ratio 0.05g : 8 ml, pH 6.6 ± 0.2

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	1.261	1.053	1.293	1.202	0.130	0.739	0.947	0.707	0.114	0.149	0.113	0.125	0.0203
4	3.404	2.757	2.917	3.026	0.337	0.596	1.243	1.083	0.092	0.195	0.167	0.151	0.0534
6	4.564	4.724	4.620	4.636	0.081	1.436	1.276	1.380	0.217	0.186	0.212	0.205	0.0168
8	6.763	6.660	6.564	6.662	0.100	1.237	1.340	1.436	0.190	0.210	0.221	0.207	0.0156
10	8.219	8.427	7.771	8.139	0.335	1.781	1.573	2.229	0.259	0.247	0.350	0.285	0.0562

Table A.27 Nalidixic acid adsorption on Ps17 sand, ratio 0.05 g : 8 ml, pH 6.6 ± 0.5

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.661	0.773	0.813	0.749	0.079	1.339	1.227	1.187	0.004	0.003	0.003	0.003	0.0002
4	1.533	1.589	1.549	1.557	0.029	2.467	2.411	2.451	0.007	0.006	0.006	0.006	0.0001
6	2.324	2.660	2.332	2.439	0.192	3.676	3.340	3.668	0.010	0.009	0.010	0.009	0.0005
8	3.580	3.332	3.460	3.457	0.124	4.420	4.668	4.540	0.012	0.012	0.012	0.012	0.0003
10	4.436	4.084	4.628	4.382	0.276	5.564	5.916	5.372	0.015	0.016	0.014	0.015	0.0007

Table A.28 Nalidixic acid adsorption on Ys11 sand, ratio 0.05 g : 8 ml, pH 7.1 ± 0.4

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.845	0.869	0.949	0.888	0.054	1.155	1.131	1.051	0.003	0.003	0.003	0.003	0.0002
4	2.181	2.173	2.228	2.194	0.030	1.819	1.827	1.772	0.005	0.005	0.005	0.005	0.0001
6	3.628	3.540	3.332	3.500	0.152	2.372	2.460	2.668	0.006	0.006	0.007	0.007	0.0004
8	5.067	5.155	4.907	5.043	0.126	2.933	2.845	3.093	0.008	0.008	0.008	0.008	0.0003
10	6.395	6.331	5.963	6.230	0.233	3.605	3.669	4.037	0.010	0.010	0.011	0.010	0.0006

Table A.29 Nalidixic acid adsorption on Ks12 sand, ratio 3.0g : 8 ml, pH 7.0 ± 0.4

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
2	0.216	0.224	0.320	0.253	0.058	1.784	1.776	1.680	0.0285	0.0284	0.0268	0.028	0.0009
4	1.112	1.104	1.112	1.109	0.005	2.888	2.896	2.888	0.0461	0.0460	0.0460	0.046	0.0001
6	2.407	2.111	2.111	2.210	0.171	3.593	3.889	3.889	0.0571	0.0616	0.0620	0.060	0.0027
8	3.167	3.759	3.671	3.532	0.319	4.833	4.241	4.329	0.0767	0.0675	0.0689	0.071	0.0050
10	4.054	4.062	4.582	4.233	0.302	5.946	5.938	5.418	0.0946	0.0948	0.0863	0.092	0.0048

Table A.30 Norfloxacin adsorption on Pc03 clay, ratio 0.1 g : 8 ml, pH 6.1 ± 0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
4	0.124	0.143	0.133	0.133	0.010	3.876	3.857	3.867	0.291	0.298	0.298	0.296	0.004
6	0.219	0.238	0.190	0.216	0.024	5.781	5.762	5.810	0.456	0.452	0.448	0.452	0.004
8	0.362	0.371	0.390	0.374	0.015	7.638	7.629	7.610	0.571	0.607	0.597	0.592	0.018
10	0.657	0.676	0.628	0.654	0.024	9.343	9.324	9.372	0.719	0.728	0.723	0.723	0.004
12	0.714	0.695	0.657	0.689	0.029	11.286	11.305	11.343	0.879	0.875	0.895	0.883	0.011
14	0.866	1.371	1.076	1.104	0.253	13.134	12.629	12.924	1.025	0.972	1.027	1.008	0.031

Table A.31 Norfloxacin adsorption on Pc10 clay, ratio 0.1g : 8 ml, pH 6.2 ± 0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
4	0.019	0.02856	0.03807	0.029	0.010	3.981	3.971	3.962	0.314	0.307	0.311	0.311	0.004
6	0.105	0.16182	0.08567	0.117	0.040	5.895	5.838	5.914	0.445	0.468	0.456	0.456	0.011
8	0.219	0.30460	0.25700	0.260	0.043	7.781	7.695	7.743	0.587	0.613	0.599	0.600	0.013
10	0.371	0.42834	0.30460	0.368	0.062	9.629	9.572	9.695	0.744	0.757	0.744	0.748	0.008
12	0.400	0.38074	0.42834	0.403	0.024	11.600	11.619	11.572	0.890	0.893	0.891	0.891	0.002
14	1.076	1.21838	1.00897	1.101	0.107	12.924	12.782	12.991	1.001	1.025	1.015	1.013	0.012

Table A.32 Norfloxacin adsorption on Ps17 sand, ratio 0.1 g : 8 ml, pH 6.6 ± 0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
4	1.409	1.599	1.799	1.602	0.195	2.591	2.401	2.201	0.185	0.184	0.173	0.181	0.006
6	2.627	2.437	2.199	2.421	0.215	3.373	3.563	3.801	0.266	0.275	0.299	0.280	0.017
8	3.141	3.474	2.837	3.151	0.319	4.859	4.526	5.163	0.374	0.317	0.394	0.362	0.040
10	4.550	5.131	4.893	4.858	0.292	5.450	4.869	5.107	0.423	0.385	0.400	0.403	0.019
12	6.406	6.358	6.558	6.441	0.104	5.594	5.642	5.442	0.429	0.409	0.421	0.419	0.010
14	6.615	6.549	7.881	7.015	0.751	7.385	7.451	6.119	0.568	0.514	0.468	0.517	0.050

Table A.33 Norfloxacin adsorption on Ys11 sand, ratio 0.1 g : 8 ml, pH 7.0 ± 0.1

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
4	1.599	1.399	1.809	1.602	0.205	2.401	2.601	2.191	0.201	0.171	0.183	0.185	0.015
6	2.580	2.770	2.389	2.580	0.190	3.420	3.230	3.611	0.254	0.275	0.263	0.264	0.011
8	3.094	3.227	2.941	3.087	0.143	4.906	4.773	5.059	0.369	0.394	0.370	0.378	0.014
10	4.293	3.798	4.131	4.074	0.252	5.707	6.202	5.869	0.483	0.463	0.463	0.470	0.011
12	5.416	4.950	4.464	4.943	0.476	6.584	7.050	7.536	0.554	0.591	0.552	0.566	0.022
14	5.997	5.797	6.187	5.994	0.195	8.003	8.203	7.813	0.627	0.602	0.617	0.615	0.013

Table A.34 Norfloxacin adsorption on Ks12 sand, ratio 0.1g : 8 ml, pH 6.5 ± 0.2

Initial Conc.	C_{eq}			Ave. (C_{eq})	Stdev	Ads. Conc. (mg/L)			q (mg/g)			Ave. q	Stdev.
(mg/L)	no.1	no.2	no.3			no.1	no.2	no.3	no.1	no.2	no.3	(mg/g)	
4	0.362	0.276	0.447	0.362	0.086	3.638	3.724	3.553	0.2769	0.2841	0.2716	0.278	0.006
6	0.714	1.085	0.885	0.895	0.186	5.286	4.915	5.115	0.4137	0.3804	0.4047	0.400	0.017
8	1.190	1.114	1.038	1.114	0.076	6.810	6.886	6.962	0.5219	0.5168	0.5373	0.525	0.011
10	1.856	1.552	2.161	1.856	0.305	8.144	8.448	7.839	0.6258	0.6661	0.6153	0.636	0.027
14	3.236	3.493	2.970	3.233	0.262	10.764	10.507	11.030	0.7980	0.8236	0.8465	0.823	0.024

APPENDIX B: COLUMN EXPERIMENT DATA

Table B.1 Acetaminophen transport through silica column, initial concentration 10 mg/l, pH 6

Sample#	Time (min)	Pore Volume	Conc. (mg/l)	C/C0
1	34.90	0.49	0.02	0.00
2	39.90	0.61	0.23	0.02
3	44.92	0.74	1.11	0.11
4	49.92	0.86	2.71	0.27
5	54.93	0.99	4.61	0.46
6	59.93	1.11	6.37	0.63
7	64.93	1.24	7.75	0.77
8	69.95	1.36	8.73	0.87
9	74.95	1.49	9.31	0.93
10	79.97	1.61	9.59	0.95
11	84.97	1.74	9.71	0.97
12	89.98	1.86	9.77	0.97
13	94.98	1.99	9.82	0.98
14	99.98	2.11	9.83	0.98
15	105.00	2.24	9.86	0.98
16	110.00	2.36	9.87	0.98
17	115.02	2.49	9.87	0.98
18	120.02	2.61	9.93	0.99
19	125.02	2.74	9.87	0.98
20	130.02	2.86	9.86	0.98
21	135.03	2.99	9.86	0.98
22	140.05	3.11	9.86	0.98
23	145.05	3.24	9.87	0.98
24	150.07	3.36	9.85	0.98
25	155.07	3.49	9.77	0.97
26	160.07	3.61	9.68	0.96
27	162.58	3.67	9.52	0.95
28	165.08	3.74	9.18	0.91
29	170.08	3.86	7.75	0.77
30	175.10	3.99	5.70	0.57
31	180.10	4.11	3.61	0.36
32	182.60	4.17	2.73	0.27
33	183.43	4.19	2.48	0.25
34	190.12	4.36	1.00	0.10
35	195.12	4.48	0.49	0.05

Table B.1 (Continued)

36	200.13	4.61	0.24	0.02
37	205.13	4.73	0.12	0.01
38	210.15	4.86	0.06	0.01
39	215.15	4.98	0.03	0.00
40	220.17	5.11	0.00	0.00
41	225.17	5.23	-0.01	0.00
42	230.17	5.36	-0.02	0.00
43	235.18	5.48	0.02	0.00
44	240.18	5.61	-0.01	0.00

Table B.2 Acetaminophen transport through alumina column, initial concentration 10 mg/l, pH 6

Sample #	Time (min)	Pore Volume	Conc. (mg/l)	C/Co
1	50.75	0.69	0.00	0.00
2	52.10	0.72	0.01	0.00
3	53.77	0.76	0.02	0.00
4	55.43	0.80	0.08	0.01
5	57.10	0.83	0.24	0.02
6	58.77	0.87	0.61	0.06
7	60.43	0.91	1.22	0.12
8	62.10	0.94	2.14	0.21
9	63.78	0.98	3.31	0.33
10	65.45	1.02	4.57	0.46
11	67.12	1.05	5.78	0.58
12	68.78	1.09	6.80	0.68
13	70.45	1.13	7.64	0.76
14	72.12	1.16	8.23	0.82
15	75.47	1.24	8.99	0.90
16	78.80	1.31	9.35	0.93
17	85.47	1.45	9.64	0.96
18	92.15	1.60	9.75	0.97
19	98.83	1.75	9.80	0.98
20	108.83	1.97	9.87	0.99
21	115.52	2.11	9.88	0.99
22	122.20	2.26	9.91	0.99
23	128.87	2.41	9.91	0.99
24	135.55	2.55	9.93	0.99
25	142.22	2.70	9.93	0.99
26	148.90	2.85	9.92	0.99
27	155.57	2.99	9.88	0.99
28	162.25	3.14	7.85	0.99
29	168.93	3.28	3.14	0.99
30	175.60	3.43	0.96	0.99
31	182.28	3.58	0.43	0.99
32	188.95	3.72	0.27	0.99
33	195.63	3.87	0.19	0.95
34	197.30	3.91	0.18	0.89
35	198.97	3.94	0.17	0.81
36	200.63	3.98	0.16	0.69
37	202.32	4.02	0.15	0.57
38	203.98	4.05	0.14	0.44

Table B.2 (Continued)

39	205.65	4.09	0.13	0.33
40	207.32	4.13	0.12	0.25
41	208.98	4.16	0.11	0.18
42	212.32	4.24	0.11	0.10
43	215.67	4.31	0.10	0.06
44	219.00	4.38	0.09	0.04
45	222.33	4.46	0.09	0.03
46	225.68	4.53	0.08	0.03
47	229.02	4.60	0.08	0.02
48	232.35	4.67	0.07	0.02
49	235.68	4.75	0.07	0.02
50	239.03	4.82	0.06	0.01
51	242.37	4.89	0.07	0.01
52	245.70	4.97	0.06	0.01
53	247.37	5.00	0.06	0.01

Table B.3 Acetaminophen transport through As10 sand column, initial concentration 10 mg/l, pH 6

Sample#	Time (min)	Pore Volume	Conc. (mg/l)	C/C0
1	0.13	0.01	0.00	0.00
2	1.13	0.06	0.00	0.00
3	4.47	0.24	0.06	0.01
4	7.80	0.43	0.06	0.01
5	11.13	0.61	0.17	0.02
6	12.80	0.70	0.57	0.06
7	14.48	0.79	1.43	0.14
8	16.15	0.88	2.73	0.27
9	17.82	0.97	4.44	0.44
10	19.50	1.07	6.16	0.62
11	21.17	1.16	7.55	0.75
12	22.83	1.25	8.55	0.85
13	26.17	1.43	9.54	0.95
14	29.50	1.61	9.85	0.98
15	31.18	1.70	9.90	0.99
16	34.52	1.89	9.95	0.99
17	37.85	2.07	9.97	1.00
18	41.18	2.25	9.98	1.00
19	44.53	2.43	9.98	1.00
20	47.87	2.62	9.98	1.00
21	51.20	2.80	9.99	1.00
22	54.55	2.98	9.98	1.00
23	57.88	3.16	9.99	1.00
24	61.22	3.35	9.99	1.00
25	64.55	3.53	9.99	1.00
26	67.90	3.71	9.99	1.00
27	71.23	3.89	9.99	1.00
28	74.57	4.08	10.00	1.00
29	77.92	4.26	9.90	0.99
30	79.58	4.35	9.50	0.95
31	81.25	4.44	8.57	0.86
32	82.92	4.53	7.05	0.70
33	84.58	4.62	5.24	0.52
34	86.25	4.71	3.51	0.35
35	87.92	4.81	2.17	0.22
36	89.60	4.90	1.27	0.13
37	91.27	4.99	0.71	0.07
38	94.60	5.17	0.25	0.02

Table B.3 (Continued)

40	101.28	5.54	0.07	0.01
41	104.62	5.72	0.06	0.01
42	107.95	5.90	0.05	0.01
43	110.95	6.06	0.05	0.00

Table B.4 17α-ethynylestradiol transport through silica column, initial concentration 9.87 mg/l, pH 6

Sample #	Time adj [min]	Pore Volume	Conc. [mg/l]	C/Co
1	4.59	0.12	0.01	0.00
2	11.26	0.30	-0.06	-0.01
3	17.94	0.48	-0.01	0.00
4	24.63	0.66	-0.13	-0.01
5	27.96	0.75	-0.03	0.00
6	31.29	0.83	0.17	0.02
7	34.63	0.92	1.08	0.11
8	37.98	1.01	2.19	0.22
9	41.31	1.10	3.74	0.38
10	44.64	1.19	4.96	0.50
11	47.99	1.28	5.92	0.60
12	51.33	1.37	6.82	0.69
13	54.66	1.46	7.48	0.76
14	57.99	1.55	8.07	0.82
15	61.34	1.64	8.41	0.85
16	64.68	1.73	8.69	0.88
17	71.36	1.90	9.14	0.93
18	78.03	2.08	9.41	0.95
19	84.71	2.26	9.57	0.97
20	91.38	2.44	9.59	0.97
21	98.06	2.62	9.66	0.98
22	104.73	2.79	9.73	0.99
23	111.41	2.97	9.78	0.99
24	118.09	3.15	9.75	0.99
25	124.76	3.33	9.78	0.99
26	131.44	3.51	9.78	0.99
27	138.11	3.68	9.78	0.99
28	141.46	3.77	9.80	0.99
29	144.79	3.86	9.78	0.99
30	148.13	3.95	9.55	0.97
31	151.48	4.04	8.89	0.90
32	154.81	4.13	7.96	0.81
33	158.14	4.22	7.10	0.72
34	161.48	4.31	6.19	0.63
35	164.83	4.40	5.51	0.56
36	168.16	4.49	4.76	0.48
37	171.49	4.57	4.08	0.41
38	174.84	4.66	3.64	0.37

Table B.4 (Continued)

39	178.18	4.75	3.17	0.32
40	181.51	4.84	2.74	0.28
41	184.84	4.93	2.53	0.26
42	191.53	5.11	2.12	0.22
43	198.21	5.29	1.83	0.19
44	204.88	5.46	1.53	0.16
45	211.56	5.64	1.33	0.13
46	218.23	5.82	0.96	0.10
47	224.91	6.00	0.65	0.07
48	231.58	6.18	0.51	0.05
49	238.26	6.36	0.26	0.03
50	244.94	6.53	0.15	0.01
51	251.61	6.71	-0.01	0.00
52	258.29	6.89	-0.13	-0.01
53	264.96	7.07	-0.19	-0.02
54	271.64	7.25	-0.22	-0.02

Table B.5 17α-ethynylestradiol transport through alumina column, initial concentration 10.11 mg/l

Sample #	Time (min)	Pore Volume	Conc. (mg/L)	C/C0
1	1.93	0.04	0.10	0.01
2	5.26	0.12	0.03	0.00
3	11.95	0.27	0.06	0.01
4	18.61	0.42	0.06	0.01
5	25.30	0.57	0.06	0.01
6	31.98	0.72	0.15	0.01
7	38.65	0.87	0.31	0.03
8	42.00	0.95	0.83	0.08
9	43.66	0.98	1.31	0.13
10	45.33	1.02	2.02	0.20
11	47.16	1.06	2.73	0.27
12	48.66	1.10	3.39	0.34
13	50.33	1.13	4.09	0.40
14	52.00	1.17	4.76	0.47
15	53.68	1.21	5.25	0.52
16	55.35	1.25	5.68	0.56
17	57.01	1.28	6.08	0.60
18	58.68	1.32	6.39	0.63
19	62.01	1.40	6.65	0.66
20	65.36	1.47	6.95	0.69
21	68.70	1.55	7.12	0.70
22	75.36	1.70	7.24	0.72
23	82.05	1.85	7.35	0.73
24	88.73	2.00	7.48	0.74
25	95.40	2.15	7.52	0.74
26	102.08	2.30	7.66	0.76
27	108.75	2.45	7.64	0.76
28	115.43	2.60	7.73	0.76
29	122.10	2.75	7.76	0.77
30	128.78	2.90	7.85	0.78
31	135.46	3.05	7.88	0.78
32	142.13	3.20	7.88	0.78
33	148.81	3.35	7.93	0.78
34	155.48	3.50	7.97	0.79
35	162.16	3.65	7.93	0.78
36	168.83	3.80	7.92	0.78
37	170.51	3.84	7.74	0.77
38	172.18	3.88	7.45	0.74

Table B.5 (Continued)

39	173.85	3.91	7.17	0.71
40	175.51	3.95	6.76	0.67
41	177.18	3.99	6.36	0.63
42	178.85	4.03	6.03	0.60
43	180.51	4.06	5.61	0.55
44	182.20	4.10	5.20	0.51
45	183.86	4.14	4.83	0.48
46	185.53	4.18	4.43	0.44
47	187.20	4.21	4.05	0.40
48	190.53	4.29	3.57	0.35
49	195.55	4.40	3.08	0.30
50	202.21	4.55	2.73	0.27
51	208.90	4.70	2.54	0.25
52	215.58	4.85	2.21	0.22
53	222.25	5.00	2.00	0.20
54	228.93	5.15	1.76	0.17
55	235.60	5.30	1.64	0.16
56	242.28	5.45	1.38	0.14
57	248.95	5.60	1.29	0.13
58	255.63	5.75	1.06	0.11
59	262.31	5.90	0.94	0.09
60	268.98	6.05		
61	275.66	6.20		
62	282.33	6.35		
63	289.01	6.51		
64	295.68	6.66		
65	302.36	6.81	0.42	0.04
66	309.05	6.96	0.37	0.04

Table B.6 17α-ethynylestradiol transports through aquifer sand column, initial concentration 9.2 mg/l

Sample #	Time (min)	Pore Volume	Conc. (mg/L)	C/C0
1	-4.21	-0.13	0.00	0.00
2	4.29	0.13	0.00	0.00
3	12.79	0.40	0.00	0.00
4	21.29	0.67	0.00	0.00
5	38.29	1.20	0.00	0.00
6	46.79	1.47	0.00	0.00
7	55.29	1.73	0.00	0.00
8	63.79	2.00	0.00	0.00
9	72.29	2.27	0.16	0.02
10	80.79	2.53	0.63	0.07
11	89.29	2.80	1.19	0.13
12	97.79	3.07	1.70	0.19
13	106.29	3.33	3.89	0.42
14	114.79	3.60	4.60	0.50
15	123.29	3.87	5.33	0.58
16	131.79	4.13	5.93	0.64
17	140.29	4.40	6.47	0.70
18	157.29	4.93	7.07	0.77
19	182.79	5.73	7.47	0.81
20	208.29	6.53	7.83	0.85
21	225.29	7.06	8.07	0.88
22	242.29	7.60	8.09	0.88
23	267.79	8.40	8.19	0.89
24	301.79	9.46	8.12	0.88
25	352.79	11.06	8.69	0.94
26	395.29	12.39	8.89	0.97
27	437.79	13.72	8.89	0.97
28	446.29	13.99	8.43	0.92
29	454.79	14.26	7.57	0.82
30	463.29	14.52	7.04	0.76
31	471.79	14.79	6.80	0.74
32	480.29	15.06	7.01	0.76
33	488.79	15.32	6.59	0.72
34	497.29	15.59	6.28	0.68
35	505.79	15.86	5.76	0.63
36	514.29	16.12	5.30	0.58
37	522.79	16.39	4.79	0.52
38	531.29	16.66	4.50	0.49

Table B.6 (Continued)

39	539.79	16.92	4.04	0.44
40	548.29	17.19	3.78	0.41
41	556.79	17.46	3.41	0.37
42	565.29	17.72	3.24	0.35
43	573.79	17.99	3.04	0.33
44	582.29	18.25	2.78	0.30
45	590.79	18.52	2.66	0.29
46	599.29	18.79	2.44	0.27
47	607.79	19.05	2.29	0.25
48	616.29	19.32	2.14	0.23
49	624.79	19.59	2.06	0.22
50	633.29	19.85	1.89	0.21
51	641.79	20.12	1.89	0.21
52	650.29	20.39	1.77	0.19
53	658.79	20.65	1.72	0.19

Table B.7 Nalidixic acid transport through silica column, initial concentration 9.66 mg/l

Sample #	Time (min)	Pore Volume	Conc. (mg/l)	C/Co
2	27.23	0.97	0.00	0.00
4	67.23	2.41	0.00	0.00
6	107.23	3.84	0.22	0.02
7	127.23	4.55	0.28	0.03
8	147.23	5.27	1.00	0.10
9	167.23	5.98	2.62	0.27
10	187.23	6.70	4.84	0.50
11	207.23	7.41	6.57	0.68
12	227.23	8.13	7.58	0.78
13	247.23	8.85	8.14	0.84
14	267.23	9.56	8.48	0.88
16	307.23	10.99	8.89	0.92
18	347.23	12.42	9.13	0.94
20	387.23	13.86	9.27	0.96
22	427.23	15.29	9.41	0.97
24	467.23	16.72	9.39	0.97
26	507.23	18.15	9.59	0.99
28	547.23	19.58	9.59	0.99
30	587.23	21.01	9.63	1.00
32	627.23	22.44	9.66	1.00
34	667.23	23.87	9.66	1.00
36	707.23	25.30	9.67	1.00
38	747.23	26.74	9.66	1.00
40	787.23	28.17	9.66	1.00
42	827.23	29.60	9.76	1.01
44	867.23	31.03	9.74	1.01
46	907.23	32.46	9.73	1.01
48	947.23	33.89	9.74	1.01
50	987.23	35.32	9.72	1.01
52	1027.23	36.75	9.77	1.01
54	1067.23	38.19	9.78	1.01
56	1107.23	39.62	9.84	1.02
58	1147.23	41.05	9.78	1.01
60	1187.23	42.48	9.78	1.01
62	1227.23	43.91	9.81	1.02
63	1247.23	44.63	9.85	1.02
64	1267.23	45.34		
65	1287.23	46.06	9.71	1.00

Table B.7 (Continued)

66	1307.23	46.77	9.46	0.98
67	1327.23	47.49	7.52	0.78
68	1347.23	48.20	6.96	0.72
69	1367.23	48.92	6.93	0.72
70	1387.23	49.63	6.93	0.72
71	1407.23	50.35	6.50	0.67
72	1427.23	51.07	5.78	0.60
73	1447.23	51.78	4.98	0.52
74	1467.23	52.50		
75	1487.23	53.21	3.69	0.38
76	1507.23	53.93	3.15	0.33
77	1527.23	54.64	2.83	0.29
78	1547.23	55.36	2.47	0.26
79	1567.23	56.07	2.19	0.23
80	1587.23	56.79	1.99	0.21
81	1607.23	57.51	1.83	0.19
83	1647.23	58.94	1.55	0.16
85	1687.23	60.37	1.35	0.14
87	1727.23	61.80	1.21	0.13
89	1767.23	63.23	1.08	0.11
91	1807.23	64.66	1.04	0.11
93	1847.23	66.09	0.89	0.09
95	1887.23	67.52	0.83	0.09
97	1927.23	68.96	0.76	0.08
99	1967.23	70.39	0.72	0.07
101	2007.23	71.82	0.66	0.07
103	2047.23	73.25	0.65	0.07
105	2087.23	74.68	0.63	0.07
107	2127.23	76.11	0.59	0.06
109	2167.23	77.54	0.55	0.06
111	2207.23	78.97	0.54	0.06
113	2247.23	80.40	0.52	0.05
115	2287.23	81.84	0.50	0.05
117	2327.23	83.27	0.47	0.05
119	2367.23	84.70	0.46	0.05
121	2407.23	86.13	0.45	0.05
123	2447.23	87.56	0.42	0.04
125	2487.23	88.99	0.41	0.04
127	2527.23	90.42	0.40	0.04
129	2567.23	91.85	0.39	0.04
131	2607.23	93.29	0.38	0.04

Table B.8 Nalidixic acid transport through As10 sand column, initial concentration 9.2 mg/l

Sample #	Time (min)	Pore Volume	Conc (mg/L)	C/C0
1	67	2.05	0.16	0.02
2	427	13.00	0.12	0.01
3	787	23.96	0.12	0.01
4	1,147	34.91	0.46	0.05
5	1,507	45.86	1.16	0.13
6	1,867	56.82	1.47	0.16
7	2,227	67.77	1.71	0.18
8	2,587	78.73	2.05	0.22
9	2,947	89.68	2.65	0.29
10	3,307	100.63	3.32	0.36
11	3,667	111.59	4.20	0.45
12	4,027	122.54	4.98	0.54
13	4,387	133.50	5.54	0.60
14	4,807	146.28	5.62	0.61
15	5,107	155.40	6.41	0.69
16	5,467	166.36	6.76	0.73
17	5,827	177.31	7.11	0.77
18	6,187	188.27	7.33	0.79
19	6,547	199.22	7.40	0.80
20	6,907	210.18	7.63	0.82
21	7,267	221.13	7.83	0.85
22	7,627	232.08	8.12	0.88
23	7,987	243.04	8.00	0.86
24	8,767	266.77	8.14	0.88
25	9,067	275.90	8.37	0.90
26	9,787	297.81	8.25	0.89
27	10,147	308.76	8.34	0.90
28	10,507	319.72	8.52	0.92
29	10,867	330.67	8.39	0.91
30	11,227	341.62	8.43	0.91
31	11,647	354.40	8.31	0.90
32	11,947	363.53	8.45	0.91
33	12,307	374.49	8.65	0.93
34	12,667	385.44	8.69	0.94
35	13,027	396.40	8.80	0.95
36	13,447	409.17	8.44	0.91
37	13,747	418.30	8.83	0.95
38	14,107	429.26	8.83	0.95

Table B.8 (Continued)

39	14,467	440.21	8.33	0.90
40	14,827	451.17	7.29	0.79
41	15,187	462.12	6.44	0.70
42	15,547	473.07	5.66	0.61
43	15,907	484.03	4.97	0.54
44	16,267	494.98	4.67	0.50
45	16,627	505.94	4.20	0.45
46	16,987	516.89	3.81	0.41
47	17,347	527.84	3.57	0.39
48	17,707	538.80	3.24	0.35
49	18,067	549.75	3.07	0.33
50	18,427	560.71	2.83	0.31
51	18,787	571.66	2.50	0.27
52	19,087	580.79	2.37	0.26
53	19,507	593.57	2.17	0.23
54	19,867	604.52	2.09	0.23
55	20,227	615.48	1.87	0.20
56	20,587	626.43	1.75	0.19
57	20,947	637.39	1.66	0.18
58	21,307	648.34	1.55	0.17
59	21,667	659.29	1.56	0.17
60	22,027	670.25	1.56	0.17
61	22,387	681.20	1.46	0.16
62	22,747	692.16	1.37	0.15
63	23,107	703.11	1.19	0.13
64	23,467	714.06	1.25	0.14
65	23,827	725.02	1.21	0.13
66	24,187	735.97	1.15	0.12
67	24,227	737.19	1.15	0.12
68	24,547	746.93	1.13	0.12
69	24,907	757.88	1.10	0.12
70	25,267	768.83	1.06	0.11
71	25,627	779.79	1.03	0.11

Table B.9 Nalidixic acid transport through As10 sand column, initial concentration 9.14 mg/l, pH 4

Sample #	Time (min)	Pore Volume	Conc. (mg/l)	C/Co
1	49.36	2.11	0.08	0.01
2	212.92	9.12	0.07	0.01
3	379.82	16.27	0.06	0.01
4	546.72	23.42	0.06	0.01
5	713.64	30.57	0.08	0.01
6	880.54	37.73	0.17	0.02
7	1047.46	44.88	0.53	0.06
8	1214.36	52.03	1.20	0.13
9	1381.27	59.18	2.07	0.23
10	1548.17	66.33	3.08	0.34
11	1715.07	73.48	4.03	0.44
12	1881.99	80.63	4.83	0.53
13	2048.89	87.78	5.51	0.60
14	2215.81	94.93	6.11	0.67
15	2382.71	102.08	6.64	0.73
16	2549.61	109.23	7.07	0.77
17	2716.52	116.38	7.37	0.81
18	2883.42	123.54	7.63	0.84
19	3217.24	137.84	8.09	0.89
20	3551.06	152.14	8.60	0.94
21	3884.87	166.44	9.00	0.99
22	4218.67	180.74	9.08	0.99
23	4552.49	195.04	9.05	0.99
24	4886.31	209.35	9.07	0.99
25	5219.82	223.63	8.70	0.95
26	5303.27	227.21	8.40	0.92
27	5386.72	230.78	8.09	0.89
28	5470.17	234.36	7.57	0.83
29	5553.62	237.94	7.13	0.78
30	5720.54	245.09	6.23	0.68
31	5887.44	252.24	5.52	0.60
32	6054.36	259.39	4.89	0.54
33	6221.26	266.54	4.34	0.48
34	6388.16	273.69	3.94	0.43
35	6555.07	280.84	3.65	0.40
36	6888.89	295.14	3.02	0.33
37	7222.71	309.44	2.49	0.27
38	7556.52	323.75	2.09	0.23

Table B.9 (Continued)

39	7890.32	338.05	1.84	0.20
40	8224.14	352.35	1.65	0.18
41	8557.96	366.65	1.40	0.15
42	8891.77	380.95	1.22	0.13
43	9225.59	395.25	1.07	0.12

Table B.10 Nalidixic acid transport through As10 sand column, initial concentration 8.67 mg/l, pH 9

Sample #	Time (min)	Pore Volume	Conc. (mg/l)	C/Co
1	1.22	0.05	0.10	0.01
2	2.88	0.13	0.10	0.01
3	6.22	0.28	0.10	0.01
4	9.57	0.43	0.10	0.01
5	17.92	0.80	0.09	0.01
6	26.25	1.18	0.09	0.01
7	34.60	1.55	0.09	0.01
8	42.95	1.93	0.15	0.02
9	59.63	2.68	1.37	0.16
10	67.98	3.05	2.57	0.30
11	76.33	3.43	3.76	0.43
12	84.67	3.80	4.76	0.55
13	93.02	4.18	5.54	0.64
14	101.37	4.55	6.16	0.71
15	109.70	4.93	6.62	0.76
16	118.05	5.30	6.97	0.80
17	126.40	5.68	7.24	0.84
18	134.75	6.05	7.45	0.86
19	143.08	6.42	7.63	0.88
20	176.47	7.92	8.04	0.93
21	209.85	9.42	8.25	0.95
22	243.23	10.92	8.39	0.97
23	276.62	12.42	8.46	0.98
24	310.00	13.92	8.49	0.98
25	343.38	15.42	8.50	0.98
26	376.77	16.92	8.50	0.98
27	410.13	18.41	8.52	0.98
28	443.52	19.91	8.54	0.98
29	476.90	21.41	8.49	0.98
30	485.25	21.79	8.45	0.97
31	493.60	22.16	8.41	0.97
32	501.93	22.54	8.13	0.94
33	510.28	22.91	7.55	0.87
34	518.63	23.29	6.79	0.78
35	526.97	23.66	6.00	0.69
36	535.32	24.03	5.27	0.61
37	543.67	24.41	4.63	0.53
38	552.02	24.78	4.08	0.47

Table B.10 (Continued)

39	560.35	25.16	3.62	0.42
40	568.70	25.53	3.21	0.37
41	577.05	25.91	2.87	0.33
42	593.73	26.66	2.32	0.27
43	602.08	27.03	2.10	0.24
44	610.43	27.41	1.92	0.22
45	643.82	28.91	1.38	0.16
46	677.18	30.40	1.06	0.12
47	710.57	31.90	0.83	0.10
48	743.95	33.40	0.68	0.08
49	777.33	34.90	0.57	0.07
50	810.72	36.40	0.50	0.06
51	844.10	37.90	0.44	0.05
52	877.48	39.40	0.40	0.05
53	910.87	40.90	0.36	0.04
54	944.25	42.39	0.34	0.04
55	977.62	43.89	0.32	0.04
56	1011.00	45.39	0.31	0.04
57	1044.38	46.89	0.29	0.03
58	1077.77	48.39	0.29	0.03
59	1111.15	49.89	0.28	0.03
60	1144.53	51.39	0.27	0.03
61	1177.92	52.89	0.26	0.03
62	1211.30	54.38	0.25	0.03
63	1244.67	55.88	0.24	0.03
64	1278.05	57.38	0.23	0.03
65	1311.43	58.88	0.22	0.03
66	1344.82	60.38	0.22	0.03

BIOGRAPHY

Mrs. Oranuj Lorphensri was born on September 26, 1965 in Bangkok, Thailand. She received her Bachelor's Degree (2nd Honour) in Geology at Chulalongkorn University and Master of Science in Civil Engineering (Groundwater Program) from Colorado State University, USA. in 1985 and 1988, respectively. After graduation, she has worked for Groundwater Division, Department of Mineral Resources and Bureau of Groundwater Conservation and Restoration, Department of Groundwater Resources for 13 years. She pursued her Degree of Doctor of Philosophy in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University, Bangkok, Thailand in May 2001. She finished her Doctoral Degree of Philishophy in Environmental Management in April 2006.