

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Pharmaceuticals

Acetaminophen (ACE) is a mild analgesic, or pain reliever, that is found in most over-the-counter medications. Its mild pain-relieving property has made it a very useful medication in the treatment of a wide variety of conditions, including migraine headaches, aches and pains due to a cold or the flu, and fever. However, this drug is a very weak anti-inflammatory agent and it is usually not used to treat stiffness, swelling of the joints, or tissue inflammation. Physicians prefer to use this drug for pain relief instead of aspirin because it works equally well without the adverse side effects often associated with aspirin. Available in both generic and brand name forms, it is an over-the-counter drug that does not require a prescription for purchase. (www.healthevolution.com/Articles/Acetaminophen.htm)

Nalidixic acid (NAL) is an antibacterial drug which is used in the treatment of lower urinary tract infections (cystitis) and it is also sometimes given for the prevention of recurrent urinary tract infections. Taken by mouth it does not accumulate in the body tissues, but is concentrated in the urine. 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 is fast acting and usually clears acute outbreaks of infection completely within a few days. Although generally safe, Nalidixic acid sometimes causes serious side effects. The drug may interfere with

some urine tests and can give a false high reading of urine sugar level. (www.cix.co.uk/~cyberville/medizine/nalidixi.htm)

17- α -Ethinylestradiol (EE2) is 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. (<http://www.cix.co.uk/~cyberville/medizine/ethinylo.htm>)

2.1.2 Subsurface Soil

Subsurface soil is a mixture containing inorganic and organic materials. The inorganic materials consist of clay, silt, sand, and gravel. The most common inorganic elements in clay are silicon, aluminum, iron, and other trace elements. These elements are in the form of metal oxides (e.g. SiO_4 , $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$). The natural soil usually has organic content about 0.2% to 3% (Lagrega et al., 2001). The organic material fraction basically consists of decomposed plant matter or humus (C 50-60%, O 30-35%, H and N 2-6%, and S 0-2% Yaron et al.; 1996).

Generally, these metal oxides and humic substances coat on clay as an outside layer, the contaminants, thus, usually react with these metal oxides humic substances rather than clay.

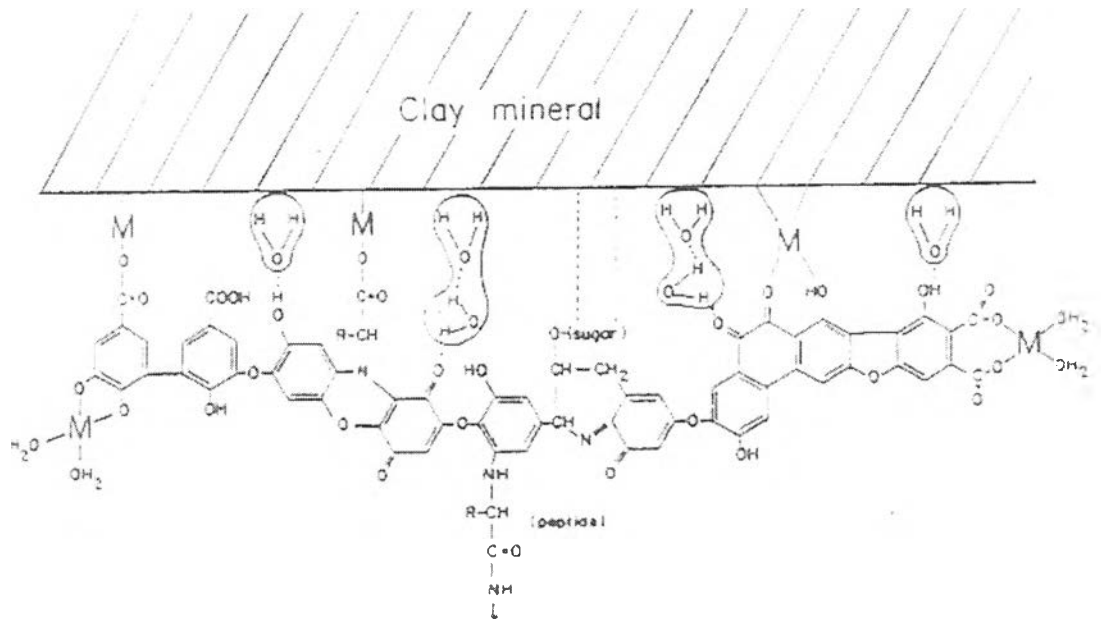


FIGURE 2.1 Clay-humate complex in soil. (Stevenson and Ardakani 1972)

2.1.3 Sorption Fundamental

The sorption process most often occurs between gas/solid interface and liquid/solid interface. In this paper, the sorption process will focus on liquid/solid interface as the most common interface occurring in the sorption process in groundwater system. Sorption is the important process governing fate and transport of sorbate attracting with aquifer materials. 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 phase (accumulation of sorbate into organic carbon) (Weber, 1972 and Weber et al., 1991).

2.1.4 Sorption of Nonionic Organic Compounds

For nonionic compounds, aqueous solubility (hydrophilic property) and hydrophobicity are the important parameters related with the sorption. In general, highly soluble nonionic compounds exhibit low hydrophobicity and low affinity for the soil surface. In contrast, low solubility nonionic compounds exhibit high hydrophobicity and high affinity for the soil surface. Hydrophobic substances which are nonpolar organic compounds will accumulate at an interface or partition into a nonpolar phase (e.g. partition into organic content of the aquifer materials) rather than remain in the water phase. For example, nonpolar organics prefer nonpolar phase to water phase (as illustrated in the adage “likes dissolved likes”) (Knox et al., 2000).

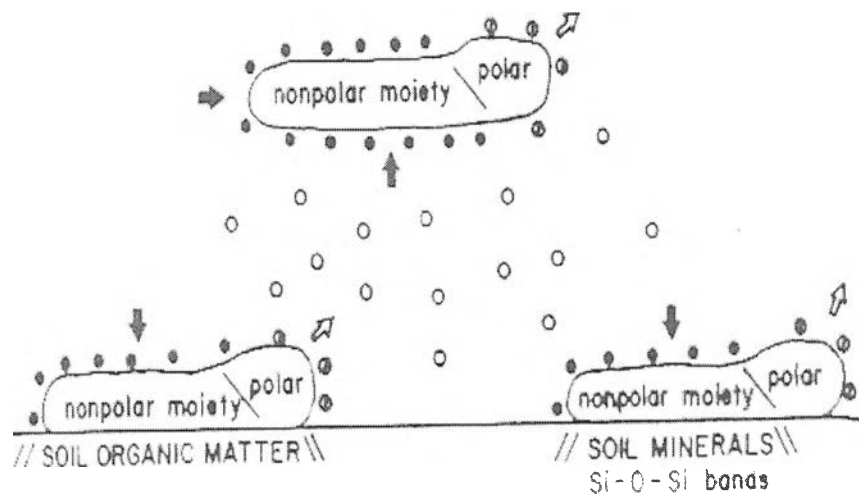
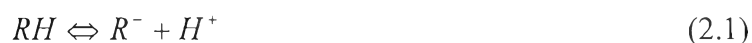


FIGURE 2.2 The sorption of nonpolar (hydrophobic) organics. The nonpolar moiety will penetrate into soil organic matter or adsorb onto soil organic matter. On the other hand, the polar moiety will dissolve in water phase. (Yaron et al. 1996)

2.1.5 Sorption of Ionic Organic Compounds

In general, the sorption process occurs when the sorbent (aquifer material) and the sorbate (contaminant) contact each other. The contaminants accumulate at the sorbent surface by the affinity of the surface. The interactions among the various components of the solid phase of the soil strongly affect its surface activity. Some organic compounds contain function groups (eg., $-\text{COO}^-$, $-\text{NH}_3^+$, $-\text{SO}_3^-$) which are ionized when they are in the aqueous solution (Lagrega et al., 2001). Chemical reaction of ionization process can be express by



Some pharmaceuticals are ionizable organic chemicals. For example, nalidixic acid contains one carboxylic group ($-\text{COOH}$) in its molecule. Nalidixic acid has the ability to donated proton when in the aqueous phase. The ionization of nalidixic acid is a function of pH. In the ionization process, nalidixic acid loses a proton. Nalidixic acid can ionize from unionized binuclear form to ionized binuclear form (anionic molecule) (Hwa Song et al., 1999). The nalidixic acid ionization process is illustrated by

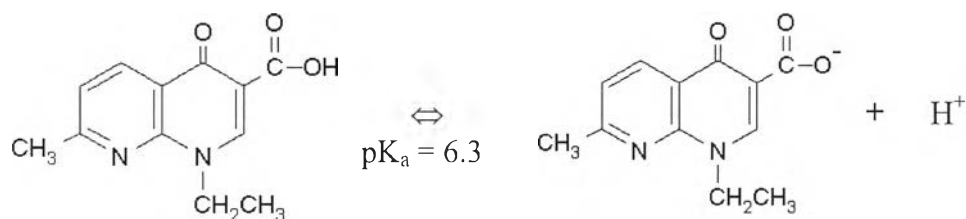


FIGURE 2.3 Ionization of nalidixic acid. Nalidixic acid is ionized to anionic molecule when $\text{pH} = \text{pK}_a = 6.3$.

TABLE 2.1 A summary of adsorption mechanisms of organic compounds in soil solutions. (After Sposito 1984, as adapted from Mortland 1970)

Mechanisms	Principal organic functional group involved
Cation exchange	Amines, heterocyclic N, carbonyl, carboxylate
Protonation	Carboxylate
Anion exchange	Amino, carboxylate, carbonyl, alcoholic OH
Water bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligan exchange	Carboxylate
Hydrogen bonding	Amines, carconyl, carboxyl, phenylhydroxyl
Van der Waals interaction	Uncharged, nonpolar organic function group

As a different functional groups of the organic compounds, various adsorption mechanisms of organic molecule on soil. A summary of the adsorption mechanisms is presented in table 2.1.

2.1.6 Sorption Kinetics

In the experiment, ground water with a known concentration of the dissolved species is conducted into contact with the adsorbent aquifer material for a period of time in which it is believed that equilibrium is achieved between the dissolved and adsorbed concentration of the species. The final concentration is measured, and the difference between initial and final concentration is used to calculate the amount adsorbed (Deutsch, 1997). The reaction can be expressed follows



In this reaction, the solid sorbent is represent as X, the dissolve species is C, and the adsorbed species on X is show as q. The rate of the forward reaction (sorption) is k_s while the rate of the reverse reaction (desorption) is k_d

The study of sorption from a kinetic perspective can lead to a better understanding of the mechanism of the process. Knox et al., 2000 has shown the kinetic expression of this reaction as follow

$$\frac{\partial q}{\partial t} = k_s \frac{\eta}{\rho_s(1-\eta)} C - k_d q \quad (2.3)$$

In the equilibrium conditions, the rate of the forward reaction is equal to the rate of the reverse reaction (although molecules are continuously sorbing and desorbing under equilibrium conditions, there is no net change in q and C). Thus, as q is no longer function as a time, the left-hand sides of the equation (2.3) equal to zero. It can be rearrange to

$$q = \left[\frac{k_s}{k_d} \frac{\eta}{\rho_s(1-\eta)} \right] C_e = K_d C_e \quad (2.4)$$

Where

- q = mass of chemical sorbed normalized by mass of adsorbent (M/M)
- k_s = first order adsorption rate constant (1/t)
- η = porosity (L^3/L^3)
- ρ_s = solid phase particle density (M/L^3)
- k_d = first order desorption rate constant (1/t)
- C = liquid phase chemical concentration (M/L^3)
- K_d = linear equilibrium partition coefficient (L^3/M)

2.1.7 Sorption Isotherms

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, a graph is obtained called the adsorption isotherm (Yaron et al., 1996). Three adsorption models are used to describe three different isotherms.

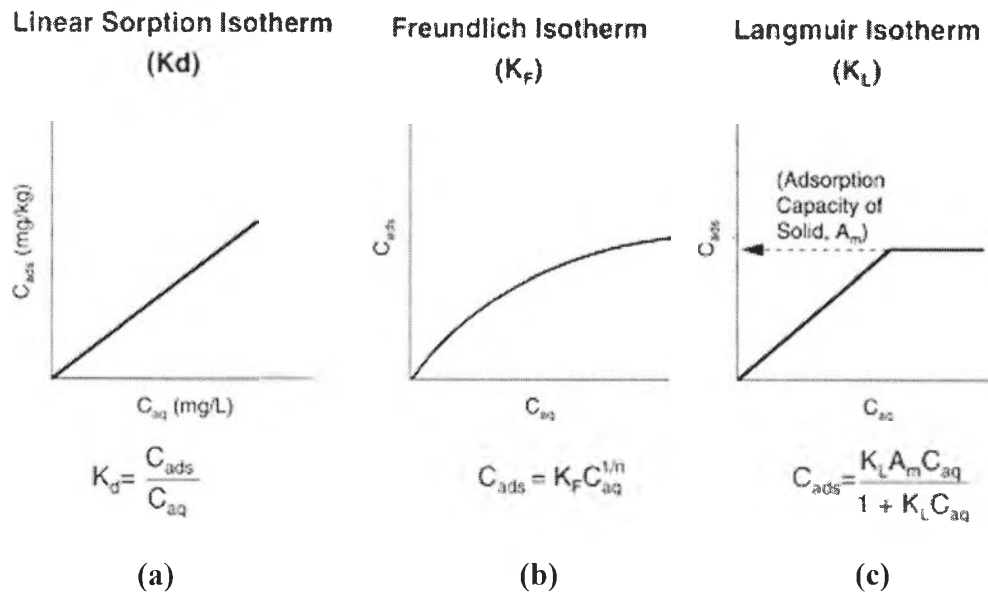


FIGURE 2.4 Sorption isotherms (a) Linear sorption isotherm (b) Freundlich Isotherm (c) Langmuir Isotherm.

A straight-line plot of adsorption implies that the process of adsorption is not affected by solute concentration and that surface of the solid has unlimited capacity for adsorption. The linear adsorption isotherm is appropriate for many species at low solution concentration, but they are not appropriate at higher concentrations when the surface sites for adsorption become saturated (Deutsch, 1997).

Each of the isotherms is linear at low adsorbate concentration; however, the Freundlich and Langmuir isotherms change slope at higher concentrations. The Freundlich isotherm becomes a curve at higher concentration reflecting lower

adsorption at these values as the adsorption sites become saturated. However, there is no total capacity term in the Freundlich isotherm equation, so there is no upper limit on adsorption. The Langmuir isotherm has a capacity term (A_m) in its definition. Once the concentration of adsorbed species reaches this capacity term, adsorption decrease to zero and any additional increase in species solution concentration remains in solution (Deutsch, 1997).

2.1.8 Transport Modeling: One Dimension

The fundamental governing equation for chemical transport under saturated ground water conditions is the advection and dispersion equation with sorption. This equation is derived from flux balance considerations about an elemental volume and, for the one-dimensional flow case, results in the partial differential equation shown in Equation 2.5 (Freeze and Cherry, 1979).

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{\eta} \frac{\partial q}{\partial t} \quad (2.5)$$

For linear equilibrium adsorption

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} = K_p \frac{\partial C}{\partial t} \quad (2.6)$$

Therefore

$$\frac{\partial C}{\partial t} = \frac{-v_x}{r_f} \frac{\partial C}{\partial x} + \frac{D_x}{r_f} \frac{\partial^2 C}{\partial x^2} \quad (2.7)$$

Where v_x = pore water (seepage) velocity (L/T)

D_x = hydrodynamic dispersion coefficient (L^2/T)

x = dimension of solute transport (L)

ρ_b = bulk density of solid phase (M/L³)

η = porosity (L³/L³)

r_f = retardation factor (dimension less)

Deutsch (1997) have showed the development retardation factor for three isotherms;

$$R = 1 + \frac{\rho_b}{\eta} K_d \quad (\text{Linear isotherm}) \quad (2.8)$$

$$R = 1 + \left(\frac{\rho_b}{\eta}\right)(K_f n)(C_{aq}^{n-1}) \quad (\text{Freundlich isotherm}) \quad (2.9)$$

$$R = 1 + \left(\frac{\rho_b}{\eta}\right)\left[\frac{K_L A_m}{(1 + K_L C_{aq})^2}\right] \quad (\text{Langmuir isotherm}) \quad (2.10)$$

2.1.9 Partition Coefficient

There are several approaches for determining the concentration of a chemical in one phase when contacted with a known concentration in another phase, under equilibrium condition. The simplest is the partition coefficient or distribution coefficient approach, which is base on the Nernst's law:

$$K_{12} = \frac{C_1}{C_2} \quad (2.11)$$

Where C_1 = concentrations in phase 1

C_2 = concentrations in phase 2

K_{12} = the partition coefficient

There are several units for the concentrations. Most commonly, C is expressed in mass/volume, e.g. mg/L or g/m³, but for solid phase, mg/kg may be preferred. K_{12} thus may be dimensionless, or it may have dimensions such as L/kg.

Hydrophobicity is a significant parameter governing the partition behavior between aqueous and nonaqueous phase in neutral, technical, and pharmacological processes. The distribution between water phase and immiscible nonpolar solvent phase is a useful descriptor for the hydrophobicity of a contaminant. Water and 1-Octanol were widely used as a two phase system indicating the partition between water and nonionic compound.

Lagrega et. al. (2001) defined the octanol-water partition coefficient is a dimensionless constant defined as a ratio of a sorbant's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol-water system. The octanol-water partition coefficient is expressed by:

$$K_{ow} = \frac{C_o}{C_w} \quad (2.12)$$

Where C_o = concentrations in octanol phase (mg/L or μ g/L)

C_w = concentrations in water phase (mg/L or μ g/L)

K_{ow} = the octanol-water partition coefficient (dimensionless)

The octanol water partition coefficient has become an important parameter in studies of the environmental fate of organic compounds. It used to indicate amount of sorbate will be absorbed by aquatic organisms. The coefficient is also useful in

evaluating fate and transport of contaminants and is related to soil sorption coefficients, the bioconcentration factor (BCF), and the water solubility.

Values for K_{ow} have been measured as low as 10^{-3} and as high as 10^7 , encompassing a range of 10 orders of magnitudes. Thus values for K_{ow} are often reported as $\log K_{ow}$, ranging from -3 to 7. Chemicals with high values of K_{ow} tend to be hydrophobic and partition to organic matter and fatty tissue. Chemicals with low values of K_{ow} tend to be hydrophilic, remain in the aqueous phase, and are generally more mobile in the environment.

2.2 Literature Reviews

2.2.1 Occurrence of Pharmaceuticals in the Aquatic Environment

Daughton and Ternes (1999) demonstrated the occurrence of pharmaceuticals and personal care products (PPCPs) in the environment. PPCPs, which are used in large amounts throughout the world, can discharge into environment via sewage treatment facilities and wet weather runoff. The literature shows some PPCPs are extremely persistent and introduced to the environment in very high quantities and perhaps have already gained ubiquity worldwide, others could act as if they were persistent, simply because their continual infusion into aquatic environment serves to sustain perpetual life-cycle exposure for aquatic organisms.

Kümmerer (2001) investigated emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals and other sources. A brief summary of input by different sources, occurrence, and elimination of different pharmaceutical groups such as antibiotics, anti-tumor drugs, anaesthetics and adsorbable organic halogen compounds (AOX) resulting from hospital effluent into sewage water and surface water is presented. The literature showed that pharmaceuticals which are

excreted by patients enter into wastewater. Furthermore, unused drugs are disposed of down the drain. Disposed of antibiotic drugs can disturb wastewater treatment processes and the microbial ecology in surface water.

Herberer (2002) showed the occurrence of pharmaceutically active compounds (PhACs) from studies carried out in Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, the Netherland, and the U.S. More than eighty pharmaceuticals and several drug metabolites have been detected in the aquatic environment. Moreover, several pharmaceutically active compounds (PhACs) from various prescription classes have been found at concentrations up to the g/l-level in sewage influent and effluent samples and also in several surface waters located downstream from municipal sewage treatment plants (STPs). The studies show evidence that some PhACs originating from human therapy are not eliminated completely in the municipal STPs and are thus discharged as contaminants into the receiving waters. To date, PhACs have also been detected in a few cases at trace-levels in drinking water.

Kolpin et al. (2002) provided the first nationwide reconnaissance of the occurrence of ninety-five organic wastewater contaminants (OWCs), including many compounds of emerging environmental concern, in 139 streams across 30 U.S. states during 1999 and 2000. OWCs were prevalent during this study, being found in 80 percents of the stream sampled. The most frequently detected compounds were coprostanol (fecal steroid), cholesterol (plant and animal steroid), *N,N*-diethyltoluamide (insect repellent), caffeine (stimulant), tricosan (antimicrobial disinfectant), tri(2-chloroethyl)phosphate (fire retardant) and 4-nonylphenol (nonionic detergent metabolite). Measured concentrations for this study were generally in the low ng/l-level. The results of this study demonstrate the importance

of obtaining data on metabolites to fully understand not only the fate and transport of OWCs in the hydrologic system but also their ultimate effect on human health and the environment

2.2.2 Kinetic and Sorption on Solid Surface

Karapanagioti et al. (2001) studied the sorption behavior of phenanthrene on different soil and sediment samples. The result has shown that as the sorption affinity increases the mechanism changes from primarily partition to soil organic matter to mainly a surface adsorption onto a small amount of opaque particles. Moreover, the study shows that the trend of K_{oc} decrease when equilibrium concentration increases.

Karapanagioti et al. (2000) investigated the equilibrium and kinetic sorption of phenanthrene with aquifer material. Subsamples containing particulate organic matter showed the highest K_{oc} , the nonlinearity of isotherms and the slowest sorption kinetics. On the other hand, soil subsamples with organic matter present as organic coatings around the quartz grains evidenced the lowest K_{oc} , the most linear sorption isotherms and the fastest sorption kinetics, since it was not limited by slow intraparticle diffusion.

Sabatini (2000) studied sorption and intraparticle diffusion of fluorescein and sulforhodamine B onto two oppositely charged consolidated aquifer materials (sandstone and limestone). Fluorescein, which has anionic carboxylic group, experienced negligible sorption onto negatively charged sandstone and sorbed much less than sulforhodamine B, with its two sulfonic groups, onto positively charged limestone. The cationic charge on sulforhodamine B caused it to adsorb onto negatively charge sandstone. Sorption kinetic rates decreased with increasing particle size, which is consistent with diffusion-limited intraparticle sorption. Diffusion-

limited sorption can impact dye transport in unconsolidated grain having internal porosity or consolidated or fractured media having dual porosity.

Kasnavia (1999) studied media properties affecting two fluorescent dyes sorption. Four fluorescent dyes (fluorescein, rhodamine B, rhodamine WT, and sulforhodamine), which are widely use as conservative tracers in surface water and ground water studies, were used to evaluate sorption characteristic onto two oppositely charged mineral surfaces (alumina and silica), and n-octanol (as a neutral organic phase). Fluorescein, which has only negative functional groups, sorbed least onto negatively charged silica but most onto positively charged alumina. The rhodamine dyes, with a permanent positively charged and negatively charged functional groups, sorbed onto both alumina and silica. Sulforhodamine B, with two strongly electronegative sulfonic groups, sorbed less onto negative charged silica than did rhodamine WT, which has two carboxyl groups. Dye partitioning onto n-octanol was strongly pH dependent with fluorescein being the most hydrophobic, follow by rhodamine WT and sulforhodamine B.

Sabatini and Austin (1991) investigated the use of RWT and fluorescein as adsorbing ground water tracers for the pesticides atrazine and alachlor. Several unique adsorption characteristics were attributed to the polar and nonionizable nature of the fluorescent dyes. First, RWT sorption was significantly greater than similar neutral organic chemicals (i.e., greater than K_{ow} -based estimates) indicating that different sorption mechanism were dominant. Second, RWT showed a two-step breakthrough curve that Shiau et al. (1993) attributed to differing transport properties of two RWT structural isomers (i.e., chromatographic separation).

Kosmulski (2002) studied electric charge density of silica, alumina, and related surfaces. This paper reported the point of zero charge (PZC) of alumina about

pH 9. Above this pH, alumina carries negative surface charge, and below this pH, alumina carries positive surface charge. For silica, the point of zero charge of silica is about pH of 2. It carries negative surface charge within the pH range of this study (4-10), and there is no evidence that silica can be positively charged at sufficient low pH. Moreover, this study shows that the density of surface charge of silica and alumina depends on pH and ionic strength.