



ENVIRONMENTAL RESEARCH BRIEF

Modeling Soil-Water Distribution of Aromatic Amines In Water Saturated Soil Systems

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Introduction

Organic bases such as aniline and aniline derivatives are important environmental contaminants because of their high potential toxicity and carcinogenicity, and the large mass produced each year (Schnell et al., 1989). These organic bases are employed as starting materials in the industrial manufacturing of synthetic chemicals such as dyes, pesticides, varnishes and perfumes (Schnell et al., 1989; Essington, M.E., 1994). Anilines are also found in wastes from coal gasification and shale oil extraction processes, and as microbial degradation products in soils treated with phenylamide herbicides (Zachara et al., 1984; Kaufman, 1974). Despite their significance as environmental pollutants, development of comprehensive quantitative relationships for describing their sorption to natural sorbents similar to those that have been developed for nonpolar organic chemicals (NOCs) have been delayed due to their intrinsic reactivity and ionogenic nature (see Lyman et al., 1990 for NOC relationships). Indeed, predictive models for sorption of organic bases are more complex because simultaneous physical and chemical reactions of the cationic and neutral species must be considered.

Research summarized in this report focuses on the abiotic interactions of aromatic amines with whole soils in aqueous systems. This work was initiated to improve our ability to predict the mobility of aromatic amines and their potential to contaminate groundwater, and to improve subsequent remediation of contaminated sites. Our work has focused on identifying and quantifying, through process algorithms and coefficients, some of the important chemical and physical-chemical interactions that occur between aromatic amines and soil constituents. In turn, process coefficients are correlated to easily measured soil and solute properties. Studies were conducted with seven aromatic amines (mostly with aniline and α -naphthylamine) and five surface soils.

The results of this work show that interaction of aromatic amines with soils over short time periods (< 24 h) can be adequately predicted on a macro-scale assuming cation exchange as the primary mechanism, utilizing the pK_a of the amine, soil cation exchange capacity, and soil-solution pH. For longer interaction times, aromatic amines undergo irreversible binding and transformation reactions. The rates, types, and extent of irreversible processes can be predicted using available intrinsic solute reactivity indices, assuming only a minor dependence on specific soil properties with regards to rate and type of reaction.

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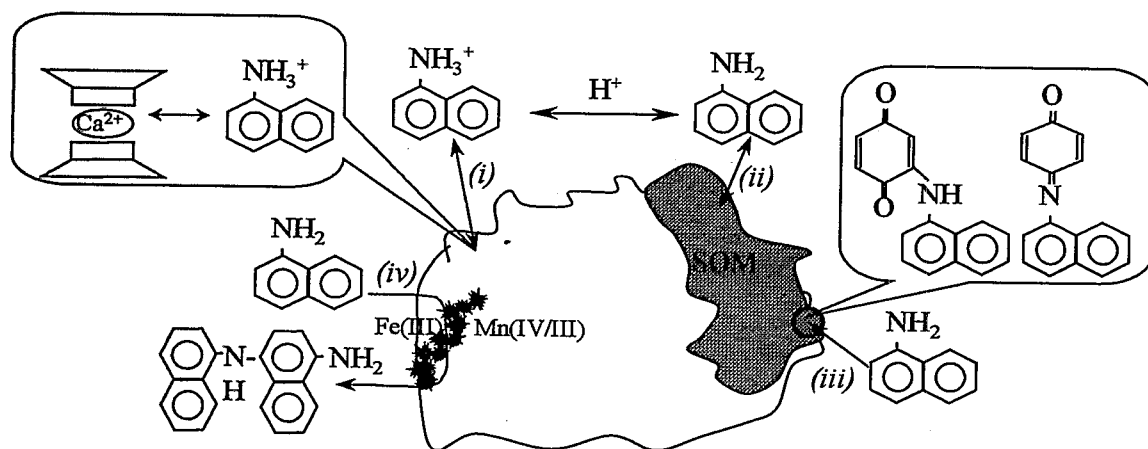


Figure 1. Conceptual schematic of the interactions of aromatic amines with soils. SOM refers to soil organic matter and italic numbers are defined in text.

Background

Aromatic amines interact with soils through both reversible and irreversible processes including: (i) exchange of the organic cation with inorganic cations on clay and soil organic matter (SOM) sites; (ii) hydrophobic interactions of the neutral organic base with SOM; (iii) covalent bonding with functional groups on SOM; and (iv) mineral-catalyzed transformation reactions (Figure 1). The individual contribution to sorption of each mechanism is dependent on the speciation of the amine as controlled by the pH- pK_a relationship, and the available soil domains (e.g., cation exchange sites and soil organic matter).

Cation exchange reactions are defined as the replacement of one adsorbed, readily-exchangeable cation by another (Sposito, 1989). Cation-exchange of organic bases is impacted by speciation as controlled by pH- pK_a relationships. As speciation of an organic base shifts towards the protonated form with decreasing pH, the contribution of cation exchange to the overall sorption process increases. Exchange of an organic cation is also impacted by the composition and concentration of other cations (Ainsworth et al., 1987; Brownawell, et al., 1990; Kosson and Byrne, 1995). Organic cations (BH^+) tend to have a higher affinity for CEC sites than inorganic cations of the same charge; however, as the concentration of the inorganic cation is increased, sorption of the organic cation will be decreased because of mass action laws governing exchange (Lee et al., 1997; Zachara et al., 1987). Among aromatic organic cations, selectivity for exchange sites increases with the number of fused rings; therefore, larger organic bases will depress sorption of smaller bases of similar structure (Zachara et al., 1987; 1990; Lee et al., 1997).

As contact time increases, aromatic amines continue to be removed from the solution phase abiotically, primarily

through irreversible processes such as covalent binding with particular constituents in soil organic matter (e.g., quinone and phenolic functional groups), and mineral-catalyzed transformation reactions. The use of quinones as a model to investigate potential reactive sites in SOM showed evidence of two reaction mechanisms: (1) the rapid but reversible addition of the amino group to the C=O group of quinone to form an imine; and (2) the slow but irreversible addition of the amino group to a C=C bond in the aromatic ring of quinone by 1,4-nucleophilic addition to produce aminobenzenquinone (Parris, 1980; Bollag et al., 1983; Ononye et al., 1994). Direct spectroscopic evidence exists for similar reactions with humic substances along with the further incorporation of aminobenzenquinone into nitrogen heterocyclic linkages (Thorn, 1996a). Nucleophilic addition is expected to accelerate with increasing pH for aromatic amines due to the concomitant increase in the fraction of neutral species. Weber et al. (1996) observed increasing covalent binding rates of aniline to Suwannee River fulvic acid with increasing pH. Iron and manganese oxides, montmorillonite clays, and biological enzymes may catalyze transformation reactions of aromatic amines such as oxidative coupling, resulting in dimerization (Laha and Luthy, 1990; Klausen et al., 1997; Ainsworth et al., 1991; Tatsumi, 1994; Thorn, 1996b). The amine dimers, in turn, may be preferentially, but not necessarily irreversibly, sorbed to soil particles. Laha and Luthy (1990) observed increasing reaction rates with decreasing pH for oxidation of aniline by δ - MnO_2 . The observed pH dependence was hypothesized to result from the enhanced formation of surface precursor complexes and not attributed to any pH-dependent speciation of the amine. Clearly, the impact of pH on the overall long-term reactivity of aromatic amines with soils is complex. At low pH, both reactivity of the soil surface and redox potential are generally increased; however, speciation of the aromatic amine shifts away from the neutral species, identified as the more reactive species for both covalent binding and oxidative transformation.

Table 1. Selected physical and chemical properties of aromatic amines used in this study.

Chemicals	S_w (g/L) ¹	log K_{ow}	pK_a ¹	$E_{1/2}$ (V) ⁴	δ^{+6}
p-Methoxyaniline (CH ₃ O-AN)	21	0.95 ³	5.34	0.393	-0.78
α -Naphthylamine (NAPH)	1.7	2.25 ²	3.92	0.54 ⁵	—
p-Methylaniline (CH ₃ -AN)	7.4	1.41 ²	5.08	0.537	-0.31
Aniline (AN)	3.4	0.90 ²	4.63	0.625	0.00
p-Chloroaniline (Cl-AN)	10	1.83 ²	4.15	0.675	0.11
p-Aminobenzoic Acid (COOH-AN)	3.4	0.68 ²	2.50;4.87	0.714	0.42
p-Nitroaniline(NO ₂ -AN)	0.8	1.39 ³	1.0	0.935	0.79

¹ Aqueous solubility (S_w) (Verschuere, 1996); ² CRC, 1982; ³ Lyman, et al., 1982; ⁴ Suatoni et al., 1961;

⁵ Pysh and Yang, 1963; ⁶ Laha and Luthy, 1990.

Table 2. Characterization data based on air-dried soils (<2 mm) for soils used in this study.

Soil	pH 1:1 soil:water	Sand %	Silt %	Clay %	OC %	CEC cmol _c /kg
Toronto	4.4	11.9	67.6	20.5	1.34	11.2
Chalmers	6.5	11.1	72.8	16.0	1.17	13.0
Drummer	7.2	13.0	66.0	21.2	2.91	26.5
Bloomfield	6.4	81.4	11.0	7.6	0.36	4.4
Okoboji	7.4	31.8	36.2	32.0	4.98	36.2

Differentiating between reversible and irreversible processes, and quantifying the parameters that control these processes, are imperative in improving the assessment and subsequent remediation of sites contaminated with aromatic amines. The impact of irreversible versus reversible processes will be a function of the residence time of the aromatic amine in the soil, the availability of reactive sites in SOM, and the type of mineral surfaces present. As aromatic amines are allowed to age within the soil matrix, the formation of soil-bound residues will increase and availability for further transport and/or microbial degradation will diminish. The interactions of aromatic amines with soil/sediment constituents or model compounds have been studied for relatively short contact times; however, results from long-term studies are sparse.

In the following sections, our experimental observations, modeling approaches, and resulting quantitative relationships are summarized for the interactions of aromatic amines in saturated soil systems during short periods in single and binary systems, and for long-term interactions using single solute systems. Studies were conducted with aniline, α -naphthylamine, five substituted anilines, and two to five surface soils. Solute and soil properties are summarized in Table 1 and Table 2, respectively. Details can be found in several publications listed in Appendices A and B.

Sorption During Short Characteristic Times

During short characteristic time periods (e.g., < 24 hours), sorption of organic amines is primarily reversible. Cation-exchange is the predominant sorption mechanism and soil-

solution pH is the most significant factor controlling the magnitude of sorption in soil systems (Lee et al., 1997; Zachara et al., 1986; Moreale and van Blandel, 1976). The hypothesis that cation-exchange largely regulates loss to the soils during a one-day incubation time can be tested for a given electrolyte matrix using a simple model that assumes all solute lost from solution is through distribution of the protonated species to cation-exchange sites on the soil. The concentration of the protonated species in solution (C_{BH^+} , $\mu\text{mol BH}^+/\text{mL}$) can be estimated using eq 1,

$$C_{BH^+} = C_T f_{BH^+} \quad (1)$$

where C_T ($\mu\text{mol}/\text{mL}$) refers to the total solution concentration of amine (i.e., neutral and protonated species) measured after a one-day equilibration, and f_{BH^+} is the fraction of base that exists as a cation in solution. Sorbed concentrations can be expressed in terms of the cation-exchange capacity (CEC) of the soil [S^* , $\mu\text{mol}/\text{mol}_c$],

$$S^* = S / \text{CEC} \quad (2)$$

where S ($\mu\text{mol}/\text{g}$) is the amount of amine lost per mass of soil and CEC is expressed in mol_c/g . This is analogous to the K_{oc} concept where the reactive domain for sorption of nonpolar organic compounds is assumed to be soil organic carbon (OC) so that normalization of sorption to OC ($S_{oc} = S/\text{OC}$) results in a single distribution plot (Lee et al., 1997). Typical sorption isotherms and isotherms normalized with respect to solution speciation and soil cation-exchange sites (eqs 1 and 2) are illustrated for aniline in Figure 2. Normalization resulted in compensation for most of the differences originally observed in sorption by the various soils from a given CaCl_2 concentration. Similar results were

obtained for α -naphthylamine. This lends support to the hypothesis that cation exchange and/or other similarly pH-dependent reactions account for most of the loss to these soils during initial contact times.

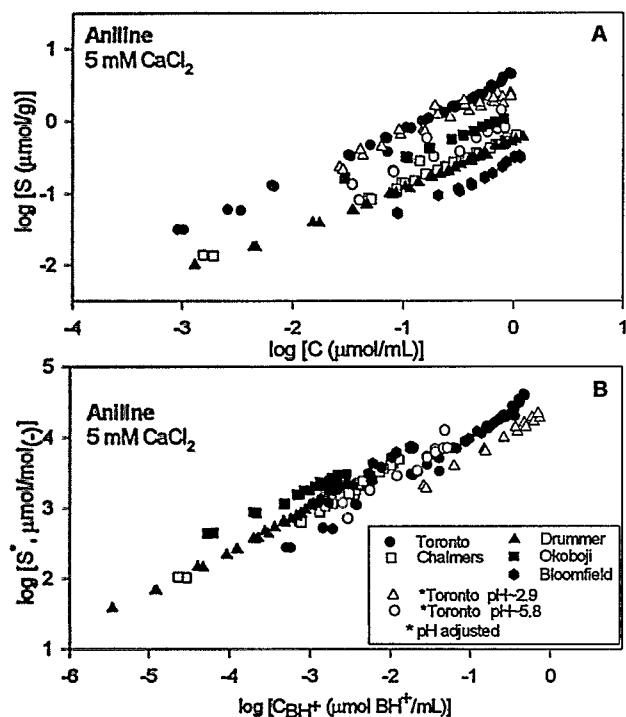


Figure 2. Aniline sorption to several soils at their natural soil-solution pH and pH-adjusted Toronto soil from 5 mM CaCl_2 solutions: (A) measured distribution; and (B) charge-normalized distribution plots.

Sorption of aniline and α -naphthylamine was measured from single organic solute solutions containing 0.5, 5, or 50 mM CaCl_2 concentrations. For aniline, a decrease in sorption with increasing CaCl_2 concentration was significant only for Toronto soil where BH^+ was abundant in the aqueous-phase. Competition between Ca^{2+} and BH^+ for CEC sites would result in decreasing amounts of BH^+ sorbed with increasing additions of Ca^{2+} consistent with a cation-exchange process. However, increasing the CaCl_2 concentration also resulted in decreases in soil-solution pH by displacement of H^+ from the soil, thereby increasing f_{BH^+} and the amount of amine available for cation-exchange. The net result was a reduced impact of Ca^{2+} additions on the sorption of aniline.

A two site (TS) and a distributed parameter (DP) model were developed to describe the primary processes affecting aromatic amine sorption for short contact time. Mass action equations considered in both models were: a) acid dissociation of the protonated organic base (eq 3); b) sorption of the neutral species to soil organic carbon through the partition coefficient K_{oc} (eq 4); and c) ion-exchange of the protonated organic base (BH^+) and inorganic divalent cations ($\text{D}^{2+} = \text{Ca}^{2+} + \text{Mg}^{2+}$) (eqs 5, 6),

$$K_a = \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} \quad (3)$$

$$K_d = f_{oc}K_{oc} = \frac{[\text{B}_s]}{[\text{B}]} \quad (4)$$

$$K_{BH} = \frac{[\text{BHS}]}{[\text{BH}^+][\text{S}^-]} \quad (5)$$

$$K_D = \frac{[\text{D}_{0.5}\text{S}]}{[\text{S}^-][\text{D}^{2+}]^{0.5}} \quad (6)$$

where K_a is the acid dissociation constant of the conjugate acid (mol/L), B represents the neutral aqueous organic base (mol/L), K_{oc} represents the partition coefficient to soil organic carbon (L/kg), f_{oc} is the fraction of organic carbon, B_s represents the concentration of B associated with the soil (mol/kg), D^{2+} represents the sum of divalent inorganic cations ($\text{Ca}^{2+} + \text{Mg}^{2+}$) (mol/L), BHS and $\text{D}_{0.5}\text{S}$ are the organic and inorganic cations, respectively, that are attached to cation exchange sites in the soil (S^-), K_{BH} and K_D are association constants for BH^+ and D^{2+} , respectively, and are related to a third constant, K_G by the following expression,

$$K_G = \frac{K_{BH}}{K_D} = \frac{[\text{BHS}][\text{D}^{2+}]^{0.5}}{[\text{BH}^+][\text{D}_{0.5}\text{S}]} \quad (7)$$

K_G ($\text{M}^{0.5}$) is the selectivity coefficient employing the Gapon cation exchange convention (Gapon, 1933). In the TS Model, cation exchange was accounted for by a single cation exchange coefficient (K_G) that is solute dependent. While this model is conceptually simple, accounting for mass transfer to two types of sites, neutral organic carbon sites and cation exchange sites, it fails to capture much of the nonlinearity observed in the distribution isotherms. Nonlinearity is likely due to the chemical heterogeneity of cation exchange sites. In the DP model, all sites are not assumed to have identical affinities for a given organic cation (BH^+). Site affinities are assumed to have a distribution of affinities, which serves as a better representation of the chemical heterogeneity of cation exchange sites on soils. The frequency distribution of sites is represented with a Gaussian probability distribution function on $\log K_{BH,i}$ with mode μ and standard deviation σ (Fernandez and Steel, 1998):

$$f(\log K_{BH,i}) = \frac{1}{\sigma\sqrt{2\pi}} \left(e^{-\frac{1}{2\sigma^2}(\log K_{BH,i} - \mu)^2} \right) \quad (8)$$

Mathematically, eqs 5 and 6 are employed in the model with organic and inorganic cations being associated with unoccupied cation exchange sites (S^-) assuming the following mass balances:

$$\text{BHS} = \sum_{i=1}^{i=n} \text{BHS}_i = [\text{BH}^+] \sum_{i=1}^{i=n} K_{BH,i} [\text{S}^-]_i \quad (9)$$

$$D_{0.5}S = \sum_{i=1}^{i=n} D_{0.5}S_i = K_D [D^{2+}]^{0.5} \sum_{i=1}^{i=n} [S^-]_i \quad (10)$$

In this way, the overall model conveniently is expressed as a system of two nonlinear equations with two unknown values (BH^+ and D^{2+}) (Fabrega et al., 1998).

The DP model was evaluated using aniline and α -naphthylamine isotherms measured after 24 h contact with three Indiana soils (ranging in pH from 4.5 to 7.0) and added calcium concentrations of 0.5 to 50 mM. The parameters K_{D0} , μ , and σ for each base were obtained by minimizing the sum of square residuals (SSR) between experimental and predicted aqueous phase organic base concentrations ($[C]_e = [B]_{aq} + [BH^+]_{aq}$) for all data at all pH and calcium concentrations, simultaneously. Examples of data and DP model results are shown for aniline in Figure 3.

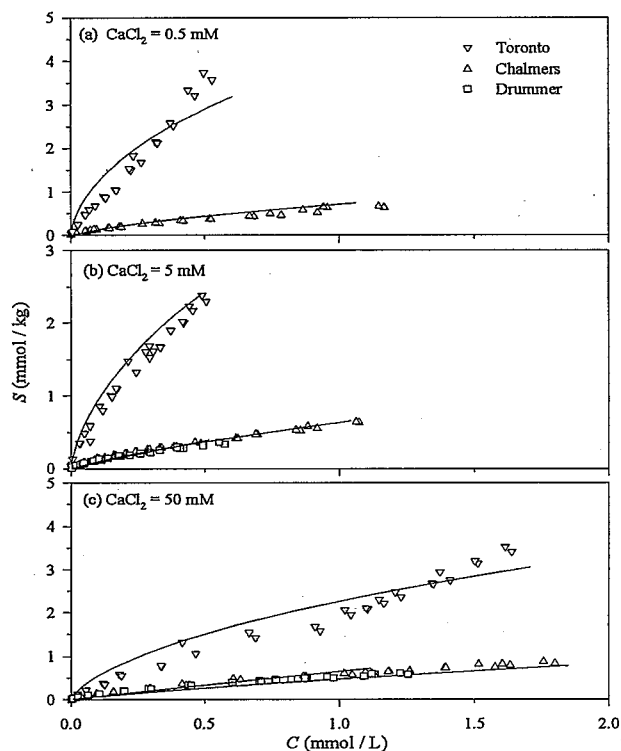


Figure 3. Aniline isotherms on Toronto, Chalmers, and Drummer soils from (a) 0.5 (b) 5 and (c) 50 mM $CaCl_2$ solutions. Solid lines are DP model predictions.

Compared to the TS model in which K_{BH} was not employed as a distributed parameter, predictions from the DP model resulted in less error between predicted and experimental isotherms for both compounds. When simultaneously fitting sorption data from various soil-solution combinations, the DP model does take into account soil-specific pH, CEC, and OC. However, since only one pair of μ and σ result, the relative magnitude and distribution of

site affinities can not be correlated directly to specific soil properties. DP model fitting of isotherms measured for a given soil across electrolyte concentrations resulted in μ and σ values for Chalmers and Drummer soils similar to what was observed in the simultaneous fit of data across soils. For the Toronto soil, μ was a little higher and σ was lower. Modeling of isotherms from additional soils is being done to observe trends between μ and σ values and soil properties.

The relative contribution from cation exchange can still be significant although the calculated f_{BH^+} in the aqueous-phase may be very small. In Figure 4, the DP model was used to simulate the distribution of the major species present in the soil and aqueous-phases at equilibrium as a function of pH. The example shown is for 1.6 mM aniline in Chalmers soil with 5 mM added $CaCl_2$. At the natural pH of 6.5 for these soil slurries, a significant amount of aniline on the soil is calculated to exist as the protonated species, despite the negligible contribution of the aqueous phase protonated species to aniline's total mass balance.

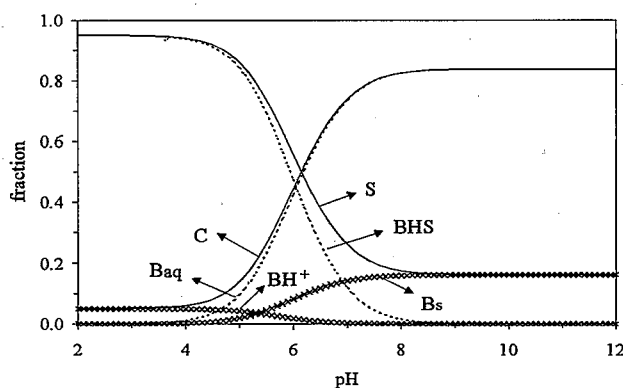


Figure 4. Aniline speciation on Chalmers soil from 5 mM $CaCl_2$ solutions as function of pH, calculated with the DP model.

Competitive Sorption and Selectivity

Sorption of aniline and α -naphthylamine onto selected soils was measured from both single and binary organic solute systems at a fixed $CaCl_2$ concentration. On the more acidic soil (Toronto), isotherms were constructed at pH values of 2.9 ± 0.15 (added HCl), 4.6 ± 0.1 (natural soil pH), and 5.8 ± 0.1 (added NaOH). Sorption of α -naphthylamine was not impacted quantitatively by the presence of aniline due to its much higher sorption to the soil and greater selectivity to exchange sites. At these pH values, cation exchange is likely to be the predominant reversible reaction occurring, and the small mass of aniline on the soil would be expected to have little effect on α -naphthylamine sorption. On the other hand, sorption of aniline was reduced by the presence of 1-naphthylamine, with the greatest effect occurring at the lowest pH values.

Both the TS and the DP model were assessed for predicting competitive sorption in binary organic solute systems (Fabrega, 1999). Predictions from the TS model were poor. The TS model is a general mass action model that does not consider the site heterogeneity of cation exchange sites, unlike the DP model. As indicated previously in the DP model, cation exchange is modeled as three independent processes involving vacant sites (S^-) (Figure 5) with a bivariate normal density function (Ang and Tang, 1975) utilized to establish a correlation between the set of $\log K_{BH,i}$ values unique for each aromatic amine. Examples of data and model results are shown for sorption of aniline and α -naphthylamine by Toronto soil in 5 mM CaCl_2 solution at $\text{pH}=2.70$ and $\text{pH}=5.78$ in Figure 6. For the binary solute isotherms, initial amine concentrations were in equal molar ratios. In all cases, the DP model successfully predicted the lack of competition by aniline for α -naphthylamine and the suppression in aniline sorption by α -naphthylamine.

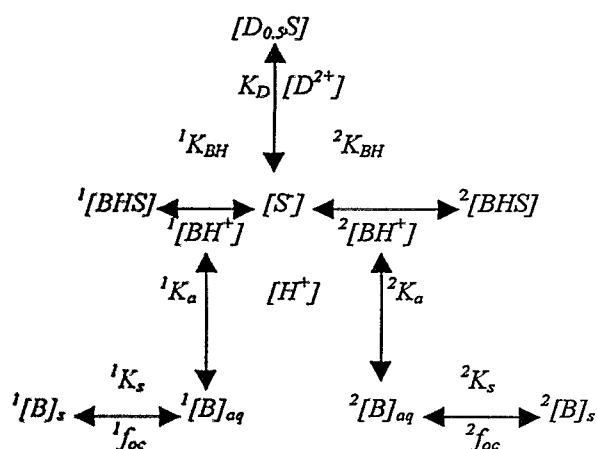


Figure 5. DP model where sorption of the neutral species is predicted from K_{oc} and cation exchange is modeled as three independent processes involving vacant sites (S) where superscripts 1 and 2 specify the two different aromatic amines.

Long-Term Sorption and Transformation Reactions

The abiotic interaction of aniline, α -naphthylamine, and five substituted anilines (Table 1) with two to five surface soils (Table 2) was investigated in sterilized systems. Solute concentrations were determined in both the aqueous and solid phases at various times throughout a two-month equilibration period. Solute extracted using a rigorous extraction method was considered to be reversibly sorbed. Solute mass not recovered was assumed to be irreversibly bound or transformed. The relative contributions from the different processes varied across soils and between solutes; however, the general dissipation was similar to what is shown for aniline with the Okoboji soil in Figure 7.

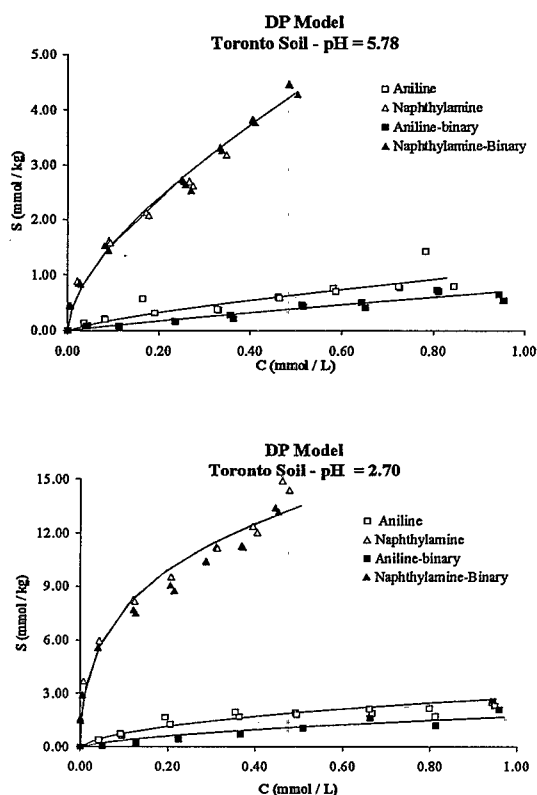


Figure 6. Single and binary (aniline and α -naphthylamine) isotherms for Toronto soil measured in a 5 mM CaCl_2 solution with pH values of 5.78 and 2.70. Solid lines are competitive DP model predictions. Values for μ and σ obtained from single solute data.

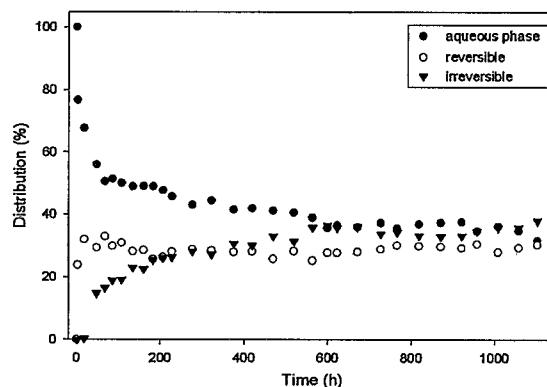


Figure 7. Percent distribution of aniline (in the aqueous phase; reversibly-sorbed; and irreversibly-bound or transformed) relative to the total aniline applied as a function of time with Okoboji soil.

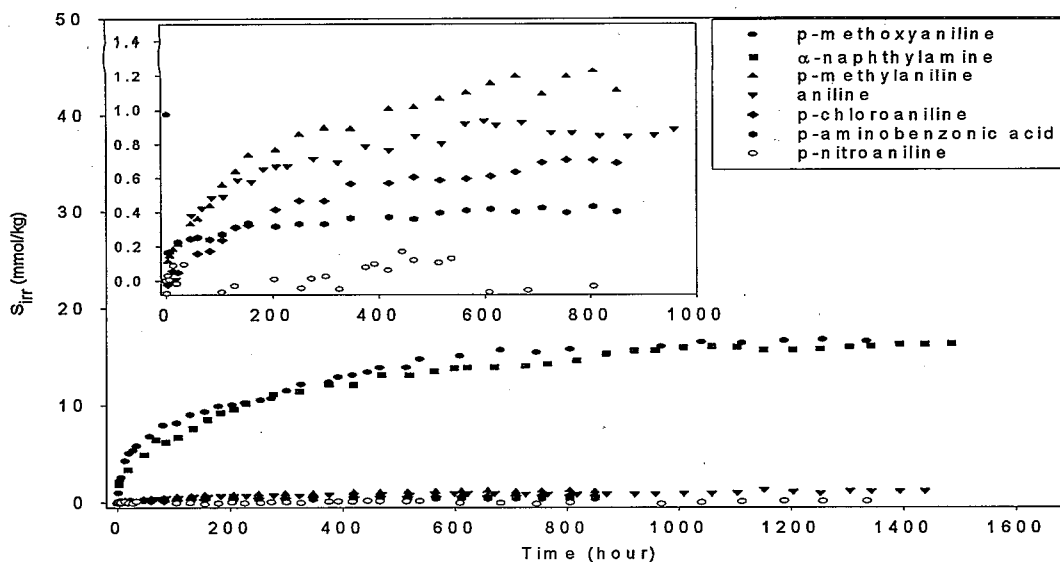


Figure 8. Irreversible binding and/or transformation of several amines (S_{irr}) in Okoboji soil with time.

Initially, most of the sorption appears to be fast and reversible, while slow chemical binding/transformation becomes increasingly more significant over time. The extractable soil-sorbed concentrations and corresponding aqueous concentrations measured at each sampling time over the two-month equilibration are in good agreement with the 24-h, nonlinear sorption isotherms indicating fast desorption of reversibly-sorbed solute as the aqueous-phase concentrations are depleted by the slower, irreversible processes (Li and Lee, 1998).

Other distribution experiments were conducted with the same initial amine concentration but at soil mass to solution ratios (m/V) varying over a factor of ten. Reversible sorption processes were not impacted over the m/V range investigated; however, the irreversible loss of amine ($\mu\text{mol/kg}$) increased with decreasing m/V. Fast, reversible sorption processes reduced aromatic amine concentrations in solution and retarded irreversible reactions indicating the concentration-dependence of the latter. With irreversible and reversible processes occurring in parallel, parameters from the reversible sorption isotherms can be used to predict amine solution concentrations available for irreversible binding and transformation.

The specific irreversible sorption/transformation process as well as the rate and extent of the reaction varied significantly among the aromatic amines. Figure 8 exemplifies the trends observed across solutes on a given soil for the amount of amine irreversibly bound or transformed (S_{irr}). The rate and extent of irreversible loss correlated very well to the intrinsic reactivity of the aromatic amine, which is reflected in the reported Hammett constants (δ^+) and half-wave potentials ($E_{1/2}$) (Pysh and Yang, 1963). Intrinsic solute reactivity increases with decreasing δ^+ and $E_{1/2}$. For p-methoxyaniline, which has the lowest δ^+ and $E_{1/2}$ values, more than 85% of the amine was

irreversibly lost during the 2-month equilibration whereas less than 12% of p-nitroaniline, with the largest δ^+ and $E_{1/2}$ values, was irreversibly lost on any soil.

Our ability to accurately define the magnitude and rate of each process contributing to irreversible binding and transformation in whole soils would result in a model with several unknown variables. Therefore, a simple heterogeneous reaction model commonly used to describe gas reaction kinetics on heterogeneous solid surfaces was modified to estimate reaction rates based on a few assumptions hypothesized to be valid for interactions of aromatic amines with whole soils. We assumed that (i) all irreversible binding and transformation reactions are first-order with respect to the aromatic amine solution concentration; (ii) activation energies vary linearly as a function of reactive sites; and (iii) available reactive soil sites change over time but remain more numerous than sites consumed. A similar approach has been used in describing the reaction kinetics of gas on heterogeneous solid surfaces (Low, 1960) and nutrient sorption/desorption (Aharoni, et al, 1991). The observed change in reaction rates with time was best described using a biphasic approach where reaction rates were estimated independently for contact times < 20 h and ≥ 20 h. The initial rate of the irreversible reaction was faster by a factor of 20 than the rate at later times. Rates are expected to retard with time because the probability of collisions with sufficient energy to activate a reaction will decline as solute molecules are depleted and remaining reactive sites have increasingly higher energies of activation. For the various amines, apparent rate constants (k_{app}) vary approximately one to two orders-of-magnitude, but for a given solute, k_{app} values across soils varied less than a factor of four. Therefore, as a first assessment of trends between amines, apparent rate constants were averaged across soils. With the exception COOH-AN, apparent reaction rates for both operationally defined time periods generally decrease in a natural log-linear manner

with decreasing solute reactivity as represented by intrinsic reactivity indices δ^+ and $E_{1/2}$ (Figure 9) as observed for other systems (Laha and Luthy, 1990). Compared to the other anilinium compounds, reaction rates with COOH-AN were almost two orders-of-magnitude faster than expected from the reported intrinsic reactivity indices, which may be due to the presence of the strong electron-donating carboxylic acid group.

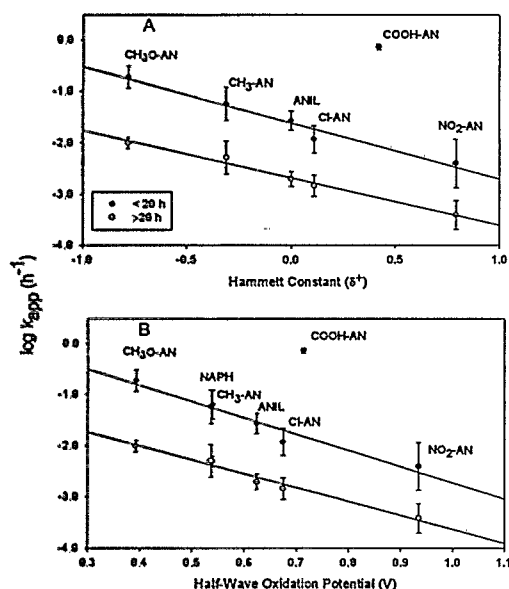


Figure 9. Average apparent reaction rates (k_{app} , h^{-1}) of irreversible process for several aromatic amines correlated to (A) Hammett constant; and (B) Half-Wave Oxidation Potential, during two characteristic time periods of ≤ 20 h and > 20 h.

During the course of the long-term study, pink-red colored substances appeared in the soil phases that had been spiked with either p-methoxyaniline, α -naphthylamine, or p-methylaniline. The colored substances were not observed in the aqueous-phase. The colored substances were extractable with an acetonitrile/acetate buffer indicating that not all of the irreversible reactions resulted in covalent bonding to the soil phase, but rather transformation to products that are strongly sorbed to the soil phase. With increasing contact times between the aqueous amine solution and the soil, the red hue in the solvent extracts of the soils became more pronounced. Multiple peaks were observed in the GC-MS analysis of the solvent extracts from the p-methoxyaniline spiked soils with the primary derivative identified as 4,4'-dimethoxyazobenzene. For the soil with α -naphthylamine, the dominant derivative identified was N-(1-aminonaphthyl)-1-naphthylamine while for p-methylaniline spiked soils, the apparent derivative concentrations were below the detection limits of the GC/MS employed. Evidence of dimer formation for at least p-methoxyaniline and α -naphthylamine is indicative of soil-catalyzed radical formation and coupling reactions as has been shown with

Fe(III) and Mn (IV/III) oxides, montmorillonite clays, and biological enzymes (Laha and Luthy, 1990; Klausen et al., 1997; Ainsworth et al., 1991; Tatsumi, 1994). Not all amines may undergo oxidative coupling. For the amine/soil combinations investigated in this study, transformation reactions were only evident for amines with $E_{1/2} \leq 0.54$ V.

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Appendix A (Published Papers)

- (1) Fabrega, J., C.T. Jafvert, H. Li, L.S. Lee, 1998. Modeling short-term soil-water phase distribution of aromatic amines. *Environmental Science and Technology*, 32:2788-2794.
- (2) Lee, L.S., A. K. Nyman, H. Li, M.C. Nyman, and C. Jafvert. 1997. Initial sorption of aromatic amines by surface soils. *Environmental Toxicology and Chemistry*, 16:1575-1582.
- (3) Nyman, M.C., A. Nyman, L.S. Lee, L. Nies and E. Blatchley. 1997. Fate of 3,3'-dichlorobenzidine in lake systems. *Environmental Science and Technology*, 31:1068-1073.
- (4) Strathmann, T. and C. T. Jafvert. 1998. Ion-pair association of substituted phenolates with K⁺ in

octanol. *Environmental Toxicology and Chemistry*, 17: 369-376.

- (5) Strathmann, T. 1997. Ion-pair association of substituted phenolates with K⁺ in octanol. M.S. thesis, Purdue University, West Lafayette, IN.
- (6) Li, H. and L.S. Lee, 1999. Sorption and abiotic transformation of aniline and 1-naphthylamine by surface soils. *Environmental Science & Technology*, 33:1864-1870.
- (7) Fabrega, J. 1999. Modeling Distribution of Aromatic Amines in Saturated Aqueous Systems. Ph.D. dissertation, Purdue University, West Lafayette, IN.
- (8) Li, Hui. 1999. Sorption and Transformation of Aromatic Amines by Surface Soils in Aqueous Systems. Ph.D. dissertation, Purdue University, West Lafayette, IN.
- (9) Fabrega, J., C.T. Jafvert, H. Li, L.S. Lee, 2000. Modeling long-term abiotic processes of aniline to water-saturated soils. *Environmental Science & Technology*, Accepted.

Appendix B (Works Submitted or in Progress)

- (1) Li, H., Lee, L.S., Fabrega, J., Jafvert, C., Graveel, J., 2000. Effect of substitution on the interaction of aromatic amines with soils in aqueous systems. *Environmental Science & Technology*, (submitted).
- (2) Fabrega, J., C.T. Jafvert, H. Li, and L.S. Lee. 2000. Modeling competitive sorption of aniline and 1-naphthylamine by water-saturated soils. (to be submitted to *Environmental Science & Technology*).
- (3) Li, H., L.S. Lee, Fabrega, J., and C.T. Jafvert. 2000. Single and binary sorption of aromatic amines on surface soils (to be submitted to *Chemosphere*).

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Quality Assurance Statement

All research projects making conclusions or recommendations based on environmentally related-measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance (QA) program. This project was conducted under an approved QA project plan. Information on the plan and documentation of the QA activities are available from the Principal Investigators (L.S. Lee and C.T. Jafvert).





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