

Sorption and Abiotic Transformation of Aniline and α -Naphthylamine by Surface Soils

HUI LI AND LINDA S. LEE*

Department of Agronomy, Purdue University,
West Lafayette, Indiana 47907-1150

Improving the assessment and subsequent remediation of sites contaminated with aromatic amines requires differentiating between reversible and irreversible sorption processes and quantifying the controlling parameters. The interaction of aniline and α -naphthylamine with five surface soils from CaCl₂ electrolyte solutions was studied for a 2 month equilibration period using a batch equilibration method. Soils varied in pH (4.4–7.4), cation exchange capacity (CEC, 4.4–36.2 cmol_c/kg), and organic carbon content (OC, 0.4–5%). Reversible sorption processes reached equilibrium within the first day of equilibration for all soil–solute combinations while irreversible binding and transformation proceeded for much longer times. After 1 day, increases over time in the ratio of reversibly sorbed concentrations to solution concentrations were shown to primarily result from nonlinear sorption coupled to decreasing aqueous solute concentrations from irreversible binding/transformation. Dimer formation hypothesized to be mineral catalyzed was confirmed with GC/MS and UV–vis detection for α -naphthylamine, but was not observed for aniline. Fast reversible sorption processes reduced aromatic amine concentrations in solution and retarded irreversible reactions indicating processes occur in parallel.

Introduction

Several aromatic amines used in the production and transformation of dyes, paints, ammunition products, and agrochemicals have been identified as potential carcinogens warranting the need for predictive tools of their environmental fate (1, 2). However, their intrinsic reactivity and ionizability have delayed the development of comprehensive quantitative relationships for predicting their interaction with soils. Aromatic amines interact with soils through both reversible and irreversible processes. Reversible sorption includes cation exchange, hydrophobic interactions by London–van der Waals forces, and dipole–dipole or induced-dipole attractions. 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). During short characteristic time periods (e.g., within 24 h), sorption of organic bases is primarily reversible with cation exchange being the predominant sorption mechanism (3). The soil–solution pH is the most significant factor controlling the magnitude of their sorption in soil systems (4–9).

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

irreversible processes such as covalent binding with particular constituents in soil organic matter (SOM) (e.g., quinone and phenolic functional groups) and mineral-catalyzed transformation reactions (10–15). 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 imine, and (2) the slow but irreversible addition of the amino group to C=C bond in aromatic ring of quinone by 1,4-nucleophilic addition to produce aminobenzenquinone (16–18). Direct spectroscopic evidence exists for similar reactions with humic substances along with the further incorporation of aminobenzenquinone into nitrogen heterocyclic linkages (19). 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. (20) observed increasing covalent binding rates of aniline to Suwannee River fulvic acid with increasing pH. Iron and manganese oxides as well as montmorillonite clays may catalyze transformation reactions of aromatic amines including oxidative coupling resulting in dimer formations (i.e., dimerization) (14, 15, 21). In this mechanism, the neutral aromatic amines first form radical cations which then couple to form dimeric species. The amine dimers then are preferentially, but not necessarily irreversibly, sorbed to soil particles. In a whole soil, SOM would have a high affinity for such dimers. Laha and Luthy (14) observed increasing reaction rates with decreasing pH for oxidation of substituted anilines by δ -MnO₂. The observed pH dependence was not attributed to any pH-dependent speciation of the amine, but to the pH-dependent formation of oxide surface precursor complexes (22). Therefore, the impact of pH on the overall long-term reactivity of aromatic amines with soils is complex. For lower pH values both reactivity of the soil surface and redox potential increase; however, speciation of the aromatic amine shifts away from the neutral species, which is identified as the more reactive species for both covalent binding and oxidative transformation.

Differentiating between reversible and irreversible processes and quantifying the parameters that control the irreversible sorption processes is imperative in improving the assessment and subsequent remediation of sites contaminated with aromatic amines. The impact of the irreversible processes relative to the reversible processes will be a function of the residence time of the aromatic amine with the soil, 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 interaction of aromatic amines with soil/sediment constituents or model compounds has been extensively studied for relatively short contact times; however, results from long-term studies are sparse. In the present study, the interaction of aniline and α -naphthylamine with five surface soils was investigated by determining solute concentrations in both the aqueous and solid phases at various times throughout a two-month equilibration period. A rigorous extraction method was used to differentiate between reversible physical sorption, irreversible chemical binding, and abiotic transformation processes. The impact of the irreversible sorption and soil-induced transformation of amines with associated mechanisms, and the time-dependent distribution of both reversible and irreversible processes will be presented.

* To whom correspondence should be addressed. Phone: (765) 494-8612. Fax: (765) 496-2926. E-mail: lslee@purdue.edu.

TABLE 1. Characterization for the Selected Soils

soil (subgroup)	pH ^a	sand (%)	silt (%)	clay (%)	OC (%)	CEC [cmol(-)/kg]	qualitative mineral identification ^{b,c}
Toronto (Typic Haplaquoll) ^b	4.4	11.9	67.6	20.5	1.34	11.2	mixed; Fe and Al oxides
Okoboji (Cumulic Endoaquoll) ^c	7.4	31.8	36.2	32.0	4.98	36.2	mixed; smectite dominated; hydroxy interlayered vermiculite; Fe and Al oxides
Chalmer (Typic Haplaquoll) ^b	6.5	11.1	72.8	16.0	1.17	13.0	mixed; Fe and Al oxides
Drummer (Typic Haplaquoll) ^b	7.2	13.0	65.8	21.2	2.91	26.5	mixed; Fe and Al oxides
Bloomfield (Psammentic Hapludalf) ^c	6.4	81.4	11.0	7.6	0.36	4.4	mixed; illite dominated; Fe and Al oxides

^a pH in 1 g/mL slurry in distilled water. ^b pH, particle size analysis, OC, and CEC from Lee et al. (3) and mineral identification from Franzmeier et al. (28). ^c All characterization data from Cox (23).

TABLE 2. Selected Physical and Chemical Properties of Solutes

chemicals	aniline	α -naphthylamine
MW (g/mol) ^a	93.14	143.18
density (g/mL) ^a	1.02	1.13
melting point (°C) ^a	-6.3	50
boiling point (°C) ^a	184-186	301
S_w (mg/L) ^a	34000-36000	1700
pK_a ^a	4.63	3.92
$\log K_{ow}$ ^a	0.90/0.98	2.22 ^b
$E_{1/2}$ (V)	0.63 ^c	0.54 ^d

^a Data from Verschuren (29) unless otherwise noted. ^b Estimated using LEO's fragment constant method according to Lyman et al. (30). ^c Suatoni et al. (31). ^d Pysh et al. (26).

Materials and Methods

Sorbents. A total of five surface horizon soils varying in pH, particle size, cation-exchange capacity (CEC), and organic carbon (OC) content were used in this study. Soil type and selected characteristics are shown in Table 1. Soil characterization methods are detailed in Lee et al. (3) and Cox (23). The Toronto, Chalmers, and Drummer soils were collected from the Purdue University Agronomy Research Center in Tippecanoe County, IN; the Bloomfield soil from the Southwest Purdue Research Center in Knox County, IN; and the Okoboji soil from Iowa. The Toronto soil is the same soil referred to in Lee et al. (3) as Chalmers-4 and was collected from a plot where lime application was prohibited such that a low soil pH would be maintained for research purposes. Soil samples were air-dried, passed through a 2 mm sieve and stored in closed containers at room temperature prior to use.

Chemicals. Aniline and α -naphthylamine, the aromatic amines selected for this study, exhibit an order-of-magnitude range in their physiochemical properties. Aniline is less hydrophobic (i.e., has a lower n -octanol/water partitioning coefficient, and a higher aqueous solubility) and is less acidic (higher pK_a), compared to α -naphthylamine. Selected properties for these amines are shown in Table 2. Aniline and α -naphthylamine were purchased from Sigma Chemical with reported purity greater than 98%. Aniline was further purified by distillation, and α -naphthylamine was used as received. Acetic acid (glacial), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), anhydrous sodium sulfate (Na_2SO_4), ammonium acetate (NH_4OAc), sodium acetate (NaOAc), and acetonitrile (CH_3CN) were purchased from Mallinckrodt at greater than 99% purity.

Batch Equilibration Studies. Sorption/transformation of aniline and α -naphthylamine from a 0.005 M CaCl_2 matrix with all five soils was assessed (1) for multiple concentrations in a 1 day batch equilibration and (2) for a single initial concentration over a 2 month period using a batch-equilibration method with destructive sampling (long-term study). A 0.005 M CaCl_2 matrix was selected because it was

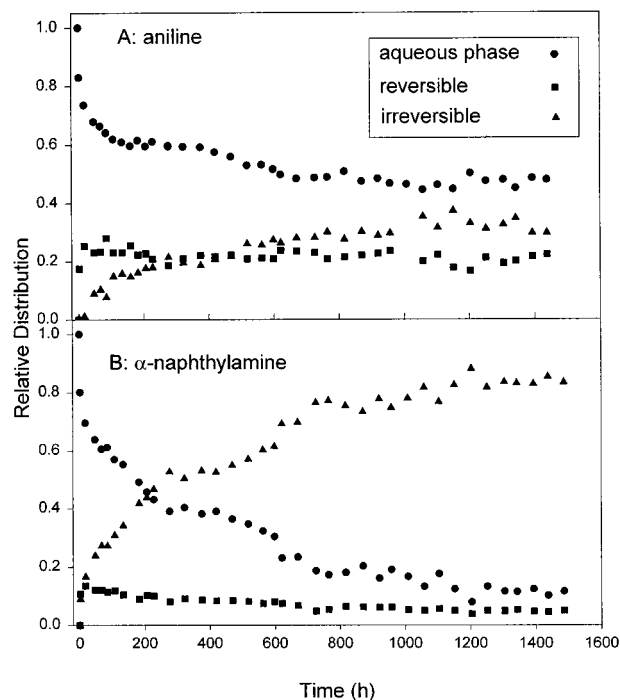


FIGURE 1. The distribution relative to the total applied solute mass of (A) aniline and (B) α -naphthylamine in the aqueous phase, reversibly sorbed, and irreversibly bound/transformed as a function of time for Chalmers soil.

representative of typical soil-solution ionic strengths with Ca^{2+} being the most relatively abundant inorganic cation for most soils. To minimize microbial degradation in the long-term study, all glassware and deionized water were sterilized by autoclaving; aniline and α -naphthylamine solutions were filter-sterilized using a 0.2 μm membrane; and soils were sterilized using ^{60}Co radiation (500 g of soil exposed at the rate of 3.0 krad/min for 16 h). Soil mass to solution volume ratios (m/V) were optimized for approximately 50% loss from solution within 1 day for each solute-soil combination. In the 1 day batch equilibration, 10 initial concentrations from 1.5×10^{-5} to 1.5 mM of either aniline or α -naphthylamine were used. In the long-term study, initial solute concentrations were approximately 0.7 mM α -naphthylamine for Chalmers soil, Bloomfield soil, and Okoboji soils; 0.91 mM α -naphthylamine for Toronto soil and Drummer soil; and 1.1 mM aniline for all soils. Soils were weighed into glass Kimax centrifuge tubes of either 8, 15, or 35 mL equipped with Teflon-line screw lids; solutions were added; contents were suspended using a vortex mixer for 10 s; covered with aluminum foil to minimize photolysis; and placed on an end-over-end rotary shaker (30 rpm) at room temperature ($23 \pm 3^\circ\text{C}$).

In the 1 day multiple concentration experiments, sorbed concentrations were estimated by difference between initial

solute mass added and solution concentrations measured at 24 h. In the long-term study, one to three samples for each solute–soil combination were sacrificed for analysis of both the solution and soil phases at several times throughout the 2 month equilibration. Contact time for each sampling was defined from the time solution was added until samples were removed for centrifugation. Sample tubes were centrifuged at 1750g for 30 min (Jouan CR312) and an aliquot of the supernatant was transferred to a clean vial for analysis. Controls consisting of aniline, α -naphthylamine, or solute-free CaCl_2 solutions in the presence or absence of soil were also analyzed at each sampling time. Soils were extracted with 3/1 (v/v) acetonitrile/0.3 M NH_4OAc solution by shaking for several hours followed by refluxing for one h in boiling flasks. During transfer to the boiling flask, tubes were rinsed three times with a total of 5 mL of clean extraction solvent. Soil–solvent slurries were centrifuged at 1750g for 10 min, and supernatants were collected for analysis. Solute mass in the residual water was determined by assuming the solute concentration in the residual water was the same as that measured in the bulk aqueous supernatant and determining content of residual water gravimetrically. The solute mass extracted is assumed to be that which is sorbed reversibly in an aqueous system. Any solute not extracted is assumed to be irreversibly bound or transformed. The extraction procedure selected was found to achieve the most effective recoveries for aniline and α -naphthylamine as well as extract transformation byproducts relative to various mixtures of methanol, acetone, acetonitrile, and ammonium acetate assessed. To ensure that the extraction solvent did not induce any sorption or transformation reactions during the extraction process, controls of 3:1 (v/v) acetonitrile/0.3 M NH_4OAc extraction solvent containing either aniline or α -naphthylamine added to clean soil were included. No sorption or transformation of either solute was observed in the controls.

Aqueous supernatant and solvent extracts were analyzed using a Shimadzu high-performance liquid chromatography (HPLC) system (LC-10AD pumps with a SIL-10A auto injector) equipped with a UV–vis detector (model SPD-10A, $\lambda=254$ nm for both aniline and α -naphthylamine) and a Supelcosil ABZ⁺ reversed-phase column (15 cm \times 4.6 mm ID). The mobile phase was 40/60 (v/v) acetonitrile/acetate buffer (pH 4.7) at a flow rate of 1.5 mL/min. If solute concentrations were out of the linear range of the standard curves, the samples were diluted and reanalyzed.

Results and Discussion

One Day Isotherms. All sorption isotherms generated from the multiple concentration 1 day batch equilibration were nonlinear; therefore, isotherms were fitted to the empirical Freundlich sorption model: $S = K_f C_w^N$ where K_f ($\mu\text{mol}^{1-N} \text{mL}^N \text{g}^{-1}$) is the Freundlich sorption coefficient and N (unitless) is a measure of isotherm linearity ($N=1$ is a linear isotherm). Sorption coefficients are reported in Table 3. For a given soil, sorption of α -naphthylamine was greater than aniline consistent with α -naphthylamine's lower pK_a and larger molecular size (3). Between soils, the magnitude of sorption is consistent with the coupled pH– pK_a relationship, available exchange sites (i.e., CEC), and soil organic carbon content in good agreement with the data reported by Lee et al. (3) and Fabrega et al. (5).

Long-Term Study. Solute mass measured in the aqueous phase and recovered from exhaustive solvent extraction of the soils at selected times was used to evaluate the magnitude of both reversible sorption and the irreversible sorption/abiotic transformation processes over time. On the basis of the total applied solute mass, the relative contributions from the different processes varied across soils and between solutes; however, the general dissipation pattern was similar to what is shown for aniline and α -naphthylamine with

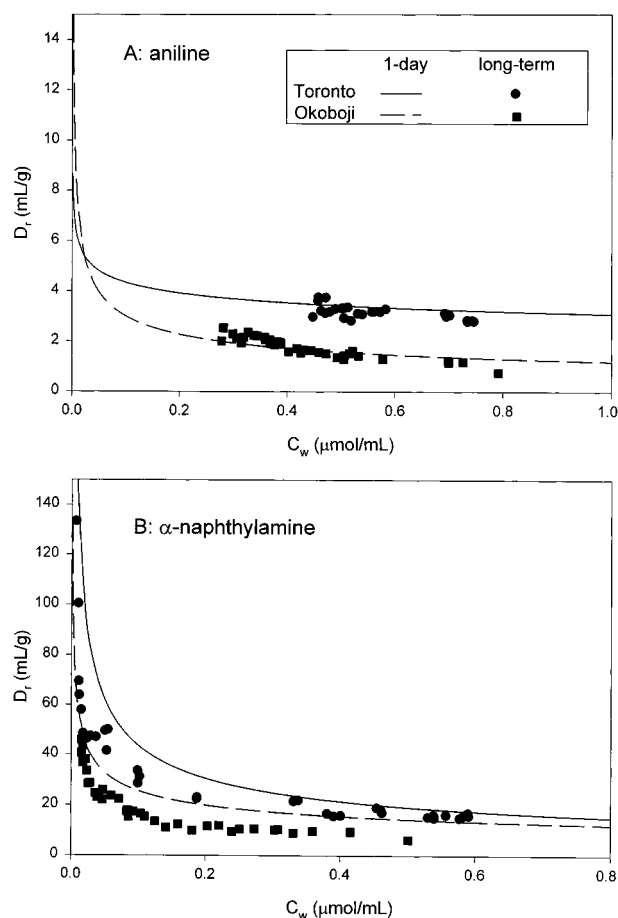


FIGURE 2. Comparison of the distribution coefficients calculated from the Freundlich fits of the 1 day isotherms (lines) with distribution coefficients measured at each sampling time in the long-term study.

Chalmers soil in Figure 1. Initially, most of the sorption appears to be fast and reversible, while slow chemical binding/transformation becomes increasingly more significant over time with regards to the total amount of amine lost from solution. Similar biphasic sorption was observed by Szecsody et al. (24) for α -naphthylamine in aqueous montmorillonite systems with cation exchange nearly complete within the first 2 h followed by transformation occurring from 50 to >1000 h. Szecsody et al. (24) attributed the rate-limiting step to chemical kinetics. In whole soils, it is also plausible that increases in irreversible chemical binding over time could result from slow diffusion to reaction sites within SOM (intraorganic matter diffusion, IOMD).

Reversible Sorption Processes as a Function of Time.

Soil–water distribution coefficients for the reversible sorption processes were estimated at selected times ($D_{r,t}$) using the following equation:

$$D_{r,t} = \frac{S_{r,t}}{C_{w,t}} \quad (1)$$

where $S_{r,t}$ is the solvent extractable solute concentration in the soil and $C_{w,t}$ is the aqueous-phase concentration at a given time (t). Average values and standard deviations for $D_{r,t}$ are shown in Table 4 for both aniline and α -naphthylamine at selected time periods for all five soils. Reversible sorption appears to increase with time for some aniline–soil combinations and for all α -naphthylamine–soil combinations. Although increases in $D_{r,t}$ over time may be attributed to slow diffusion to additional sorptive domains, it may also be a result of nonlinear sorption. Decreases in solution

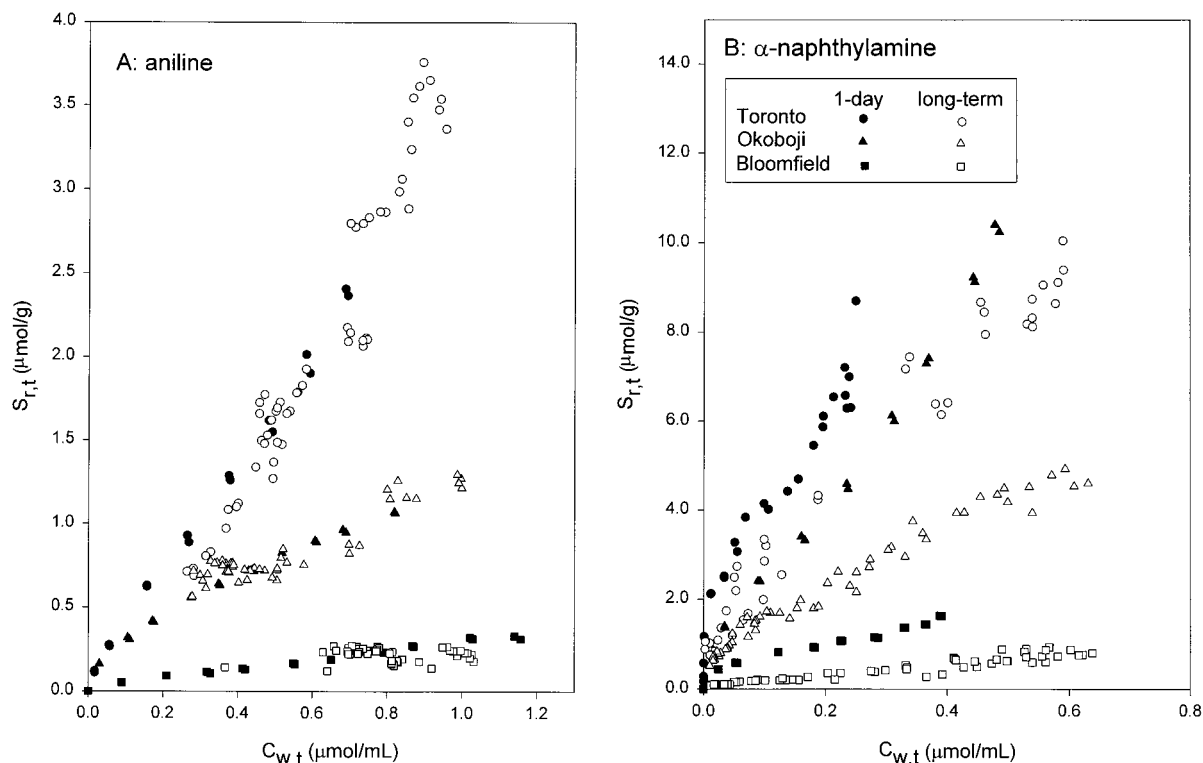


FIGURE 3. Comparison of 1 day sorption isotherms with isotherms constructed from extractable solute concentration ($S_{r,t}$) and aqueous-phase concentration ($C_{w,t}$) at each sampling time in the 2 month and 1 week study for (A) aniline and (B) α -naphthylamine.

TABLE 3. Summary of the Soil Mass to Solution Volume Ratios (m/V , g/mL), Corresponding Soil-Solution pH Values, and Freundlich Parameters for the 1-D Isotherms

soil ID	aniline					α -naphthylamine				
	m/V	pH \pm 0.1	K_f^a	N	r^2	m/V	pH \pm 0.1	K_f^a	N	r^2
Toronto	1:10	4.55	3.10	0.85	0.99	1:32	4.55	13.5	0.49	0.96
Okoboji	2.5:5	7.20	1.20	0.60	1.00	0.2:5	7.48	11.2	0.64	1.00
Drummer	5:10	7.23	0.50	0.75	0.99	5:10	7.28	4.23	0.54	0.98
Chalmers	4:10	6.72	0.53	0.65	1.00	4:10	6.76	4.06	0.31	0.98
Bloomfield	5:5	6.44	0.29	0.84	0.99	5:10	6.55	2.36	0.49	0.98

^a $\mu\text{mol}^{1-N} \text{mL}^N \text{g}^{-1}$.

concentration as irreversible processes proceed will result in increasing $D_{r,t}$ when sorption isotherms have Freundlich N values less than unity. The impact of decreasing aqueous-phase concentrations C_w on D_r can be predicted by defining D_r in terms of the Freundlich sorption model and using the Freundlich model fits estimated from the 1 day isotherms (Table 3) assuming all sorption is reversible within this period,

$$D_r = \frac{S}{C_w} K_f C_w^{N-1} \quad (2)$$

Equation 2 predictions of D_r as a function of C_w are shown in Figure 2 for both aniline and α -naphthylamine from Toronto and Okoboji soils along with $D_{r,t}$ and $C_{w,t}$ measured over time in the long-term study. Similar data were observed for all soil-solute combinations. Likewise, reversible sorption isotherms constructed from the long-term study ($S_{r,t}$ versus $C_{w,t}$) for both solutes are compared with the 1 day multiple concentration isotherms for Toronto, Okoboji, and Bloomfield soils in Figure 3. Excellent agreement observed for aniline in both Figures 2A and 3A confirms fast equilibrium of the reversible sorption processes and the dominance of reversible processes at early contact times. For α -naphthylamine, trends

TABLE 4. $D_{r,t}$ (L/kg) as a Function of Time for Aniline and α -Naphthylamine on Five Surface Soils^a

time (day)	Aniline				
	Toronto (2:10) ^b	Okoboji (4:10) ^b	Drummer (4:4) ^b	Chalmers (7:10) ^b	Bloomfield (4.5:5) ^b
1	3.07	1.18	0.58	0.49	0.20
1-5	3.23	1.48	0.55 (0.08)	0.53 (0.06)	0.22 (0.06)
6-15	3.16	1.47	1.00	0.54	0.24 (0.07)
16-25	3.13	1.69	1.04	0.56	0.32
26-35	3.25	2.96	1.26	0.65	0.34
36-65	3.24 (0.46)	2.15	1.33	0.66	0.35

time (day)	α -Naphthylamine				
	Toronto (0.75:25) ^b	Okoboji (1:25) ^b	Drummer (1.6:25) ^b	Chalmers (1.8:25) ^b	Bloomfield (2:10) ^b
1	15.3	9.49	2.66	2.69	1.71
1-5	17.2	9.80	4.44	2.71	1.4 (0.2)
6-15	22.4	11.0	4.61	2.96	1.5 (0.2)
16-25	31.2	15.4 (2.6)	3.86	3.25	1.8 (0.4)
26-35	47.0	19.4 (3.6)	5.5 (0.5)	4.2 (0.5)	2.1 (0.5)
36-45	56.8	23.7	4.6 (0.5)	4.68	3.0 (1.2)
46-55	101(32)	30.8 (5.2)	5.0 (2.1)	5.6 (0.9)	5.2 (1.4)
56-65	377	40.9	4.3 (0.7)	6.2 (0.8)	5.8 (0.8)

^a Standard deviations for $D_{r,t}$ are less than 10% unless shown otherwise in parentheses. ^b Soil mass to solution volume ratios (g/mL).

between the 1 day multiple concentration data and the long-term data are similar (Figures 2B and 3B); however, sorption estimated from the 1 day study is consistently greater than that estimated from the long-term study. Recall sorbed concentrations for the 1 day isotherm were estimated by difference and assumed to be reversible whereas $D_{r,t}$ in the long-term study was determined by extraction. Differences for α -naphthylamine are due to the occurrence of some irreversible binding and/or transformation within the first day of equilibrium. Good agreement for aniline and the general agreement in trends for α -naphthylamine (Figure 2) indicates that increasing D_r with time is primarily due to the

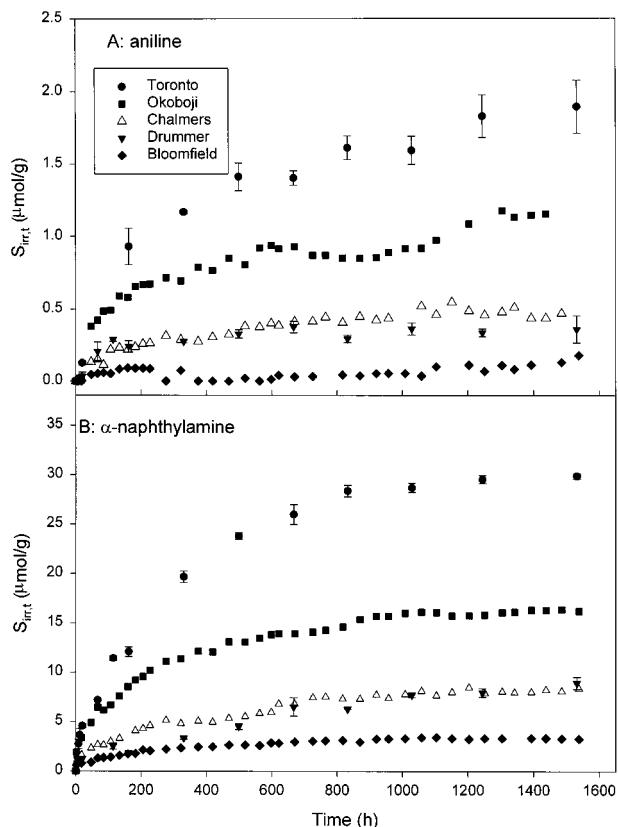


FIGURE 4. Irreversible binding/transformation versus time with five soils using the following m/V ratios listed in Table 4.

coupled effect of nonlinear sorption and decreasing aqueous solute concentrations from irreversible binding/transformation, and not necessarily from diffusion to additional reversible sorption sites.

Irreversible Binding and Transformation. Nonextractable soil concentrations of aniline and α -naphthylamine (S_{irr} , $\mu\text{mol/g}$) over time are shown for all soils in Figure 4. For all soil-solute combinations, the loss of solute to irreversible processes became increasingly more significant over time although rates appear to retard after 1–2 weeks (i.e., S_{irr} appears to be approaching a plateau). Recall no loss of solute was observed in the absence of soil; therefore, the soil mediates the irreversible loss of the solute whether bound or transformed. The amount of solute lost to irreversible processes is much greater for α -naphthylamine compared to aniline. Among soils, trends in the magnitude of S_{irr} are similar for both solutes with Toronto > Okoboji > Chalmers \approx Drummer > Bloomfield. During the course of the long-term study, pink-red-colored substances appeared in the α -naphthylamine contaminated soil phase. The colored substances were extractable with the acetonitrile/acetate buffer, indicating that transformation products are not necessarily irreversibly bound, but rather sorbed much more strongly than the parent compound. The red hue in the solvent extracts of the soils became more pronounced with increasing contact time of the aqueous α -naphthylamine solution with all soils. In an attempt to identify and semiquantify the extractable red-colored derivatives observed in the α -naphthylamine soil systems, GC-MS analysis and UV-vis scanning analysis were employed.

GC-MS Analysis. The sample prepared for GC-MS analysis was from an equilibration of 10 mL of 7 mM α -naphthylamine with 4 g of Chalmers soil for 120 h. Pure acetonitrile was used to extract the soil and residual water removed by passing through oven-dry NaSO_4 . GC-MS analysis was performed on a HP5890 capillary gas chromatograph coupled with a HP

5970 mass spectrometer. The total ion chromatogram is shown in Figure 5A with the mass spectra for peaks 2 (retention time = 28.09 min), 3 (retention time = 28.27 min), and 4 (retention time = 28.65 min) in panels B–D of Figure 5, respectively. The mass spectra of the primary transformation product (peak 4; Figure 5D) shows the dimer molecule peak at m/z 284 and the fragment at m/z 267 resulting from the loss of the amino group (MW = 17 g/mol); therefore, the proposed product is *N*-(4-aminonaphthyl)-1-naphthylamine. Ainsworth et al. (21) observed the same primary product in α -naphthylamine-montmorillonite systems and attributed it to the formation of a radical cation-clay complex. They identified iron (Fe^{3+}) substitution in montmorillonite as the key component responsible for the reaction because (1) sorbed α -naphthylamine did not transform on iron-free hectorite, but (2) transformation was observed in the presence of freshly sorbed Fe^{3+} on the hectorite surface. Specific chemical structure for the two smaller peaks (peak 2 and 3) was not identified; however, mass fragments of m/z 284 and 267 dominant in their mass spectra are indicative of dimer derivatives.

UV-Vis Scanning Analysis. Tracking the formation of the colored derivatives with a UV-vis scanning detector was selected as a simple approach to semiquantifying the dimerization reaction observed with α -naphthylamine. To allow direct comparison of UV-vis results between soils, the same soil mass to solution volume ratios (m/V) were used for all five soils. Samples were prepared by equilibrating 10 mL of 0.77 mM α -naphthylamine with 1 g soil samples for 20, 45, 62, 86, and 111 h. In the visible range, an absorption maximum at 498 nm ($A_{\lambda=498}$) was observed in extracts from all α -naphthylamine contaminated soils. $A_{\lambda=498}$ increased with aqueous equilibration times for all soils as shown in Figure 6A. The corresponding plot for $S_{irr,t}$ estimated from HPLC-UV analysis as previously described is shown in Figure 6B. The general trends observed with time between $A_{\lambda=498}$ and S_{irr} are similar, suggesting that for α -naphthylamine irreversible loss is primarily due to transformation rather than covalent binding for the time period investigated. However, S_{irr} appears to be increasing at a faster rate than $A_{\lambda=498}$ which may be due to the covalent binding of α -naphthylamine or subsequent transformation products to soil.

For extracts from the aniline-soil systems, no colored substances or UV-vis peaks other than aniline and soil blank peaks were observed. Thorn et al. (25) using NMR and ^{15}N -labeled-aniline showed that incorporation of aniline into soils only occurs through nucleophilic addition; however, in the presence of peroxidase or MnO_2 , oxidative coupling did occur. Laha and Luthy (14) and Klausen et al. (15) noted a log-linear decrease in oxidation rates of substituted anilines in MnO_2 suspensions as a function of solute half-wave potential ($E_{1/2}$) where dimerization was confirmed. $E_{1/2}$ values are inversely proportional to the intrinsic reactivity of the solute (26). The $E_{1/2}$ value of aniline ($E_{1/2} = 0.63$ V) is higher than that of α -naphthylamine ($E_{1/2} = 0.54$ V).

For both covalent binding and dimerization, the neutral amine is hypothesized to be the more reactive species inferring enhanced reactivity with increasing pH; however, the more acidic soil (Toronto) exhibited the highest initial rate of irreversible loss for both aromatic amines (Figures 4 and 6A). Similar results were also observed for the transformation product formation of α -naphthylamine (Figure 6B). The lower pH of the Toronto soil may have resulted in a higher redox potential which would have facilitated electron transfer needed for dimer formation and covalent binding. Although not all redox reactions are pH coupled, Bass Becking et al. (27) have demonstrated a general pattern of increasing redox potential with decreasing soil-solution pH.

Impact of Reversible Processes on Irreversible Reactions. To elucidate the impact of reversible sorption on the

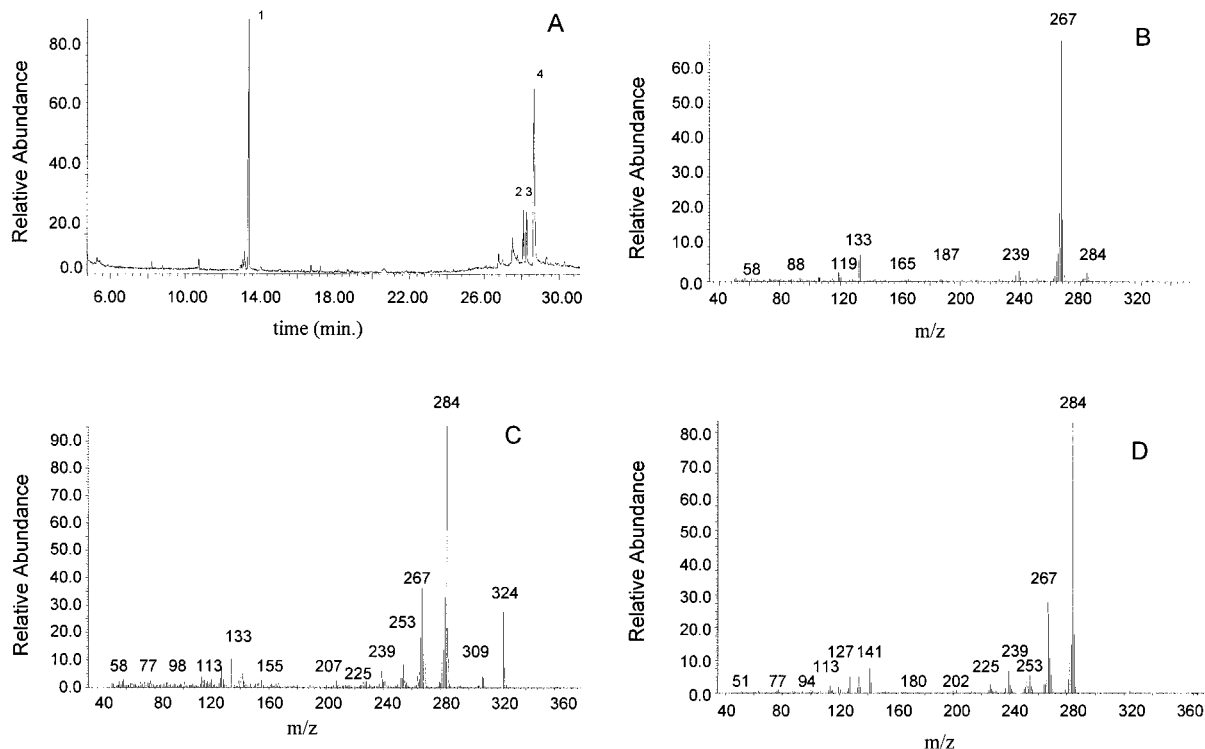


FIGURE 5. (A) Total ionic chromatograph of an acetonitrile extraction from Chalmers soil with peak 1 being α -naphthylamine and peaks 2, 3, and 4 transformation products; (B) mass spectra of unidentified peak 2; (C) mass spectra of unidentified peak 3; and (D) mass spectra of peak 4 proposed to be *N*-(aminonaphthyl)-1-naphthylamine.

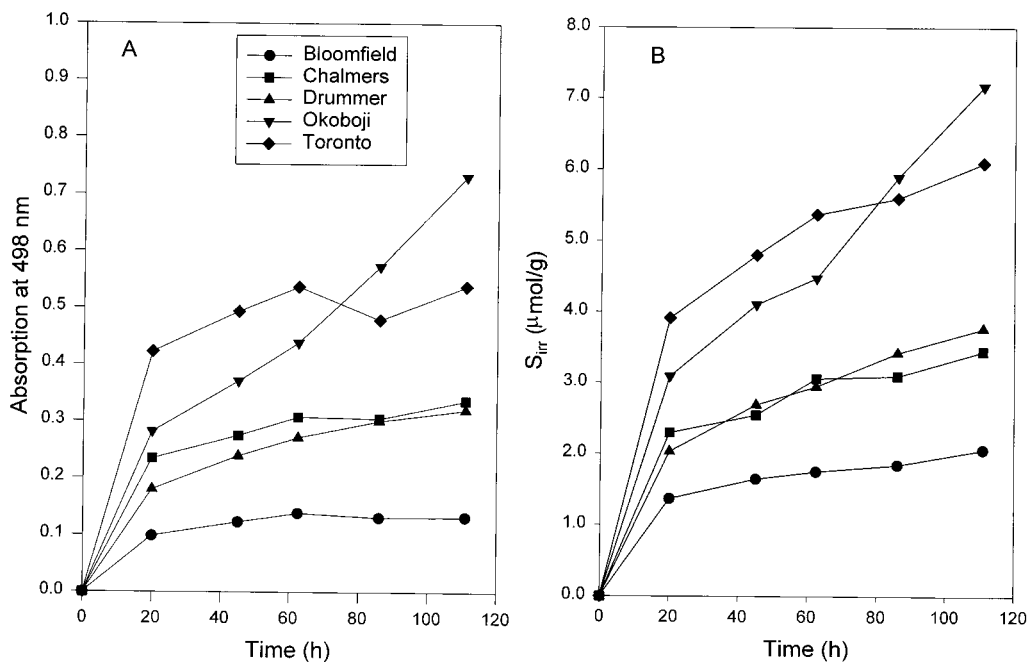


FIGURE 6. Transformation and irreversible binding of α -naphthylamine with five soils at fixed m/V ratios as a function of time as shown by (A) absorption at 498 nm of transformation products, and (B) $S_{irr,t}$ values estimated by mass not recovered in solution or soil extracts.

irreversible solute loss, experiments of 1 week duration were conducted for both aniline and α -naphthylamine on selected solute-soil combinations where soil mass to solution volumes were varied over a factor of 10 at a single solute concentration. Samples were sacrificed at 8 times during the 1 week experiment. Isotherms constructed in Figure 3 included the $S_{e,t}$ and $C_{v,t}$ values from the 1 week experiment where m/V ratios varied. No differences were observed, indicating that reversible sorption processes are independent of m/V ratios in the range investigated. However, the apparent

rate of the irreversible processes increased with decreasing soil mass. Fast reversible sorption processes reduced aromatic amine solution concentrations and retarded irreversible reactions suggesting that irreversible processes occur in parallel to reversible processes rather than in series. Therefore, any parameter impacting reversible sorption including inorganic cation concentrations, CEC, pH, and OC may impact irreversible processes. Given fast equilibrium of the reversible sorption processes and the m/v independence of $D_{t,t}$, outputs from an appropriate model for predicting

reversible sorption processes (5) can be used to predict amine solution concentrations available for irreversible binding and transformation.

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