The Terrestrial Fate of Coal-Liquid Constituents: Behavior of Alkyl Anilines in Soil

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July 1982

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SUMMARY

The low molecular weight aromatic amines (anilines) are important water soluble constituents of coal liquids. In the event of an accidental product spill, these components will be susceptible to leaching, possibly affecting local biota and water quality which may result in adverse human health effects. The impact of anilines released to the terrestrial environment will largely depend on their mobility and persistence. Studies were conducted to investigate those processes governing the mobility and persistence of the alkylanilines, namely, soil sorption and chemical/microbial degradation.

Soil sorption measurements were conducted on aniline and several methyl substituted anilines on A and B horizons of a soil profile collected from Davies County, Kentucky. The magnitude of sorption was large in all horizons. Sorption in the B horizons was larger than in the A horizon for many of the anilines studied, indicating the importance of both the mineral matrix and organic carbon content of the soil in determining the magnitude of sorption. In all cases, sorption could be described by the linear form of the Freundlich equation with Freundlich K constants of 3.93 to 6.91 for the A horizon and 6.54 to 10.47 for the B₂₂ horizon. Results of these measurements indicate that movement of the anilines through the soil would be significantly attenuated by sorption reactions.

Aniline sorption was measured in the A horizon after removal of the organic matter (hydrogen peroxide oxidation) and in the B₂₂ horizon after removal of amorphous iron oxides (oxalate extraction) and crystalline iron oxides (sodium dithionite/citrate extraction). Results of these experiments indicate that organic matter largely controls aniline sorption in the A horizon, while crystalline iron oxides and phyllosilicates are important in the B horizons. The effects of pH on aniline sorption was also examined and shown to have significant effects on the magnitude of sorption in both A and B horizons.

Soil degradation studies using ¹⁴C-3-methylaniline as a model for alkyl aniline degradation show that 3-methylaniline is readily metabolized by soil microorganisms during the 32-day period examined. However, less than 5% of

the methylaniline is converted to CO_2 during this time. It appears that as the 3-methylaniline is metabolized, the metabolic products are removed from solution and sorb to the soil. There is no accumulation of metabolites in solution, but several pools of 3-methylaniline derived products form on the soil with time--an acetone extractable, a sodium hydroxide extractable and a non-extractable pool. The result of microbial metabolism is the removal of methylaniline from solution and the formation of less mobile species. However, neither the nature of the metabolites nor their ultimate fate is known at this time.

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INTRODUCTION

In the event of a coal-liquid spill to the environment, the ecological and human health impacts will depend on a variety of environmental processes acting on the liquid. Toxicological properties alone cannot be used to assess the environmental hazard of the liquid, but must be used in conjunction with information on the fate of the material in the environment. This report summarizes results of studies undertaken to elucidate the fate of selected SRC components (alkyl anilines) in the terrestrial environment. The objective of the studies was to examine in detail the parameters affecting the environmental transport and persistence of alkyl anilines in soil. Emphasis was given to experiments that would give insight into the parameters that control the mobility and the chemical and biological degradation of the anilines. Effort was directed to obtain data that has broad application and that could eventually be used for the mathematical modeling of the transport of these compounds.

The initial studies focused on the alkyl anilines for a variety of reasons. Work at Pacific Northwest Laboratory (PNL) and at other laboratories has shown alkyl anilines to be present in many coal-derived liquids (1,2). At PNL, alkyl anilines were determined to comprise approximately 10% of the water-soluble organic fraction of a solvent refined coal (SRC) distillate (3). The water solubility, combined with the toxicity of the anilines (4,5), raises concern over the potential for ground and surface water contamination with anilines in the event of a terrestrial coal-liquid spill. The study of the alkyl anilines represents the first in a series of studies which will eventually deal with the higher molecular weight aromatic amines. Information generated in these studies will facilitate work with the higher molecular weight compounds. In spite of the mutagenic activity of the larger amines (6,7), they will be relatively immobile in the terrestrial environment, and the more immediate concern is with the low molecular weight compounds.

The fate of the anilines in the terrestrial environment will largely depend on the interaction of the anilines with soils and on their chemical and

biological degradation in soils. Therefore, studies were conducted to investigate the sorption of aniline and several alkyl substituted anilines and their chemical and biological stability in soils.

SORPTION OF ALKYL ANILINES

A coal liquid spilled on the soil surface will be susceptible to leaching, and may possibly affect local biota or water quality as the water soluble constituents pass through soil. The potential effects of these compounds will, to a large degree, be determined by their sorption to soil resulting in a reduced mobility. To evaluate the importance of sorption in determining the mobility of anilines, the sorption of several anilines on the individual horizons of an eastern soil was measured. Several alkylated anilines having different degrees of substitution were studied to evaluate the effects of increasing substitution and molecular weight. A number of studies were found in the literature which dealt with the interaction of anilines with soils (8-12). However, the majority of the studies dealt with herbicide-derived chloroanilines and not with the alkyl substituted anilines. In such earlier studies, soil materials from only the upper surface soil horizons were used. In contrast, we used the entire soil profile and, thus our information is of greater use for assessing potential impacts due to migration of coal liquid constituents through soil.

Soils were selected that are representative of a large region of the southeastern U.S. where coal conversion technology may be located. Sorption studies were performed on aniline and several alkyl substituted anilines using individual horizons of a soil profile in an effort to determine the variation of sorptive behavior with the physicochemical properties of the horizons. Several alkyl anilines were selected for study based on their occurrence in coal-liquids and to observe the change in sorption due to increasing compound hydrophobicity. Additional experiments were conducted using aniline as a model compound to elucidate the mechanisms of sorption and to determine which parameters control aniline sorption.

METHODS

Chemical and Mineralogic Analyses of Soils

Soil materials at their field moisture status were passed through a 2-mm-mesh sieve and air dried. Soil pH was determined on a saturated paste

after one hour of equilibration. Organic and inorganic carbon were determined by wet oxidation ($K_2Cr_2O_7$) and vacuum distillation (HCL as the liberant), respectively, with measurement of evolved CO_2 . Cation exchange capacity was determined by column elution with cesium (Cs) saturation. Amorphous oxides of iron were extracted using acid ammonium oxalate (13,14). In this procedure, 0.25- to 0.50-g subsamples of soil were extracted (in the dark) for 4 hr with 50 ml of ammonium oxalate-oxalic acid buffer adjusted to pH 3 with concentrated HCl. Dithionite soluble (total nonsilicate iron) was determined by three successive extractions with sodium dithionite/citrate-bicarbonate buffer (DCB). Both oxalate and dithionite treatments were performed in triplicate and extracts were analyzed for iron, aluminum and manganese by atomic absorption spectrophotometry. Total iron and aluminum were determined by Inductively Coupled Argon Plasma (ICP) emission analysis of nitric acid digests of <2.0 mm soil materials (ground to <150 μm) performed in a teflon-lined digestion bomb.

Particle size analysis was performed according to the method of Kittrack and Hope (15) following H_2O_2 (3%) oxidation of organic material and DCB treatment (deferration). The isolated clay subfractions (<0.2 μm and 0.2-2.0 μm) were flocculated with NaCl, washed free of chloride, frozen and lyophilized. Oriented slides were prepared with 50-mg subsamples of deferrated clay and analyzed by x-ray diffraction with Ni filtered Co K α radiation using a 1° divergence slit, a 0.1° receiving slit, and a diffracted beam monochrometer. Standard chemical (K, Mg, glycerol solvation) and thermal treatments were employed. A separate sample was subjected to DMSO intercalation to confirm the presence of kaolinite. Additionally, the clay fraction (<2.0 μm) was isolated from the untreated B_{22} horizons by centrifugation following ultrasonic dispersion (150 W, 15 min) in water at pH 8.5 (NaOH). The untreated clay fraction was boiled in 5 N NaOH to concentrate iron oxide minerals, and the residue was subjected to x-ray diffraction analysis.

Aniline and Alkyl Aniline Sorption Measurements

Initially, 1-g subsamples of each major soil horizon were equilibrated with 5 ml of a 100 ppm aniline solution and the aqueous equilibrant samples

over a 32-hr time period to define time required for sorption and to evaluate compound stability over this time interval. It was determined that with this solution to solids ratio, aniline sorption to soil was rapid and equilibrated within two hours. Following sorption, aniline concentrations in solution remained constant for 24 hr indicating the chemical/microbiologic stability of this compound over the time interval.

A variety of sorption experiments were performed to define the mode of interaction of aniline with the individual soil horizons. In all cases, sorption was followed in the batch mode by equilibrating 1 g of soil with 5 ml of an aqueous aniline solution in 35 ml-Corex tubes with teflon-lined screw caps at 25°C for 4 hr. The samples were then centrifuged for 5 min at 7700 g, decanted, and the supernatant centrifuged again at 7700 g for 20 min. The supernatant was analyzed for aniline by direct liquid chromatographic analysis with UV detection.

Sorption to Natural Soil Horizons

Sorption isotherms were determined for each of the anilines in each soil horizon over the concentration range of 25 to 400 ppm aniline. This concentration range was chosen to bracket aniline concentrations that could be produced by laboratory water extraction (1:2 oil to water) or environmental leaching of spilled coal liquids. Additional electrolytes were not added to these suspensions, but Inductively Coupled Argon Plasma (ICP) and ion chromatographic analyses indicated that the prominent inorganic ions in the aqueous phase of the equilibration were Ca^{2+} and SO_4^{2-} , in a concentration approximately 0.15 mM.

Sorption of Phenols

Sorption of phenols on soils was measured as described for anilines, except that the soil to solution ration was 1:1 and samples were equilibrated for 19 hr.

Sorption to Treated Horizons

Sorption isotherms for aniline were determined on A_1 horizons subjected to H_2O_2 oxidation and B_{22} horizons extracted with acid ammonium oxalate

and dithionite-citrate-bicarbonate (DCB). Following treatment all horizons were washed successively with distilled water to remove residual extractant, saturated with 1 N CaCl_2 at pH 5, washed free of chloride, frozen, and lyophilized. Prior to use in sorption experiments, treated horizons were washed twice with 0.15 mM CaSO_4 at pH 5. Sorption experiments were carried out over the concentration range 25 to 400 ppm aniline, with 0.15 mM CaSO_4 at pH 5 as the supporting electrolyte.

Effects of pH on Sorption

Because the natural pH of the soil horizons approached the pKa of aniline (4.63), sorption of aniline (50 ppm) was determined as a function of pH in the A and B₂₂ horizons. Soil pH was adjusted over the range of 3.0 to 8.0 with microliter additions of 1 or 0.1% H_2SO_4 or 0.1, 1, or 5% NaOH to the soil suspensions (1 g soil/5 g H_2O) on the day preceding and at the time of aniline addition. Soil pH was measured upon initiation and completion of the sorption equilibration.

RESULTS AND DISCUSSION

Soil Characteristics

The soil used in our study was from the Ohio/Illinois basin, a geographic region where a variety of coal conversion projects have been proposed. The Elk soil, an acidic Alfisol, was sampled in Davies County, Kentucky, and is characteristic of well-drained, mature alluvial soils of the Ohio and Green river valleys. This soil type (Alfisols) is common to many geographic localities where coal liquefaction processing sites may be located.

A variety of soil characteristics have been shown to influence the adsorption of organics. The most important of these include the amount and chemical characteristics of organic materials, clay mineralogy, particle size distribution (surface area), and soil pH. Each horizon of the Elk soil has been analyzed for these as well as other chemical characteristics important in determining the surface chemical properties of the soil. Results of these analyses are summarized in Table 1.

The Elk soil is acid in pH and contains significant exchangeable acidity (pH of 0.1 M CaCl_2). The soil profile contains an argillic horizon with clay accumulation in the B_{22} horizon. Extractable iron forms (dithionite and oxalate) increase with depth along with the clay content. The ratio of oxalate to dithionite extractable iron (Fe_o/Fe_d) decreases with depth, indicating an increase in crystalline secondary iron compounds relative to amorphous forms (oxalate-extractable) in the lower B horizon. Cation exchange capacity (CEC) also increases with depth, paralleling the trend in clay content and extractable iron. Vermiculite, quartz and mica are the predominant minerals in the coarse clay fraction. An expanding phyllosilicate (smectite) was seen in all horizons, while a trace of goethite was found only in the B_{22} horizon after oxides concentration.

Sorption of Aniline and Alkyl Anilines

For the most part, the sorption isotherms of the anilines studied were curvilinear over the concentration range examined with the exception of several anilines on the B_{22} horizon (Figures 1-5). The sorption isotherms had a shape similar to the L (normal) curves of Giles et al. (16), which are characteristic of sorption in dilute solution where available binding sites become a limiting factor with increasing concentration. In several cases sorption in the B_{22} horizon gave isotherms representative of the S-curved isotherms of Giles et al. (16), which result when the percent sorption increases with increasing concentration of the solute or sorbate over a portion of the isotherm.

At low equilibrium solution concentrations (approximately less than 75 $\mu\text{g/ml}$), the sorption isotherms are linear or nearly linear with the magnitude of sorption of a particular aniline being similar in all three horizons. Generally, sorption in the A horizon is somewhat greater than in the B horizons at these concentrations. At higher solution concentrations (greater than 100 $\mu\text{g/ml}$) the isotherms diverge; sorption becomes greatest in the B_{22} horizons and lowest in the A_1 horizon with the exception of 2,4,6-trimethylaniline. The most striking feature of the aniline sorption is the magnitude of sorption in the B_{22} horizon. The sorption of numerous compounds has been shown to correlate with the organic content of the soil, including the chloroanilines.

The sorption, however, observed in the B₂₂ horizon suggests an inorganic or mineralogic control and illustrates the importance of inorganic mechanisms in aniline binding.

The sorption isotherms of all the anilines could best be described by the empirical Freundlich equation:

$$S = KC^{1/n}$$

where

S is the quantity sorbed in moles/g

C is the equilibrium solution concentration in $\mu\text{moles/ml}$

K is a constant related to the partitioning of the solute between solution and its solid

1/n is a constant describing the nonlinearity or concentration dependency of the isotherm.

Values of K and 1/n were determined by linear regression of the log form of the Freundlich equation:

$$\log S = 1/n \log C + \log K$$

These constants are summarized in Table 2. Using the K values as a measure of adsorption, it is seen that the B₂₂ horizon in all cases binds more of each aniline than the B₁ or A horizons. For example, sorption of aniline increases with depth through the profile with a maximum K value of 8.04 in the B₂₂ horizon. As the degree of substitution increases, the relative differences between the magnitude of sorption in the A and B₂₂ horizons decrease. This results from the increasing hydrophobicity and the basicity of the compounds with alkyl substitution and suggests a shift in the relative importance of different attraction mechanisms such as ion exchange and hydrophobic attraction to organic matter. In the case of 2,4-dimethylaniline, the Freundlich K values for the A horizon, 6.91, and B horizon, 6.71, are almost the same. The addition of another methyl group (2,4,6-trimethylaniline) increases compound affinity for the organic fraction and therefore sorption is greater in the A horizon (K = 5.4) than in the B (K = 4.48).

Two previous studies (9,10) suggested that soil organic matter content and chemical status (e.g., ratio of hydrophilic to hydrophobic sites) was the key factor accounting for aniline sorption in surface soils. Results of this study indicate that at certain times other factors may be equally or more important in controlling sorption in both surface and in deeper horizons of the soil profile. For example, sorption increased in the B₂₂ horizons relative to the A horizon in most cases even though organic carbon was at a minimum in the B₂₂ horizon. This suggests the interaction of aniline with the inorganic or mineralogic matrix of the soil.

Results of the sorption measurements suggest that the movement of the anilines would be retarded significantly by soil, because the rate of compound relative to water movement during leaching is largely determined by the degree of sorption. Compound movement relative to water movement can be determined by calculating the Retardation Factor from the following relationship:

$$\text{Retardation Factor} = \frac{V_s}{V_e} = \frac{d_s}{d_e} = \frac{1}{1 + (bp/\theta)}$$

where

V_s and V_e are the flow rates of the solute and water, respectively

d_s and d_e are the distances moved in a given time

p is the dry bulk density of the soil

θ is the volumetric water content at which mass flow occurs

b is the adsorption coefficient

This relationship was used to estimate the movement of aniline and 4-methylaniline through the Elk soil profile. The calculation of water infiltration depth and the retardation factors were based upon a precipitation of 101.6 cm, a volumetric water content (θ) of 0.25 and a bulk density (P , g/cm³) for the individual horizons of 1.15 for the A₁, 1.22 for the B₁, and 1.30 for the B₂₂. The results are illustrated in Figure 6. In the absence of appreciable microbial degradation, aniline and 4-methylaniline move only 21.3 cm and 15.2 cm, respectively, relative to the 406 cm depth of water penetration. It is informative to compare the mobility of the anilines to

compounds such as phenols, which are less strongly sorbed. In some preliminary experiments, the sorption isotherms for phenol and 4-methylphenol major constituents of the water-soluble fraction of SRC were measured in the A and B₂₂ horizons. The magnitude of phenol and 4-methylphenol sorption (Figures 7, 8) is much less than that of aniline and 4-methylaniline, respectively, even though the sorption of the phenols was conducted at a higher soil to solution ratio (1:1).

In contrast to the anilines, sorption of phenols in the B₂₂ horizon is barely measureable. Sorption of phenol and 4-methylphenol appears to be controlled by the organic content of the soil with little or no contribution from the inorganic or mineral matrices of the B₂₂ horizon. The same soil and water parameters used to calculate anilines were used to calculate the retardation factor for phenol and 4-methylphenol. The distance of phenol and 4-methylphenol movement is 167 cm and 354 cm, respectively, relative to a 406 cm depth of water infiltration. The phenols move well into the B₂₂ horizon, while the anilines are contained in the A horizon, again illustrating the importance of sorption in controlling mobility. The mathematical expression for the retardation can be combined with equations describing unsaturated/saturated water movement, compound dispersion and the rate of degradation (17,18) to give a mathematical expression that will more realistically predict environmental concentrations of a compound with time at various depths in the soil or subsoil profile.

Sorption to Treated Horizons

Aniline sorption was evaluated on soil horizons subjected to chemical extraction to remove specific components. It is recognized that these chemical treatments affect a variety of physicochemical parameters of the soil. Thus results will be used to qualitatively suggest the relative importance of selected soil chemical parameters on aniline sorption.

The partial oxidation of organic material in the Elk A₁ horizon using hydrogen peroxide significantly affected the sorptive behavior (isotherm shape) and the magnitude of aniline bound (Figure 6). The oxidation with hydrogen peroxide removed more than 75% of the organic matter and resulted in a

significant reduction in the quantity of aniline bound. This indicates relative importance of the organic fraction in sorbing aniline. After oxidation, the resulting isotherm was S-shaped, which is characteristic of the sorption of several anilines in the B₂₂ horizons. It must be recognized that the surface chemistry of the inorganic or mineral fraction and distribution of saturating cations may have been altered appreciably by oxidant contact and repeated washings. These changes, in addition to removal of organic material, are likely to contribute to the reduction in aniline sorption observed.

In an attempt to evaluate whether specific chemical interaction was occurring between aniline and secondary hydrous iron oxides, sorption isotherms were performed on the lower B horizons after extraction with acid ammonium oxalate and sodium dithionite in a citrate bicarbonate buffer (DCB) (Figure 9). These extractions were intended to remove primarily amorphous (oxalate) and crystalline forms (DCB) of iron oxides. Following extraction, soils were Ca saturated and isotherms were run at a pH 5 and with a supporting electrolyte (0.15 mM CaSO₄) comparable to that found in the natural horizons. Extraction with acid ammonium oxalate had little effect in the Elk B₂₂ horizon. The S-shaped isotherms of the oxalate-extracted soils were similar to the natural horizons, suggesting a comparable mechanism of binding.

Extraction with DCB significantly affected the magnitude of sorption and shape of the isotherm in the B horizon (Figure 10). In the treated soil, aniline sorption is likely controlled solely by interaction with layer lattice silicates in the clay fraction. Although these results suggest that aniline may be interacting with crystalline (DCB extractable) hydrous iron oxides, it is more plausible that dithionite extraction and Ca saturation has altered the exchangeable acidity and distribution of exchangeable cations on phyllosilicate minerals. The latter mechanism is preferred simply because of the lack of effect seen on aniline sorption following removal of amorphous oxides by oxalate extraction. Amorphous hydrous oxides should have greater surface area and surface reactivity than crystalline forms. In contrast, Moreale and Van Bladel (8) and Bailey et al. (12) found that the saturating cation (e.g., H⁺, Al³⁺, Fe³⁺, Mg²⁺, Ca²⁺, K⁺, Na⁺) had a profound effect on aniline sorption by montmorillonite, influencing both the Freundlich K and 1/n. Generally, the

highest sorption was found on H-saturated clays, while sorption on other acid clays (Al^{3+} and Fe^{3+}) was strongly concentration dependent, producing S-shaped isotherms with Freundlich $1/n$ values greater than unity. Calcium saturated montmorillonites were least effective in sorbing aniline. Direct analogy of aniline behavior on montmorillonite to that anticipated on the vermiculites and hydroxy-interlayered vermiculites of these soils is difficult because of the higher surface charge density of these minerals which effect surface and inter-layer acidity and the dissociation potential of hydrated water associated with adsorbed cations. In spite of this, it is likely that extraction with Na dithionite and attempted saturation with Ca has reduced the exchangeable acidity (H^+ , Al^{3+}) of the vermiculite present, thus reducing the affinity for aniline. Curiously, aniline sorption isotherms in the deferrated soil horizons (DCB treated) mimic those seen, in terms of S-curvature, in the Fe and Al saturated montmorillonite systems of Moreale and Van Bladel (8).

Effects of pH

Sorption of aniline varies significantly depending on the equilibrium solution pH in the A and B horizons (Figure 11). The effect of pH below 5 in the A horizon differs from the B horizon and may reflect different sorptive sites in these two horizons.

Aniline behaves as a weak base in aqueous systems. At a pK_a or pH of 4.63, 50% of the aniline is in the protonated form; thus, it is not surprising to see a significant change in sorption as the pH is varied. In addition to affecting the form of aniline, the pH change also affects the surface characteristics of the solid phase and the presence of competing ions.

It appears that aniline sorption in the A horizon occurred by interaction with both the organic material and with the inorganic matrix (phyllosilicates and hydrous oxides) and with the inorganic matrix in the B_{22} horizons. The increasing sorption with decreasing pH seen in the A horizon (Figure 11) could be the result of an ion exchange mechanism in this horizon, most likely with the organic fraction. As the pH is decreased, the concentration of the protonated species increased resulting in an increase binding due to ion exchange. Based on a pK_a of 4.63, it is expected that a sharp rise in sorption would

begin at approximately pH 5 and rise sharply between pH 4 and pH 5. However, in this case, the most rapid sorption increase occurred below pH 4. This could be a result of differences in the measured solution pH and the pH at the binding surface and also due to the resulting changes in ionizable surface functionalities. As the pH decreases there is also a decrease in binding to inorganic phases; this simultaneous decrease in inorganic binding will change the shape and location of the sorption versus the pH curve.

In the B₂₂ horizon, maximum sorption (binding) occurred with the equilibrium solution pH on the basic side of the pKa. At this point aniline is primarily in the neutral form and three mechanisms, in addition to physical attraction (Van der Waals) and hydrogen bonding, likely predominate. In the first, aniline may, by proton association, bind to exchangeable protons on layer silicates or amphoteric hydrous oxide surfaces. The charge status of hydrous oxides in these soils is difficult to estimate. First, although the zero point of charge (pzc) of pure hydrous iron oxides ranges from 6.5 to 8.0, naturally occurring iron hydrous oxide with coreacted silica even in small concentration, have a pzc considerably lower in pH. Second, aniline may interact with hydrated exchangeable cations on layer silicates and be sorbed by indirect coordination through a water bridge. For more electronegative exchangeable metals (e.g., Al³⁺, Fe³⁺) proton transfer to aniline may occur leading to sorption of the anilide ion and a hydrolyzed form of the participant metal (e.g., Al(OH)²⁺). Third, aniline may react by direct coordination (electron transfer) with select exchangeable metals (e.g., Cu²⁺) on layer silicates or possibly even with soil hydrous metal oxides. As the equilibrium of the soil suspension pH is reduced below the pKa, ion exchange reactions predominate and decreasing sorption may well result from competition with the hydronium ion for available negatively-charged exchange sites. In contrast, decreasing sorption above a pH of 5.5 may have resulted from the neutralization of sites of surface acidity, by the added hydroxide as well as by hydroxide inhibition of proton transfer reactions between aniline and adsorbed hydrated metals on phyllosilicates.

DEGRADATION OF ANILINES

Metabolism by soil microorganisms will play a major role in determining the fate of alkyl anilines in the terrestrial environment. A number of studies have shown that anilines are readily degraded in soil (19-21). As is the case with soil sorption, the majority of the soil degradation studies that appear in the literature deal with chloroanilines. The objective of this study was to obtain information on the degradation of alkyl anilines and specifically to determine how microbial action would affect the availability of anilines to man in the event of a terrestrial coal-liquid spill. To obtain this information, ^{14}C -3-methylaniline was incubated in a soil-water system, and the concentration of the aniline and its metabolites were monitored with time in various extractable phases of the system.

METHODS

Degradation Study

The degradation of ^{14}C -3-methylanilines was carried out in 125-ml brown bottles that contained 2 g soil and 10 ml of a solution of 3-methylaniline (200 $\mu\text{g/ml}$) to which ^{14}C -3-methylaniline had been added and incubated at ambient ($\sim 28^\circ\text{C}$) temperature (Figure 12). At intervals, triplicate reactions were terminated by the addition of acetone (4 ml) and analyzed for the formation of $^{14}\text{CO}_2$. A second triplicate set of samples were terminated at the same time by centrifugation (10,000g, 15 min) and the supernatant decanted and extracted with ethyl acetate (10 ml, 2x). A portion of the supernatant was analyzed for 3-methylaniline by high performance liquid chromatography before the ethyl acetate extraction. The soil pellet was extracted with acetone (10 ml, 3x) and, after air drying, was further extracted with 0.5N NaOH (910 ml) for 8 hr at 80°C to remove the alkali-soluble humic acid fraction. The NaOH solution was removed from the soil after centrifugation at 10,000g for 15 min and extracted with ethyl acetate (10 ml, 2x). All fractions were assayed for ^{14}C -activity by liquid scintillation counting. All solvent extracts were concentrated under a stream of nitrogen after drying over Na_2SO_4 and adding 1 ml DMF as a keeper. The concentrates were analyzed for

3-methylaniline and its degradation products by silica thin-layer chromatography using a benzene methanol (95:5) mobile phase. Thin-layer chromatography (TLC) plates were analyzed by autoradiography or by cutting plates into 2.0 x 0.5 cm pieces and assaying by liquid scintillation counting.

RESULTS AND DISCUSSION

Degradation of 3-Methylaniline

The microbial degradation of 3-methylaniline was examined in a soil suspension system (Figure 13). Degradation caused a significant reduction in solution concentration over the 32-day study period. After 32 days, approximately 6% of the original 3-methylaniline remained in solution, whereas 30% remained in the sterile control. The initial rapid decrease in the 3-methylaniline concentration is primarily due to soil sorption. The differences in concentrations of 3-methylaniline at 32 days between soil suspensions and sterile controls strongly suggest that microbial activity or soil enzymes of microbial origin are responsible for a significant portion of the decrease. However, the production of $^{14}\text{CO}_2$ from the degradation of 3-methylaniline was not significant over the 32-day incubation period (Table 3). The production of $^{14}\text{CO}_2$ was only marginally detectable with less than 0.3% of the ^{14}C -activity added as 3-methylaniline recovered as $^{14}\text{CO}_2$. Analysis of the aqueous phase by liquid chromatography showed no buildup of metabolites. Over 95% of the activity in the aqueous phase was present as 3-methylaniline. The 3-methylaniline is effectively removed from solution, and after 32 days almost all the aniline added is contained in the soil as 3-methylaniline or its degradation products.

Analysis of the residual ^{14}C -activity in the soil indicated the presence of at least two (acetone and NaOH extractable) pools and possibly a third, non-extractable pool of ^{14}C -activity (Table 3). Carbon-14 profiles of thin-layer chromatograms of the acetone and NaOH extracts (Figures 14 and 15) show the development of at least three radiolabeled components. Both the acetone and NaOH extracts showed similar carbon-14 profiles with the greatest increase of degradation products occurring at the origin. However, the TLC profiles should only be considered qualitative because losses during TLC analysis cannot be

determined. The fraction of activity extractable with acetone appeared constant over the entire incubation period, whereas the NaOH extractable fraction increased six-fold over this period. The fraction of ^{14}C -activity extractable from control vessels (day 16 and 32) was ~50% less for the acetone extract and ~25% less for NaOH extraction. The total recoverable ^{14}C -activity (sum of the residual aqueous, acetone and NaOH extracts) decreased from ~93% at 4 hr to ~49% after 32 days. Control samples showed a 80% recovery at 32 days. Apparently microbial metabolism of 3-methylaniline produces degradation products that are volatile and lost during workup, or products that become an integral part of the soil organic matter and are not extracted by NaOH or are degraded to volatile components by NaOH treatment.

The changes in distribution of the 3-methylaniline and ^{14}C -activity between aqueous and the soil matrix with time of incubation is probably due to the production of metabolites, which are insoluble in water or bind strongly to the soil. Metabolites are effectively removed from solution as they are formed. The strong binding of the 3-methylaniline degradation products to soil may make these products unavailable for further degradation and could explain the very low conversion of 3-methylaniline to CO_2 .

The strong binding of 3-methylaniline metabolites is not surprising since oxidation of anilines can result in a variety of intermediates which can polymerize and would be expected to bind strongly to the soil. In fact, many of the oxidation and polymerization reactions of anilines are similar to those occurring during the formation of soil humic acids, and it is likely that anilines and their degradation products are incorporated into the humic acid fraction of soil. Hsu and Bartha (11) have shown that chloroaniline is irreversibly bound to the soil humic acid fraction, and Bollag et al. (22) have demonstrated the polymerization of anilines with phenols in humic-acid-forming type reactions. Results of this study are consistent with those findings. The fraction of ^{14}C -activity extractable by NaOH only shows an increase with time and is probably a result of the incorporation of 3-methylaniline or its degradation products into the soil humic acids. The behavior of anilines is not unique, because a number of pesticide-derived components have been shown to irreversibly bind to soil. The ultimate fate and, therefore the environmental significance, of organic components irreversibly bound to soil is not known.

CONCLUSION

The soil sorption of aniline as affected by varying degrees of methyl substitution has been studied and found to be similar for all compounds examined. Anilines were strongly sorbed in all horizons. The sorptive behavior was somewhat surprising, because sorption in the B₂₂ horizons was generally greater than or equal to that in the A horizon. Studies of chloroanilines have shown that soil organic matter was the most important soil property controlling sorption, whereas the magnitude of binding in the B₂₂ horizon obtained in this study clearly indicates the importance of soil mineral phases in controlling sorption. The relatively high degree of soil sorption should severely limit movement of anilines into groundwaters, if spilled to the terrestrial environment. In the case of spillage of limited quantities of anilines, movement may very well be restricted to the surface horizon. The attenuation of aniline mobility would be most effective in acidic soils or in acidic leachates, because the degree of sorption is dramatically reduced at neutral and basic pH.

The action of soil microorganisms would also serve to reduce the concentrations of anilines available for transport to surface and groundwaters. Although 3-methylaniline is not readily degraded to CO₂, it is metabolized to products that are strongly sorbed to soil. The result of microbial action is a reduction in the solution concentration of both the alkyl aniline and its metabolites and, thus, a decrease in the concentration of species available for transport. Although this process appears to be favorable in the short term, the ultimate fate and effects of the soil-bound metabolites are not known.

The results of these preliminary studies indicate that the two major environmental processes, soil sorption and microbial metabolism, may act to reduce the impact of a release of alkyranilines. However, before such a conclusion can be made, several aspects of both the sorption reactions and the microbial degradation should be examined. Soil desorption studies should be undertaken to determine the reversibility of aniline sorption. Our studies, as well as literature reports of chloroaniline sorption, show that a significant quantity of sorbed anilines may be irreversibly bound and would, therefore, be unavailable for transport. The generality of the results obtained in

3-methylaniline degradation studies should be determined by expanding the microbial studies to include additional aromatic amines. A major effort should be made to determine the type of products generated from alkyl aniline metabolism and to determine the fate of soil-bound metabolites. Soil sorption and degradation studies should be expanded to include the behavior of the aromatic amines in the presence of coal liquids and also include the larger molecular weight aromatic amines.

TABLE 1. Selected Physical and Chemical Soil Properties

Horizons	pH (H ₂ O)	pH 0.01 M CaCl ₂	Part. Size Dust weight %			Dry C (% C)	weight %			Fe _d / Fe _t	Fe _d / Fe _d	weight %			CEC ^(a) (meq/100 g)	Mineralogy ^(b,c) (0.2 - 2 μ)
			Sand	Silt	Clay		Fe _d	Fe _o	Fe _t			Al _d	Al _o	Al _t		
A1	4.71	4.16	30.3	59.1	10.5	1.66	0.819	0.194	1.85	0.443	0.234	0.099	0.091	4.01	5.51	V, M, Q, S
B1	4.66	3.92	21.4	62.0	16.5	0.454	1.37	0.184	2.75	0.498	0.134	0.161	0.118	5.56	6.92	V, Q, M, S
B ₂₂ t	4.76	3.90	28.7	48.0	23.4	0.271	1.96	0.295	3.76	0.521	0.150	0.191	0.149	6.51	10.0	V, Q, M, S, G(t)

^(a) Cs exchange capacity.
^(b) Listed in descending order of occurrence.
^(c) S-smectite, V-vermiculite, H-hydroxy interlayered, M-mica, Q-quartz, G-goethite, t-trace.

TABLE 2. Freundlich Constants for Elk Soil

Horizon	Aniline		3-Me		4-ME		2,4 DiME		2,4,6 TRiME	
	K	1/n	K	1/n	K	1/n	K	1/n	K	1/n
A ₁	3.93	0.790	3.09	0.675	5.59	0.383	6.91	0.424	5.41	0.313
B ₁	6.01	1.23	4.83	1.11	7.06	0.927	6.71	0.816	4.48	0.541
B ₂₂	8.04	1.40	7.37	1.18	10.47	1.10	9.70	0.932	6.54	0.742

TABLE 3. Recovery of ^{14}C -Activity from Cultures Containing ^{14}C -3-methylaniline

Incubation	^{14}C Recovered ^(a)				
	CO_2	In Aqueous Phase	In Soil		Total Recovered
			Acetone Extractable	NaOH Extractable	
4 h	0.01 $\pm$ 0.005	67.6 $\pm$ 0.8	20.9 $\pm$ 0.6	4.6 $\pm$ 0.2	93.2 $\pm$ 1.1
12 h	0.01 $\pm$ 0.001	61.3 $\pm$ 1.3	24.9 $\pm$ 2.0	7.5 $\pm$ 0.1	93.6 $\pm$ 0.9
24 h	0.01 $\pm$ 0.005	55.1 $\pm$ 1.3	22.1 $\pm$ 0.4	12.2 $\pm$ 0.3	89.3 $\pm$ 1.6
2 d	0.02 $\pm$ 0.01	52.2 $\pm$ 1.0	21.5 $\pm$ 0.3	14.8 $\pm$ 0.5	88.5 $\pm$ 0.2
4 d	0.03 $\pm$ 0.02	44.6 $\pm$ 2.0	17.4 $\pm$ 0.6	18.4 $\pm$ 0.8	80.4 $\pm$ 1.5
8 d	0.08 $\pm$ 0.02	36.3 $\pm$ 0.1	20.8 $\pm$ 0.4	18.6 $\pm$ 1.0	75.7 $\pm$ 0.8
16 d	0.06 $\pm$ 0.01	23.1 $\pm$ 1.6	17.4 $\pm$ 0.8	22.0 $\pm$ 0.7	62.6 $\pm$ 2.4
32 d	0.27 $\pm$ 0.27	5.7 $\pm$ 1.0	18.1 $\pm$ 0.2	24.7 $\pm$ 0.2	48.5 $\pm$ 0.8
Control ^(b)					
16 d	0.01 $\pm$ 0.01	57.9 $\pm$ 0.9	9.7 $\pm$ 0.3	16.7 $\pm$ 1.2	84.2 $\pm$ 0.4
32 d	0.02 $\pm$ 0.01	49.4 $\pm$ 5.8	10.2 $\pm$ 0.2	18.3 $\pm$ 0.6	77.9 $\pm$ 6.0

^(a) Mean $\pm$ S.D. (n = 3).

^(b) Autoclaved soil.

FIGURE 1. Sorption Isotherms of Aniline on Elk Soils

FIGURE 2. Sorption Isotherms of 3-methylaniline on Elk Soils

FIGURE 3. Sorption Isotherms of 4-methylaniline on Elk Soils

FIGURE 4. Sorption Isotherms of 2,4-dimethylaniline on Elk Soils

FIGURE 5. Sorption Isotherms of 2,4,6-trimethylaniline on Elk Soils

- PRECIPITATION OF 40-(101.6cm) INFILTRATES SOIL
- SOIL EQUILIBRATES AT A VOLUMETRIC WATER CONTENT OF 0.25 (25% MOISTURE)
- DEPTH OF WATER INFILTRATION IS 406cm
- SORPTION IS LINEAR OVER THE CONCENTRATION RANGE PRESENT

FIGURE 6. Soil Mobility of Phenols and Anilines

FIGURE 7. Sorption Isotherms of Aniline and Phenol

FIGURE 8. Sorption Isotherms of 4-methylaniline and 4-methylphenol

FIGURE 9. Aniline Sorption on the A Horizon After Peroxide Oxidation of Soil Organics.

FIGURE 10. Aniline Sorption on the B₂₂ Horizon After Removal of Amorphous (Oxalate Treatment) and Crystalline (DCB Treatment) Iron Oxides

FIGURE 11. Effects of pH on Aniline Sorption in the A and B₂₂ Horizons

FIGURE 12. Analytical Scheme for the Isolation of ¹⁴C-3-methylaniline and Metabolites from the Soil Incubation System

FIGURE 13. Solution Concentration of ^{14}C -3-methylaniline Versus Time of Incubation

FIGURE 14. TLC Chromatograms of Acetone Extract of Soil after Incubation with ^{14}C -3-methylaniline

FIGURE 15. TLC Chromatograms of NaOH Extract of Soil After Incubation with ^{14}C -3-methylaniline

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