

Sorption of Triazine and Organophosphorus Pesticides on Soil and Biochar

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S Supporting Information

ABSTRACT: Sorption and degradation are the primary processes controlling the efficacy and runoff contamination risk of agrochemicals. Considering the longevity of biochar in agroecosystems, biochar soil amendment must be carefully evaluated on the basis of the target agrochemical and soil types to achieve agricultural (minimum impact on efficacy) and environmental (minimum runoff contamination) benefits. In this study, sorption–desorption isotherms and kinetics of triazine (deisopropylatrazine) and organophosphorus (malathion, parathion, and diazinon) pesticides were first investigated on various soil types ranging from clayey, acidic Puerto Rican forest soil (PR) to heavy metal contaminated small arms range (SAR) soils of sandy and peaty nature. On PR, malathion sorption did not reach equilibrium during the 3 week study. Comparison of solution-phase molar phosphorus and agrochemical concentrations suggested that degradation products of organophosphorus pesticides were bound on soil surfaces. The degree of sorption on different soils showed the following increasing trend: deisopropylatrazine < malathion < diazinon < parathion. While sorption of deisopropylatrazine on SAR soils was not affected by diazinon or malathion, deisopropylatrazine suppressed the sorption of diazinon and malathion. Deisopropylatrazine irreversibly sorbed on biochars, and greater sorption was observed with higher Brunauer–Emmett–Teller surface area of biochar (4.7–2061 mg g⁻¹). The results suggested the utility of biochar for remediation of sites where concentrations of highly stable and mobile agrochemicals exceed the water-quality benchmarks.

KEYWORDS: organophosphorus pesticide, deisopropylatrazine, competitive sorption, degradation, hysteresis, surface area

INTRODUCTION

The long-term fate of agrochemicals in soils depends upon a number of complex and interrelated phenomena, especially the rate, extent, and reversibility of sorption, including competition with other contaminants and natural organic matter (NOM), as well as degradation.^{1,2} Triazine and organophosphorus pesticides are among the most well-studied agrochemicals with respect to the sorption on various soil components as a function of controlling parameters such as pH. However, systematic studies are lacking to directly compare and predict the fate of agrochemicals having different susceptibilities for hydrolysis and other degradation pathways in a given soil sample. Triazine and organophosphorus compounds such as atrazine and malathion are the most frequently detected agrochemicals in U.S. agricultural and urban streams throughout the year.³ Concentrations are typically in the ppb range⁴ and often exceed water-quality benchmarks for aquatic life and fish-eating wildlife.³ Especially in agriculturally impacted watersheds, agrochemicals are not detected alone but as a mixture of as many as 10 agrochemicals.³

Especially for organophosphorus pesticides, metal (hydr)-oxide and clay components of soils can serve as a direct adsorption site⁵ and can also catalyze hydrolysis and other degradation pathways.^{6,7} Some organophosphorus pesticides such as diazinon can form a bidentate complex with Cu^{II} and other Lewis acids resulting in a six-membered ring complex, which simultaneously decreases the electron density at the phosphorus atom and increases the leaving ability of ester

during hydrolysis.⁶ The complex formation between diazinon and the geothite surface was proposed to be the rate-determining-step in surface-catalyzed hydrolysis of diazinon.⁶ In a similar fashion, soluble Cu^{II}, Zn^{II}, Co^{II}, and Mg^{II} can enhance hydrolysis of phosphate, phosphorothioate, and other acid esters.⁶

In addition to NOM and mineral surfaces, surface-active soil amendments such as biochar will impact both the bioavailability and mobility of agrochemicals.⁸ Biochar benefits soil biology (plant–microbe interactions within agroecosystems), and that can lead to increased crop yield. Potential limitation of biochar use in agriculture is the reduced efficacy of agrochemicals due to biochar's high sorption capacity for both polar and nonpolar compounds.⁸ Longevity of biochar in agroecosystems⁹ may compromise pesticide applications for generations of farming practice. Sorption of diuron on sandy loam soil became greater and more irreversible in the presence of 0.1–5 wt % wood chip biochars pyrolyzed at 450 and 850 °C.¹⁰ Increased Freundlich sorption coefficient, isotherm nonlinearity, and apparent sorption–desorption hysteresis were attributed to high Brunauer–Emmett–Teller (BET) surface areas and micropore volume of biochars (especially 850 °C biochar with 556 m² g⁻¹ BET surface area).¹⁰ Similar controlling roles of BET surface

Received: December 12, 2011

Revised: March 5, 2012

Accepted: March 6, 2012

Published: March 6, 2012

area were observed for the sorption of deisopropylatrazine on broiler litter biochars in the absence of soil.¹¹ Sorption of organic contaminants is often enhanced when biochar and other black carbon samples are acid-washed to remove mineral components and to increase the BET surface area,^{11,12} further suggesting the importance of the surface adsorption mechanism.

The objective of this study was to systematically investigate the sorption (in single and binary solute systems), desorption, and degradation of triazine (deisopropylatrazine) and organophosphorus (malathion, parathion, and diazinon) pesticides to understand the specific pesticide and soil types that should be targeted for biochar amendment. Acidic (pH 5.01 ± 0.14), clayey, highly weathered, and leached Ultisol (Puerto Rican humid tropical forest soil; PR)¹³ and heavy metal (especially Pb) contaminated small arms range (SAR) soils of organic peaty and sandy nature¹⁴ were employed. Kinetic experiments were first carried out on PR to understand sorption behaviors of agrochemicals having varying tendencies for hydrolysis and other degradation pathways. Sorption–desorption and competitive sorption (between triazine and organophosphorus pesticides) experiments were then performed on SAR soils by monitoring solution-phase pesticide and phosphorus concentrations to distinguish sorption from degradation. For the least sorbing compound that is likely to cause surface/groundwater contamination (deisopropylatrazine), sorption–desorption isotherms were obtained for selected unactivated and activated biochar samples with BET surface areas ranging from 4.7 to 2,061 m² g^{−1}.

MATERIALS AND METHODS

Chemicals. Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (Millipore, Milford, MA) was used for all procedures. Analytical standard grade (>95% purity by HPLC assay) malathion, parathion, diazinon, and deisopropylatrazine were obtained from Sigma-Aldrich (Milwaukee, WI). Figure 1 presents the structures and relevant physical properties of agrochemicals investigated in this study. Stock solutions (145 mg L^{−1} malathion, 23 mg L^{−1} parathion, 40 mg L^{−1} diazinon, and 250 mg L^{−1} deisopropylatrazine; see Figure 1 for the solubility of each compound) were freshly prepared daily in DDW.

Biochar and Soil Samples. As described in detail previously,¹⁵ cottonseed hull biochars were prepared using raw materials from

Planters Cotton Oil Mill (Pine Bluff, AK) without pretreatments as a mixture of hulls and cottonseeds. Cottonseed hulls were pyrolyzed at 350, 650, and 800 °C for 4 h under 1,600 mL min^{−1} nitrogen flow rate using a box furnace (22 L void volume) with a retort (Lindberg, Type 51662-HR, Watertown, WI). The resulting chars (CH350, CH650, and CH800) were allowed to cool to room temperature overnight under nitrogen atmosphere.

Steam activated biochar from flax shive (hereby denoted flax) was prepared by pyrolysis at 700 °C for 1 h under 1,600 mL min^{−1} nitrogen flow rate and subsequent steam activation at 850 °C for 1.5 h under nitrogen atmosphere with 3 mL min^{−1} water flow rate.¹⁶ To remove excess ash, CH350, CH650, CH800, and flax were washed with 0.1 M HCl (27 g char L^{−1}) by constant stirring for 1 h, rinsed three times with DDW, and dried overnight at 80 °C.

Rice husk KOH activated carbon (KOH) that was developed for hydrogen storage application was obtained from Nagaoka University of Technology, Japan. As described in detail previously,^{17,18} rice husk was heated at 500 °C for 1 h under 45 g min^{−1} steam gas flow rate to produce steam activated rice husk. The product was milled to <150 μm and then mixed with KOH (5:1 = KOH/steam activated rice husk by weight) and was heated at 850 °C for 2 h. The product was neutralized by washing in DDW and dried at 120 °C for 24 h. The BET surface areas of biochar samples were reported previously (in m² g^{−1}): 4.7 ± 0.8 for CH350, 34 ± 3 for CH650, 322 ± 1 for CH800, 650 ± 11 for flax,¹⁹ and 2,061 for KOH.¹⁷

As described in detail previously,¹⁴ the top few inches of heavy metal contaminated small arm range soil samples from Maryland (MD2) and Alaska (AK) were obtained from Aberdeen Proving Ground and were air-dried and sieved (<250 μm). The MD2 (composite sample) was characterized as sandy, slightly acidic (pH 6.11) soil containing low total organic carbon (TOC; 1.966%) and low cation exchange capacity (CEC; 1.1 cmol_c kg^{−1}).¹⁴ The AK sample was acidic (pH 4.4) organic (31.63% TOC) peaty soil with much higher CEC (13.36 cmol_c kg^{−1}).¹⁴

Puerto Rican humid tropical forest soil (PR) was obtained from University of California, Berkeley. As described in detail previously,¹³ soil samples (0–5 cm depth) were collected at a valley site of a toposequence in Puerto Rico and were air-dried and sieved (<2 mm). Puerto Rican valley soil is acidic (pH 5.01 ± 0.14), clayey (predominantly kaolinite and chlorite), highly weathered, and leached Ultisol and contains 9.24% total organic matter and 5.36% TOC.¹³

Stability of Pesticides. Hydrolysis half-lives of malathion and other organophosphorus pesticides from different literature sources vary from days to months with confounding pH dependence.^{2,6,20} Because centrifugation was necessary to obtain desorption isotherms by successive supernatant replacement,²¹ the stability of parathion, diazinon, and malathion was tested in fluorinated ethylene propylene (FEP) and polypropylene centrifuge tubes (50 mL nominal volume, Thermo Scientific Nalgene centrifuge ware; Thermo Fisher Scientific, Waltham, MA) as well as amber glass vials. Deisopropylatrazine did not degrade in DDW for more than a month and was employed as a model agrochemical having high stability. After 24 h in DDW, all pesticides were stable in FEP and amber glass vials (Table S1, Supporting Information). In polypropylene centrifuge tubes, however, the concentration ratio (final:initial in moles L^{−1}) of organophosphorus pesticides decreased to 0.1 for parathion and diazinon, and 0.5 for malathion after 24 h (Table S1, Supporting Information). The concentration decrease can result from degradation or sorption on the reactor. The HPLC chromatogram for parathion in the polypropylene centrifuge tube showed an upward baseline shift as well as a new, broad peak indicative of degradation products (Figure S1, Supporting Information). After 6 days of equilibration (Table S1, Supporting Information), diazinon concentration decreased in FEP, while parathion, malathion, and deisopropylatrazine concentrations did not decrease in FEP and glass vials (Table S1, Supporting Information). On the basis of these results, all desorption experiments involving organophosphorus pesticides were conducted using FEP centrifuge tubes with a 24 h equilibration period, in order to minimize the degradation of the parent compounds. Similar instability was reported for the catecholate ligand in a polypropylene container.²²

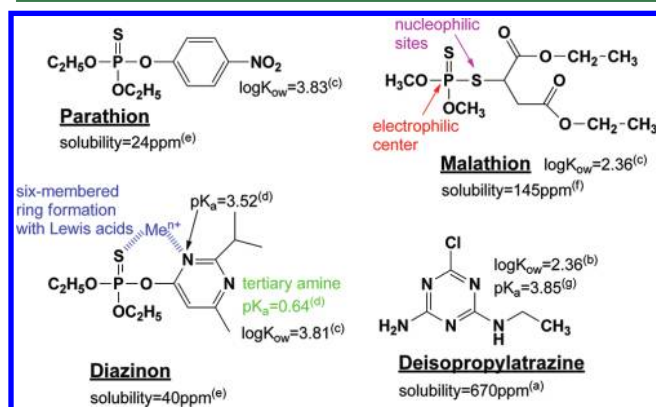


Figure 1. Physical properties of agrochemicals investigated in this study. Values were obtained from (a) Jiang and Adams,³⁷ (b) Ghose and Crippen,⁴⁹ (c) Bartelt-Hunt et al.,⁵⁰ (d) Smolen and Stone,³⁴ (e) Cornell University Pesticide Management Education Program (<http://pmep.cce.cornell.edu>), (f) Tomlin,⁵¹ and (g) SciFinder Scholar (2012).

Because deisopropylatrazine was stable in all reactors (Table S1, Supporting Information), single-solute experiments were conducted with 3 days of equilibration in a glass (sorption only) or polypropylene (sorption–desorption) container, based on the predetermined time required for deisopropylatrazine sorption to reach apparent equilibrium.¹¹

Sorption Kinetics of Malathion and Diazinon on PR. The sorption experiment was initiated in amber glass vials by adding a known volume of malathion (145 ppm) or diazinon (40 ppm) stock solution to PR soil suspension (20 g soil L⁻¹ in DDW for 30 mL total volume). Initial concentrations were set to 30, 60, 90, 120, and 145 ppm for malathion and 20, 30, and 40 ppm for diazinon. All sorption experiments were conducted in duplicate. Reactors were equilibrated by shaking end-over-end at 70 rpm. At successive time intervals (1, 2, 6, and 9 days, and 2 and 3 weeks), suspensions were removed from the end-over-end shaker. The pH (Oakton pH/Ion 510 benchtop pH meter, Oakton Instruments, Vernon Hills, IL) of soil suspension was determined. The soil suspension was filtered (0.2 μ m Millipore Millex-GS; Millipore, Billerica, MA), and the filtrate (\approx 1 mL) was directly injected into an isocratic HPLC system with a diode array detector (Agilent Technologies, Inc., Santa Clara, CA) equipped with a μ Bondapak C₁₈ column (3.9 \times 300 mm column). Depending upon the analyte under investigation, different ratios of (i) acetonitrile and (ii) water (both HPLC-grade, Fisher Scientific) were required for a set flow rate of 1.0 mL min⁻¹. Malathion, diazinon, and deisopropylatrazine were quantified at 214 nm, and parathion was quantified at 275 nm.

Sorption–Desorption of Malathion and Diazinon on SAR Soils, and Competition with Deisopropylatrazine. Competition experiments were conducted for malathion and diazinon on MD2 and AK (20 g soil L⁻¹ in DDW for 40 mL total volume) in the presence of deisopropylatrazine in FEP centrifuge tubes. The reaction was initiated by adding equal concentration (20, 30 ppm) of each solute. Single-solute control experiments were performed separately for malathion, diazinon, and deisopropylatrazine. After 24 h of equilibration, soil suspension was centrifuged at 9,180 rpm (11,950g) for 20 min at 4 °C. Supernatant (20 mL determined gravimetrically) was carefully decanted into a clear glass vial, filtered (0.2 μ m), and analyzed by HPLC as described above. In order to separately account for the degradation of malathion and diazinon, portions of filtered samples were acidified to 4% (v/v) nitric acid (trace metal grade, Sigma-Aldrich) for the determination of soluble P concentration using an inductively coupled plasma atomic emission spectrometer (ICP-AES; Profile Plus, Teledyne/Leeman Laboratories, Hudson, NH). Soil-only control (without pesticide addition) was employed for the ICP-AES analyses.

Sorption and Desorption of Deisopropylatrazine on Biochars. Deisopropylatrazine sorption isotherms (20–100 ppm initial concentration) were obtained in DDW for CH350, CH800, and flax using polypropylene centrifuge tubes. After 3 days of equilibration, pH of the char suspension was measured. The suspension was then centrifuged, and the supernatant (20 mL determined gravimetrically) was carefully decanted into a clear glass vial, filtered (0.2 μ m), and analyzed by HPLC as described above. Immediately following the sorption step, desorption was initiated by a successive replacement of 20 mL of supernatant by DDW for 3, 2, and 2 day equilibration periods. Deisopropylatrazine sorption isotherms were obtained using the following equation:^{21,23,24}

$$q_s = \frac{V_s}{m}(C_i - C_s) \quad (1)$$

where q_s (in mg g⁻¹) is the mass of solute sorbed on a dry weight basis, C_s (in mg L⁻¹) is the solution-phase solute concentration at the end of the sorption experiment, C_i (in mg L⁻¹) is the initial solute concentration, V_s is the total volume, and m is the dry weight of sorbent (in g).²¹

Desorption isotherms were obtained by calculating the mass of solute that remained sorbed at each desorption step (q_d in mg g⁻¹) using the following equation:²³

$$q_d = \frac{V_d}{m} \left(C_{d-1} \left(\frac{V_{d-1,r}}{V_d} \right) - C_d \right) + q_{d-1} \quad (2)$$

where $V_{d-1,r}$ is the volume remaining in soil suspension after the supernatant removal in the ($d-1$) desorption step (determined gravimetrically), V_d is the sum of volume added for the d th desorption step (20 mL) and $V_{d-1,r}$, and C_d is the equilibrium solution-phase solute concentration for the d th desorption step.

Analogous sorption experiments (without desorption steps) were conducted in 0.1 M acetate buffer (pH 4.9) for CH350, CH650, and KOH. The pH buffer was employed to set the ionizable fraction of solute to understand electrostatic interactions²⁵ with biochars having diverse pH and point of zero charge (PZC). In all experiments, biochar loadings were set to 5 g L⁻¹ for flax, CH350, CH650, CH800, and 0.3 g L⁻¹ for KOH for the total volume of 30 mL.

RESULTS AND DISCUSSION

Sorption Kinetics of Malathion and Diazinon on PR Soil. Figure 2 presents single-solute sorption isotherm results

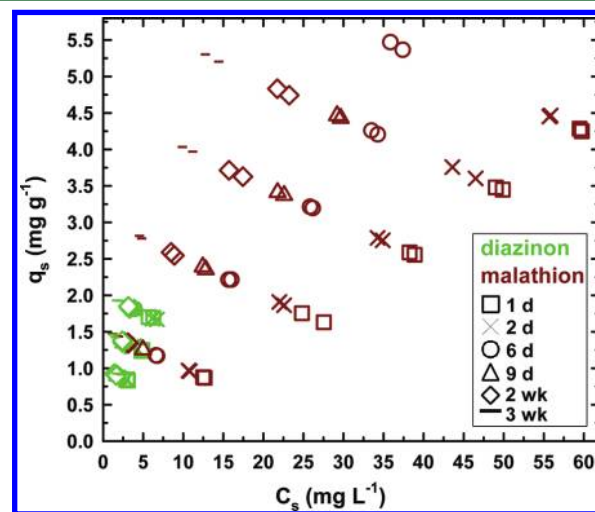


Figure 2. Changes in single-solute malathion and diazinon sorption isotherms on Puerto Rican forest soil (PR) over a 3 week period. Initial concentrations were 30, 60, 90, 120, and 145 mg L⁻¹ for malathion and 20, 30, and 40 mg L⁻¹ for diazinon in 20 g soil L⁻¹ DDW (without buffer).

obtained for different equilibration periods: 1, 2, 6, and 9 days, and 2 and 3 weeks. Malathion and diazinon were added to PR (20 g soil L⁻¹) in amber glass vials without buffer. The pH of soil suspension was 5.9 ± 0.0 (6 reactors) for diazinon and 5.8 ± 0.1 (10 reactors) for malathion. In an analogous experiment, parathion concentration decreased to below the detection limit within 24 h. Continuous leftward shift in sorption isotherms of malathion (with greater equilibration period from 1 day to 3 weeks) indicates that the reaction did not reach equilibrium over the 3 week period. At each sampling point, sorption of diazinon on PR soil was significantly greater than malathion. The degree of change in the malathion sorption isotherm after 2 weeks (Figure 2). Because malathion is stable in amber glass vials for 6 days (Table S1, Supporting Information), the initial shifts in Figure 2 likely resulted from slow sorption

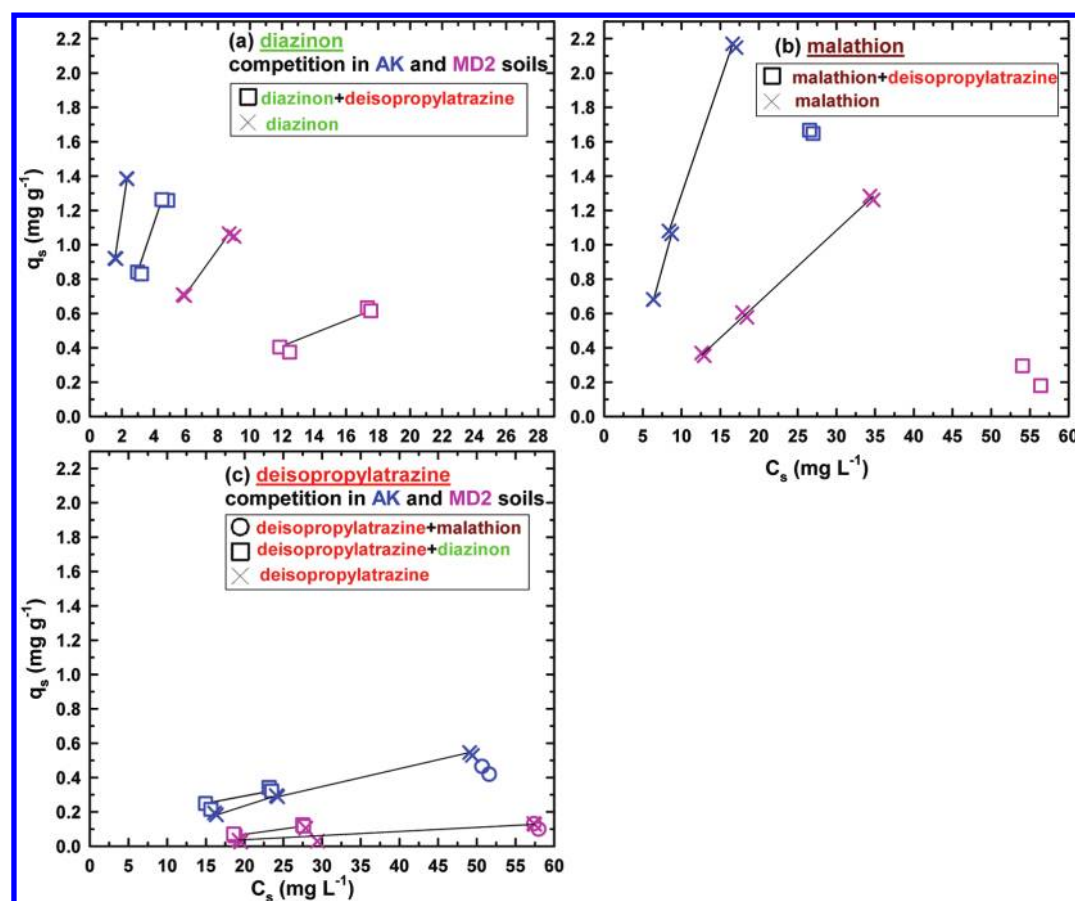


Figure 3. Sorption of diazinon, malathion, and deisopropylatrazine in single (crosses) and binary-solute experiments. Equal concentration (20–30 mg L⁻¹) of each pesticide was added together to AK (blue) or MD2 (pink) soil (20 g soil L⁻¹) and were equilibrated for 24 h. Deisopropylatrazine suppressed sorption of diazinon and malathion (a–b), while sorption of deisopropylatrazine was unaffected by malathion and diazinon (c). Lines are drawn for visual aid and do not represent model fits.

kinetics. However, degradation of malathion and diazinon^{6,26,27} is likely to be enhanced by PR soil.

A plot of C_s as a function of time shows an initial rapid disappearance and subsequent, much slower decrease for malathion (Figure S2, Supporting Information). Between 1 day and 2 weeks, malathion concentration continued to decrease by as much as 50% (depending on the initial concentration, Figure S2, Supporting Information). In contrast, diazinon concentration decreased to 6 ppm or lower (for all initial concentrations) within 1 day and did not show a significant decrease between 1 day and the 3 week period (except for the highest initial concentration, Figure S2, Supporting Information). Like diazinon, sorption of deisopropylatrazine on broiler litter biochars (in pH 5.5 acetate buffer) rapidly reached apparent equilibrium within 1 day, and the concentration did not change thereafter.¹¹ In a separate report, sorption of pyridine on Cherokee Park sediment (pH 5.5) reached equilibrium within 1–2 h.²⁸ In contrast, aniline sorption kinetics was characterized by a rapid initial loss followed by a much slower rate of disappearance.²⁸ These different kinetic behaviors were attributed to reversible sorption of pyridine through the cation exchange mechanism, as opposed to covalent, irreversible sorption of aniline, on sediment.²⁸ Like aromatic amines,^{28,29} malathion possesses a nucleophilic sulfur functional group that can covalently bind on carbonyl and other functional groups of soil components. Diazinon and deisopropylatrazine are di- and triazines

containing low pK_a tertiary amines (Figure 1), and protonated species (at experimental pH near pK_a) can sorb via the cation exchange mechanism.²⁸ In addition, diazinon possesses a tertiary amine group that can form a six-membered ring with metal cations and other Lewis acids (Figure 1). Metal ion (e.g., Cu^{II})³⁰ and clay³¹ are often intentionally added to diazinon and other pesticide formulations to increase the shelf life and persistence of pesticides, and to allow more controlled release of pesticide. Overall, Figures 2 and S2 (Supporting Information) suggest the more irreversible nature of sorption for malathion, relative to diazinon on PR soil.

Competitive Sorption on SAR Soils. Figure 3 presents (a) diazinon, (b) malathion, and (c) deisopropylatrazine sorption isotherms on AK (blue) and MD2 (pink) soils in the presence of a secondary solute: deisopropylatrazine for diazinon and malathion; diazinon and malathion for deisopropylatrazine. The experiment was conducted to investigate the competition between triazine and organophosphorus pesticides. Single-solute control experiments were conducted for each pesticide (crosses in Figure 3). The AK soil was more acidic (4.9 ± 0.3 for all experiments presented in Figure 3) than MD2 (6.2 ± 0.4), as reported previously.¹⁴ For all pesticides, sorption was greater on AK than MD2 in both single and binary solute experiments. The AK contains nearly 16-fold greater TOC than MD2.¹⁴ Organic matter content is often a controlling parameter of pesticide sorption on soils,²⁷ and sandy soil is the least capable of sorbing pesticides.³² In

both soils, greater sorption was observed in the following order (regardless of single/binary solute): deisopropylatrazine < malathion < diazinon. Greater sorption of diazinon than malathion is in agreement with PR soil results presented in Figure 2. Deisopropylatrazine suppressed sorption of diazinon (Figure 3a) and malathion (Figure 3b) in both AK and MD2. The presence of second solute (malathion or diazinon in Figure 3c) did not significantly suppress sorption of deisopropylatrazine on AK or MD2. The single-solute isotherms for deisopropylatrazine nearly overlapped with binary-solute isotherms (see Figure S3, Supporting Information for Figure 3c in a reduced y-axis).

Figure 4 presents sorption–desorption isotherms corresponding to Figure 3a and 3c (competition between

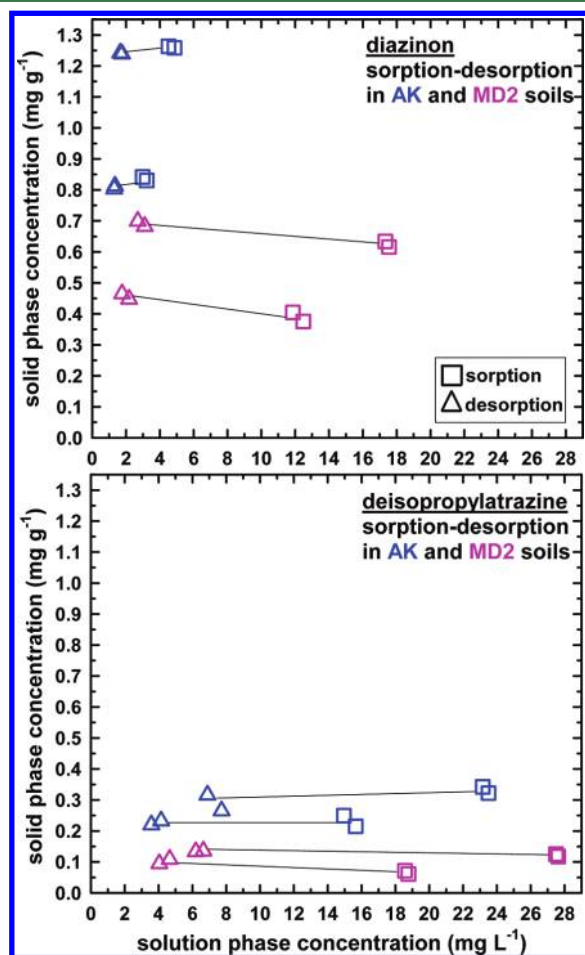


Figure 4. Sorption (squares) and desorption (triangles) isotherms for diazinon (top) and deisopropylatrazine (bottom) in competition experiments (Figure 3a,c). Equal concentration (20–30 mg L⁻¹) of each pesticide was added together to AK (blue) or MD2 (pink) soil (20 g soil L⁻¹) and were equilibrated for 24 h. Lines are drawn for visual aid and do not represent model fits.

deisopropylatrazine and diazinon). Both diazinon and deisopropylatrazine showed significant hysteresis on AK and MD2. In conclusion, deisopropylatrazine competed with diazinon and malathion, while neither diazinon nor malathion competed with the sorption of deisopropylatrazine on AK or MD2 (Figure 3). In the same binary solute experiment, hysteresis was observed for both diazinon and deisopropylatrazine on AK and MD2 (Figure 4). Irreversible sorption of deisopropylatrazine¹ and

atrazine³³ on different soil types has been reported. Distinct kinetic behaviors of malathion and diazinon (Figure S2, Supporting Information) likely reflect different degrees of sorption reversibility, and sorption on soil is not fully reversible even for the least sorbing pesticide investigated: deisopropylatrazine (Figure 4). Irreversible sorption observed in Figures 4 and S2 (Supporting Information) likely resulted from a combination of factors, especially degradation and short equilibration period (that was necessary to minimize the degradation of organophosphorus pesticides, Table S1, Supporting Information).

In an effort to differentiate sorption from degradation, Figure 5 compares solution-phase molar concentrations of phosphorus and pesticides (malathion, diazinon, and deisopropylatrazine) in Figures 3 and 4. Horizontal lines in Figure 5 show “background” solution-phase phosphorus concentrations originating from AK (blue) and MD2 (pink) soils (from soil-only control experiments without pesticide addition). The black line represents the slope of 1 corresponding to equimolar solution-phase concentrations of phosphorus and pesticide. The solution phase molar concentration of organophosphorus pesticide (malathion or diazinon) is expected to equal P (after taking into account the background P in soils) if no degradation occurs.

Deisopropylatrazine does not contain P (Figure 1) and is not expected to influence solution-phase P concentrations (Figure 5). In a single-solute experiment, P concentration does not change as a function of deisopropylatrazine concentration and consistently equals background concentrations for AK and MD2 (squares in Figure 5a). For diazinon and malathion, P concentration followed the 1:1 slope (black line in Figure 5a). Diazinon is consistently shifted to the left of malathion, suggesting that diazinon released greater amounts of P than malathion for a given C_s (eq 1). However, when background P in AK and MD2 (horizontal lines) were subtracted from data points in Figure 5, diazinon data points for both AK and MD2 closely followed the 1:1 slope (Figure S4, Supporting Information). The results suggest negligible degradation of diazinon after 24 h of equilibration to obtain the sorption isotherms. Malathion data points, however, were shifted rightward of the 1:1 line (Figure S4, Supporting Information), suggesting the sorption of P-containing degradation products on soils. Hydrolysis of phosphorothionate triesters, regardless of leaving group, results in P-containing degradation products.³⁴ Sorption of P-containing degradation products on soil surfaces will result in a rightward shift from the 1:1 line (Figure S4, Supporting Information). Organophosphorus pesticides undergo complex abiotic (hydrolysis, isomerization, oxidation, and photolysis) and biotic decomposition pathways with half-lives ranging from hours to days.⁷ Solid and liquid state ³¹P NMR investigation of parathion-clay systems indicated that decomposition products are more tightly bound to clay than parathion that was originally physisorbed.⁷ In the presence of Cu^{II}-montmorillonite, oxidation was the predominant degradation mechanism of parathion, and Cu^{II}-catalyzed decomposition of organophosphorus compounds is widely reported in the literature.⁷ Further investigation of the degradation pathways using radiolabeled compounds and NMR analysis is the subject of a future study.

Figure 5b compares solution-phase molar P concentrations for diazinon (in the presence of deisopropylatrazine) at sorption (x-axis) and desorption (y-axis) steps corresponding to Figure 4 in AK (blue) and MD2 (pink) soils. Data points for

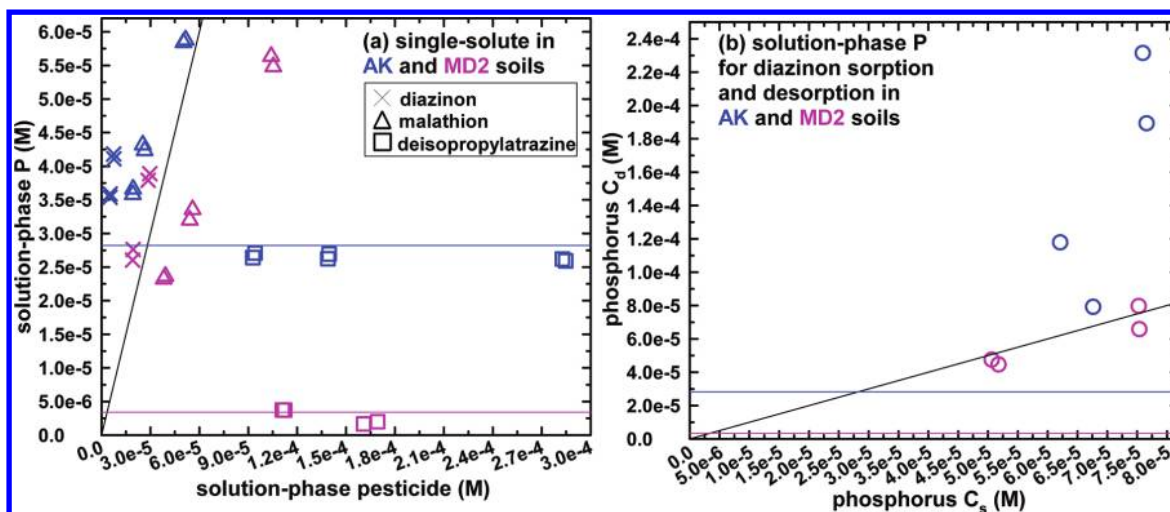


Figure 5. Solution-phase molar P and pesticide concentrations for single-solute (malathion, diazinon, deisopropylatrazine) systems in AK and MD2 (a). Solution-phase P concentrations for sorption and desorption steps are provided in panel b for the binary solute (diazinon and deisopropylatrazine) system. Lines represent background (soil-only without pesticide addition) AK (pink) and MD2 (blue) P concentrations and 1:1 slope (black).

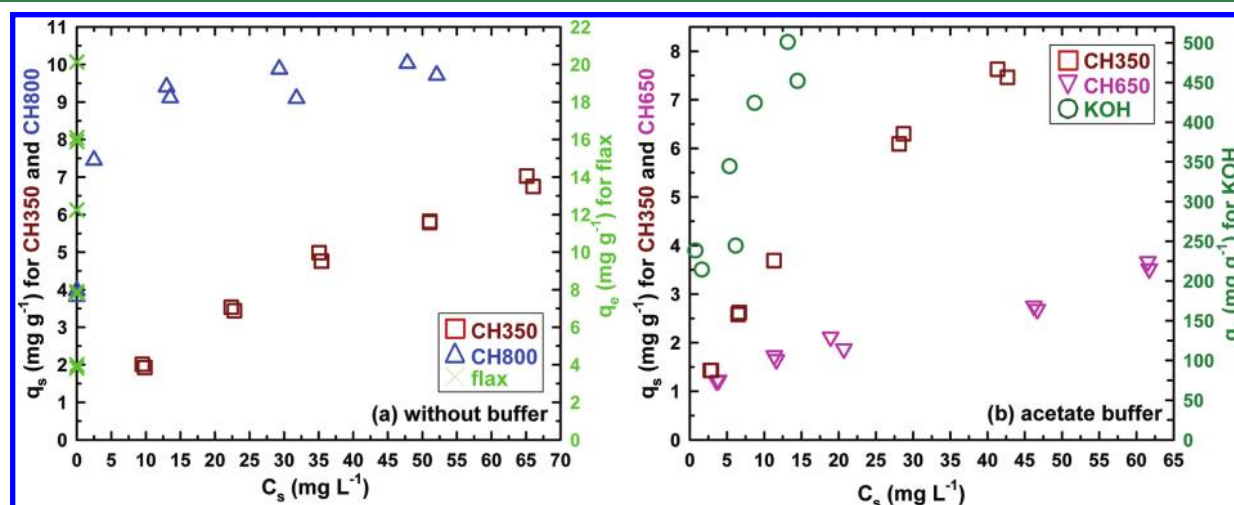


Figure 6. Deisopropylatrazine sorption isotherms after 3 d equilibration on (a) CH350, CH800, and flax in DDW and (b) CH350, CH650, and KOH in acetate buffer. Biochar loadings were 5 g L⁻¹ for CH350, CH650, CH800, and flax, and 0.3 g L⁻¹ for KOH.

the MD2 soil (pink) closely followed the 1:1 slope (black line), indicating negligible difference in P concentrations at sorption and desorption steps. For AK (blue), in contrast, P concentration for desorption significantly exceeded that of sorption. Excess P in the desorption step can arise from diazinon degradation as a result of prolonged contact with soil and suggests enhanced degradation in peaty AK soil, compared to sandy MD2 soil. Diazinon is expected to be sensitive to metal (e.g., Fe, Al) (hydr)oxide surface-catalyzed hydrolysis because it is able to form a six-membered ring complex (Figure 1) at the rate-limiting-step.⁶ Hydrolysis of diazinon is also catalyzed by Cu^{II} in homogeneous systems.³⁴ The MD2 and AK soils are heavy metal (especially Pb and Cu to a lesser extent) contaminate soils, and metal ions can also compete with pesticide sorption on soil components.^{11,35} Clay is also known to catalyze hydrolysis (at phosphate ester bond) of adsorbed parathion, malathion, and diazinon.³⁶

In conclusion, deisopropylatrazine was stable and highly mobile especially in low TOC soil and suppressed sorption of coexisting agrochemicals (Figures 3 and 4). In addition,

deisopropylatrazine has significantly higher solubility (670 ppm, Figure 1) than the parent compound atrazine (33 ppm),³⁷ and poses greater surface/groundwater contamination risk. Soil is an ultimate sink for applied pesticides whose bioavailability strongly depends upon the inherent sorption capacity of soil that can be enhanced by means of biochar amendment.⁸ Depending on the solute concentration (C_e) to solubility (S_w) ratio at equilibrium, biochar can sorb up to its own weight of organic compounds.³⁸ Because the smallest pores are filled first, sorption is more favorable at low surface coverage (C_e/S_w).³⁹ Plant-derived chars formed at incremental pyrolysis temperatures (e.g., 300–700 °C in 100 °C intervals⁴⁰) suggested that polarity, aromaticity, surface area, and pore size distribution of char control the sorption capacity for nonpolar and polar solutes.^{40,41} For ionizable compounds, additional sorption mechanisms exist: electrostatic interactions, cation exchange, and various hydrogen bonding interactions.^{25,42}

Sorption of Deisopropylatrazine on Biochars. In order to investigate the utility of biochar for retaining the highly mobile contaminant, deisopropylatrazine sorption–desorption

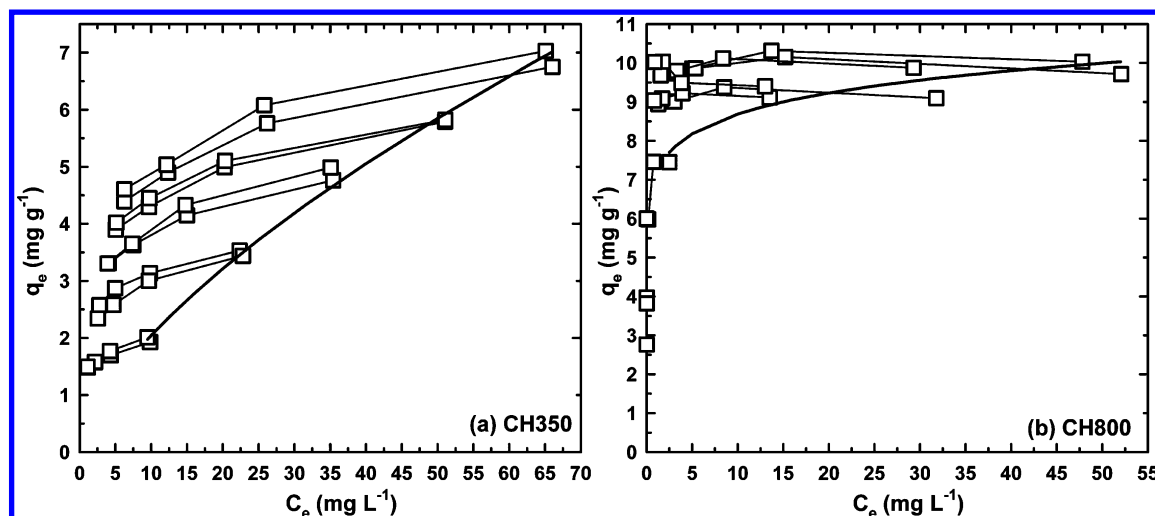


Figure 7. Deisopropylatrazine sorption–desorption isotherms on 5 g L^{−1} (a) CH350 and (b) CH800 in DDW (without buffer). The thick line represents Freundlich fittings for the sorption isotherm: $\log K_F$ (L kg^{−1}) = 2.7 and n_F = 0.65 (r^2 = 0.99) for CH350; $\log K_F$ (L kg^{−1}) = 3.9 and n_F = 0.09 (r^2 = 0.84) for CH800. The thin line connects sorption and desorption steps for each reactor.

experiments were conducted for selected biochar samples. Figure 6 shows a clear influence of BET surface area on biochar's ability to sorb deisopropylatrazine with and without buffer (pH 4.9 acetate). Without buffer, pH after 3 days of equilibration (to obtain sorption isotherms in Figure 6a) ranged from 3.8 ± 0.1 for flax, 8.5 ± 0.1 for CH350, to 10.6 ± 0.0 for CH800. Progressively greater deisopropylatrazine sorption was observed as a function of BET surface area (in m² g^{−1}): CH350 (4.7 ± 0.8) < CH800 (322 ± 1^{15}) < flax (650 ± 11 ;¹⁹ note that the y -axis for flax is provided on the right). The reaction pH for flax (3.8 ± 0.1) coincided with pK_a of deisopropylatrazine (3.85, Figure 1). However, because PZC of flax is estimated to be 4.1,⁴³ electrostatic interactions between positively charged deisopropylatrazine species and negatively charged surfaces of flax are not expected to be a significant driving force for sorption.

In pH 4.9 acetate buffer (Figure 6b) where the fraction of ionized solute was set constant, CH350 was able to sorb more deisopropylatrazine than CH650 (34 ± 3 m² g^{−1}), despite the lower BET surface area. However, KOH, having the highest BET surface area of all samples employed in Figure 6 ($2,061$ m² g^{−1},¹⁷ note y -axis for KOH is provided on the right) sorbed several orders of magnitude greater amount of deisopropylatrazine (on mg g^{−1} basis, Figure 6b), compared to CH350 and CH650. Within the range of initial concentration employed (that was limited by the solubility of deisopropylatrazine), KOH sorbed as much as half of its own weight of deisopropylatrazine (Figure 6b).

Sorption Hysteresis. Reversibility of deisopropylatrazine sorption was investigated by conducting successive desorption experiments on CH350 and CH800 without buffer (Figure 6a). Thick lines in Figure 7 represent Freundlich isotherm fittings for the sorption step. Freundlich parameters were $\log K_F$ (L kg^{−1}) = 2.7 and n_F = 0.65 (r^2 = 0.99) for CH350; $\log K_F$ (L kg^{−1}) = 3.9 and n_F = 0.09 (r^2 = 0.84) for CH800. Compared to similar experiments for broiler litter biochars produced at 350 (60 ± 20 m² g^{−1}) and 700 °C (94 ± 5 m² g^{−1}),¹¹ sorption on cottonseed hull biochars (CH350 and CH800) was lower (lower $\log K_F$) and more linear (higher n_F , thick lines in Figure 7).

As shown in Figure 7, significant hysteresis was observed for both CH350 and CH800. Observed irreversible sorption is not likely to arise from an insufficient equilibration period (based on kinetic experiments) or degradation: deisopropylatrazine was stable for the duration of the experiment (no additional HPLC peaks were observed at selected wavelengths between 210 and 450 nm). However, there are other sources of artificial hysteresis such as the changes in the composition of NOM and nonsettling particles during the desorption experiments.^{21,44} While further investigation on the artificial hysteresis is the subject of our future reports, irreversible sorption in Figure 7 may reflect the pathway of sorption being different from the pathway of desorption,⁴⁵ as widely discussed in detail for biochar,³⁸ peat, and other sorbents.⁴⁵ Sorption of organic compounds on char is strongly hysteric,^{38,46} and “true hysteresis” has been attributed to pore elasticity, that is, “pore deformation by the solute results in the pathway of sorption being different from the pathway of desorption leading to entrapment of some adsorbate as the polyaromatic scaffold collapses during desorption”.³⁸ Biochar occurs in agricultural soils either as a result of deliberate addition or as a naturally occurring component.^{47,48} Biochars having high surface areas are expected to be beneficial for mitigating watershed contamination by deisopropylatrazine (metabolite of herbicide atrazine) and other agrochemicals that are highly stable, water-soluble, and mobile. To maintain the efficacy of agrochemicals, biochar application should be carefully attenuated and engineered based on the contamination level, soil property, type of crop, and history of pesticide application at the target site.

■ ASSOCIATED CONTENT

📄 Supporting Information

Stability of pesticides, timecourses of soluble malathion and diazinon concentrations, competitive sorption for deisopropylatrazine in reduced y -axis, and phosphorus concentration in Figure 5a corrected for soil background. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

This work was partially funded by the Defense Threat Reduction Agency Project #CBS.SIM.03.10.ER.PP.002.

Notes

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Professor Garrison Sposito (UC Berkeley) for providing the Puerto Rican valley soil sample, Dr. Desmond Bannon (US Army Public Health Command, Army Institute of Public Health) for providing arms range soil samples, and Ikumi Toda (Nagaoka University of Technology) for providing rice husk KOH activated carbon sample.

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