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ARTICLE

Photolysis of Chlortetracycline on a Clay Surface

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Chlortetracycline, an antibiotic commonly used as a growth promoter in livestock, enters the environment primarily through application of animal waste to open fields. The photochemical loss of chlortetracycline in sunlight-exposed soils is a potentially important process in its environmental fate, especially because it is photochemically labile and sorbs strongly to mineral surfaces. In this study, photolysis on kaolinite clay under simulated sunlight was used as a model system to elucidate the mechanistic kinetics of chlortetracycline photolysis on soil surfaces. The results suggest that photolysis may be an important loss process for chlortetracycline sorbed to sunlight-exposed soils, as well as to suspended clays in surface waters. Under direct irradiation equivalent to noon-time, summer sunlight in the midwestern United States, chlortetracycline at the outer clay surface (before light attenuation) degraded with a rate constant of $k^0_p = 0.65 \pm 0.30\ h^{-1}$. The depth at which photochemical action was reduced by 50% ($z_{0.5}$), one of the parameters of the mechanistic model, was found to be 0.014 ± 0.004 mm. The quantum yield on the clay surface was estimated to be $(1.3 \pm 0.7) \times 10^{-4}$, an order of magnitude lower than the quantum yield of the aqueous chlortetracycline zwitterion [$(1.3 \pm 0.3) \times 10^{-3}$; pH 5], although still significant.

KEYWORDS: Antibiotics; soil photolysis; quantum yield; hydrolysis; kinetics

INTRODUCTION

Among pharmaceuticals and personal care products (PPCPs), a diverse class of pollutants detected in the environment (*1*−*4*), antibiotic compounds used as growth promoters in livestock feed, including chlortetracycline, have been observed to make their way to downstream surface waters (*5*). In contrast to wastewater-derived pharmaceutical pollution, the pathway for veterinary pharmaceuticals from use to contamination of surface water may involve the additional intermediate step of incorporation into soil. Animal waste is either excreted directly onto the soil surface, or, commonly in swine, poultry, and dairy operations, it may be stored and spread onto fields at a later time. Pharmaceutical residues in animal wastes can persist throughout the storage conditions until the waste is spread onto fields. For example, chlortetracycline has been found in swine lagoons at concentrations up to 1 mg/L (*6*). In one field study, chlortetracycline was observed to persist in soil after application with a half-life of 25 days (*7*). Compared to other antibiotics with relatively lower sorption coefficients, tetracyclines applied to fields have the potential to accumulate (*8*). The impact of antibiotics in such systems will be a function of their application rate and their persistence. Accordingly, further work is needed to quantify specific loss processes.

Søeborg et al. (*9*) observed that photolysis was an important factor in the stability of chlortetracycline in soil interstitial water. Many veterinary pharmaceuticals, including the tetracycline class, are expected to be primarily sorbed to organics and clay surfaces, with only a small fraction of the total compound in the aqueous phase (*10*). Meaningful numbers for the photolysis of trace organics sorbed to soil organics or minerals are difficult to elucidate.

The photolysis of organic compounds on soil has been investigated in engineered systems for the remediation of contaminated soils, such as removal of PCBs (*11*). Natural photolysis conditions have also been the subject of study, with the goal of quantifying photochemical parameters used to predict the fate of pollutants such as chlorinated dioxins (*12*), polybrominated diphenyl ethers (*13*), pesticides (*14*−*16*), and veterinary antibiotics (*17*).

Photolysis experiments on soil media present many challenges not present in aqueous photolysis. Aqueous systems can be considered to be well-mixed, and light attenuation is precisely defined. In soil photolysis, compounds sorbed to clay or soil organics often have a poorly defined partition coefficient, and diffusion to sunlit surfaces may be slow compared to photolysis kinetics. Light attenuation by the soil is difficult to define, especially with field samples that consist of a heterogeneous mixture of different materials with a wide distribution of particle sizes. Whereas light is dramatically attenuated with depth in a soil, the volatility of some sorbed compounds allows for their diffusion to areas of higher light intensity (*18*, *19*). With increases in soil moisture, an increase in observed photolysis rate constants and a simplification of kinetics to a pseudo-first-order process

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have been observed for several pesticides (*15*, *20*, *21*), indicating that desorption into and diffusion in the aqueous phase are possible. Chlortetracycline is essentially nonvolatile and sorbs strongly to soils [log$K_d \sim 3-6$ (*22*, *23*)], and thus soil moisture may play a role in its photochemical loss, due to desorption and transport to regions of higher light intensity. To simplify the system so that photolysis on a soil surface may be modeled mechanistically, Balmer et al. (*18*) and later Ciani et al. (*19*) developed a method to observe photolysis of compounds sorbed to dry, thin films of kaolinite clay with a controlled thickness. This method allows the variables for light attenuation and volatility to be defined explicitly, so that a fundamental rate constant and quantum yield (i.e., the fraction of photon absorption events that lead to transformation) may be calculated.

The goal of this study was to investigate the photolysis of chlortetracycline on a dry clay surface using the method of Balmer et al. (*18*). We chose this method and simple system to gain a basis for understanding of the photochemical behavior of chlortetracycline in sunlit soil surfaces. A surface rate constant under simulated sunlight is reported, as is the quantum yield for direct photolysis.

MATERIALS AND METHODS

Chemicals. All aqueous solutions were made using Milli-Q ultrapure water (Millipore Corp.). Chlortetracycline (Aldrich Chemical; 95+%) solid was stored at −5 °C; a fresh stock solution was prepared daily to avoid hydrolysis. Glassware containing aqueous chlortetracycline was wrapped in aluminum foil to avoid photodegradation. *p*-Nitroacetophenone (PNAP; 98%) and pyridine (PYR; 99+%) were used as supplied from Sigma-Aldrich. Ethylenediaminetetraacetic acid (EDTA) disodium salt was obtained from Fisher Chemical. Isochlortetracycline was prepared from an aqueous solution of 100 μM chlortetracycline by adjusting the pH to a value of 10 and allowing it to stand at room temperature for 24 h (*24*).

Aqueous Photolysis. Aqueous chlortetracycline (10 μM, pH 5) was irradiated under natural sunlight using quartz tubes (OD = 1.3 cm, i.d. = 1.1 cm, volume = 10 mL) placed perpendicular to the sun on August 14, 2003, in Minneapolis, MN (45° latitude), average T = 31 °C. Photochemical loss was quantified as a function of time using aliquots taken at regular time intervals, which were analyzed by high-pressure liquid chromatography (HPLC) with UV−vis detection. Light intensity was monitored using the PNAP/PYR actinometer method of Dulin and Mill (*25*). The relative solar spectrum used to calculate quantum yield was predicted using the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS) (*26*, *27*).

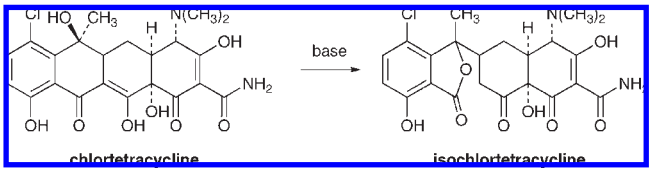
Preparation of Clay Layers. Quartz plates (8.9 cm × 8.9 cm × 1.5 mm) were plated with a kaolinite (Kaolin finest powder, Riedel-de Haen; N_2 BET surface area = 9.4 $m^2\ g^{-1}$; CEC = 6.08 mequiv/100 g) clay layer of variable, controlled thickness using the method developed by Balmer et al. (*18*, *28*). Kaolinite clay was suspended in Milli-Q water using a magnetic stir bar in a 250 mL Erlenmeyer flask. Clay was applied to the quartz glass surface using a single aliquot (8 to 12 mL) of the suspension poured onto the center of the plate using a 25 mL graduated pipet. The area filled by the clay suspension was controlled by a square, 2 mm thick Teflon gasket with inner edges 6.4 cm in width, resulting in a total surface area of 41 cm^2 to which the clay was applied. The clay was dried for 24−48 h, and thickness was determined from the mass of dry clay and the bulk density of kaolinite (1.8 g/cm^3). The concentration of clay in the suspension and the volume applied were varied to achieve the desired thickness, according to **Table 1**. The assumption of homogeneity of the clay distribution was tested by recording the dry mass of the clay delivered from multiple aliquots throughout the range of clay concentrations used in this study. Chlortetracycline was sorbed to the dry clay surface at a concentration of 1 mg g^{-1} by the addition of a chlortetracycline aqueous stock solution to the aqueous clay suspension before application to the plate. Chlortetracycline/clay suspensions were allowed to equilibrate for 15 min before application, and chlortetracycline was not detectable in the aqueous phase after this period. When photolysis experiments were conducted, a second quartz plate was placed on the Teflon gasket and the quartz plates and gasket were held together with binder clips (*18*).

Table 1. Kaolinite Clay Layer Thickness Values Resulting from Various Preparation Procedures

kaolinite in slurry (g/L)	vol of slurry applied (mL)	thickness[a] (mm)
51	8	0.055 ± 0.001
51	10	0.068 ± 0.001
51	12	0.084 ± 0.003
120	8	0.130 ± 0.001
120	10	0.160 ± 0.003
120	12	0.193 ± 0.002

[a] Thickness was calculated from the measured dry mass of the plate, area, and bulk density of the clay. Error values represent standard deviation, N = 4.

Scheme 1. Base-Catalyzed Hydrolysis of Chlortetracycline to Isochlortetracycline



Irradiation of Clay Samples. Clay plates of six different thicknesses, 0.055−0.19 mm, containing chlortetracycline were prepared and irradiated for a series of time periods: 0, 10, 15, and 30 h. Data designated time point 0 h were dark controls, wrapped in aluminum foil and irradiated for 15 h. Photolysis was carried out using an Atlas Suntest CPS+ solar simulator with a UV-Suprax optical filter, a lamp/filter combination that is designed to closely mimic the UV-A and UV-B portions of the terrestrial solar spectrum. The second clean quartz plate sealed to the Teflon gasket above the clay plate prevented disturbance of the clay by the cooling fan. It should be noted that using a solar simulator has the potential to slightly overestimate quantum yield values, because of UV light with wavelength of < 290 nm that is incompletely removed by the filters, as was observed by Kromer et al. (*29*). However, the error from additional UV light is more significant for compounds with absorbance profiles that have limited overlap with the solar spectrum, and the error was assumed to be insignificant for chlortetracycline.

Clay Transfer. The chlortetracycline concentration on dry clay was analyzed by saturating the clay layer with dropwise additions of the extraction solution (described below) and transferring it into a centrifuge tube using a 0.5 cm Teflon straight-edge. The clay remaining on the plate was dried, and its mass was recorded. The difference between this mass and the total mass was assumed to be the mass of clay transferred to the centrifuge tube.

Extraction. Approximately 10 mL of the extraction solution (10 mM EDTA adjusted to pH > 10.5 using NaOH) was added to the tube containing the clay sample slurry. Because the clay already contained some of the extraction solution, the total volume of extraction solution in the vial was determined from the mass of the vial. Care was taken to use only acid-washed glassware and to otherwise avoid the introduction of polyvalent metal cations, including calcium, magnesium, and iron, at any step of extraction and analysis. The presence of EDTA in the extraction solution to chelate metal ions was essential for desorption of chlortetracycline from the clay surface. The high pH value of the extraction solution accomplished two important extraction steps: (1) desorption of chlortetracycline as a dianion and (2) quantitative hydrolysis of chlortetracycline to isochlortetracycline (**Scheme 1**). The samples were allowed to react and equilibrate for 24 h. The tubes were centrifuged for 5 min at 2000 rpm, and the supernatant was sampled and analyzed for isochlortetracycline concentration by HPLC.

The complete hydrolysis of chlortetracycline to isochlortetracycline was verified by monitoring at selected lower pH values (pH 8.5 and 9.5), as well as performing the hydrolysis of chlortetracycline in the extraction solution with no clay present to create a calibration curve. No other significant chromophores were observed in these experiments. As extraction was not complete, a sorption isotherm was created for isochlortetracycline in a

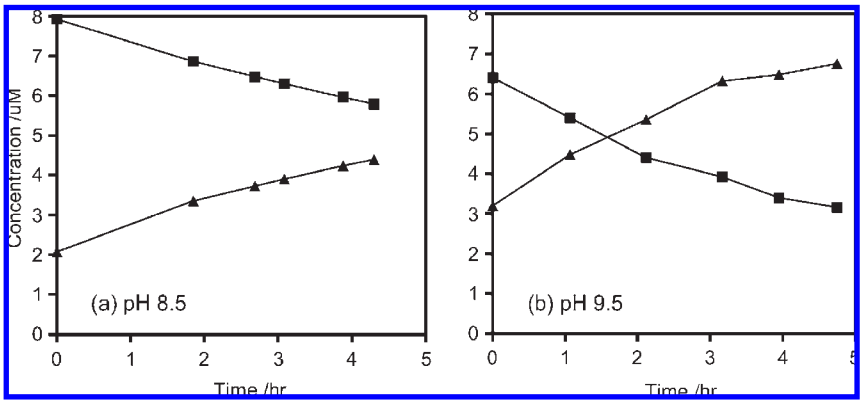


Figure 1. Hydrolysis of chlortetracycline (squares) to isochlortetracycline (triangles) at (**a**) pH 8.5 and (**b**) pH 9.5. Time 0 represents the start of the HPLC sample analysis, which began over an hour after the hydrolysis experiment had been initiated. The original 10 μM chlortetracycline solution contained no isochlortetracycline.

1:1 mass slurry of clay/extraction solution. For every fresh batch of extraction solution, a linear sorption isotherm within the relevant concentration range was formed from six chlortetracycline concentrations at a constant clay/water mass ratio. Analysis of the sorption isotherm was accomplished by measuring the isochlortetracycline concentration in the EDTA/NaOH/H_2O phase after 24 h via HPLC-UV−vis. The resultant distribution coefficient, K_d, was used to calculate total isochlortetracycline in the experimental sample tubes from knowledge of the concentration in water.

Analysis. Chlortetracycline and isochlortetracycline were separated and quantified by HPLC (Hewlett-Packard 1100) using a chromatographic column, a Supelco RP-Amide C_{16} 150 × 4.6 mm, 5 μm particle size column with an in-line RP-Amide C_{16} guard column, and the following solvent gradient: 1 mL min^{-1} flow rate, acetonitrile/pH 3 phosphate buffer 10:90 at 0 min, 28:72 at 5 min, 55:45 at 8 min, and re-equilibration at the starting solvent mixture for 5 min. UV−vis absorbance was monitored at 310 nm. Chlortetracycline eluted at 6.5 min and isochlortetracycline at 7.2 min. The limit of quantification was not determined, as all analyses yielded clear peaks well over the signal-to-noise ratio threshold of 10-fold.

Data Analysis. For the aqueous photolysis experiments, chlortetracycline disappearance was fit using first-order kinetics. The photolysis rate constant is

$$k_s = 2.303 \sum_{\lambda} \varepsilon_{s\lambda} I_\lambda \Phi_{s\lambda} \quad (1)$$

where $\varepsilon_{s\lambda}$ is the decadic (base 10) molar absorptivity of the compound at wavelength λ, I_λ is the intensity of the light source at wavelength λ, and $\Phi_{s\lambda}$ is the quantum yield of the substrate at wavelength λ. The quantum yield was assumed to be wavelength independent and was determined by comparison of the rate constant with that of the actinometer, correcting for differences in light absorption rate as described by Zepp (*30*)

$$\Phi_s = \frac{k_s \sum_{\lambda} \varepsilon_{a\lambda} I_\lambda}{k_a \sum_{\lambda} \varepsilon_{s\lambda} I_\lambda} \Phi_a \quad (2)$$

where Φ_a and $\varepsilon_{a\lambda}$ are the relevant known values for the actinometer.

A full mathematical treatment of photolysis of a compound on a thin clay medium of a controlled depth is available in Balmer et al. (*18*) and is expanded in Ciani et al. (*19*). Light is assumed to be attenuated homogeneously, such that light intensity is reduced exponentially as a function of depth (z). The photolysis rate constant at depth z [$k_p(z)$] therefore decreases exponentially as a function of z

$$k_p(z) = k_p^0 \, e^{-z/1.443 z_{0.5}} \quad (3)$$

where $z_{0.5}$ is the depth at which half of the influent light has been attenuated and k^0_p is the photolysis rate constant at the upper surface [i.e., $k_p(z)$ at $z = 0$].

The experimental data obtained from the analytical methods used in this study yield the average concentration of chlortetracycline over the total depth of the clay layer used, z_{total}. It was noted that the total mass of compound remaining, M_{total}, is a more meaningful value to be used as the dependent experimental value (*18*). Integrating eq 3 over the total depth z_{total} and applying the appropriate correction factors to maintain consistent units gives eq 4

$$\frac{\partial M_{total}}{\partial t} = A \rho_{bulk} \int_{z=0}^{z=z_{total}} -k_p^0 \, e^{-z/1.443 z_{0.5}} C(t,z) \, dz \quad (4)$$

where A is the surface area of the plate and ρ_{bulk} is the bulk density of kaolinite clay (1.8 g cm^{-3}).

This equation, a simplified version of the one used in Balmer et al. (*18*), was used to fit experimental data and obtain the two unknowns, $z_{0.5}$ and k^0_p. The system in ref *18* takes into account diffusion of the analyte concurrent with photolysis, which is a case that is more complex than that of the system studied here. Chlortetracycline is a polar, low-volatility compound, and it was assumed to have no significant diffusion through air on the time scale of the experiment. The fit of eq 4 to experimental data was defined as the minimum of rms error.

With knowledge of k^0_p, the calculation of quantum yield requires only knowledge of incident light intensity as a function of wavelength and the absorptivity of chlortetracycline as a function of wavelength (*19*). Light intensity was monitored using chemical actinometry as described above for aqueous photolysis. The change in geometry from the cylinder holding the actinometer to the flat surface of the clay plate was corrected using an approximate lens effect of 2.0. Absorptivity of chlortetracycline as a function of wavelength was approximated as that of the zwitterion in aqueous solution.

RESULTS AND DISCUSSION

Hydrolysis. The hydrolysis of chlortetracycline to isochlortetracycline in alkali solution is well established (*24*, *31*, *32*). Hydrolysis was monitored at pH values of 8.5 and 9.5, as shown in **Figure 1**. A representative chromatogram is given in the Supporting Information. Successful monitoring of the kinetics requires the reaction to occur over time scales much greater than that of an HPLC chromatographic run, a limitation which resulted in the much more rapid kinetics of the isomerization in the extraction solution (pH > 10.5) being faster than what could be observed. Using a calibration curve developed with the synthesized isochlortetracycline, the hydrolysis of chlortetracycline in the extraction solution was verified (by retention time and peak area) to quantitatively produce isochlortetracycline, which was observed to be stable in the extraction solution for over 24 h. No other product peaks were observed by the analytical method used.

Sorption Isotherm. Figure 2 shows the sorption isotherm for the isochlortetracycline/clay/extraction solution system. For each batch of extraction solution prepared, K_d was similar to that shown in **Figure 2** ($K_d = 4.51 \pm 0.14$ L kg^{-1}) with the exception of

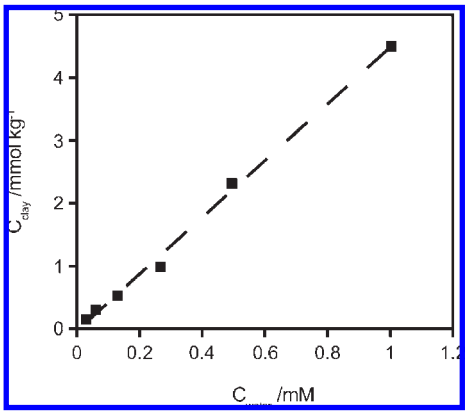


Figure 2. Concentration of isochlortetracycline sorbed to kaolinite clay (C_{clay}) versus concentration in water (C_{water}). Aqueous phase is the extraction solution (10 mM EDTA at pH >10.5). Linear regression yields $K_d = 4.51 \pm 0.14$ L kg^{-1}, $R^2 = 0.996$.

one, for which the data were discarded. The inconsistent batch was later observed to have a pH value of 9.9, which was too low for the extraction to be effective. In addition to the need for high pH (>10.5), EDTA was also necessary in the extraction procedure. Chlortetracycline (and presumably isochlortetracycline) strongly chelates polyvalent metal cations, which can neutralize the charge of the anion or dianion, facilitating sorption to clay surfaces even at high pH values (*22*). Aqueous isochlortetracycline remained below the detection limit in initial attempts to measure aqueous concentration without the presence of EDTA, indicating strong sorption to the clay surface facilitated by bridging metal ions.

Preparation of Clay Plates. Formation of clay layers was found to be predictable and reproducible. **Table 1** shows the procedure used to obtain plates of various thicknesses and the error in reproducibility for four replicates.

Aqueous Photolysis. Photolysis of aqueous chlortetracycline was performed at pH 5 to observe the photochemistry of the zwitterion species, expected to most closely represent the surface-adsorbed chromophore of chlortetracycline (*22*). The low pH also prevented conversion of the chlortetracycline to isochlortetracycline. Under natural sunlight, the rate constant for direct photolysis was observed to be $(5.0 \pm 1.2) \times 10^{-4}$ s^{-1}. The quantum yield for direct photolysis was calculated to be $(1.3 \pm 0.3) \times 10^{-3}$. When the rate constant for the $\times 2$ lens effect of the test tube is adjusted for, photolysis of the chlortetracycline zwitterionic species at the surface of a sunlight-exposed surface water at noon in Minneapolis, MN, is expected to have a half-life of 46 min. Kinetics were rapid compared to the direct photolysis of tetracycline under similar conditions (also primarily the zwitterion), which had a half-life of 190 min (*33*).

Photolysis on a Clay Surface. The photolysis of chlortetracycline, measured as extracted isochlortetracycline, on the kaolinite surface is shown in **Figure 3**. A sample chromatogram is available in Supporting Information Figure S2. The fit of eq 4 to the concentration data yielded $z_{0.5} = 0.014 \pm 0.004$ mm and $k^0_p = 0.65 \pm 0.30$ h^{-1}, where the error represents the range for which the residuals remained within the tested standard error of the analytical method. Note that by fitting the entire data set to eq 4, biphasic kinetics are not needed, as detailed in Balmer et al. (*18*). The $z_{0.5}$ value found in this study seems to be reasonable in comparison to that found by Balmer et al. for trifluralin: 0.016 ± 0.0099 mm. Light attenuation within the clay layer is wavelength-dependent, and $z_{0.5}$ therefore depends on the clay used, the light source used, and the absorbance spectrum of the compound of

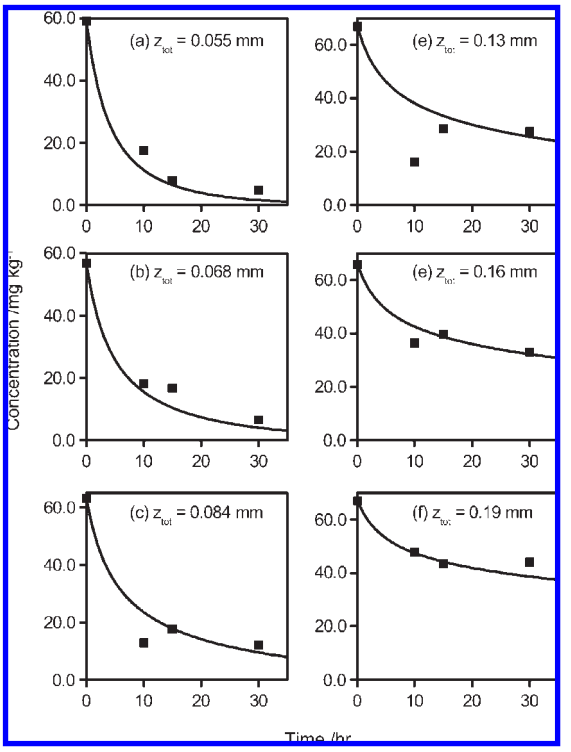


Figure 3. Average concentration of chlortetracycline in dry kaolinite clay plates of various thicknesses ($z_{total} = 0.055-0.19$ mm; **a**−**f**) as a function of photolysis time. Lines represent a global fit of the entire data set to eq 4, yielding $z_{0.5} = 0.014 \pm 0.004$ mm and $k^0_p = 0.65 \pm 0.30$ h^{-1}.

interest. The light source and clay used in this study were similar to those of Balmer et al. (*18*), and the peaks of photochemical action for chlortetracycline and trifluralin are expected to be relatively similar. The close agreement of $z_{0.5}$ between the two studies is therefore not unexpected, although it indicates that the values obtained in this study are of a reasonable magnitude.

The quantum yield for the photolysis of chlortetracycline sorbed to the kaolinite surface was estimated to be $(1.3 \pm 0.7) \times 10^{-4}$, on the basis of the value of k^0_p and the absorbance spectrum of the aqueous chlortetracycline zwitterion. The reported error for this value represents only the error in kinetic rate constants used for its calculation. Any error introduced from the assumption of a comparable light flux seen by the actinometer test tube and the flat quartz plate are not included (although efforts were made to ensure a similar distance to the light source); differences in the geometry of placement within the solar simulator have been ignored, except for the $\times 2$ lens effect of the test tube, which was incorporated. The calculation of quantum yield using the absorbance spectrum of aqueous chlortetracycline is an approximation. It would have been preferable to have measured the absorbance spectrum of surface-sorbed chlortetracycline (*34*), although such a technique was outside the scope of this study. The fact that the quantum yield for photolysis of chlortetracycline on a clay surface is lower (by approximately 1 order of magnitude) is likely because the compound was sorbed to a dry mineral surface. Ciani et al. (*19*) found quantum yields of sorbed species were 2−10 times lower than those in aqueous solution. The underlying reasons for the lower quantum yield for clay-bound chlortetracycline are not known, but may include changes in chemical environment upon solvation, surface-facilitated deactivation of the excited state, or conformational rigidity in the bound state that inhibits some of the reaction pathways. In aqueous solution, photolysis of tetracycline compounds proceeds by intramolecular rearrangements and loss of the dimethylamine,

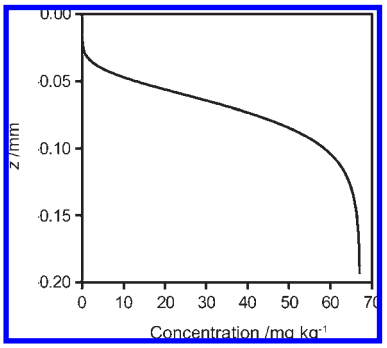


Figure 4. Predicted concentration of chlortetracycline as a function of z (depth) after 30 h of photolysis using a clay layer of z_{total} = 0.2 mm. The starting concentration is 68 mg/kg.

and these pathways may be sensitive to conformational flexibility (*35*).

It is also possible that transformation of chlortetracycline to isochlortetracycline may have occurred on the clay surface, and the photochemical kinetics we observed were those of a mixture of both compounds. However, attempts to extract chlortetracycline from the kaolinite using neutral conditions and added organic solvents such as acetonitrile yielded only the chlortetracycline parent compound (data not shown). This suggested that, if surface-catalyzed hydrolysis occurred during sorption, it was limited. Unfortunately, organic extraction methods had recoveries that were both too low and too variable to be used for kinetic analysis.

The depth profile of photolysis will vary among compounds, depending on the action spectrum of the compound compared to wavelength-dependent light attenuation of the medium. The compound-specific variation of the parameter $z_{0.5}$ of Balmer et al. (*18*) reflects this photochemical action of the compound. The depth profile for chlortetracycline within a 0.2 mm clay layer after 30 h of photolysis is shown in **Figure 4**, on the basis of the model calculations used to fit the data in **Figure 3**.

Environmental Application. Although the dissipation of chlortetracycline by photolysis seems, in **Figure 4**, to be limited to a depth of about 0.1 mm, photolysis is expected to be far more significant in systems with higher moisture. Chlortetracycline sorption is likely dominated by reversible electrostatic interactions with mineral surfaces (*22*, *23*, *36*). Sorption is therefore expected to be labile enough to allow for significant diffusion along a concentration gradient such as that formed in **Figure 4**, resulting in dissipation of chlortetracycline originating at greater depths. This would be analogous to the gas diffusion considered as a component of photolysis on dry clay (*18*). Further investigations of chlortetracycline photolysis on kaolinite with added moisture, on other clay minerals (with higher exchange capacities or swelling properties that may affect chlortetracycline sorption/retention and thus photochemical behavior), and in systems with organic matter are needed to fully evaluate the role of photolysis in chlortetracycline persistence in soil systems.

The data presented here are also of interest in aquatic systems containing suspended sediment. With the strong sorption of chlortetracycline to clays [log $K_d \sim 3-4$ (*22*)], the photochemistry of mineral surface-sorbed chlortetracycline may be of a greater importance than photolysis of the dissolved compound. Because of the high quantum yield observed in this study for sorbed chlortetracycline, within an order of magnitude of that of the aqueous zwitterion, the photochemical loss of chlortetracycline in a system containing suspended sediment is potentially significant. The quantum yield reported here offers the basis for environmental fate calculations that take into account the photochemistry of the mineral-associated compound.

ACKNOWLEDGMENT

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Supporting Information Available: Example chromatograms from the hydrolysis and photolysis experiments. This information is available free of charge via the Internet at http://pubs.acs.org.

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