Bioavailability of s-Triazines Adsorbed on Montmorillonite

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Interaction of s-triazine herbicides with montmorillonite surfaces may produce protonation and/or hydrolysis of s-triazine compounds. Upon protonation the s-triazines are transformed into organic cations and adsorbed in the interlamellar region of the montmorillonite. If a s-triazine adsorbed on montmorillonite resists hydrolysis, it may be biologically active upon desorption. The bioavailability of four s-triazines adsorbed on montmorillonite but not undergoing hydrolysis was studied by using the green alga *Chlamydomonas* as a bioassay technique. The infrared and X-ray data showed that protonated s-triazine molecules in the interlamellar spaces of montmorillonite could be deprotonated and displaced to external surfaces by NH_3 treatment. Bioassay results showed that s-triazines desorbed from montmorillonite were in a biologically active form and their bioavailability was greatly increased by NH_3 treatment.

The s-triazines are among the most widely used soil applied herbicides in the world. From the first communication published by Gast et al. (1955) until today, considerable research concerned with the nature, fate, and behavior of s-triazines has been published, including an extensive review of the mechanisms of adsorption of s-triazines by clay colloids (Weber, 1970).

The lack of biological activity of a pesticide adsorbed on soil colloids is the ultimate criterion for characterization of the compound as a bound or unavailable residue. However, relatively little is known concerning the biological activity of herbicides that have been adsorbed by interacting with soil surfaces and are then desorbed into the soil solution. Weber and Weed (1974) summarized the effects of soil constituents on the biological activity of pesticides as related to the mechanism by which the compounds were bound. They reported that diquat and paraquat, when adsorbed in the interlayer region of montmorillonite in amounts less than the cation-exchange capacity, are biologically unavailable to both plants and microorganisms. Except for diquat and paraquat, there is very little specific information on the fate of pesticide compounds strongly adsorbed in the interlamellar region of swelling soil clay minerals.

Russell et al. (1968a) showed that amitrole could be protonated and adsorbed as a cation in interlamellar spaces of the montmorillonite; they postulated that it would be biologically active if it were exchanged or desorbed. The factors affecting adsorption of s-triazines by soils have been considered in detail by Weber (1966, 1970) and Bailey et al. (1968). Infrared studies (Russell et al., 1968b; Cruz et al., 1968; Brown and White 1969; Cruz and White, 1972) of the interaction of s-triazines with mineral surfaces have shown that adsorption usually produces degradation of the herbicides through protonation and hydrolysis. In the case of certain s-triazines, they are protonated and subsequently hydrolyzed to form hydroxytriazines that have no biological activity (Cruz et al., 1968). The ease of protonation and hydrolysis varies among the s-triazines (White, 1975). It is possible that adsorption on the soil surface may occur after protonation while hydrolysis may or may not occur. Cruz et al. (1968) showed that hydroxypropazine adsorbed in montmorillonite interlamellar spaces could be deprotonated and displaced to the external surface when exposed to NH_3 gas. If the protonated and adsorbed s-triazine molecule resists hydrolysis, the triazine compound should show biological activity when it is desorbed.

The object of this study was to examine the biological activity of a series of s-triazines adsorbed on montmorillonite when treated to produce desorption. The biological activity of desorbed herbicides was measured by using the green alga *Chlamydomonas* as a bioassay technique. The use of *Chlamydomonas* to detect bioavailability of growth inhibitor and photosynthetic inhibitor herbicides has been described recently (Hess, 1980).

EXPERIMENTAL SECTION

Materials. The adsorbent used in this study was the <2-μm fraction of montmorillonite separated by sedimentation from Wyoming bentonite (Upton, WY). The montmorillonite was saturated with calcium by three treatments with 1 M calcium chloride and then dialyzed until salt free.

The s-triazine compounds used (prometryn, sebuthylazine, terbuthylazine, and GS 18183) were high-purity compounds, obtained from Ciba-Geigy Corp., Ardsley, NY, and Ciba-Geigy A.G., Basel, Switzerland. These s-triazines were chosen because, according to White (1975), they do not undergo hydrolysis when adsorbed on montmorillonite. The structural formula of these triazines and other properties are shown in Table I.

Infrared and X-ray Techniques. For IR studies of the s-triazine–montmorillonite complexes, self-supporting films of montmorillonite were prepared by pipetting appropriate volumes of a 2% suspension of the calcium-saturated montmorillonite onto Mylar film. The air-dried montmorillonite films were readily detached from the Mylar and then placed in aqueous solutions of s-triazines at pH 3.5 (5×10^{-3} M HCl) for a period of 3 days, removed, rinsed twice with water, and air-dried. The concentration of the s-triazines in the aqueous solutions was 8 ppm except for prometryn which was 40 ppm due to its higher solubility. Differential spectra of the complex films, before and after NH_3 treatment (described below), were recorded with a Perkin-Elmer Model 180 spectrophotometer. An untreated calcium–montmorillonite film was used in the reference beam. The IR spectra of s-triazines were recorded for specimens as KBr pellets.

The X-ray diffractograms of the triazine–montmorillonite complexes before and after NH_3 treatment were obtained on oriented films in a N_2 atmosphere after vacuum treatment overnight. The X-ray equipment used was

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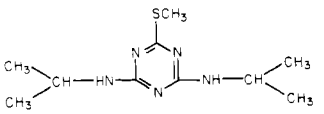
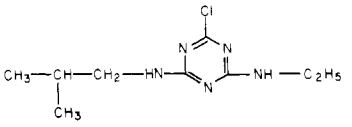
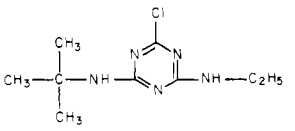
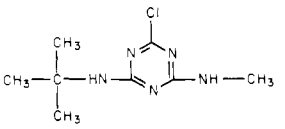
Table I. Herbicides Used in This Study

common name	code no.	structure and chemical denomination	M_r	sensitivity of *Chlamydomonas* bioassay: I_{50}, ppm	sensitivity of *Chlamydomonas* bioassay: lower limit detectability, ppm
prometryn	G 34161	 2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine	241.4	0.02	0.005
sebuthylazine	GS 13528	 2-(*sec*-butylamino)-4-chloro-6-(ethylamino)-*s*-triazine	229.6	0.07	0.01
terbuthylazine	GS 13529	 2-(*tert*-butylamino)-4-chloro-6-(ethylamino)-*s*-triazine	229.6	0.10	0.02
	GS 18183	 2-(*tert*-butylamino)-4-chloro-6-(methylamino)-*s*-triazine	215.6	0.10	0.02

a Siemens AG Kristalloflex 4 generator, Type F diffractometer.

Preparation of *s*-Triazine–Montmorillonite Complexes. The herbicide–montmorillonite complexes were prepared by adding 5 mL of 2% calcim–montmorillonite suspension to 100 mL of an aqueous solution at pH 3.5; the concentration of *s*-triazines was 8 ppm except for prometryn which was 40 ppm. These suspensions were shaken for 24 h, centrifuged, and filtered. The complexes were washed twice with water at pH 4.2 and air-dried. The amount of herbicide adsorbed on the complexes was calculated from the difference between initial and final concentrations of triazines in the aqueous solutions and with correction for the herbicide removed by washing. The *s*-triazine concentration in aqueous solution was determined spectrophotometrically at an appropriate wavelength (223 nm) by using a Beckman Acta II UV–vis spectrophotometer. For production of desorption by deprotonation, portions of air-dried complexes were placed in a controlled atmosphere chamber for 0.5 h and flushed alternately with NH_3 gas and humidity-controlled air (relative humidity = 30.5%). The films of the herbicide–montmorillonite complexes were treated in the same way for both IR and X-ray analysis. The treatment with HCl vapors for IR was carried out in the same manner as the NH_3 treatment.

***Chlamydomonas* Bioassay.** The bioactivity of *s*-triazines adsorbed on montmorillonite before and after NH_3 treatment was monitored by using *Chlamydomonas* as a bioassay technique. This bioassay measured the evolution of oxygen during the light reaction of photosynthesis with an oxygen electrode and amplifier (YSI Model 53) equipped with a recorder (Fassan Model 100). Three replicates of each sample were carried out.

The maintenance and preparation of the *Chlamydomonas* cultures were carried out as previously described by Hess (1980). The evolution of oxygen was measured by placing 2.5 mL of algal culture (cell density = 1×10^6/mL), 2.5 mL of either water (for control), herbicide solution, (for standard curves) or herbicide–montmorillonite complex suspension, and 0.02 mL of 1 M $NaHCO_3$ in the sample chamber. Dissolved oxygen in the sample chamber solution was removed by bubbling N_2 gas through the solution for 30 s. For maintenance of uniformity the samples were constantly stirred during analysis. Curves of oxygen evolution vs. time were obtained upon illumination (400 μEinstein m^{-2} s^{-1}) of the sample chamber. Net oxygen evolution was determined by correcting for measured oxygen consumption in the dark. Standard curves for each herbicide were obtained by plotting the inhibition of oxygen evolution, as compared to the control, vs. concentration. Figure 1 shows the standard curve obtained for terbuthylazine. In Table I, the sensitivity of this bioassay for the *s*-triazine compounds is summarized.

For measurement of the possible influence of the montmorillonite clay on the bioassay procedure, a clay control was run for calcium–montmorillonite. An accurate amount of calcium–montmorillonite (1, 2, 3, 10, 20, and 30 mg) was weighed and made to a volume of 100 mL with distilled water and shaken thoroughly for 5 min. Aliquots (2.5 mL) of these various concentrations were placed in the sample chamber with 2.5 mL of algal culture and 0.02 mL of 1 M $NaHCO_3$, N_2 gas was bubbled through the chamber for 30 s, and the oxygen evolution was measured as indicated above. The measurements were made in quadruplicate and the results are shown in Table II. Since the standard error for LSD (0.239) is less than the standard deviation (0.31), there is no significant difference between the water control and the clay control, and we may conclude that the presence of from 1 to 30 mg/100 mL calcium–montmorillonite in the suspension from which an aliquot is taken for the bioassay test has no significant

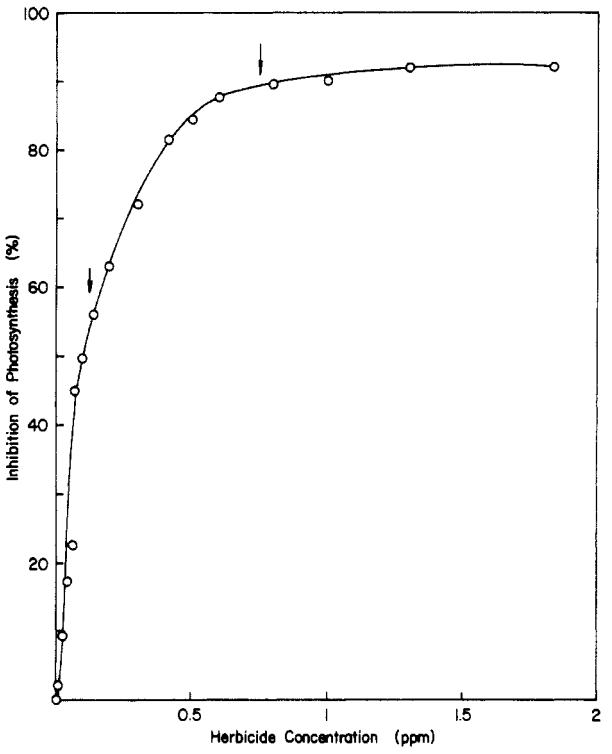


Figure 1. Bioassay standard curve for terbuthylazine (GS 13529). The arrows indicate the range in which the quantitative measurements were made.

Table II. Influence of Calcium-Montmorillonite on the *Chlamydomonas* Bioassay[a]

mg of clay/ 100 mL	% increase in O_2/min				
	rep I	rep II	rep III	rep IV	mean
0	4.45	3.46	4.35	4.55	4.20
1	4.55	5.13	3.56	4.45	4.42
2	4.55	4.35	4.35	4.05	4.33
3	3.75	4.35	4.05	4.35	4.13
10	4.15	3.95	4.15	4.35	4.15
20	4.25	4.34	4.15	4.15	4.22
30	3.95	4.35	4.35	4.54	4.30
0	4.15	4.35	4.54	4.35	4.35

[a] ANOVA (analysis of variance) calculations gave the following data: grand mean = 4.26; standard deviation = 0.31; standard error for LSD = 0.240.

effect on the measrement of oxygen evolution by the algae.

The bioassay of the herbicide–montmorillonite complexes before and after NH_3 treatment were carried out by weighing an accurate amount of complex, adding 100 mL of distilled water, and shaking thoroughly for 5 min. These suspensions (2.5 mL) were placed in the sample chamber, and the evolution of oxygen was recorded as described above. The amount of active herbicide desorbed from the complexes was calculated from the standard curve for the herbicide.

RESULTS AND DISCUSSION

Infrared and X-ray Data. Adsorption of *s*-triazines from aqueous solution on montmorillonite yielded phases whose infrared spectra differed from those of pure *s*-triazines in KBr disks. The changes in intensities and frequencies of the absorption bands occurred at 3200–3250 cm^{-1} (NH stretching), 1510–1550 cm^{-1} (in-plane vibrations of the triazine ring and NH in-plane deformation), and near 1600 cm^{-1} (C=N skeletal vibrations). The general features of the interaction are illustrated in Figure 2 for prometryn. The shifts of these bands to higher frequencies in the complexes (Figure 2a), compared to pure prometryn (Figure 2b), are due to the protonation of the triazine molecules when adsorbed in the interlamellar spaces of montmorillonite (Russell et al., 1968b; Cruz et al., 1968; White, 1975).

After the initial analysis, the films of the complexes were exposed to NH_3 gas and the infrared spectra recorded again. The infrared spectrum showed shifting of NH stretching bands from 3400–3340 cm^{-1} in the untreated complex (Figure 2a) to 3240 cm^{-1} in the NH_3–treated complex (Figure 2c), indicating that a major portion of the prometryn had been deprotonated and displaced to external surfaces (Cruz et al., 1968; White, 1975). For purposes of comparison, the spectra of prometryn and protonated prometryn are shown in parts a and b of Figure 3. The occurrence of deprotonation and desorption of the prometryn is further supported by the appearance of an intense Christensen effect around 1600 cm^{-1} due to the formation of a crystalline prometryn phase on external surfaces of the montmorillonite particles in the clay film. The details of the 1600-cm^{-1} region that were obscured in the infrared spectrum of the NH_3-treated prometryn–montmorillonite film due to the Christensen effect were readily observed by recording the spectra of untreated and NH_3-treated prometryn–montmorillonite complexes in KBr pellets (Figure 4). The virtual disappearance of the band near 1640 cm^{-1} and the development of the prominent shoulder at 1590 cm^{-1} are clearly seen in Figure 4b. Comparison of the spectrum in Figure 4b and that of the pure prometryn in Figure 3a shows the desorbed and deprotonated prometryn spectrum to have features very similar to those of the pure prometryn. Slight differences in the peak positions in Figures 3 and 4 and those in Figure 2 are due to differences between instruments used in recording the spectra and effects of the KBr matrix on the interaction of the prometryn–montmorillonite complex with infrared radiation. The spectrum of the NH_3-treated samples showed a band at 1420 cm^{-1} (Figure 2c), corresponding to the deformation band of NH_4^+ ions, indicating that NH_4^+ cations were in the interlamellar spaces of the montmorillonite.

The NH_3-treated film was then treated with HCl vapors. The band at 3590 cm^{-1} in Figure 2d is too high to be associated with NH stretching bands of prometryn or NH_4^+ and is attributed to OH stretching vibrations of water and/or hydronium strongly associated with the clay surface as a result of the HCl–H_2O vapor treatment. The spectrum also showed bands at 1685 and 1655 cm^{-1} that correspond to protonated prometryn. It is postulated that the band at 1655 cm^{-1} corresponds to protonated prometryn in the interlamellar region of montmorillonite while the band at 1685 cm^{-1} may be due to protonated prometryn on external surfaces with a proton concentration higher than that in the interlamellar region of the clay. The broad band at 3280 cm^{-1} probably contains contributions corresponding to neutral molecules of prometryn as well as NH_4^+ cations that were not replaced by the HCl treatment. The strong band at 1420 cm^{-1} is evidence for the persistence of the NH_4^+ ions. These changes suggest that some of the external prometryn was protonated by HCl; a portion of these protonated molecules was readsorbed into the interlamellar space of the montmorillonite. The rest of the protonated molecules of prometryn remained on the external surfaces along with molecules that may not have been protonated.

The X-ray diffractograms of the prometryn–montmorillonite complexes, before and after NH_3 treatment, are shown in parts a and b of Figure 5 ,respectively. The d_{001} spacing of the prometryn–montmorillonite complex before

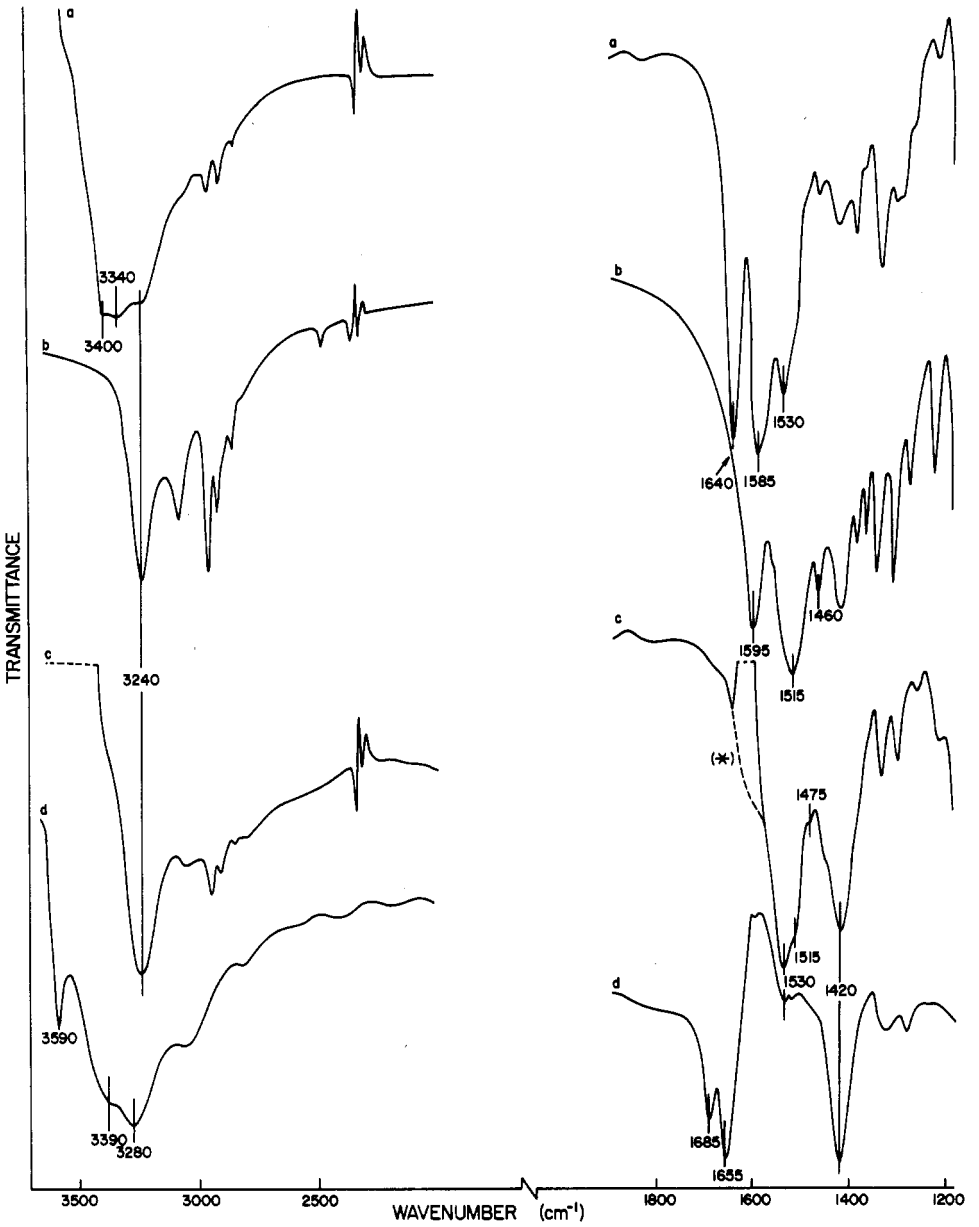


Figure 2. Infrared spectra of (a) the film of the prometryn–montmorillonite complex, (b) prometryn in the KBr disk, (c) sample a after NH_3 treatment [(*) dotted line indicates the approximate shape of 1590-cm^{-1} shoulder obscured by the Christensen effect at 1600 cm^{-1}; approximation based on spectrum of the KBr disk, Figure 4b], and (d) sample c after HCl vapor treatment.

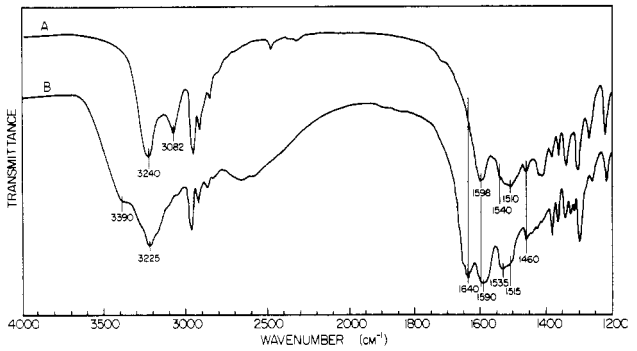


Figure 3. Infrared spectra of prometryn: (a) untreated; (b) protonated with HCl. KBr pellets (1 mg of sample/300 mg of KBr).

NH_3 treatment was 12.6 Å; this spacing corresponds to a single layer of prometryn molecules in the interlamellar spaces with the triazine ring parallel to the montmorillonite layers (Cruz et al., 1968). The d_{001} spacings of Ca–montmorillonite and NH_4–montmorillonite recorded under the same conditions as the prometryn–montmorillonite complex were 9.6 and 10.4 Å, respectively. After NH_3 treatment, the basal spacing of the prometryn–montmorillonite complex decreased to 10.5 Å, indicating that prometryn had been displaced from the interlayer region to the external surface.

In summary, the IR and X-ray data showed that *s*-triazines adsorbed on montmorillonite can be deprotonated and displaced to external by NH_3 treatment.

Bioassay Data. The bioassay data obtained for the *s*-triazine-montmorillonite complexes before and after NH_3 treatment established that all the herbicides studied were active upon desorption and the NH_3 treatment increased their biological activity. This feature is illustrated in Figure 6 for the GS 18183–montmorillonite complex, showing curves of oxygen evolution obtained in the *Chlamydomonas* bioassay for the control (curve a), for the untreated complex (curve b) and for the NH_3-treated complex (curve c). It can be observed that herbicide adsorbed on montmorillonite is desorbed in a bioactive form, producing inhibition of photosynthesis. A more severe

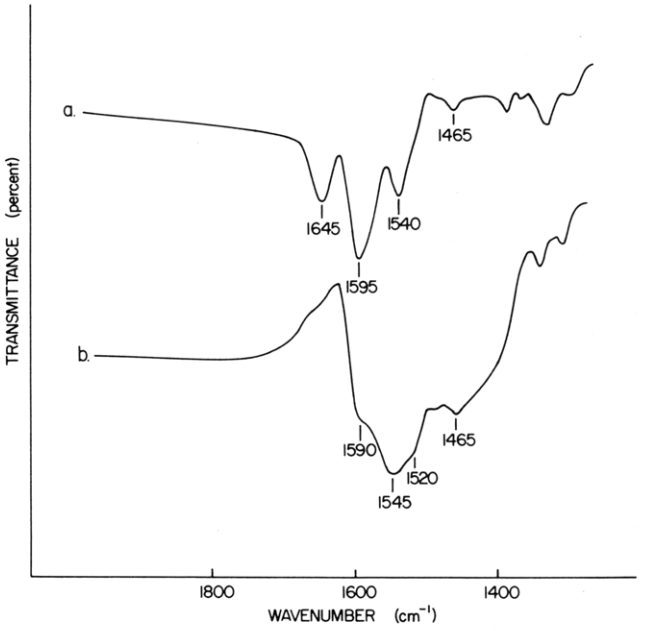


Figure 4. Differential infrared spectra of KBr pellets (5 mg of sample/300 mg of KBr) of the prometryn–montmorillonite complex: (a) untreated; (b) after treatment with NH_3 gas. Ca–montmorillonite in KBr pellet was placed in the reference beam.

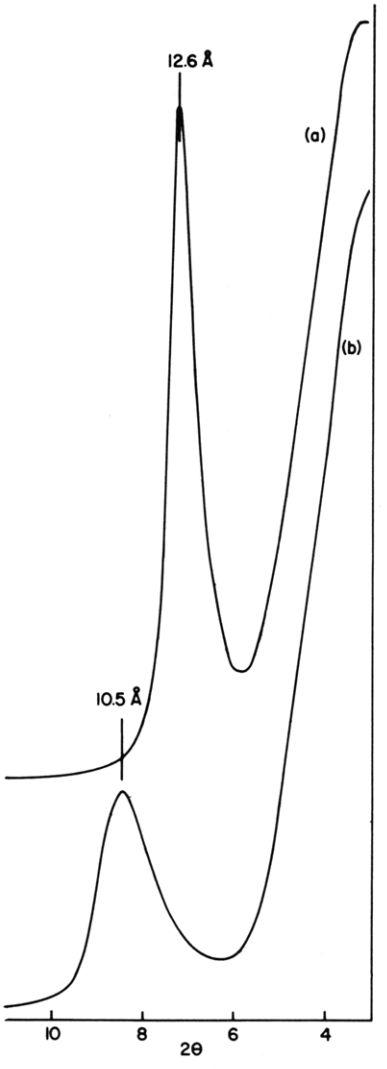


Figure 5. X-ray diffraction tracings of the oriented film of (a) the prometryn–montmorillonite complex and (b) sample a after NH_3 treatment.

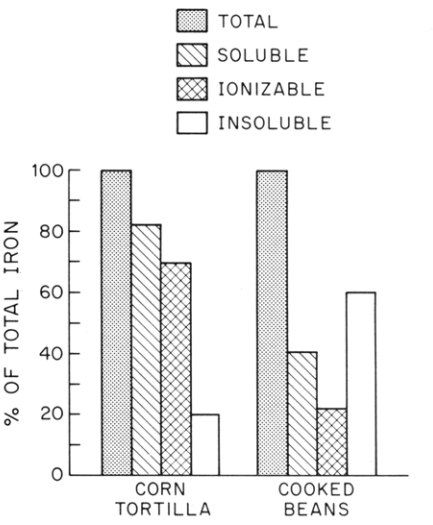


Figure 6. Oxygen evolution curves from *Chlamydomonas* bioassay of (a) control culture, (b) culture with 30 mg/100 mL suspension of the GS 18183–montmorillonite complex, and (c) the same as b for the NH_3-treated complex. The position of the arrow by each curve indicates the point at which respiration measurements were begun.

inhibition of photosynthesis occurring in the NH_3-treated complex (Figure 6c), when compared to the untreated complex (Figure 6b), proves that the NH_3 treatment resulted in an actual increase in the bioavailability of herbicide to the test organism.

The results obtained by bioassay for the different *s*-triazine–montmorillonite complexes before and after NH_3 treatment are shown in Table III. The amount of herbicide desorbed was calculated from the standard curves of inhibition vs. concentration (as shown in Figure 1), previously obtained for each herbicide. The analysis of the data in Table III permits the observation that, in all cases, the herbicides adsorbed on montmorillonite were desorbed in bioactive form, producing inhibition of photosynthesis. This fact indicates that an equilibrium exists between the molecules of *s*–triazine adsorbed on montmorillonite and the molecules in solution. This can be explained by taking into account the different equilibria that govern the adsorption of *s*–triazines on montmorillonite in aqueous medium (Weber, 1970):

$$R + H^+ \rightleftharpoons RH^+ \quad (1)$$

$$RH^+ \text{ X–mont.} \rightleftharpoons \text{RH–mont.} + X^+ \quad (2)$$

$$\text{RH–mont.} + H^+ \rightleftharpoons \text{H–mont.} + RH^+ \quad (3)$$

where R = triazine compound, RH^+ = triazine cation, X–mont. = montmorillonite with exchangeable cation X, H–mont. = hydrogen (aluminum) montmorillonite, and H^+ = hydrogen ion as hydrated H_3O^+ species. In this way, the adsorbed *s*-triazines which do not undergo hydrolysis can be biologically available when desorbed. The bioavailability of the adsorbed *s*-triazine will depend upon the equilibrium constants of eq 1–3, as well as factors affecting such parameters (pH, cation concentration, temperature, etc.).

The percentage of adsorbed herbicide that is bioavailable depends also on the relative degree of protonation of the herbicide. Table IV shows the values of the relative degree of protonation (White, 1975) and the desorption percentange ranges obtained by bioassay for the different complexes before and after NH_3 treatment. One can observe that a relationship exists between the relative degree of protonation and herbicide desorption percentages. Prometryn has the highest protonation degree and showed the

Table III. Desorption of Herbicides Adsorbed on Montmorillonite As Measured by *Chlamydomonas* Bioassay

concn of the complex suspension, mg/100 mL		inhibition of photosynthesis, %	concn of the desorption solution, ppm	amt of herbicide desorbed, mg/g	desorption, %
Prometryn-Montmorillonite Complex (Initial Amount Adsorbed = 192.0 μmol/g)					
1:	untreated	65.6 ± 1.4[a]	0.06	6.01	12.9
	NH_3 treated	82.2 ± 0.8	0.15	15.00	32.4
2:	untreated	72.9 ± 1.5	0.08	4.00	8.6
	NH_3 treated	79.5 ± 0.4	0.12	6.02	13.0
3:	untreated	74.1 ± 1.5	0.08	2.81	6.0
	NH_3 treated	79.2 ± 1.0	0.12	4.00	8.6
Sebuthylazine-Montmorillonite Complex (Initial Amount Adsorbed = 10.9 μmol/g)					
10:	untreated	50.0 ± 0.2	0.13	1.31	52.4
	NH_3 treated	57.0 ± 0.6	0.15	1.50	60.0
20:	untreated	52.7 ± 0.7	0.14	0.70	28.0
	NH_3 treated	57.0 ± 1.4	0.16	0.74	29.6
30:	untreated	55.7 ± 0.8	0.15	0.50	20.0
	NH_3 treated	60.0 ± 1.3	0.17	0.57	22.8
Terbuthylazine-Montmorillonite Complex (Initial Amount Adsorbed = 22.9 μmol/g)					
10:	untreated	57.6 ± 0.6	0.10	1.06	20.1
	NH_3 treated	82.0 ± 0.7	0.26	2.60	49.4
20:	untreated	73.8 ± 1.0	0.60	3.00	57.0
	NH_3 treated	81.7 ± 1.0	0.76	3.80	72.2
30:	untreated	68.2 ± 0.4	0.48	1.60	30.4
	NH_3 treated	83.3 ± 1.7	1.14	3.80	72.2
GS 18183-Montmorillonite Complex (Initial Amount Adsorbed = 11.8 μmol/g)					
10:	untreated	35.5 ± 0.6	0.08	0.80	31.5
	NH_3 treated	43.0 ± 1.3	0.18	1.80	70.8
20:	untreated	56.5 ± 0.9	0.26	1.30	51.2
	NH_3 treated	65.5 ± 1.4	0.42	2.10	82.6
30:	untreated	52.8 ± 1.2	0.22	0.73	28.7
	NH_3 treated	71.9 ± 0.8	0.60	2.00	78.7

[a] Standard deviation from triplicated bioassay.

Table IV. Relationship between Protonation Degree and Desorption

herbicide	rel degree of protonation[a]	desorption % range from the herbicide-montmorillonite complexes[b]	
		untreated	NH_3 treated
prometryn	3.4	6-13	8-32
sebuthylazine	1.5	20-52	23-60
terbuthylazine	1.6	20-57	49-72
GS 18183	1.5	29-51	70-82

[a] After White (1975). [b] From Table III.

lowest desorption percentages. This fact suggests that the protonation–deprotonation process is an important factor in influencing the biological availability of s-triazine herbicides adsorbed on montmorillonite.

As data in Table III show, the NH_3 treatment of the s-triazine–montmorillonite complexes greatly increased the bioavailability of the adsorbed herbicide. The reason for this increase in bioavailability was shown by infrared and X-ray analyses that established that NH_3 molecules deprotonated and displaced the herbicide adsorbed in the interlamellar spaces of montmorillonite.

According to Weber (1970) the adsorption of s-triazines by soil colloids depends upon many factors: rate of removal of the s-triazine from the soil solution by plant roots, type and concentration of other ions or molecules in the system, constituency of the particles that make up the system, pH, etc. In the same way, the desorption and bioavailability of these herbicides in a bioassay will depend on all these factors. The results reported in this communication concerning desorption and bioavailability of s-triazines correspond only to the conditions used for the bioassay (pH, culture solution composition, clay/water ratio, etc.). The data show that certain s-triazines that do not undergo hydrolysis when adsorbed on montmorillonite can be biologically available and their bioavailability is greatly increased by treatment with a base stronger than s-triazines, (e.g., NH_3). This can be very important for the behavior and fate of these herbicides in soils. The fertilization of soils containing s-triazines with ammonia will affect the bioavailability of these herbicides and, in turn, influence all those factors governing their fate and behavior in soils: adsorption–desorption by soil colloids, plant and organism uptake, movement, chemical or photochemical decomposition, volatilization, etc.

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