



The Adsorption of Herbicides and Pesticides on Clay Minerals and Soils. Part 1. Isoproturon

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Abstract

The adsorption of isoproturon and two model compounds, *N,N*-dimethylurea and 4-isopropylaniline, on clay minerals (bentonite, montmorillonite and kaolinite), organic matter (humic acid) and soil (with and without organic matter) has been studied using FT- infrared spectroscopy (IR), thermogravimetric analysis (TGA), high pressure liquid chromatography (HPLC) and X-ray diffraction (XRD). *N,N*-dimethylurea interacted with bentonite and montmorillonite by the coordination of the carbonyl group, directly or indirectly through water molecules, with exchangeable cations. Adsorption on humic acid was due to hydrogen bonding with the active sites of the adsorbent. The amino group of *N,N*-dimethylurea appears to be relatively inactive during adsorption. The mechanisms involved in the adsorption of 4-isopropylaniline were hydrogen bonding and protonation. No adsorption of 4-isopropylaniline was observed on kaolinite. The investigation of isoproturon suggested that both the carbonyl and amino groups of isoproturon were involved in interactions with the active sites of the adsorbents. Both the clay minerals and organic matter of soil contribute to the adsorption of organic compounds on soil but the clay minerals bentonite and montmorillonite play a major role in their adsorption on soil.

Introduction

The past few decades have seen increasing use of a wide range of organic herbicides and pesticides in agriculture which ultimately find their way directly or indirectly into soils. The risk of these compounds entering the human food chain via drinking water has given rise to a need for extensive research into the fate and behaviour of pesticides and other organic molecules. The latter are not classified as pesticides but they are found as degradation products of pesticides and can also act as model compounds in soil. The fate and behaviour of the pesticides in soil environments are governed by various retention, transportation and transformation processes. These processes determine both the efficacy of pesticides in controlling target organisms and their potential for environmental hazards. Transportation and transformation processes of pesticides in soils depend strongly on their retention by the solid organo-mineral phase. Although retention includes all the processes that prevent or retard movement of pesticides in soils, the primary means of retention is adsorption of pesticides on soil constituents. The most important soil constituents for adsorption are clay minerals and organic matter [1, 2].

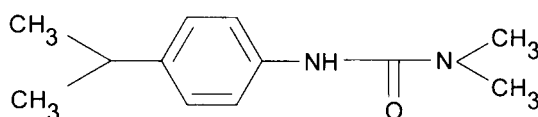
Isoproturon was chosen for study because of its widespread agricultural use [3] and it has been widely detected in ground water [4]. Spark and Swift [5] studied the ad-

sorption of substituted-urea herbicides on soil humic acid and suggested that both the amino group and carbonyl group of isoproturon could interact with humic functional groups through H-bonding to the similar types of functional groups of the humic molecule. Recent studies of the adsorption of isoproturon on soils [2, 6] and clays [2, 7] have used techniques such as adsorption-desorption measurements and FT-IR spectroscopy.

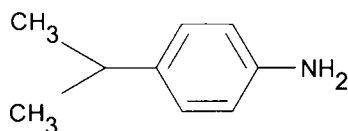
The objectives of this study are to provide a better understanding of the interaction mechanisms involved in the adsorption of isoproturon (Figure 1) on soil and its constituents using clay minerals (bentonite and kaolinite, together with an acid treated montmorillonite (K10)), humic acid, air-dried soil, and soil with and without organic matter. The organic compounds *N,N*-dimethylurea and 4-isopropylaniline were also used as model compounds (Figure 1). The complementary techniques used were:

- (i) Fourier transform-infrared spectroscopy (FT-IR) to identify the interacting moieties,
- (ii) thermogravimetric analysis (TGA) to provide quantitative information about the complexes formed,
- (iii) X-ray diffraction (XRD) to confirm formation of intercalation complexes,
- (iv) high pressure liquid chromatography (HPLC) to provide information on the desorption of the organic component.

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Isoproturon



4-Isopropylaniline

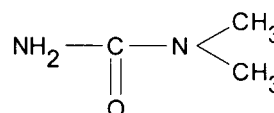
*N,N*-dimethylureaFigure 1. Structures of isoproturon (IPU), 4-isopropylaniline (IPA) and *N,N*-dimethylurea (DMU).

Table 1. Selected physiochemical properties of clays

	Bentonite	Montmorillonite	Kaolinite
SiO ₂ (wt%)	63.40	72.36	47.40
TiO ₂ (wt%)	0.15	0.59	0.05
Al ₂ O ₃ (wt%)	19.90	16.17	36.52
Fe ₂ O ₃ (wt%)	3.74	3.20	0.78
CaO (wt%)	1.11	0.22	0.06
MgO (wt%)	2.32	1.40	0.21
MnO (wt%)	0.01	0.01	0.01
Na ₂ O (wt%)	1.82	0.14	<LOD*
K ₂ O (wt%)	0.28	1.71	1.56
CEC** meq/100 g	71.00	51.08	3.13
pH	6.00	3.5	4.5

*Below lower limit of detection.

**Cation exchange capacity.

Experimental

Chemicals

All the chemicals were research grade, (solids having 98% purity and liquids 99%). *N,N*-dimethylurea (DMU), and 4-isopropylaniline (IPA) were obtained from Lancaster Synthesis Ltd. Isoproturon (IPU) was supplied by Ciba Agriculture. BDH Hiperolve UV grade acetonitrile, Hiperolve methanol and chloroform were used throughout this study. The organic free distilled water was prepared by using milli pore Milli-RO and Milli-Q purification systems.

Clays

Bentonite was obtained from Aldrich. Montmorillonite (K10) and kaolinite were obtained from Fluka. Their properties are summarised in Table 1.

Humic acid

Humic acid was obtained from Aldrich as the sodium salt. It was converted into the acid form by passing a 5% solution

of the sodium salt through a column of Amberlite IR-120 (H) cation exchange resin. The resulting solution was freeze dried and stored.

Soils

The soil sample was obtained from Brimstone Experimental Farm, Oxfordshire, United Kingdom. Comprehensive details of the farm and soil sample are given in [8]. Three kinds of soil samples were used in this study.

1. Air-dried soil (AS)
2. Carbonate and soluble salt free soil (CSS)
3. Organic matter free soil (OMS)

Air dried soil (AS)

The soil obtained from the field was air-dried and gently ground to <2 mm and stored in polythene bags. Its composition and some properties are: organic matter 9.01 wt%; sand 8.6 wt%; silt 30.7 wt%; clay 60.7 wt%; cec 33.6 meq/100 g; pH 6.50 [8].

Carbonate and soluble salt free soil (CSS)

Carbonates and soluble salts were removed from the air-dried soil by using the method of Gee and Bauder [9]. 10 g of the air-dried soil was placed in a 250 mL centrifuge bottle and mixed with 100 mL of water and 10 mL of 1M NaOAc (adjusted to pH 5). The mixture was centrifuged for about 10 minutes at 1500 rpm and the supernatant discarded. The remnant was washed three times by shaking with 50 mL of water, centrifuged and the supernatant was discarded. The soil was freeze dried and stored in a pyrex bottle.

Organic matter free soil (OMS)

After removing the carbonates and soluble salts (as mentioned above), 10 mL of H₂O₂ were added for each 10 g of soil in a pyrex beaker, stirred and left for about an hour. A further 5 mL of H₂O₂ were added, stirred and left for half an hour. The sample was heated at 90 °C to evaporate the excess water and destroy the remaining H₂O₂. The residue

was washed with water, freeze-dried and stored in a pyrex bottle.

CEC and pH

The cation exchange capacity was determined by shaking approximately 4 g of each clay, humic acid and soil sample with 33 mL of 1M sodium acetate solution for 15 minutes. The mixture was centrifuged for 5 minutes at 3000 rpm and the supernatant was discarded. The remnant was washed twice with industrial methylated spirit. Finally ammonium acetate was used to flush off the sodium. The total amount of sodium was then measured by using a flame photometer.

The pH of two duplicates of each clay, humic acid and soil samples was determined by shaking a mixture of the samples and water for 1 hour at a ratio of 1:2.5.

Adsorption experiments

Adsorption on clays and soil samples

1 g of each clay and soil sample was immersed in 10 mL methanol solution of DMU, 15 mL methanol solution of IPU or in 5 mL of IPA in a 50 mL conical flask. These were kept on a magnetic stirrer for about 24 hours at room temperature. The solutions were filtered at the pump without washing and dried over silica gel for a minimum of 24 hours. To observe any intercalation by a solid – solid exchange reaction physical mixtures were prepared by grinding 1 g clay or soil with DMU or IPU. The weight of DMU or IPU used was approximately equal to the weight loss observed by the thermogravimetric analysis of the model compound treated samples.

Adsorption on humic acid

These samples were prepared by immersing 1 g of humic acid in 10 mL methanol solution of DMU, 15 mL methanol solution of IPU or in 5 mL of IPA in a 50 mL conical flask. These were kept on a magnetic stirrer for 24 hours at room temperature and then transferred to 50 mL propylene centrifuge tubes and centrifuged for about 30 minutes at 3500 rpm. The supernatant solutions were decanted in the pyrex bottles and stored in a refrigerator while the remnant was dried over silica gel for at least 24 hours. To observe any solid-solid interaction physical mixtures of humic acid were prepared by grinding and mixing 0.1 g DMU or IPU with 1 g of humic acid.

Desorption experiments

0.1 g of model compound treated samples were mixed separately in 2.5 mL of 80% methanol and 20% water solution, (60/40 acetonitrile/water for the IPU treated sample), in 50 mL propylene centrifuge tubes on a rotary shaker for 24 hours. The tubes were centrifuged at 4000 rpm for 30 minutes and then the supernatant solutions were decanted in

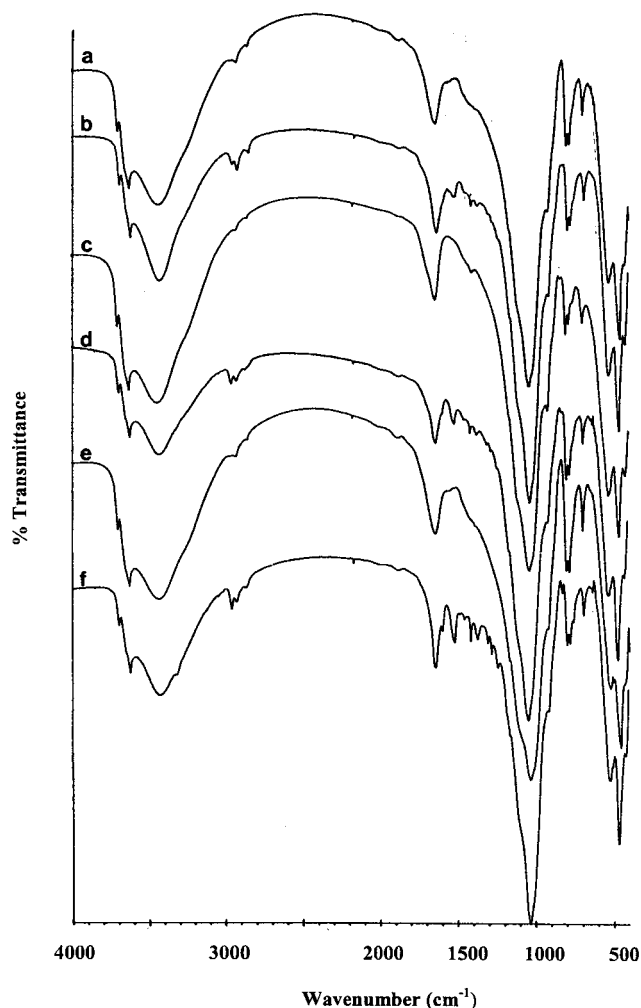


Figure 2. Infrared spectra of (a) AS, (b) isoproturon (IPU) treated AS, (c) CSS, (d) IPU treated CSS, (e) OMS, (f) IPU treated OMS.

pyrex bottles and stored in a refrigerator. Solutions were diluted and filtered through Nalgene 0.22 μm cellulose acetate filters prior to HPLC analysis.

Instrumentation

Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer purged with dried air. Solids were examined in the form of KBr discs. Solutions were examined in a 1 mm path length cell with NaCl windows. Liquid phase spectra were examined as capillary films between sodium chloride plates. Spectral subtractions were done by subtracting the spectrum of untreated samples from that of the model compound and pesticide treated samples, by using the standard Nicolet software. Figure 2 shows typical IR spectra obtained in this study.

Thermogravimetric (TGA) traces were obtained using a Perkin Elmer 7 series thermal analysis system using a temperature range of 30–850 $^{\circ}\text{C}$ at a ramp rate of 20 $^{\circ}\text{C min}^{-1}$. The sample chamber was purged with dry air. Figure 3 shows typical TGA traces obtained from clay/guest systems in this study. The three weight losses represent desorption of physically adsorbed water (100 $^{\circ}\text{C}$ region), loss of the guest

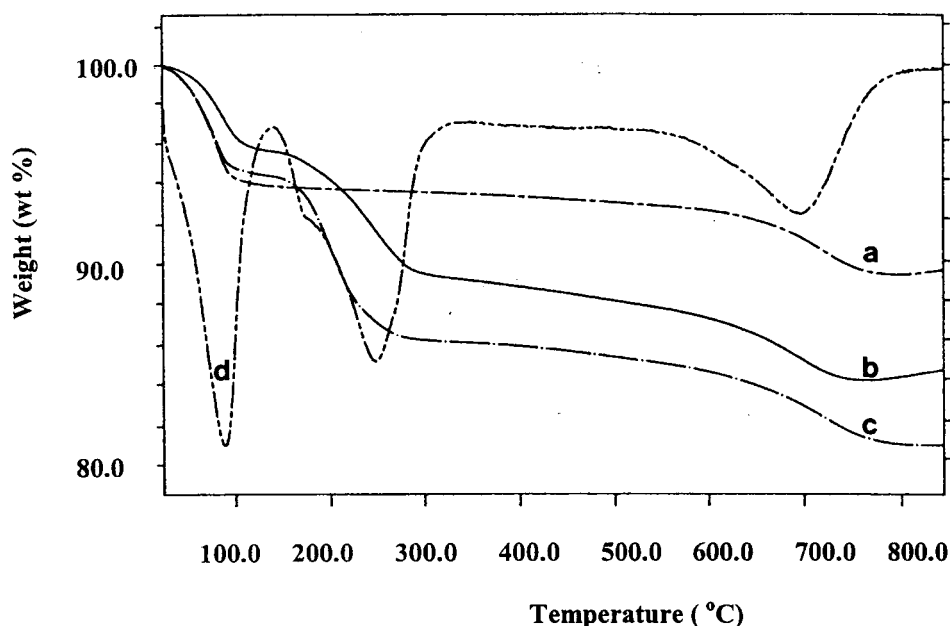


Figure 3. Thermogravimetric analysis of (a) bentonite, (b) isotreturon (IPU) treated bentonite, (c) physical mixture of IPU and bentonite, (d) derivative thermogram for IPU treated bentonite.

(300 °C region) and dehydroxylation of the aluminosilicate layer (700 °C region)

The HPLC system consisted of a Merck Hitachi LC organizer fitted with a rheodyne injection port with a 20 μm sample loop and L-6200 and L-3000 photo-diode array detectors. These were controlled by a Merck Hitachi D-6000 DAD Manager and HPLC manager software packages on an IBM model AT computer. The chromatography column used was a Hibar Merck Lichrospher C18 reversed phase column (250 \times 4mm i.d.) with 4 μm beads. Solvents used in the study were water, acetonitrile and methanol.

The X-ray diffraction studies were carried out on a Philips X-ray diffraction unit consisting of a table top X-ray generator PW 1720 and a PW 1050/70 vertical goniometer. All the patterns were recorded by using Cu $K\alpha$ radiation at 40 kV and 40 mA. Each sample was scanned at a rate of 2 θ 1° min⁻¹.

XRF analyses were carried out using a Philips PW 1400 instrument.

Results and discussion

N,N-dimethylurea (DMU)

IR Studies

Table 2 summarises the positions of the IR bands of *N,N*-dimethylurea (DMU) after contact with the various supports. A dilute solution of DMU in CHCl_3 , i.e., a non-interacting DMU molecule, was used as reference. The NH and CO stretching modes have lower cm^{-1} values whilst the NH bending and CN stretching modes have higher cm^{-1} values than the solution phase values. These observations are consistent with interactions of the DMU molecule through the CO and NH bonds. The relatively small decrease in the NH band positions suggests that the main interaction involves

Table 2. IR band positions (cm^{-1}) of *N,N*-dimethylurea in the crystalline and solution phases and adsorbed on different media

	NH ₂ asym stretch	NH ₂ sym stretch	CO stretch	NH ₂ bend	CN stretch
Crystalline	3406	3208	1660	1610	1515
CHCl_3 solution	3530	3428	1657	1594	1501
Bentonite	3514	3406	1649	1603	1518
DMU PM ¹	3485	3416	1650	1607	1518
Montmorillonite	3493	3412	1646	1605	1519
DMU PM ¹	3507	3415	1646	1616	1519
Kaolinite	3409	3212	1644	1616	1518
DMSO-kaolinite ²	3514	3407	1652	1606	1516
Humic acid	3451	3367	1635	1590	1513
Air dried soil	3409	3360	1650	1602	1523
CSS ³			1647	1606	1520
OMS ⁴			1645	1610	1519

¹Physical mixture of DMU and the clay.

²Displacement of intercalated DMSO by DMU [12].

³Carbonate and soluble salt free soil.

⁴Organic matter free soil.

the carbonyl group. The DMU band positions in the spectra of physical mixtures with bentonite and montmorillonite also show similar shifts which are indicative of interactions occurring in the solid mixtures. Comparison of the spectra of the supports before and after treatment with DMU suggests the following interactions between the two components:

- Changes in the bands in the OH stretching region indicate that DMU and bentonite interact by coordination of the carbonyl group oxygen, either directly or indirectly through a water molecule, with the exchangeable cations of bentonite as suggested by Farmer and Ahlrichs [10] and Akyüz *et al.* [11].

Table 3. Basal spacings (Å) for clay minerals, after treatment with DMU, IPA and IPU and for DMU and IPU physical mixtures (PM)

	Untreated	DMU treated (d_t)	DMU PM (d_t)	IPA treated (d_t)	IPU treated (d_t)	IPU PM (d_t)
Bentonite	12.26	13.38 (3.78) ^a	15.49 (5.89)	13.19 (3.59)	14.71 (5.11)	14.47 (4.87)
Montmorillonite	12.15	14.24 (4.64)	14.24 (4.64)	14.96 (5.36)	14.71 (5.11)	13.81 (4.21)
Kaolinite	7.26	12.61 ^b	^c	^c	^c	^c

^a $\Delta d = d_t - 9.6 \text{ \AA}$.

^bValues obtained by treatment of DMSO-kaolinite.

^cValues as for kaolinite.

- DMU and montmorillonite interact in a similar way but solely through water molecules.
- The absence of changes in the OH stretching bands of kaolinite, coupled with the observation that the DMU bands have values similar to those in the crystalline state, suggest that surface adsorption occurs when treated directly with DMU. It has been shown that DMSO in the DMSO-kaolinite complex can be displaced by other species [12], and this procedure leads to the formation of an intercalation complex with weak kaolinite-DMU interactions.
- Changes in the positions of the OH and carbonyl band positions of humic acid suggest that the main interaction between DMU and humic acid involves the carbonyl group of the former and the OH or COOH groups of the acid. No interaction was observed in the physical mixture.
- The IR spectrum of air-dried soil (Figure 2a) is very similar to that of montmorillonite, but with additional bands which can be assigned to kaolin group minerals, quartz and organic matter. The C=O stretching mode band decreases in the order AS>CSS>OMS which suggests that the soil-DMU interaction increases in this order.

TGA studies

Figure 3 illustrates typical TGA traces obtained from clay-guest systems. The three weight losses represent desorption of physically adsorbed water (100 °C region), loss of the guest (300 °C region) and dehydroxylation of the aluminosilicate layer (700 °C region) [13]. The weight losses observed for DMU in the bentonite and montmorillonite complexes were 12% and 7% respectively, indicating the very different nature of these two materials. Kaolinite and DMSO-kaolinite treated with DMU showed weight losses of 5% and 15% respectively, confirming the IR data that surface adsorption occurs in the former and intercalation in the latter. The desorption of DMU from the soil samples gave similar weight losses of 6% (AS), 5% (CSS) and 4% (OMS). Solution desorption measurements could not be made due to incomplete resolution of the DMU and solvent peak.

XRD studies

Intercalation of DMU into clay minerals would lead to an expansion of the basal spacing. Table 3 summarises the XRD results. An increase was observed with DMU treated bentonite and montmorillonite, but no increase was observed with

kaolinite confirming the conclusion of the IR study of surface adsorption. Treatment of DMSO kaolinite with DMU did however result in an increase in the basal spacing indicating formation of an intercalate, in agreement with the IR and TGA data. Physical mixtures of DMU with bentonite and montmorillonite also showed an increase in the basal spacing indicating that an intercalate was formed during the grinding process, in agreement with the IR results.

The expansion in the d(001) basal spacing of the clay minerals due to the intercalation of DMU was calculated as $\Delta d = d_t - 9.6 \text{ \AA}$, where d_t is the basal spacing obtained after adsorption, and 9.6 Å is the thickness of a 2:1 clay layer. The Δd values (Table 3) observed for all the samples ranged from 3.78–5.89 Å. The large spacing observed in the bentonite physical mixture sample could be indicative of a greater DMU content than in the treated sample leading to a different orientation of the guest.

DMU treated kaolinite did not show any expansion in the basal spacing while intercalation was observed by the replacement of DMSO by DMU in the DMSO-kaolinite complex. The XRD pattern of DMU treated DMSO-kaolinite showed two peaks: one at 11.18 Å which shows the expansion in the basal spacing due to DMSO and the other at 12.61 Å, the expansion due to the adsorption of DMU. This further suggests that DMU has not replaced all the DMSO molecules.

4-Isopropylaniline (IPA)

IR Studies

Table 4 compares the positions of the IR bands of 4-isopropylaniline (IPA) in the liquid and solution phases and after contact with the various supports. Compared with the spectrum of the CHCl₃ solution the NH₂ and CN stretching modes have lower cm⁻¹ values, indicating interaction involving the NH₂ group. Comparison of the spectra of the supports before and after treatment with IPA suggests the following interactions between the two components:

- IPA and bentonite interact by both direct coordination of the nitrogen atom of aniline with the interlayer cations and via a water bridge, the type I and type II complexes suggested by Yariv *et al.* [14] for adsorbed aniline. The former is characterised by a weak band in the 3220–3270 cm⁻¹ region and the latter by a downward shift of the 3636 cm⁻¹ band of bentonite.

Table 4. IR band positions (cm^{-1}) of 4-isopropylaniline in the liquid and solution phases and adsorbed on different media

	NH_2 asym stretch	NH_2 sym stretch	CN stretch
Liquid	3430	3351	1274
CHCl_3 solution	3447	3372	1271
Bentonite	3391	3353	1267
Montmorillonite	3395	3325	1257
Kaolinite ¹			
Humic acid	3413	3368	
Air dried soil	3395	3346	1264
CSS ²	3388	3332	1265
OMS ³	3381	3339	1264

¹No adsorption.

²Carbonate and soluble salt free soil.

³Organic matter free soil.

- The spectrum of the IPA/montmorillonite system shows a weak band at 1581 cm^{-1} indicative of protonation of the aniline as suggested by Cloos *et al.* [15]. The absence of a band in the $3220\text{--}3270 \text{ cm}^{-1}$ region indicates no type I complex but there is evidence for the formation of a type II complex. Bentonite and montmorillonite therefore give very different adsorption behaviour, as was the case for DMU.
- There was no spectroscopic evidence for adsorption of IPA by kaolinite.
- Changes in the positions of the OH and carbonyl band positions of humic acid suggest that the main interaction between IPA and humic acid involves the amino group of the former and the OH or COOH groups of the acid.
- The relative values of the NH_2 stretching modes of IPA adsorbed on the different soil samples suggests the interaction increases in the order $\text{OMS} > \text{CSS} > \text{AS}$, the same order as observed for DMU adsorption.

TGA Studies

The TGA curves obtained for the clay-IPA systems are similar to those shown in Figure 3 with three weight loss regions. In the $150\text{--}550 \text{ }^\circ\text{C}$ region the bentonite sample gave a major weight loss of 22% at $170 \text{ }^\circ\text{C}$ and a minor loss of 3% at $450 \text{ }^\circ\text{C}$. These two peaks are assumed to arise from the type I and II complexes suggested by the IR study. Similar effects were observed in the TGA curve of the montmorillonite sample corresponding to the loss of the protonated and type II complexes. The desorption of IPA from the soil samples gave weight losses of 10% (AS), 11% (CSS) and 21% (OMS).

Desorption of IPA from the solid samples into a methanol/water mixture was also studied using HPLC and compared with the thermal desorption values (Table 5). The TGA analysis showed greater desorption of IPA as compared to the HPLC analysis due to the higher temperatures used. In the case of the clay minerals, the HPLC analysis gave about 50% of the weight loss observed in the TGA analysis.

Table 5. Comparison of guest desorption % weight loss values obtained using thermal and solution desorption

	DMU ¹		IPA desorption		IPU desorption	
	TGA	TGA	HPLC	TGA	HPLC	
Bentonite	12.0	25.0	14.0	7.0	5.6	
Montmorillonite	7.0	31.0	18.9	7.0	4.6	
Kaolinite	5.0	na	na	3.0	2.7	
Humic Acid	nd	nd	19.1	nd	9.5	
AS	6.0	10.0	9.8	2.0	2.0	
CSS	5.0	11.0	8.2	2.0	2.3	
OMS	4.0	21.0	12.9	4.0	3.2	

¹The DMU and solvent peaks could not be satisfactorily resolved.

n.a. – no adsorption.

n.d. – not determined.

The organic matter free soil (OMS), showed more affinity for the adsorption of IPA (12.9% weight loss) as compared to the other two types, AS and CSS, (9.8% and 8.2% respectively). This suggests that the clay minerals are important in the adsorption of IPA on this type of soil and removal of the organic matter from the soil increases the availability of the clay surfaces for adsorption [16].

XRD Studies

An increase was observed in the basal spacing with IPA treated bentonite and montmorillonite, indicating the formation of intercalates, but no increase was observed with kaolinite (Table 3).

Greene-Kelly [17], reporting on the adsorption of aniline, inferred that a 15 \AA basal spacing corresponded to a perpendicular arrangement of the aniline ring with respect to the silicate layers whilst a 12.6 \AA spacing required an arrangement of the aniline molecules with their planes parallel to the silicate layers. Farmer and Mortland [18] and Yariv *et al.* [14] suggested a tilted configuration of the ring to explain their results. In the present study IPA treated bentonite (13.19 \AA) showed a tilted arrangement of the IPA molecules with respect to the surface of the silicate layers, while in the case of IPA treated montmorillonite (14.96 \AA) the IPA may be perpendicular to the surface of the silicate layer.

The quantitative analysis shows that a higher amount of IPA was adsorbed on montmorillonite as compared to bentonite. This favours the perpendicular arrangement of the molecules since an increase in the amount of adsorption changes the orientation of the ring from horizontal to vertical [14].

Isoproturon (IPU)

IR Studies

Table 6 summarises the positions of the IR bands of isoproturon (IPU) after contact with the various supports. Compared with the spectrum of the CHCl_3 solution, the NH , CO and $\text{C-N}(\text{CH}_3)_2$ stretching modes have lower cm^{-1} values whilst the C-N(H) stretching mode value remains virtually

Table 6. IR band positions (cm^{-1}) of isoproturon in the crystalline and solution phases and adsorbed on different media

	NH stretch	CO stretch	C–N(H) stretch	C–N(CH ₃) ₂ stretch
Crystalline	3313	1649	1518	1371
CHCl ₃ solution	3460	1662	1517	1362
Bentonite	3318	1639	1518	1372
IPU PM ¹	3315	1640	1518	1371
Montmorillonite	3315	1636	1518	1372
IPU PM ¹	3319	1638	1518	1371
Kaolinite	3325	1646	1518	1370
Humic acid	3314	1636	1517	1372
Air dried soil	3315	1637	1519	1375
CSS ²	3322	1641	1519	1372
OMS ³	3314	1636	1519	1375

¹Physical mixture of IPU and the clay.

²Carbonate and soluble salt free soil.

³Organic matter free soil.

unchanged. Similar results were reported by Pantani *et al.* [7] for IPU adsorption on montmorillonite. These observations are consistent with interactions of the IPU molecule through the CO and NH bonds. Comparison of the spectra of the supports before and after treatment with IPU and using the criteria considered for DMU and IPA suggest the following interactions between the two components:

- IPU is adsorbed on bentonite and montmorillonite by the interaction of both the CO and NH groups with the exchangeable cations.
- No intercalation occurs with kaolinite, only surface adsorption
- Comparison with the studies of urea derivative herbicides on humic acid reported by Senesi and Testini [19] and Spark and Swift [5] indicates that adsorption on humic acid involves the hydrogen bonding of the CO and NH groups of IPU with the COOH, C=O, OH and NH groups of humic acid.
- The relative values of both the NH and carbonyl stretching modes of IPU adsorbed on the different soil samples suggests the interaction increases in the order OMS~AS>CSS, an order slightly different from that observed with DMU and IPA (OMS>CSS>AS).

TGA Studies

The TGA curves obtained for the clay-IPU systems are similar to those shown in Figure 3 with three weight loss regions. The weight losses in the IPU desorption region were 7%, 7%, 3%, 2%, 2% and 4% for bentonite, montmorillonite, kaolinite, AS, CSS and OMS respectively.

Comparison of these values with those obtained by desorption of IPU by an acetonitrile/water mixture (Table 5) indicates stronger adsorption of IPU by the OMS as compared to the AS and CSS soil samples. This further suggests that the clay minerals are important in the adsorption of isoproturon in the soil studied.

XRD Studies

Increases in the basal spacings were observed for bentonite and montmorillonite but not for kaolinite (Table 3), confirming the IR results that surface adsorption occurs on kaolinite. The spacings for the IPU treated samples are identical at 14.71 Å. This large value is unlikely to be due to a perpendicular arrangement of the IPU molecules due to their greater length when compared with IPA, but rather to a tilted or parallel arrangement.

Conclusions

The combination of the results from various techniques employed to study the adsorption of isoproturon on clay minerals, humic acid and soil samples leads to the following conclusions.

The results of the infrared study show that the isoproturon molecule gives a decrease in the CO and NH stretching vibrations and an increase in the C–N(CH₃)₂ stretching vibrations. This suggests that both the carbonyl and amino groups of isoproturon interact with the active sites of the adsorbents.

An interaction was observed between isoproturon and the clay minerals (bentonite and montmorillonite) in the physical mixture. No interaction was observed in the physical mixtures of isoproturon with kaolinite, humic acid and soil samples.

The TGA quantitative analysis shows significant differences between the amount of DMU, IPA and IPU adsorbed by each support. The clay minerals do however play an important role in the adsorption and desorption of isoproturon in the soil type used in the present study.

Isoproturon was intercalated into the layers of bentonite and montmorillonite. No intercalation was observed in the case of kaolinite.

Acknowledgements

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