Table III. Monthly Rainfall (cm)

			Month				
Year	June	July	Aug	Sept	Oct	Nov	Dec
1972	8.7	6.6	14.5	22.0	5.4	10.6	12.5
1973	17.9	23.4	7.7	7.6	7.4	6.3	12.2

than 1% was recovered. In contrast, from 74 to 97% of the applied bentazon leached through soil columns in the laboratory (Abernathy and Wax, 1973). Most of the bentazon evidently was adsorbed in the lysimeters in the field, because it is not metabolized rapidly enough to disappear in 30 days. Bentazon half-life ranges from 10 to 30 days (Drescher, 1972). The differences in the quantity adsorbed between the field and laboratory studies could result from the bentazon not reaching adsorption equilibrium in the laboratory studies like it did in the field. Leachate was collected within hours after application on the laboratory columns, but not for days after application in the field. Bentazon may be completely adsorbed at equilibrium, but this may not occur for 30 or more days, as evidenced by the absence of bentazon in leachates from the lysimeters after the initial surge terminated. In addition, no bentazon leached in lysimeters where no leachate appeared for 60 days.

If bentazon ionizes in aqueous solution as proposed (Abernathy and Wax, 1973), then only less than 1 mequiv of anion exchange capacity per 100 kg of soil in the upper 15 cm of soil would be required to satisfy the exchange capacity of the 3.36 kg/ha of bentazon applied. Even these soils should have this amount of anion exchange. Bentazon ap-

pears not to be completely adsorbed by this means, because it was easily transported through the soils.

No AIBA was detected in any of the leachates analyzed in 1973.

Our results indicate that some of the soil-applied bentazon can leach through some Illinois soils, provided it rains enough to cause water movement through the soil within 60 days after application. Even though we applied four times the recommended rate to the soil (normal applications are applied to foliage), less than 2% of the applied bentazon was ever recovered in the leachate. Although some bentazon can leach through soils, its presence in aquatic systems is probably not a threat to aquatic food chains, because aquatic organisms do not accumulate the chemical to any significant degree nor is this herbicide greatly toxic to these organisms (Booth and Hansen, 1973).

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Effect of Associated Anions on Ammonium Adsorption by and Desorption from Soils

Ram C. Dalal

The effect of associated anions, $H_2PO_4^-$, SO_4^{2-}, and NO_3^-, on NH_4^+ adsorption by 14 Trinidad soils showed that the NH_4^+ adsorption maxima obtained from $(NH_4)_2SO_4$ and NH_4NO_3 were 63 and 45%, respectively, of that from $NH_4 H_2PO_4$. Conversely, NH_4^+ desorption from soils was less when it was adsorbed from $NH_4 H_2PO_4$ than from either $(NH_4)_2SO_4$ or NH_4NO_3. These effects were ascribed to the specific adsorption of $H_2PO_4^-$ and SO_4^{2-} by soils. NH_4^+ adsorption maxima were correlated positively with CEC and negatively with total nitrogen content irrespective of associated anions. In addition, it was also correlated with oxalate extractable iron, base saturation, and dithionite extractable iron when the associated anions were $H_2PO_4^-$, SO_4^{2-}, and NO_3^-, respectively. The application of these observations to $(NH_4)_2SO_4$, $NH_4H_2PO_4$, and NH_4NO_3 fertilization of soils in the humid tropics was indicated.

The nature of the anion associated with ammonium ion has been found to influence the capacity for ammonium fixation. This was generally ascribed to be due to the effect of the anion on the pH of the soil. The effect of the anion on the adsorption capacity of the associated cation should also be considered. Thus, Leggett (1958) showed that in a number of different ammonium salts tested, the highest

sorption by soils and minerals was obtained with $(NH_4)_2HPO_4$. Stojanovic and Broadbent (1960) found that a small but consistently greater proportion of the ammonium ions added to soils as $(NH_4)_2HPO_4$ or NH_4NO_3 could be recovered by acidified salt solutions than when the ammonium ions were added as NH_4OH or NH_4Cl. However, Harada and Kutsuna (1954) observed that the ammonium fixation was the same, independent of whether ammonium was added as sulfate or chloride. In Hawaiian soils, Kanehiro et al. (1960) found that the sorption of ammonium ions was higher when applied as $NH_4 H_2PO_4$ or $(NH_4)_2HPO_4$ than when applied as $(NH_4)_2SO_4$ or NH_4Cl. Thus, the na-

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Table I. Some Properties of the Soils

Soil no.	Soil series[a]	Tentative soil[b] subgroup	pH	Clay content, %	CEC, mequiv/100 g of soil	Exch. cations			Base satn., %	Org. C, %	Total N, %	Oxalate extr.		Dithionite extr.	
						Ca	Mg	K				Fe, %	Al, %	Fe, %	Al, %
1	L'Ebranche C	Entic Pelludert	5.7	66	23.2	14.8	4.8	1.17	94	2.7	0.22	1.30	0.16	2.11	0.78
2	Freeport Cl	Aric Tropaquult	4.9	34	12.3	1.4	2.0	0.45	30	1.2	0.13	0.50	0.15	1.67	0.69
3	Talparo C	Aquentic chromodert	5.2	45	10.8	6.2	2.7	0.53	81	2.3	0.19	1.18	0.11	2.84	1.08
4	Tarouba C	Aquentic chromodert	5.2	72	35.0	8.3	6.9	0.68	47	2.8	0.29	1.45	0.16	9.01	1.26
5	Bois Neuf C	Entic Pelludert	4.6	70	45.7	7.2	9.7	0.94	38	8.5	0.88	0.29	0.20	0.38	0.23
6	Siparia Ls	Arenic Haplustult	6.3	11	3.9	2.4	0.7	0.22	67	1.6	0.12	0.03	0.01	0.21	0.02
7	River Estate Cl	Fluventic Eutropept	5.1	35	9.1	3.0	2.6	0.23	49	1.2	0.13	0.57	0.06	2.43	0.72
8	Sevilla C	Aquentic Chromodert	6.8	51	25.6	23.7	3.4	0.39	100	1.8	0.18	0.57	0.08	2.83	1.09
9	Mayaro Sl	Typic Tropopsamment	4.3	13	9.2	0.3	2.0	0.21	15	2.1	0.16	0.08	0.03	0.39	0.08
10	Montserrat C	Typic Tropudoll	6.8	47	39.6	37.7	7.6	0.67	100	3.4	0.40	1.35	0.76	12.30	2.47
11	Navet C	Entic Pelludert	5.1	51	29.4	17.8	5.6	1.23	87	5.8	0.44	1.31	0.14	2.56	0.98
12	Bejucal C	Entic Pelludert	5.1	45	25.2	9.5	4.6	0.72	64	2.3	0.23	0.86	0.18	2.36	1.12
13	Maracas Cl	Oxic Tropudult	5.7	31	13.4	10.6	3.2	0.31	97	3.2	0.35	0.28	0.25	10.42	1.75
14	Barataria peat	Fluvaquentic Tropohemist	4.9	52	68.9	57.6	4.1	0.31	86	17.6	1.62	1.78	0.67	3.93	1.61

[a] Ls, loamy sand; Sl, sandy loam; C, clay; Cl, clay loam. [b] Dr. Guy D. Smith, personal communication, 1974.

ture of associated anions may influence the extent to which ammonium ions containing fertilizer enter into adsorption and fixation reactions with soil constituents. In the present study, the effects of associated anions, SO_4^{2-}, $H_2PO_4^-$, and NO_3^-, that accompany the NH_4-N containing fertilizers, $(NH_4)_2SO_4$, $NH_4 H_2PO_4$, and NH_4NO_3, respectively, on ammonium ion adsorption by some Trinidad soils were investigated.

MATERIALS AND METHODS

Fourteen surface soil samples (0–15 cm depth) were collected from different parts of Trinidad. The soil samples were air-dried, ground to pass a 2 mm sieve, and stored in plastic containers. Some properties of the soils are given in Table I.

The soil samples were analyzed for pH, clay content, CEC, exchangeable cations, organic carbon, and total nitrogen according to Metson (1956). Oxalate (pH 3.0) and dithionite (+EDTA) extractable iron and aluminum were extracted according to the procedures of Schwertmann (1964) and Asami and Kumada (1959), respectively. Iron in the extracts was determined by the o-phenanthroline method (Asami and Kumada, 1959) and aluminum by the haematoxylin method (Dalal, 1972).

For ammonium adsorption studies, a 5-g soil sample was shaken with 50 ml of 0.01 M $CaCl_2$ solution containing 10 to 1000 μg of NH_4-N/ml obtained from $(NH_4)_2SO_4$, $NH_4 H_2PO_4$, or NH_4NO_3. After shaking the soil suspension for 1 hr in a reciprocating shaker, the suspension was centrifuged for 5 min at 2000 rpm and the pH of the supernatant solution was recorded. Then it was filtered through Whatman No. 42 filter paper. A suitable aliquot from the filtrate was taken for ammonium determination by steam distillation with MgO (Bremner, 1965). The amount of ammonium adsorbed by the soil was calculated from the difference in the amount of ammonium added to that found in the solution after the shaking. Also, the amount of ammonium adsorbed was corrected for by the exchangeable ammonium (in 1 M KCl extract) already present in the soil.

For ammonium desorption studies, a 5-g soil sample was shaken for 1 hr with 50 ml of 0.01 M $CaCl_2$ solution containing 1.0 mg of NH_4-N/ml as $(NH_4)_2SO_4$, $NH_4 H_2PO_4$, or NH_4NO_3. After centrifugation and filtration of the soil suspension, the ammonium adsorbed by the soil was extracted into 0.01 M $CaCl_2$ solution by shaking the soil suspensions for 1 hr each, successively for four times (soil:solution ratio, 1:10).

All the experiments were performed at least in duplicate and contained 0.25 ml of chloroform to retard microbial activity. The filtrates from both adsorption and desorption studies were also analyzed for combined nitrite and nitrate (Bremner, 1965) to ascertain whether ammonium added had been nitrified during the experimental period; no significant amounts of nitrate (<2%) could be observed.

The experiments were conducted at room temperature (27–30°).

RESULTS AND DISCUSSION

NH_4^+ **Adsorption.** The effect of associated anions on ammonium adsorption by soil 1 plotted according to the Langmuir adsorption isotherm is shown in Figure 1. The Langmuir isotherm is:

$$c/(x/m) = 1/kb + c/b \qquad (1)$$

where c is the equilibrium ammonium concentration (mequiv/l.), x/m is the amount of ammonium adsorbed (mequiv/100 g of soil), and b and k are constants. b is the adsorption maxima (mequiv/100 g of soil) and k is the bonding energy term.

The ammonium adsorption maxima (b) of the soils as affected by the associated anions are given in Table II. It is seen that ammonium adsorption maxima of the soils, in
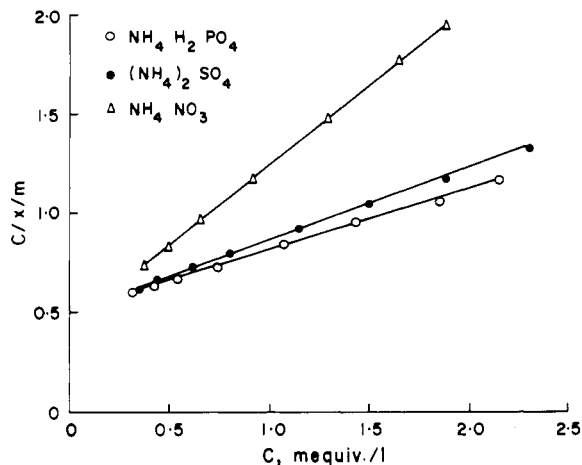
Figure 1. Effect of associated anions on Langmuir adsorption isotherm for NH_4^+ adsorption (soil 1).

Figure 2. Ammonium desorption by 0.01 M $CaCl_2$ solution from soil 1 previously treated with NH_4 H_2PO_4, $(NH_4)_2SO_4$, or NH_4NO_3 (1.0 mg of NH_4–N/ml).

Table II. Effect of Associated Anions on Ammonium Adsorption Maxima (b) of Soils

Soil no.	NH_4^+, mequiv/100 g of soil		
	$H_2PO_4^-$	SO_4^{2-}	NO_3^-
1	3.261	2.775	1.241
2	2.250	1.609	0.838
3	1.877	1.309	0.838
4	5.271	3.102	2.421
5	2.135	2.201	1.240
6	0.983	0.824	0.428
7	1.734	1.309	0.997
8	3.698	3.306	1.320
9	1.159	1.088	0.858
10	4.500	3.354	3.055
11	3.791	2.933	1.738
12	4.397	3.071	1.699
13		1.284	
14		3.244	

Table III. Effect of Associated Anions on Desorption of Adsorbed Ammonium from Soils by Four Successive Extractions with 0.01 M $CaCl_2$ Solution

Soil no.	NH_4^+ desorbed, %		
	$H_2PO_4^-$	SO_4^{2-}	NO_3^-
1	64.9	76.4	79.7
2	63.6	72.3	73.3
3	63.9	68.5	72.1
4	49.6	52.7	56.8
5	65.1	71.1	83.3
6	70.1	86.6	91.9
7	84.3	92.6	97.7
8	66.0	80.6	96.1
9	76.0	80.0	89.7
10	86.1	91.6	97.7
11	70.0	76.5	93.9
12	75.0	86.5	88.5
Mean	69.6	77.9	85.0

general, were in the following order: NH_4 H_2PO_4 > $(NH_4)_2SO_4$ > NH_4NO_3. The regression equations are:

$$b((NH_4)_2SO_4) = 0.399 + 0.630b(NH_4\ H_2PO_4) \qquad (2)$$
$$r = 0.9350\ (P < 0.001)$$

$$b(NH_4NO_3) = 0.062 + 0.454b(NH_4H_2PO_4) \qquad (3)$$
$$r = 0.8666\ (P < 0.001)$$

Thus, ammonium adsorption maxima of the soils obtained from $(NH_4)_2SO_4$ and NH_4NO_3 were 63 and 45%, respectively, of that from NH_4 H_2PO_4. This is to be expected from Paneth–Fajans–Hahn rule, that is, an anion which is strongly adsorbed by soil may increase the adsorption of the associated cation. Since the soils, in general, would retain $H_2PO_4^-$ more strongly and NO_3^- more weakly than SO_4^{2-} (Kinjo and Pratt, 1971b), more ammonium would be adsorbed from NH_4 H_2PO_4 than from $(NH_4)_2SO_4$ (Leggett, 1958; Kanehiro et al., 1960) and more ammonium would be adsorbed from $(NH_4)_2SO_4$ than from NH_4NO_3. However, two soils (soils 5 and 9) adsorbed nearly as much ammonium from NH_4 H_2PO_4 as from $(NH_4)_2SO_4$. This is probably because the gradient of SO_4^{2-} adsorbed/pH is greater than that of $H_2PO_4^-$ adsorbed/pH (see Figures 1(b) and 1(d) in Hingston et al., 1972) so that at low pH values (soil 5, pH 4.6; soil 9, pH 4.3) both SO_4^{2-} and $H_2PO_4^-$ ions may be equally effective in increasing NH_4^+ adsorption.

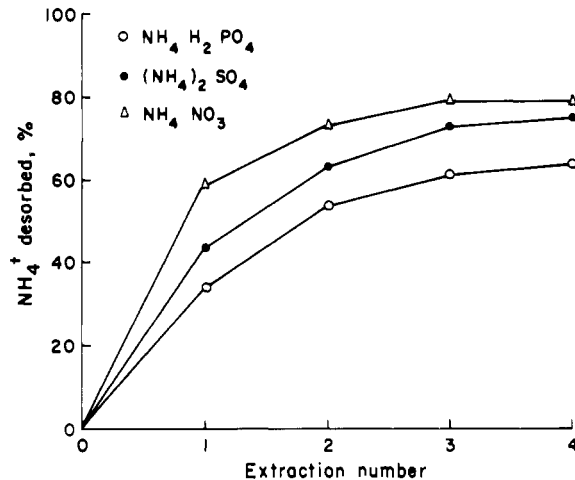The specific adsorption of $H_2PO_4^-$ and SO_4^{2-} by iron and aluminum oxides (Muljadi et al., 1966; Hingston et al., 1968; Chao et al., 1964) and possibly by kaolinite (Hingston et al., 1972) and ferruginous tropical soils (Mekaru and Uehara, 1972) would increase the ammonium adsorption by the soils. The effect of the specific adsorption of SO_4^{2-} ions is to reduce the positive charges on the soil surface and that of $H_2PO_4^-$ ions is to make a negative surface more negative (Hingston et al., 1972). Hence due to these processes the SO_4^{2-} and $H_2PO_4^-$ adsorption by the soils would result in the increase in NH_4^+ adsorption from $(NH_4)_2SO_4$ and NH_4 H_2PO_4 over that from NH_4NO_3.

The mean percentages of cation exchange sites occupied by NH_4^+ at adsorption maxima ($b100/CEC$) were 15, 11, and 7 when NH_4^+ was adsorbed from NH_4 H_2PO_4, $(NH_4)_2SO_4$, and NH_4NO_3, respectively. Thus, at adsorption maxima, only a fraction of the sites of equal bonding energy were occupied by NH_4^+ and were adsorbed possibly with little interaction between the NH_4 ions. This satisfied the two conditions necessary for the application of the Langmuir isotherm, that is, localized binding spots of equal energy on the surface of the solid and no interaction between adsorbed molecules.

NH_4^+ Desorption. The effect of associated anions on the desorption of adsorbed NH_4^+ from soil 1 by four suc-

Table IV. Coefficients of Correlation between Soil Characteristics and Ammonium Adsorption Maxima (b) of Soils[a]

Soil factor	Corr coeff for associated anions		
	$H_2PO_4^-$	SO_4^{2-}	NO_3^-
pH	0.3118	0.2723	0.3203
Clay	0.6688*	0.6079	0.5319
CEC	0.6916*	0.7472**	0.7549**
Exch. Ca	0.6433	0.6804**	0.7546**
Exch. Mg	0.5851	0.6238*	0.7053*
Exch. K	0.5144	0.5215	0.4080
Base saturation	0.4444	0.4508	0.3654
Org. C	0.1377	0.3831	0.2543
Total N	0.1796	0.3941	0.3328
Oxalate extractable Fe	0.7630**	0.7172**	0.7018*
Oxalate extractable Al	0.5134	0.5427	0.8040*
Dithionite extractable Fe	0.7172**	0.3406	0.9038***
Dithionite extractable Al	0.7528**	0.5612	0.8529***

a ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$.

cessive extractions with 0.01 M $CaCl_2$ solution is shown in Figure 2.

In the first extraction, only 34.6% of the NH_4^+ adsorbed from NH_4 H_2PO_4 by the soils could be desorbed as compared to 44.2 and 59.1% desorbed when NH_4^+ was adsorbed from NH_4SO_4 and NH_4NO_3, respectively. Thus, the nature of associated anion accompanying NH_4^+ adsorption by soil influences NH_4^+ desorption from soil as well. This is amply illustrated in Table III for 12 soils. Therefore, the desorption of NH_4^+ after, for example, four extractions would be less when it is adsorbed from NH_4 H_2PO_4 than when it is adsorbed from $(NH_4)_2SO_4$ or NH_4NO_3 (Table III).

Soil Characteristics Affecting Ammonium Adsorption. The coefficients of correlation between soil characteristics and ammonium adsorption maxima are given in Table IV.

Since most of the soil properties which are significantly correlated with ammonium adsorption maxima are interrelated, the stepwise multiple regression analysis was attempted to select those properties which contributed significantly to the variation in the ammonium adsorption maxima.

The following multiple regression equations with three soil properties were obtained.

$$b(NH_4\ H_2PO_4) = 0.977 + 0.141CEC - 6.095 \times \text{total N} + 0.627\text{oxalate extractable Fe} \quad (4)$$
$$R^2 = 0.9349$$

$$b((NH_4)_2SO_4) = 0.463 + 0.093CEC - 2.754 \times \text{total N} + 0.007\text{base saturation} \quad (5)$$
$$R^2 = 0.9284$$

$$b(NH_4NO_3) = 0.431 + 0.036CEC - 0.820 \times \text{total N} + 0.12\text{dithionite extractable Fe} \quad (6)$$
$$R^2 = 0.9428$$

Thus, irrespective of associated anions, $H_2PO_4^-$, SO_4^{2-}, and NO_3^-, the ammonium adsorption maxima increased with the increasing CEC of the soils and decreased with the increasing total nitrogen content. Also, ammonium adsorption maxima obtained from NH_4 H_2PO_4, $(NH_4)_2SO_4$, and NH_4NO_3 increased with the increasing content of oxalate extractable (amorphous) iron, base saturation, and dithionite extractable (crystalline) iron, respectively. The effect of associated anions, $H_2PO_4^-$ and SO_4^{2-}, on NH_4^+ adsorption is due to their specific adsorption by soils. The correlation of dithionite extractable iron with NH_4^+ adsorption maxima in the case of NH_4NO_3 is not clear because generally NO_3^- is negatively adsorbed by soils although Singh and Kanehiro (1969) and Kinjo and Pratt (1971a) have shown that NO_3^- could be adsorbed by acidic soils containing amorphous inorganic materials.

In the humid tropics where considerable losses of fertilizer nitrogen may occur due to leaching of NO_3^-, much less N would be lost from the application of NH_4 H_2PO_4 as compared to that from $(NH_4)_2SO_4$ or NH_4NO_3. This may be due to the fact that more NH_4^+ would be adsorbed by soil and retained against leaching when NH_4 H_2PO_4 is used as when $(NH_4)_2SO_4$ or NH_4NO_3 is used as the N source. Furthermore, since nitrification of NH_4^+ in soil is slower when it is adsorbed than when it is not adsorbed (Nommik, 1965), a lower percentage of the added NH_4^+ would be nitrified from NH_4 H_2PO_4 than from either $(NH_4)_2SO_4$ or NH_4NO_3, although pH changes as a result of nitrification of these fertilizers may modify nitrification rates. One possible explanation is that the availability of adsorbed (and fixed) NH_4^+ to nitrifiers will gradually decrease as the incubation proceeds, possibly as a consequence of a migration of NH_4^+ from the outermost cavities to the interior of the mineral particles. Similarly, more NH_4^+ would be adsorbed by soil and retained against leaching when NH_4^+ is added as $(NH_4)_2SO_4$ than when it is added as NH_4NO_3. Besides the possible differences in nitrification rates, NO_3^- accompanying NH_4^+ in NH_4NO_3 would be lost rapidly under heavy rainfall conditions.

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