

THE ADSORPTION OF YEAST RNA BY ALLOPHANE

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Abstract—Phosphate in the form of organic compounds can be bound in soils containing the aluminosilicate allophane. A significant part of this phosphorus is believed to be present as nucleic acids. The interaction of yeast RNA with allophane was studied to further the understanding of the allophane/organic macromolecule interaction as well as the binding of organic phosphorus by allophanic soils. The extent of RNA adsorption on the allophane was dependent upon the pH, the charge and concentration of simple cations, the concentration of RNA, and the time of interaction. From a mixture containing 145 mg/liter RNA and 2.9 g/liter allophane in 10^{-2} M NaCl, the amount of RNA adsorbed increased from 6% at pH 10 to 98% at pH 3. The adsorption also increased as the concentration of added NaCl was increased from 10^{-4} M to 10^{-1} M, but only when the pH was greater than 5, *i.e.*, above the isoelectric point of the clay. Mg^{2+} and Ca^{2+} were equally much more effective at promoting adsorption than Na^+ at the same concentrations. There was no difference in the effectiveness of SO_4^{2-} , Cl^- , or NO_3^- at pH 5 or higher. The adsorption isotherm at pH 7 can be described by the Langmuir equation; the apparent adsorption maximum was 38 mg/g. Van der Waals and simple electrostatic forces appear to dominate the interaction leading to the adsorption of RNA by allophane.

Key Words—Adsorption, Allophane, Electrolytes, Phosphate, RNA.

INTRODUCTION

The amorphous, aluminosilicate allophane is commonly the predominant clay material found in soils developed from recent deposits of volcanic ash. Although allophane exerts profound influences upon the structure and chemistry of these soils, studies of its own chemistry have concentrated on its composition and structure, its physical properties, and its interactions with only a few selected materials, notably inorganic phosphate. Comparatively little is known of the interactions of allophane with many of the other materials with which it comes into contact in the soil or those which it would encounter if it were used as an agent for water treatment, an application for which it shows promise. These materials include soluble organic substances of high molecular weight and low isoelectric point (IEP) such as those derived from the degradation and decay of plant and animal tissues or those found in the wastewaters of food-processing industries. In general, the adsorption of substances of this nature by common clay minerals, such as montmorillonite and kaolinite, is promoted by decreasing pH and increasing electrolyte concentration in the solution phase and also by the adsorption of multivalent cations by the mineral, *i.e.*, by increasing positive surface charge (Greenland, 1965; Swartz-Allen and Matijević, 1974).

A number of organic materials bind readily and firmly to allophane, *e.g.*, allophanic topsoils are typically dark-colored from the accumulation of humic substances and other organic matter (Gradwell and Birrell, 1954; Wada and Harward, 1974). This is due, in part, to the decrease in the activity of humus-degrading en-

zymes in the presence of allophane (Aomine and Kobayashi, 1964, 1966) and to the affinity that humic materials display for this clay (Wada and Inoue, 1967; Inoue and Wada, 1968). Because the concentration of an indifferent electrolyte, sodium chloride, had no influence upon the adsorption of humic materials onto allophane, it was proposed that humus carboxyl groups were incorporated into the coordination sphere of aluminum at the clay surface, *i.e.*, that the organic matter was specifically adsorbed. The mode of interaction of proteins with allophane has not been thoroughly established although they bind to a greater extent as the solution pH approaches the IEP of the protein (Milestone, 1971). Proteins are also thought to bind to both cationic and anionic adsorption sites at the mineral surface (Aomine and Kobayashi, 1964, 1966). However, a combination of Van der Waals forces and the development of net positive charge at pH below 6 was considered to be responsible for the strong affinity of allophane for two viruses (organic colloids of low IEP) (Taylor *et al.*, 1979), *i.e.*, it was a colloid–colloid type of interaction.

Nucleic acids are relatively well characterized, soluble macromolecular materials of low IEP. They are representative of the organic phosphates that make up a significant proportion of the total pool of phosphorus in the plow layers of soils (Black, 1968). Their adsorption behavior has been found to be typical of acidic, organic matter in that it is controlled predominantly by pH (Goring and Bartholomew, 1952; Flaig *et al.*, 1955; Greaves and Wilson, 1969). In this manner they may represent much of the organic matter found in soils or in some wastewaters.

The purpose of this study was to determine the factors that influence the ability of allophane to adsorb an acidic organic material of moderately high molecular weight from aqueous solution. Particular interest was

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focused upon pH as, in the absence of extensive specific adsorption, pH dominates the surface charge of the mineral and thus is an important parameter in the interaction of allophane with other charged materials.

MATERIALS AND METHODS

Allophane

The allophanic clay studied was taken from the C horizon (60–80 cm) of an Ohaupo silt loam, Ohaupo, New Zealand (site reference NZMS 1 N65/769341). The clay-size fraction, $<2 \mu\text{m}$, was extracted by dispersion in dilute sodium carbonate at pH 9 followed by differential centrifugation. Organic matter was removed by treating the clay with hot, 2% hydrogen peroxide. The clay was then concentrated by centrifugation at 8000 g and resuspended in twice-distilled water. The pH of the suspension was adjusted to 5.5 with dilute HCl to induce coagulation and the clay again concentrated by centrifugation. This process was repeated until the concentration of sodium in a 5% weight-per-volume suspension was less than 10^{-4} M. These suspensions were further diluted with twice-distilled water to give the stock material used for the adsorption experiments. Suspension concentrations were determined by drying aliquots to constant weight at 105°C . Material prepared in the above manner, but freeze-dried, was found to have a total surface area of $250 \text{ m}^2/\text{g}$ (measured by adsorption of nitrogen at 77.4°K). X-ray powder diffraction and electron microscopy studies showed a trace ($<10\%$) of halloysite; the remainder of the material was assumed to be allophane.

RNA

Yeast RNA, from British Drug Houses Ltd., Poole, England, was dissolved in twice-distilled water at room temperature. The solutions were freed of bacteria and undissolved solid by filtration through sterile $0.2\text{-}\mu\text{m}$ Millipore filters into sterile glass vessels. They were then stored at 4°C until needed. Fresh solutions were prepared daily.

Adsorption experiments

Aliquots of stock clay suspension were placed in polyethylene centrifuge tubes to which suitable amounts of electrolyte were added, if necessary. The pH was adjusted with dilute HCl or NaOH, the final volume was made up with distilled water, and the tubes were closed and agitated by end-over-end rotation at 6 rpm for several hours to stabilize pH. A suitable aliquot of RNA solution was then added, and agitation at room temperature was recommenced. After 24 hr, or as required, the pH of the mixtures was determined, and the clay with adsorbed RNA was sedimented by centrifugation at 8000 g for 10 min followed, if necessary, by centrifugation at 20,000 g for a further 20 min. The absorbance of the supernatant was recorded at 320

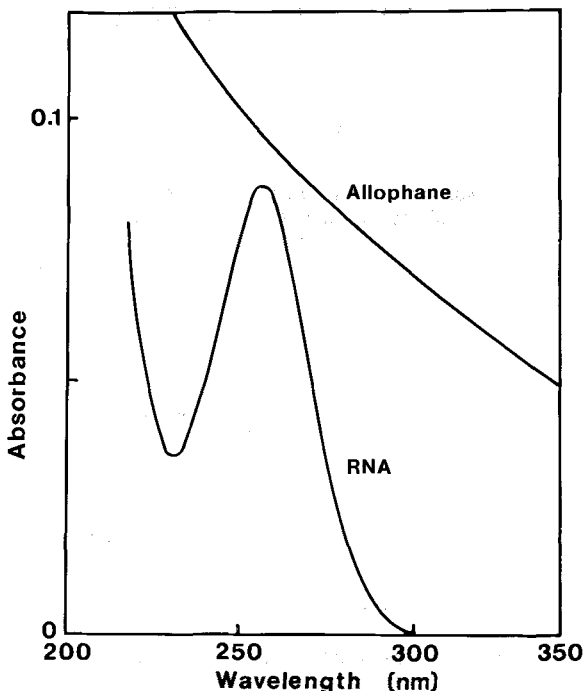


Figure 1. Absorbance spectra of a solution of yeast RNA and of a stable suspension of Ohaupo allophane after centrifugation at 20,000 rpm for 10 min.

and 258.5 nm. Samples were diluted with twice-distilled water if the absorbance exceeded 1.0; below this value the Beer-Lambert law held for RNA solutions. Although the absorbance varied with pH, the variation within the range pH 3 to 9 was less than 2% and was not corrected for; outside this range the solutions were diluted with phosphate buffer which returned the pH to neutrality.

In stable suspensions of allophane, such as those found at low or high pH where there is little coagulation, some of the clay was of such a small particle size that it remained in suspension during both centrifugations. This residue interfered with the spectrophotometric determination of the RNA concentration at 258.5 nm. The absorbance spectra of a stable suspension of allophane, after centrifugation as described above, and of a solution of RNA were determined (Figure 1). RNA solutions did not adsorb at 320 nm. As a RNA solution containing 10 mg/liter had an absorbance at 258.5 nm of 0.254, the following equation was used to obtain the nucleic acid concentration.

$$[\text{RNA}] = (A_{258.5} - 1.65A_{320})/0.0254 \quad (1)$$

Adsorbed RNA was taken as the difference between the amount added and that amount found to be remaining in solution.

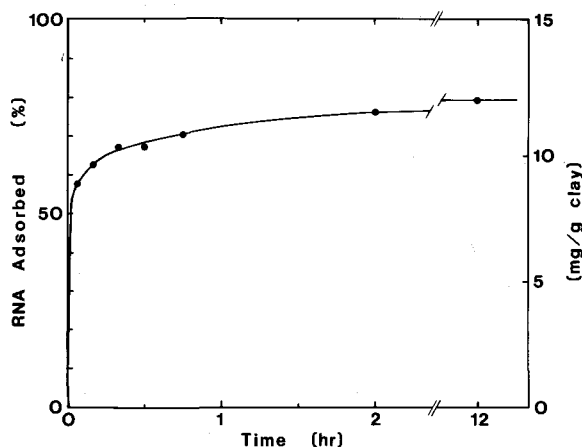


Figure 2. Adsorption of RNA on allophane as a function of time at pH 7.3. 2.9 g/liter allophane, 45 mg/liter RNA, free sodium concentration 2×10^{-4} M.

RESULTS

Rate of adsorption

The initial rate of adsorption of RNA from a neutral solution by Ohaupo allophane was rapid. Within 30 min 85% of the maximum adsorption had occurred (Figure 2); 95% had occurred within 2 hr, but adsorption did not appear to approach equilibrium until at least 12 hr had elapsed. For all subsequent experiments a period of 24 hr was allowed for the reaction. This rate is comparable, although a little slower, to that reported for nucleic acid adsorption by montmorillonite (Greaves and Wilson, 1969).

pH and electrolyte effects

The interaction of RNA with allophane was highly dependent upon pH and proceeded more readily if the solutions were acidic (Figure 3a). The change was continuous, and the adsorption curve was sigmoidal. The actual amount adsorbed increased with electrolyte (sodium chloride) concentration above pH 5.

The pH dependence of the distribution of a substance between the dissolved and adsorbed states may also be presented by plotting the variation of the logarithm of the distribution coefficient, log D, where D is defined by

$$D = \frac{\text{proportion substance adsorbed}}{\text{proportion substance in solution}} \quad (2)$$

For the interaction of RNA with allophane a linear relationship between log D and pH became evident (Figure 3b) for both concentrations of sodium chloride. The least squares regression lines were calculated and found to intersect near pH 5; i.e., at pH greater than 5, RNA adsorption increased with sodium chloride

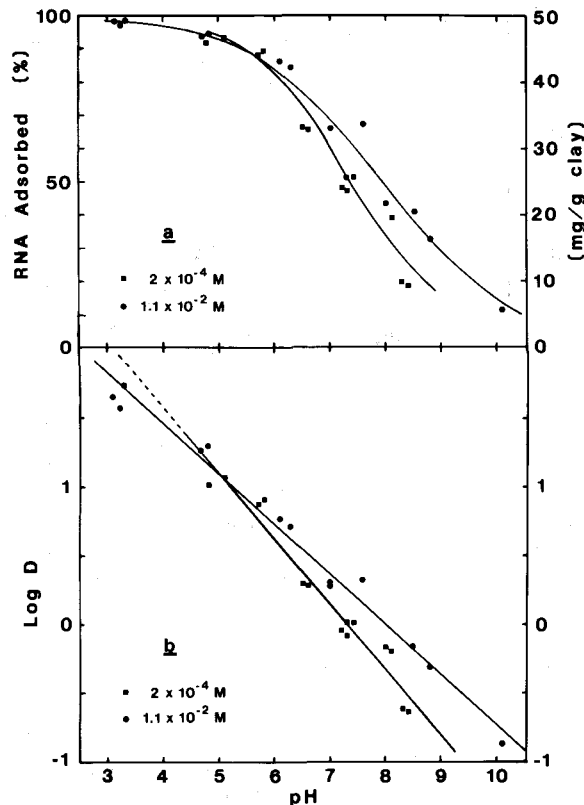


Figure 3. Adsorption of RNA on allophane as a function of pH at two different electrolyte concentrations. 2.9 g/liter allophane, 145 mg/liter RNA. (a) RNA adsorbed. (b) log (distribution coefficient); linear regression equations: 2×10^{-4} M NaCl; $\log D = -0.49 \text{ pH} + 3.61$ ($r = 0.97$); 1.1×10^{-2} M NaCl; $\log D = -0.37 \text{ pH} + 2.97$ ($r = 0.99$).

concentration, but at pH 5 the salt concentration had no influence.

The nature of the anion of the electrolyte, whether chloride, nitrate, or sulphate, made no difference to the adsorption from 10^{-2} M solutions of the sodium salt (Figure 4). However, there was a large difference in the influences of mono- and divalent cations, sodium and calcium, when they were added to give the same initial concentration (Figure 4). The enhancement of adsorption by the divalent cation was even more pronounced when the effect of electrolyte concentration at constant pH was measured. This effect was measured with various nominal concentrations of the chlorides of sodium, magnesium, and calcium at pH 7 and pH 9 (Figure 5). (All solutions were at least 2×10^{-4} M in sodium because the RNA was obtained as the sodium salt.) There appears to be no significant difference in the effect of either calcium or magnesium; both were able to enhance greatly the adsorption of RNA by allophane and were effective at one hundredth the concentration of sodium required for the same result.

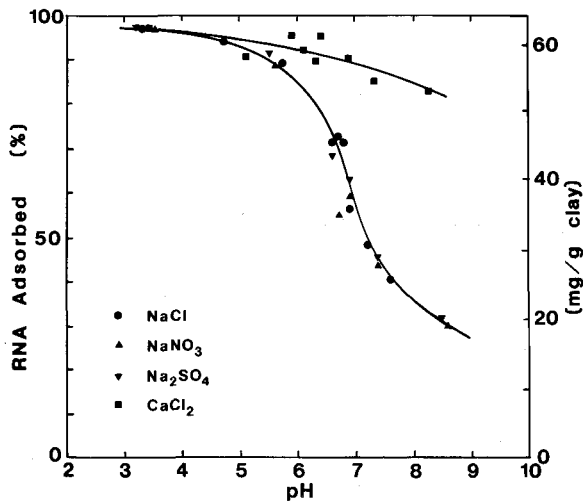


Figure 4. Adsorption of RNA on allophane as a function of pH and electrolyte nature. 2.9 g/liter allophane, 185 mg/liter RNA, 1.1×10^{-2} M electrolyte (5.5×10^{-3} M Na_2SO_4).

Effect of RNA concentration

The isotherm for RNA adsorption on allophane at constant pH and at low electrolyte concentration showed typical Langmuir characteristics (Figure 6a), i.e., the amount of RNA adsorbed increased with the equilibrium solution concentration towards a maximum value. The Langmuir adsorption equation used to describe reversible adsorption to form a monolayer may take the form

$$\frac{C_e}{X} = \frac{C_e}{X_{\max}} + \frac{1}{\alpha X_{\max}} \quad (3)$$

where C_e is the equilibrium solution concentration of the adsorbate, X is the amount of adsorbate taken up

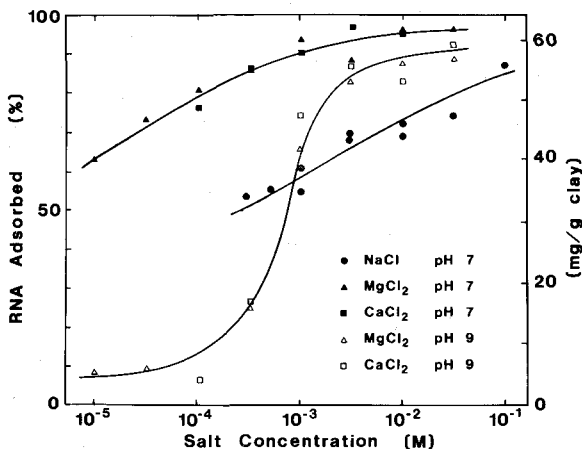


Figure 5. Adsorption of RNA on allophane as a function of cation type and added concentration at two pHs. 2.9 g/liter allophane, 185 mg/liter RNA.

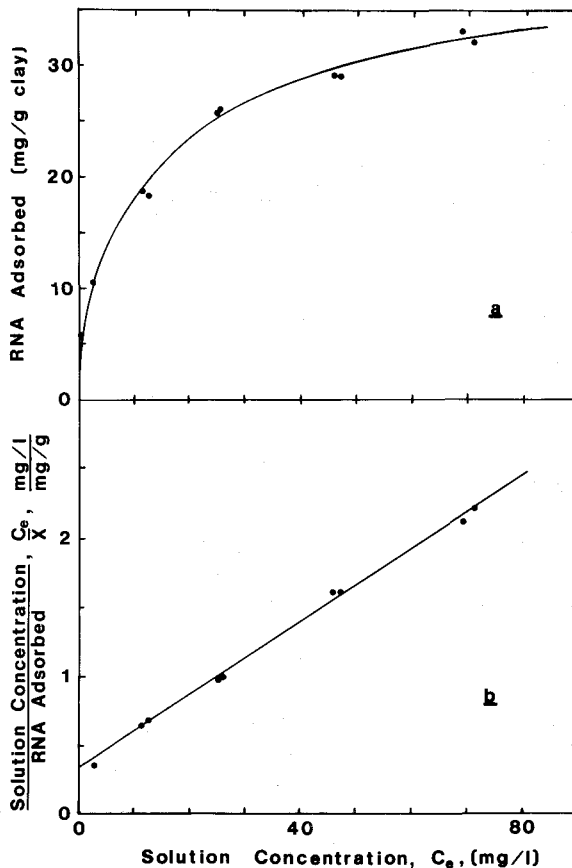


Figure 6. Adsorption of RNA on allophane as a function of solution concentration (C_e) at pH 7.0. 4.55 g/liter allophane. (a) RNA adsorbed (X). (b) Langmuir representation (C_e/X).

per unit mass of adsorbent, X_{\max} is the maximum amount of adsorbate that may be bound, and α is a constant related to the rates of the adsorption and desorption reactions.

When C_e/X was plotted against C_e for RNA adsorption, a linear relationship was found indicating that the adsorption can be adequately described by the Langmuir equation (Eq. 3) (Figure 6b). The least squares regression line (regression coefficient $r = 0.99$) gave saturation at pH 7 as 38 mg/g. This is about 40 times greater than the amount of RNA bound by alumina under similar conditions (Upadhyay and Chatteraj, 1968), but considerably less than that adsorbed by montmorillonite (Greaves and Wilson, 1969).

DISCUSSION

A number of observations of the interaction of RNA with allophane can be made from the results of this study:

- (1) Adsorption occurred over a wide pH range; the amount of adsorption increased steadily with decreasing pH.

(2) The amount of RNA adsorbed increased with the concentration of indifferent electrolyte (sodium chloride) above pH 5. It also increased steadily with the concentration of divalent cations; these were much more effective at promoting adsorption than were monovalent cations.

(3) No significant difference was observed in the adsorption from solutions containing either monovalent or divalent anions.

(4) The adsorption isotherm at pH 7.0 obeyed the Langmuir equation.

The major conclusion of these observations is that the ionic composition of the solution phase, i.e., the pH and the nature and concentration of the electrolyte, dominates the interaction.

Allophane is believed to consist of an aluminosilicate core, of about 50 Å diameter, coated to a variable extent with amorphous aluminum hydroxide (de Villiers *et al.*, 1967; Cloos *et al.*, 1969; Henmi and Wada, 1976). The clay surface has hydroxyl and hydronium groups associated with the polymeric hydroxide and the aluminosilicate which, by their protonation and deprotonation, are responsible for the pH-dependent particle charge developed in aqueous systems (Fey and Le Roux, 1976). This pH-dependent charge is displayed not only by the cation and anion exchange capacities (Fieldes and Schofield, 1960) but also by the electrophoretic properties (Horikawa, 1975). The variation with pH of the electrophoretic mobility of a different preparation of Ohaupo allophane is shown in Figure 7. The clay used for the electrophoresis experiment had been resuspended only in distilled water following dispersion and centrifugation. As no acid was added, only relatively free anions and cations were washed from the clay; very little of the native divalent cationic material or surface aluminum would have been displaced, and so this sample had a higher IEP than that used for the RNA interaction experiments. The allophane actually used for the RNA adsorption studies had an IEP, estimated from its coagulation behavior, of 5.6 (Taylor, 1977).

At pH below its IEP, allophane bears a net positive charge and has a positive electrophoretic mobility. RNA, as a consequence of the acidic nature of its groups which have a pK_a of about 0.7 to 1.0 (Bloomfield *et al.*, 1974), has a low IEP. In the systems studied here the nucleic acid would have had a net negative charge, although the magnitude of this charge would be expected to vary with pH. Thus for those systems in which the pH was below the allophane IEP, i.e., 5.6, the two interactants would have had opposite electric charges. The attractive coulombic forces these induced would have encouraged adsorption. With decreasing pH the positive charge on the clay particle is enhanced by further protonation; this in turn would have increased adsorption. (As the pH approaches 3, the solubility of RNA rapidly decreases. This may also con-

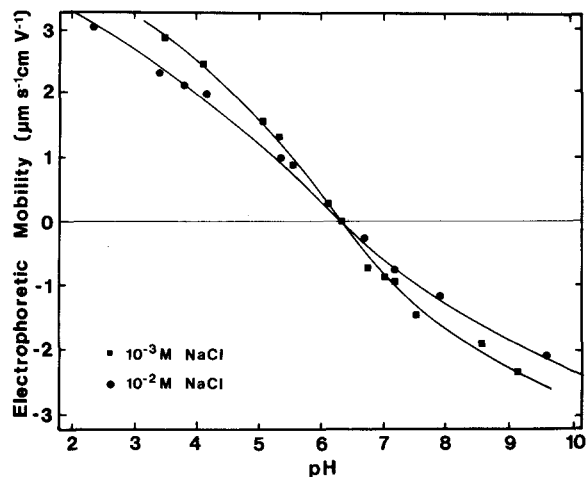


Figure 7. Variation of the electrophoretic mobility of allophane with pH. (Determined with a zetameter.)

tribute to an enhanced tendency to adsorb to suitable substrates at low pH.)

Above pH 5.6 both the allophane and the nucleic acid would bear net negative charges. For adsorption to occur under these conditions there must be a relatively strong attractive force to which Van der Waals interactions would make a significant contribution. In addition, there may be a high specific adsorption potential arising from the formation of bonds with a high degree of covalent nature between the nucleic acid and the clay surface. Such bonds would be similar to those suggested by Gordon and Kleinschmidt (1970) for the interaction of DNA with aluminum-treated mica or for humic material adsorption by allophane (Inoue and Wada, 1971). Generally, specific interactions of ionic species are influenced by the concentrations of indifferent electrolytes such as sodium chloride. If the nucleic acid was bound primarily by adsorption of anionic groups into the Stern layer of the clay, the layer close to the surface in which specifically adsorbed ions are presumed to reside, it should compete with other anions for adsorption sites. Under these circumstances an increase in the electrolyte concentration would bring about less anion adsorption. Such an effect has been reported for the adsorption of the relatively small acidic compound pentachlorophenol on allophane (Choi and Aomine, 1974). However, in this study it was found that an increase in the concentration of the indifferent electrolyte was accompanied by greater adsorption of RNA, and so it is likely that the sodium chloride concentration influenced the interaction between allophane and RNA in some other manner.

As allophane is a composite material with both a high IEP component (aluminum hydroxide) and a low IEP component (aluminosilicate), at pH above the net particle IEP there will still be regions of the surface with

positive charge even though the net particle charge is negative. Coulombic attraction between these regions of the surface and the dissolved RNA, coupled with the attractive Van der Waals forces, would lead to extensive adsorption. Increasing the concentration of sodium chloride in the suspending medium has strong effects on the surface electrochemistry of allophane, as displayed, for example, by both electrophoretic mobility (Figure 7) and colloid coagulation. At higher salt concentrations, the net particle charge, and hence the electrophoretic mobility of the clay, is reduced by greater adsorption of the surface charge counter-ion (Na^+ at pH above the IEP and Cl^- below) within the shear plane at the surface. (A similar reduction of apparent surface charge occurs simultaneously with the nucleic acid.) Above the allophane IEP a reduction in the repulsive coulombic forces between the negatively charged surfaces of the clay particles and other similarly charged colloids (including molecules of nucleic acid) takes place, which would encourage adsorption. At the IEP the concentration of sodium chloride has no influence on the net particle charge (which is, of course, zero). Consequently, adsorption of charged colloids is also independent of the concentration of sodium chloride. Below the allophane IEP the net particle charge becomes less positive with increasing electrolyte concentration, and coulombic attraction and adsorption of negatively charged RNA would also be reduced, a situation suggested by extrapolation of Figure 3b. Thus, RNA behaves like a colloid, rather than a simple ion, on adsorption by allophane.

The preferential adsorption of divalent cations over monovalent cations on allophane has been well documented (e.g., Birrell, 1961; Harada and Wada, 1973). This behavior is analogous to that observed with hydrous oxides for which a major result is a general reduction in the negative component of the net particle charge and an increase in the apparent IEP (Huang and Stumm, 1973). As this adsorption increases the positive component of the net particle charge on the clay, it brings about a stronger coulombic attraction for anionic colloids. Furthermore, coulombic repulsion between negative charges on the clay and the polymer would be further reduced by association of the divalent cations with the anionic phosphate groups of the acid. Such charge shielding also allows the RNA to adopt a more compact conformation which has a reduced solubility in water. Although the concentration of RNA did not exceed its solubility in the presence of the electrolytes (Bacher and Allen, 1950), and no precipitation was observed, the reduced solubility in the presence of calcium or magnesium may have contributed to the tendency of the nucleic acid to become adsorbed.

The maximum surface area that can be totally covered by a close-packed layer of RNA molecules, assuming they lie on the surface as cylinders of diameter 18 \AA [the thickness of a layer of RNA adsorbed on

montmorillonite (Greaves and Wilson, 1969)], is $\sim 500 \text{ m}^2/\text{g}$. Based on this value the apparent maximum surface concentration on allophane at pH 7.0 corresponds to a surface coverage of $19 \text{ m}^2/\text{g}$. The surface area of this allophane, after freeze-drying, was $250 \text{ m}^2/\text{g}$ when determined by nitrogen adsorption. This discrepancy may stem from changes in the morphology of allophane on drying (Fieldes and Claridge, 1975). Alternatively, the apparently low coverage may be due to the fact that allophane is a porous material and a significant proportion of its total surface area is "internal" surface (Gradwell and Birrell, 1954; Fieldes and Claridge, 1975). This internal surface may be accessible to small molecules but not to larger ones, such as nucleic acids, which are unable to penetrate the narrow pores and interstices between the aluminosilicate particles. In addition, for the adsorption of ionic materials on hydrous oxides and allophane, the apparent Langmuir maximum surface concentration, X_{max} , is pH dependent. For example, X_{max} decreases with increasing pH for anion adsorption on goethite (Bowden *et al.*, 1973); while for the adsorption of strontium on allophane, X_{max} increases logarithmically with pH (Taylor, 1977). Thus, with decreasing pH allophane should display an increasing apparent maximum capacity for RNA.

The ability of allophane to remove acidic organic materials of high molecular weight from aqueous solution has implications in two fields. In allophanic soil the adsorption of such materials may bring about fixation of potential nutrients. In the case of organic phosphates this will be a further contribution to the removal of phosphate from the biological cycle and to the phosphate fixation problems that allophanic soils experience. (The pool of available phosphorus in allophanic soils is already small as a consequence of the ability of allophane to bind and fix inorganic phosphate.) The second field of interest is the treatment of aqueous wastes containing this type of dissolved organic matter. Treatment with suspensions of allophanic clays or permeation through filters containing allophane would bring about a significant reduction in their ability to pollute their receiving waters.

REFERENCES

- Aomine, S. and Kobayashi, Y. (1964) Effects of allophane on the enzymic activity of a protease: *Soil Sci. Plant Nutr. (Tokyo)* **10**, 28–32.
- Aomine, S. and Kobayashi, Y. (1966) Effects of allophanic clays on the enzymic activity of β -amylase: *Soil Sci. Plant Nutr. (Tokyo)* **12**, 7–12.
- Bacher, J. E. and Allen, F. W. (1950) Solubility and sedimentation studies on certain pentose nucleic acids: *J. Biol. Chem.* **186**, 511–516.
- Birrell, K. S. (1961) The adsorption of cations from solution by allophane in relation to their effective size: *J. Soil Sci.* **12**, 307–316.
- Black, C. A. (1968) *Soil Plant Relationships*: 2nd Ed., Wiley, New York, 792 pp.
- Bloomfield, V. A., Crothers, D. M., and Tinoco, I., Jr.

- (1974) *Physical Chemistry of Nucleic Acids*: Harper and Row, New York, 517 pp.
- Bowden, J. W., Bolland, M. D. A., Posner, A. M., and Quirk, J. P. (1973) Generalized model for anion and cation adsorption at oxide surfaces: *Nature (London) Phys. Sci.* **245**, 81–83.
- Choi, J. and Aomine, S. (1974) Mechanisms of pentachlorophenol adsorption by soils: *Soil Sci. Plant Nutr. (Tokyo)* **20**, 371–379.
- Cloos, P., Leonard, A. S., Moreau, S. P., Herbillon, A., and Fripiat, J. J. (1969) Structural organization in amorphous aluminosilicates: *Clays & Clay Minerals* **17**, 279–287.
- de Villiers, S. M. and Jackson, M. L. (1967) Cation exchange capacity variations with pH in soil clays: *Soil Sci. Soc. Amer. Proc.* **31**, 473–476.
- Fey, M. V. and Le Roux, J. (1976) Electric charges on sesquioxide soil clays: *Soil Sci. Soc. Amer. J.* **40**, 359–369.
- Fieldes, M. and Claridge, G. G. C. (1975) Allophane: In *Soil Components, Vol. 2, Inorganic Components*, J. E. Gieseking, ed., Springer-Verlag, New York, 351–393.
- Fieldes, M. and Schofield, R. K. (1960) Mechanisms of ion adsorption by inorganic soil colloids: *N.Z. J. Sci.* **3**, 563–579.
- Flaig, Von W., Kuron, H., and Kaul, R. (1955) Über die Sorption von Nucleinstoffen an Tonkolloiden: *Z. Pflanzen-ernaehr. Dueng. Bodenkd.* **71**, 141–154.
- Gordon, C. N. and Kleinschmidt, A. K. (1970) Electron microscopic observation of DNA adsorbed on aluminum-mica: *J. Colloid Interface Sci.* **34**, 131–141.
- Goring, C. A. I. and Bartholomew, W. V. (1952) Adsorption of mononucleotides, nucleic acids and nucleoproteins by clays: *Soil Sci.* **74**, 149–164.
- Gradwell, M. and Birrell, K. S. (1954) Physical properties of certain volcanic clays: *N.Z. J. Sci. Tech., Sect. B*, **36**, 108–122.
- Greaves, M. P. and Wilson, M. J. (1969) The adsorption of nucleic acids by montmorillonite: *Soil Biol. Biochem.* **1**, 317–323.
- Greenland, D. S. (1965) Interactions between clays and organic compounds in soils: *Soils Fert.* **28**, 415–425.
- Harada, Y. and Wada, K. (1973) Release and uptake of protons by allophanic soils in relation to their CEC and AEC: *Soil Sci. Plant Nutr. (Tokyo)* **19**, 73–82.
- Henmi, T. and Wada, K. (1976) Morphology and composition of allophane: *Amer. Mineral.* **61**, 379–390.
- Horikawa, Y. (1975) Electrokinetic phenomena of aqueous suspensions of allophane and imogolite: *Clay Sci.* **4**, 255–263.
- Huang, C. P. and Stumm, W. (1973) Specific adsorption of cations on hydrous γ - Al_2O_3 : *J. Colloid Interface Sci.* **43**, 409–420.
- Inoue, T. and Wada, K. (1968) Adsorption of humified clover extracts by various clays: *Trans. 9th Int. Congr. Soil. Sci. Adelaide* **3**, 289–298.
- Inoue, T. and Wada, K. (1971) Reactions between humified clover extract and imogolite as a model of humus-clay interaction: Parts I and II: *Clay Sci.* **4**, 61–70, 71–80.
- Milestone, N. B. (1971) Allophane—Its structure and possible uses: *J. N.Z. Inst. Chem.* **35**, 191–197.
- Swartzén-Allen, S. L. and Matejević, E. (1974) Surface and colloid chemistry of clays: *Chem. Rev.* **74**, 385–400.
- Taylor, D. H. (1977) The colloid and surface chemistry of allophane: D. Phil. Thesis, University of Waikato, Hamilton, New Zealand, 430 pp.
- Taylor, D. H., Bellamy, A. R., and Wilson, A. T. (1979) The interaction of bacteriophage R17 and reovirus type III with allophane: *Water Res.* (in press).
- Upadhyay, S. N. and Chatteraj, D. K. (1968) Adsorption of nucleic acids at the alumina-water interface: *Biochim. Biophys. Acta* **161**, 561–563.
- Wada, K. and Harward, M. E. (1974) Amorphous clay constituents of soils: *Adv. Agron.* **26**, 211–254.
- Wada, K. and Inoue, T. (1967) Retention of humic substances derived from rotted clover leaves in soils containing montmorillonite and allophane: *Soil Sci. Plant Nutr. (Tokyo)* **13**, 9–16.

(Received 15 September 1978; accepted 1 March 1979)

Резюме—Фосфат в форме органических соединений образуется в почвах, содержащих алюмосиликатный аллофан. Считается, что значительная часть этого фосфора существует в виде нуклеиновых кислот. Для более глубокого понимания взаимодействия макромолекул аллофана и органики а также связывания органического фосфора аллофановыми почвами изучалось взаимодействие дрожжевой РНК с аллофаном. Степень адсорбции РНК аллофаном зависела от pH, заряда и концентрации элементарных катионов, концентрации РНК, и времени взаимодействия. В растворе 10^{-2} M NaCl, содержащем смесь 145 мг/литр РНК и 2,9 г/литр аллофана, количество адсорбированной РНК возросло от 6% при pH = 10 до 98% при pH = 3. Адсорбция также возрастала при увеличении концентрации NaCl от 10^{-4} M до 10^{-1} M, но при условии, что pH был больше 5, т.е. выше изоэлектрической точки глины. Mg^{2+} и Ca^{2+} обеспечивали значительно более эффективную адсорбцию, чем Na^{+} при той же концентрации. Не наблюдалось различий в эффективности SO_4^{2-} , Cl^{-} , или NO_3^{-} при pH = 5 или выше. Адсорбционная изотерма при pH = 7 может быть описана уравнением Лангмуира. Очевидная максимальная адсорбция достигала 38 мг/г. Силы Ван-дер-Ваальса и простые электростатические силы по-видимому доминируют во взаимодействиях, приводящих к адсорбции РНК аллофаном.

Resümee—Organische Phosphatverbindungen können in Erden gefunden werden, die das Aluminiumsilikat Allophan enthalten. Es wird geglaubt, daß ein großer Teil dieses Phosphors als Nucleinsäuren vorkommt. Die Wechselbeziehung zwischen Hefe-RNA und Allophan wurde weiterhin untersucht, um das Verständnis der Allophan-organischen Makromolekül Wechselbeziehung sowohl wie auch die Bindung zwischen organischem Phosphor und allophanischen Erden zu fördern. Der Ausmaß der RNA Adsorption auf Allophan war von dem pH, der Ladung und Konzentration von einfachen Kationen, der Konzentration von RNA, und der Dauer der Einwirkung abhängig. Von einer Mischung, die 145 mg/Liter RNA und 2,9 g/Liter Allophan in 10^{-2} M NaCl enthält, nimmt der Anteil von adsorbiertem RNA von 6% bei pH 10 zu 98% bei pH 3 zu. Die Adsorption nahm auch zu, als die Konzentration des zugesetzten NaCl von 10^{-4} M auf 10^{-1} M erhöht wurde, aber nur, wenn der pH größer als 5 war, das

heißt höher als der isoelektrische Punkt des Tons. Mg^{2+} und Ca^{2+} waren beide mehr effektiv in der Förderung der Adsorption als Na^+ bei gleichen Konzentrationen. Es gab keinen Unterschied in der Wirkungsweise von SO_4^{2-} , Cl^- , oder NO_3^- bei pH 5 oder höher. Die Adsorptionsisotherme bei pH 7 kann durch die Langmuirgleichung erklärt werden; das scheinbare Adsorptionsmaximum war 38 mg/g. Van der Waalsche- und einfache elektrostatische Kräfte scheinen die Wechselwirkungen, die zur Adsorption von RNA durch Allophan führt, zu dominieren.

Résumé—Le phosphate sous la forme de composés organiques peut être lié dans des sols contenant l'aluminosilicate allophan. On pense qu'une part significative de ce phosphore est présent en tant qu'acides nucléiques. L'interaction de la levure RNA avec l'allophan a été étudiée pour mieux comprendre l'interaction de la macromolécule allophan/organique aussi bien que la liaison du phosphore organique par des sols allophaniques. L'étendue de l'adsorption RNA sur l'allophan dépendait du pH, de la charge et de la concentration de cations simples, de la concentration de RNA, et de la durée d'interaction. D'un mélange contenant 145 mg/litre de RNA et 2,9 g/litre d'allophan dans 10^{-2} M NaCl, la quantité de RNA adsorbée a augmenté de 6% à un pH de 10 à 98% à un pH de 3. L'adsorption a aussi augmenté lorsque la concentration de NaCl ajouté était augmentée de 10^{-4} M à 10^{-1} M, mais seulement quand le pH était plus élevé que 5, au-delà du point isoélectrique de l'argile. Mg^{2+} et Ca^{2+} étaient également beaucoup plus efficaces à promouvoir l'adsorption que Na^+ aux mêmes concentrations. Il n'y avait pas de différence dans les effets de SO_4^{2-} , Cl^- , ou NO_3^- à un pH de 5 ou plus élevé. L'isotherme d'adsorption à un pH de 7 peut être décrit par l'équation Langmuir, le maximum d'adsorption apparent était 38 mg/g. De simples forces électrostatiques et de Van der Waals semblent dominer l'interaction conduisant à l'adsorption de RNA par l'allophan.