Exchange Reactions Between Phosphates and Soils: Hydroxylic Surfaces of Soil Minerals

C. D. McAuliffe, N. S. Hall, L. A. Dean, and S. B. Hendricks

Isotopic tracers are of value in following exchange reactions between surfaces and components of contiguous solutions. They were first used in this way by Paneth (13) for determining specific surfaces of insoluble lead salts by exchange with the radioactive isotope of lead known as Th B, which is $^{212}$Pb and is hereinafter referred to as Pb*. Kolthoff and his students (8, 9) greatly extended work with this isotope and formulated clear concepts of the surface of PbSO$_4$. The basic reaction is,

$$\text{PbSO}_4 \text{ (solid surface)} + \text{Pb* (solution)} \leftrightarrow \text{Pb*SO}_4 \text{ (solid surface)} + \text{Pb (solution)}$$

The equilibrium constant for this isotopic exchange reaction is, of course, equal to 1; hence,

$$\frac{\text{Pb* (surface)}}{\text{Pb (surface)}} = \frac{\text{Pb* (solution)}}{\text{Pb (solution)}}$$

In work reported here this principle is applied to soil reactions involving phosphate and hydrogen, use being made of P$^{32}$ and deuterium.

Phosphate reactions in acid soils may involve the hydroxylic surfaces of clay minerals and hydrous oxides, such as goethite (10, 11). These reactions can be schematically represented by,

(A) Surface $-$ OH $+$ phosphate (in solution) $\leftrightarrow$ Surface $-$ phosphate + change in pH

which is ambiguous in that neither the form of phosphate taking part, whether PO$_4^{3-}$, HPO$_4^{2-}$, or H$_2$PO$_4^-$ is known nor the equivalence of change in pH toward a more alkaline system (7). The nature of the surface phosphate which is generally spoken of as “adsorbed” is also unknown.

Radioactive P$^{32}$ can be used to test the reversibility of reaction (A) through use of the reaction:

(B) Surface phosphate $-$ P$^{31}$ + solution phosphate $-$ P$^{32}$ $\leftrightarrow$ Surface phosphate $-$ P$^{32}$ + solution phosphate $-$ P$^{31}$

The extent of surface reaction can be estimated from equilibrium for reaction (B), namely

$$\frac{\text{Surface phosphate P}^{32}}{\text{Solution phosphate P}^{32}} = \frac{\text{Surface phosphate P}^{31}}{\text{Solution phosphate P}^{31}}$$

The kinetics of reaction (A) or (B) can be followed, that is, the progress of the reactions as a function of time.

Reaction (A) might involve the total surface or only a part such as the fraction in base-exchange as usually considered. The acidic hydrogen is measured by base exchanging a reaction such as,

(C) Surface $-$ OH$_{ad}$ + Na* $\leftrightarrow$ Surface $-$ ONa + H* + Na$^+$

Isotopic exchange with deuterium is used for measurement of total hydroxylic surface making use of the reaction,

(D) Surface $-$ OH $+$ DOD $\leftrightarrow$ Surface $-$ OD $+$ H* + D$_2$O

Deuterium oxide (heavy water) has previously been used in this way for determining the number of hydroxyl groups upon surfaces of cellulose.

KINETIC EXCHANGE WITH PHOSPHATE

The rate of reaction (B) has been measured for several soils having different levels of fertility. In these experiments 5.0 grams of soil were mixed with 1 ml of water were shaken together for 4 hours to establish an equilibrium. The phosphorus in the solution was then determined and 1 ml containing 25 microcuries of carrier free P$^{32}$ was added. This essentially did not change the solution since only $8 \times 10^{-5}$ microcuries were added and the volume change was only 4%, 1 ml in 25. After various elapsed times the introduction of the P$^{32}$, samples of the solution separated by high speed centrifugation, the specific activities determined.

Results obtained are shown in Table 1. For the Caribou soil 451588 are plotted in Fig. 1 it can perhaps be seen that the initial increase in P$^{32}$/P$^{31}$ solution changes at first logarithmically with respect to time and later linearly. The results for the Moyock soil 451586 that gave an equilibrium in 1 hour solution containing about 10 times as much phosphate as soil 451588 and for the Caribou soil E787 for which the phosphate concentration is lower, 25 micrograms of phosphorus per ml, the phosphate concentration in the solution is very low, 0.005 ppm of P$^{32}$, behavior is connected in part with the difficulty in handling extremely dilute solutions without introducing reactions with glassware, stopcocks, etc.