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INTERACTIONS OF MOLYBDATE
AND PHOSPHATE WITH SOILS

A thesis presented in partial fulfilment of
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of Philosophy in Soil Science at
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Graeme d'Egville Hope
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ABSTRACT

Using four New Zealand soils, it was found that pH, extractable Al, citrate-dithionite-bicarbonate-Al, oxalate Fe, and crystalline Fe appeared to be important soil properties in both P and Mo sorption. Allophane appeared less important in the sorption of Mo than in the sorption of P.

For the sorption of Mo, the initial, rapid removal of Mo was followed by a slow, continuing removal of Mo from solution. An estimate of equilibrium Mo concentration was obtained by extrapolation of the relationship between solution Mo and $^1/t$ to $^1/t = 0$, i.e. $t = \infty$. The effect of ionic strength on Mo sorption appeared to be kinetically controlled at low final Mo concentrations ($< 5\ \mu mol\ l^{-1}$), but appeared to be absolute at high final concentrations ($> 10\ \mu mol\ l^{-1}$).

Isotherms for the sorption of Mo by both topsoils and subsoils, at equilibrium and 40 hr, and by synthetic hydrous ferric oxide gel (Fe gel) and allophane at 40 hr, could be described by three Langmuir equations. Values for the free energies of sorption for each region of sorption, which were remarkably similar for the different sorbents, indicated that sorption in regions I and II corresponded to chemisorption reactions, whereas sorption in region III involved a more-physical type of sorption. Fe gel appeared to be a satisfactory model for Mo sorption by soils.

Isotherms for the sorption of P by the four soils, Fe gel, and allophane during 40 hr were described by three Langmuir equations. Because the free energies of sorption for each region, for both Mo and P, were very similar, the sites for sorption and types of sorption reaction for both anions are probably similar. Synthetic allophane chemisorbed much less Mo than P, relative to Fe gel, and this was attributed to kinetic charge effects.

Sorption of Mo by Fe gel in each region was affected differently by changes in pH and ionic strength, and the charge relationships for each region were also different. These data, along with the three distinct free energies of sorption obtained for Mo, suggested that three distinct sorption reactions were involved. The data suggested that sorption of Mo in regions I and II involved ligand-exchange chemisorption of MoO_4^{2-} for $-OH_2^+$ and $-OH$, respectively, resulting in the formation of a bidentate complex. Sorption in region III was considered to involve sorption at a plane distant from the sorbing surface.

The Langmuir equation developed to describe competitive sorption was not obeyed for Mo and P, but the sorption of Mo, in the presence of P, could be described by three simple Langmuir equations. It appeared that Mo and P competed for similar surface sites.

Solution P increased the amounts of sorbed Mo that could be desorbed, relative to Cl. The amounts of Mo desorbed by both Cl and P decreased with time after addition of Mo to soils. This was attributed to a shift in the form of sorbed Mo. Chemical fractionation of sorbed Mo suggested that the absorption of adsorbed Mo was also occurring. For several soils to which Mo had been added in the field, no Mo was desorbed by P solutions.

Solution:soil ratio affected only the rate at which P was removed from solution, not the final equilibrium concentrations. Incubating soil with P prior to the addition of Mo reduced both chemisorption and more-physical sorption of Mo. For a soil that had received annual additions of phosphate and lime for 22 yr, the chemisorption of added Mo was reduced by both fertilizer P and lime, whereas the more-physical sorption maxima were only reduced by lime additions. The results were discussed in terms of both the persistence and plant-availability of Mo added in the field situation.

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