MANGANESE-PHOSPHATE REACTIONS IN AQUEOUS SYSTEMS AND THE EFFECTS OF APPLICATIONS OF MONOCALCIUM PHOSPHATE, ON THE AVAILABILITY OF MANGANESE TO OATS IN AN ALKALINE FEN SOIL

by S. G. HEINTZE *

Rothamsted Experimental Station, Harpenden, Herts.

INTRODUCTION

Others have studied the effects of phosphates applied to the soil on the availability to plants of native or added manganese, either by following changes in water soluble or exchangeable soil manganese, or by measuring the effects on yields and on manganese uptake by plants. For instance Lindsay and Stephenson 12 13 studied the reactions between pellets of monocalcium phosphate and soils; while the phosphate dissolved, pH values of the soil were lowered and considerable amounts of several soil constituents (such as iron, manganese and aluminium) also dissolved concomitantly. Several workers have found that adding an acid phosphate increased exchangeable or water-soluble manganese, and also manganese concentrations in plants growing on the soils 8 10 14 15 16 17 18 19. Bingham and Garber 3 obtained large increases in manganese concentrations in citrus leaves by adding ammonium phosphate which lowered the soil pH more than the other phosphates tested. Increases in water-soluble manganese were not, however, always associated with changes in soil reaction and they concluded that phosphates directly affect the solubility of soil manganese. Albrecht

* Now at: The Royal Veterinary and Agricultural College, Department of Soil Fertility and Plant Nutrition, Kobenhavn, Denmark.
and Smith, and Bingham found that applied phosphate increased manganese uptake in bean leaves but decreased it in citrus and tomato. From field experiments, Spencer and Page et al. concluded that effects on manganese availability from applying superphosphate were mainly from changes in pH values though they emphasised that it was difficult to know whether the effects of pH changes were direct or indirect. Larsen concluded that the effect of phosphate on yield could not be attributed to pH changes, and suggested that large applications of superphosphate form soluble manganese phosphate complexes in soil. Phosphate may also lessen the availability of manganese. Teakle concluded that manganese and iron were partly responsible for maintaining small phosphate concentrations in acid soils.

TVA workers, studied the reactions of phosphate in soils and synthesised and identified many phosphate compounds, but have not worked with manganese phosphates. Most investigations on the effects of phosphate on manganese availability have been with soils not deficient in manganese. The present work therefore studied the types of compounds formed in aqueous manganese sulphate-phosphoric acid systems at various pH values and initial Mn : P molar ratios; effects of phosphate applications (with or without added manganese) on the availability of manganese in an Mn-deficient soil to oats were also followed.

**PART I. AQUEOUS MANGANESE PHOSPHATE SYSTEMS**

**Methods**

The procedures for potentiometric analyses and estimations of solubility were: To a series of mixtures of manganous sulphate and phosphoric acid, at initial Mn/P molar ratios of 0.1, 1 and 10, increasing amounts of potassium hydroxide were added and the total volume adjusted to 50 ml by adding distilled water. During mixing and measuring pH values, oxygen-free nitrogen was bubbled through, but it was not possible to prevent oxidation of Mn

Manganese concentrations were 10⁻² and 10⁻³ molar. The mixtures were left in stoppered tubes for various times with intermittent shaking. pH was measured with a glass electrode. The supernatant liquid and precipitates were analysed after several weeks' equilibration.

Manganese was estimated colorimetrically as permanganate and phosphorus as phosphomolybdovanadate. X-ray diffraction patterns of the washed and dried precipitates were obtained with Fe-Kα radiation.