

ANNUAL REPORT -- 1986-87

1. Title of Project: Influence of Potassium Chloride and Polyphenols on the Dynamics of the Release of Manganese from Soils
2. Project leader: P.M. Huang
3. Location of research: Department of Soil Science, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 0W0
4. Objectives of the Study:
 - (1) To investigate the effect of KCl on the release of Mn from a series of Mn-bearing minerals and representative soils from temperate and tropical regions.
 - (2) To study the release of Mn from a series of Mn-bearing minerals in relation to their ability to catalyze the polymerization of polyphenols and the subsequent formation of humic substances.
5. Specific results and conclusions for each objective:

The dynamics of soil manganese and its availability to plants are determined by many factors including pH, Eh, the nature and concentration of cations and anions, clay mineralogical composition and microorganisms. Therefore, the nature and properties of soils and agricultural practices should have important bearings on the mobility of manganese in soils. Little is known on the influence of KCl on the release of Mn from Mn-bearing minerals and soils representing different taxonomic orders in both temperate and tropical regions, however. The data obtained show that the release of Mn from Mn oxides common in soils increased consistently with increasing concentration of KCl (0, 0.01, and 1M). As the concentration was increased from 0 to 1M, the release after a 20-h reaction period at 297 K increased 7.2, 2.9 and 1.6 times at pH 5.0 and 7.6, 2.0 and 1.4 times at pH 7.0 for pyrolusite, hausmannite and cryptomelane, respectively. The release of Mn from the minerals was attributed partly to the reduction of Mn(IV) to Mn(II) as confirmed by ESR spectroscopy, and partly to the formation of $MnCl^+$ complex. The Mn release was rapid initially (0-0.25 h) and then decreased subsequently (1-20 h), following a multiple zero order kinetics. The rate constants of the Mn release are in the same order as the specific surface of the minerals i.e., cryptomelane > hausmannite > pyrolusite. The kinetic data indicate that more than one factor controlled the Mn release from the three Mn oxide minerals. The dependence of Mn release on KCl concentration, temperature, and time was evaluated and an equation derived relating these variables. The results indicate that the Mn release significantly varies with the nature of Mn-bearing minerals studied.

The amounts of the Mn released from fourteen soils representing different taxonomic orders from six countries (China, Canada, Japan, Israel, Brazil and India) located in temperate and tropical regions were very significantly (13 to infinite times) increased with the increasing KCl concentration (0, 0.01, 0.1 and 1 M). The rate of Mn release was examined by a series of kinetic equations, namely zero order, first order, second order, diffusion, Elovich and modified Freundlich. The curvilinear relationship between Mn release and time suggests that the release of Mn involved multiple rate processes. Reduction of Mn(IV) to Mn(II) by Cl^- is only thermodynamically feasible for certain Mn-bearing minerals as indicated by their standard electrode potentials (E_0). Therefore, the enhancement of the release of Mn by KCl cannot be entirely attributed to the redox reactions. The complexation of solution

Mn²⁺ by Cl⁻ appears to be partly responsible for the increase of Mn released by KCl from the soils. An equation was derived to relate the Mn release from the soils with KCl concentration, time and temperature. The Mn release is correlated significantly with square root of molarity of KCl concentration, logarithm of time (s), and temperature (K). Multiple regression analysis of the data show that 87% to 96% of the Mn release can be explained by the model developed in this study.

The data obtained show that the release of Mn from birnessite (δMnO_2) was enhanced by pyrogallol which is a common polyphenol in soils. Furthermore, the Mn release was related to the catalytic power of birnessite in the polymerization of pyrogallol. The humic polymers derived from pyrogallol resembled soil humic substances in IR and ¹³C NMR CPMAS spectra.

Future research (1987-88) will be directed to the following:

- (1) Physicochemical factors determining the release of Mn from a series of particle size fractions of Mn-bearing minerals and of soils from both temperate and tropical regions.
- (2) The kinetics of Mn release from selected soils where the stimulating action of KCl dressings on Mn concentration in palm fronds was observed in Indonesia and where excessive release of Mn resulted in crop toxicity in Oregon (personal communication with J.D. Beaton).
- (3) The influence of polyphenols on the dynamics of Mn release from Mn-bearing minerals and selected soils representing different taxonomic orders.

Research Papers Presented at Scientific Meetings

- (1) G.S.R. Krishnamurti and P.M. Huang. 1986. Kinetics of the release of manganese from selected manganese-bearing minerals as influenced by potassium chloride. Abstract p.17. The 1986 Annual Meeting of the Canadian Society of Soil Science, Saskatoon, SK.
 - (2) M.C. Wang and P.M. Huang. 1986. Polyphenol transformations as catalyzed by oxides of Mn, Fe, Al and Si. The 1986 Annual Meeting of the Soil Science Society of America, Agronomy Abstract p.173, New Orleans, LA.
 - (3) G.S.R. Krishnamurti and P.M. Huang. 1987. Influence of potassium chloride on the kinetics of Manganese release from soils representing different taxonomic orders. To be presented at the 1987 Annual Meeting of Soil Science Society of America, Atlanta, GA.
6. Planned changes for next year: The project will continue as originally planned.
7. Can PPI/FAR cite data: Yes



**NEWS
RELEASE**

POTASH HELPS SOILS RELEASE MANGANESE - Beaton

FOR IMMEDIATE RELEASE

"It now seems clear that potash applied to certain soils effects a release of manganese which should make this key micronutrient more available to plants," says Dr. J.D. Beaton, Vice President of the Potash & Phosphate Institute of Canada (PPIC).

Dr. Beaton was commenting on recent studies carried out by Dr. P.M. Huang of the University of Saskatchewan Department of Soil Science. The studies were partially financed by PPIC's Foundation for Agronomic Research (FAR). Crops which are sensitive to insufficient manganese include wheat, alfalfa, barley, oats, potatoes and sugar beets among others and some agriculturalists believe that lack of manganese is the most common micronutrient problem in soybean production.

Dr. Huang's research initially focused on the effect of potash applications on known manganese bearing soil minerals and then was widened to include 14 different soils from six countries (China, Canada Japan, Israel, Brazil and India) varying from temperate to tropical in climate. His findings showed that the release of manganese from common manganese oxides found generally in soils, and from the 14 specific soil increased consistently with increasing potash additions.

MEMBERS

• Chevron Chemical Company
• Kalium Chemicals
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• Cominco American Incorporated
• Mississippi Chemical Corporation
• Western Ag-Minerals Company

• Great Salt Lake Minerals & Chemicals Corporation
• Potash Company of America
• Potash Company of Canada Limited

• International Minerals & Chemical Corporation
• Potash Corporation of Saskatchewan

The influences of time and temperature on the liberation of soil manganese were also studied as part of the overall project.

"The complex nature of the chemistry involved is an open invitation to further research," Dr. Beaton says. "This is a new area and we have much to learn, however it is certain that potash will unlock this valuable nutrient from the soil. This discovery opens a whole set of possibilities in North East Saskatchewan for example, where some soils are deficient in manganese."

Manganese is also known to be deficient in certain soil areas of Alberta and Manitoba.

Dr. Beaton also notes that as more and more research is carried out on the use of potash in agriculture a whole spectrum of benefits to crop growth is emerging.

"We have been excited about the positive effects of the chloride in potash on the control of plant diseases such as common root rot and take-all root rot" Dr. Beaton notes, "and now we seem to be on the threshold of a whole new set of possibilities with the research on potash and the important micronutrient manganese, especially in the area of plant uptake and use."

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For more information contact:

Dr. J.D. Beaton
Potash & Phosphate Institute
Ste. 704, CN Tower, Midtown Plaza
SASKATOON, SK S7K 1J5

Mr. Don Leitch
Potash & Phosphate Institute
Ste. 704, CN Tower, Midtown Plaza
SASKATOON, SK S7K 1J5

Phone: 652-3535

Adsorption of sulfate by kaolinite and amorphous iron-oxide in the presence of humic and tannic acids.

W.P. INSKEEP, Montana State Univ.

The sorption of sulfate in acid forest soils is an important process which influences cation transport through soil profiles. The objective of the present study was to determine the influence of representative soil organic ligands on the sorption of sulfate by kaolinite (KGa-2) and amorphous Fe-oxide at pH 4.3. Sorption was studied over a range in SO_4^{2-} (TS=total soluble) from 0.012 mM to 2-3 mM, in the presence of humic and tannic acids at C_{TS} values ranging from 1 to 3 mM C_{TS} . Sorption of sulfate by kaolinite at 12g L⁻¹ was reduced by 50 and 90% at low sulfate levels in the presence of 1.4 mM C_{TS} and 2.4 mM C_{TS} present as humic acid. At 6g L⁻¹ kaolinite, sorption of sulfate was reduced by 100% at low sulfate levels in the presence of 2.4 mM C_{TS} as humic or tannic acid. Sorption of sulfate by amorphous Fe-oxide at 0.8g L⁻¹ was reduced anywhere from 10 to 100 percent at 1.3 mM C_{TS} as humic, tannic, or citric acid. Organic acids common in soil solutions reduce sulfate adsorption apparently by competing for surface sites. This may indirectly affect the transport of cations in acid soil profiles receiving inputs of sulfate.

Herbicide Adsorption by Coastal Plain Soils.

R. M. JOHNSON*, J. T. SIMS, University of Delaware
The adsorption of alachlor, atrazine, cyanazine, dicamba, metolachlor and 2,4-D-amine by six Delaware soils was investigated. The soils are representative of the major soil series in the state and include well and somewhat poorly drained soil series. Soil sampling was conducted by soil horizon, to a depth of approximately 1/2 meters. Soil horizons were characterized for several physical, chemical and mineralogical properties that influence adsorption. Adsorption isotherms were constructed utilizing a batch equilibrium technique with radiolabeled herbicides. Five herbicide concentrations were used based on currently recommended herbicide rates. Results from the herbicide adsorption study were correlated with soil characterization data by employing a stepwise multiple regression procedure.

Organic Molecules at Mineral Surfaces - FTIR and Raman Studies.

C. T. JOHNSTON*, Univ. of Florida
In-situ spectroscopic studies of adsorption processes are necessary for a more detailed understanding of the fundamental interactions between an adsorbate and a mineral surface. As a prototypical example of this approach, non-invasive FT-IR and Raman spectra of clay-organic complexes will be presented. Direct optical evidence for the chemical transformation of the adsorbed species on the clay mineral surface has been obtained. The influence of the interlayer water content and the nature of the exchangeable cation on these surface induced reactions will be presented. In addition, the complementary nature of in-situ vibrational spectroscopic methods to other physical methods will be discussed.

Phosphate Adsorption by a Mixture of Reference Oxides.

N. KHOURI*, P. L. M. VENEMAN, and J. H. BAKER, Univ. of Massachusetts.

The "linear additivity" concept of anion adsorption was validated in this batch study of P adsorption on binary mixtures of oxides. Goethite (FeOOH) and gibbsite (Al(OH)₃) colloids were prepared in the laboratory and characterized in pure suspensions. Mixtures containing 1.9 g L⁻¹ of each oxide were then equilibrated with (i) increasing levels of P concentration (0 to 300 μmol L⁻¹) at pH 5, and (ii) the same initial P level but varying pH (3 to 12). Although some aggregation was observed in the mixtures, the amount of P adsorbed in each experiment was the sum of P adsorbed by each oxide in pure systems and under similar experimental conditions. This was observed even at low pH levels (<4) where gibbsite was partially dissolved and goethite remained unaffected. At initial P of 200 μmol L⁻¹, maximum adsorption for goethite, gibbsite, and the mixture reached 100, 75, and 90 mmol kg⁻¹, respectively, at pH 3, 4, and 4. Results will be discussed with respect to the need to evaluate the additivity concept in order to study environmental effects on particular heterogeneous systems- especially in view of recent research contradicting its universal applicability.

Soil pH Effects on the Distribution and Plant Availability of Heavy Metals in Three Coastal Plain Soils.

J. S. KLINE* and J. T. SIMS, University of DE.

Assessment of the hazards of utilizing sewage sludges or sludge-based organic wastes on agricultural lands requires an understanding of the fate of potentially toxic heavy metals contained in these wastes. The objectives of this study were to (i) examine under greenhouse conditions, the influence of soil pH and soil type on plant uptake of Cd, Cr, Ni and Pb by wheat and soybeans; (ii) to determine the fate of metals not taken up by the plant through a chemical fractionation procedure and (iii) to evaluate the ability of routine soil testing methodology to identify plant available heavy metals. Three coastal plain soils were limed to four pH levels (5.5 - 7.0). Four rates of a co-composted organic waste (produced by aerobic digestion of a mixture of anaerobically digested sewage sludge and municipal solid waste) were added to each soil. Data to be presented include the relationships between plant uptake, heavy metal fractions, and metals extracted by two soil tests.

The Effect of Soil Type, Concentration, and Waste Material on the Transport of Pb and Cd in Soil.

J. KOTUBY-AMACHER* and R.P. GAMBRELL, Laboratory for Wetland Soils and Sediments, Louisiana State University.

The transport of Pb and Cd through packed soil columns in the laboratory was studied using various soil types. Two concentrations of Pb and Cd were used - 500 ppm Pb with 50 ppm Cd and 50 ppm Pb with 5 ppm Cd. Various waste materials were also used in conjunction with the two Pb and Cd concentrations including 0.005M Ca(NO₃)₂ as a background, an aerobic synthetic municipal leachate, and a simulated metal-plating waste. Cd breakthrough occurred prior to Pb breakthrough. At low Pb concentrations, there was very little transport of Pb through the columns even after leaching with 20 pore volumes of 0.005M Ca(NO₃)₂. Pb and Cd transport was fastest in the acidic metal-plating waste and slowest in the 0.005M Ca(NO₃)₂. The synthetic leachate produced two separate peaks for each Pb and Cd concentration - the first a rose-colored solution and the second a clear solution with a longer retention time than Ca(NO₃)₂.

The Influence of Potassium Chloride on the Kinetics of Manganese Release from Soils Representing Different Taxonomic Orders.

G. S. R. KRISHNAMURTI* and P. M. HUANG, University of Saskatchewan.

The kinetics of manganese release from fourteen soils, representing different taxonomic orders, was studied as a function of concentration of potassium chloride (0, 0.01, 0.1 and 1.0M), time (0.25-216 h), and temperature (4, 25 and 44°C). The soils were selected from six countries located in temperate and subtropical regions. The total Mn content of the soils varied from 2.9 to 32.5 mmol/kg, with more than 50% in the <2 μm mechanical size separates. The Mn release increased consistently by 10 to infinite times as the concentration of KCl increased from 0 to 1.0M. The Mn release increased 1.3 to 3.4 times with temperature (4 - 44°C) by M KCl and was examined by a series of kinetic models. The Mn release had two distinct reaction rates, medium (1-24 h) and slow (24 - 216 h), following the fast release observed initially (0-1 h). The rate constants of Mn release at different temperatures were calculated based on zero order kinetics as no significant improvement in r² and S.E. values was observed using the first and second order kinetic models. The rate constants during the medium reaction stage (1- 24 h) were 6-12 times larger than those during the slow reaction stage (24 - 216 h). The activation energy of Mn release varied from 0.5 to 27.4 kJ mole⁻¹ amongst the soils. The Mn release from the calcareous Vertisols was the lowest (15 - 29 μmol/kg) even though the total Mn content was the highest (25.1 - 32.5 mmol / kg). Redox, complexation and exchange reactions appear to be the mechanisms governing the dynamics of Mn release from soils.

Oxidation Reactions of Hydroquinone on Fe and Mn Oxides.

K.-H. KUNG* and M. B. McBRIDE, Cornell Univ.

The oxidation of hydroquinone on Mn and Fe oxides was studied kinetically in aqueous solution by an on-line analysis using UV and ESR spectrometry. The p-Benzosemiquinone anion radical was found as an intermediate in the reaction. The radical-mediated reaction suggests that the reduction of the oxide proceeds via one-electron transfer processes. In Mn oxide systems, the radical persisted in aqueous solution at pH 6, decreasing simultaneously with the consumption of dissolved O₂. With different Fe oxides, the extent of oxidation and adsorption of organics were different. All Fe oxides were much weaker than Mn oxides for oxidizing ability. Dissolution of Mn²⁺

Kinetics of the release of manganese from selected manganese-bearing minerals as influenced by potassium chloride. G.S.R. Krishnamurti* and P.M. Huang, University of Saskatchewan.

The influence of KCl on the rates of release of Mn from selected MnO_2 minerals was studied. The release of Mn from these minerals consistently increased with increasing concentration of KCl (0, 10^{-1} , 1 M). The Mn release from birnessite, pyrolusite and cryptomelane increased 23, 7.5 and 1.5 times respectively, as the KCl concentration increased from 0 to 1 M after a 20 hr reaction period. The Mn release was rapid initially (0 to 1 hr) and then the rate of release decreased (1 - 20 hrs). The release of Mn was evidently related to the reduction of Mn(IV) to Mn(II) as confirmed by ESR spectroscopy. The increase in Mn release from different metal chlorides was in the order: $CaCl_2 > KCl > NH_4Cl = NaCl$. The results indicate that the influence of KCl on the Mn release varies with the nature of Mn-bearing minerals commonly present in soils.

Potassium Fixation in Coarse Textured Soils. M.A. Lathiff* and R.J. Soper, University of Manitoba.

Potassium fixation was measured for twelve coarse textured Almasippi soils of Manitoba with a range of applied potassium (0 to 1000 mg Kg^{-1}). The fixed potassium was measured and defined in this study by the difference between the amount of applied K and the increase in the extractable K after equilibration, using 1N ammonium acetate as an extractant. At application rates of 50 and 1000 mg Kg^{-1} the fixed potassium varied from 12% to 100% and 12% to 53% respectively. All soils showed a trend of increasing amounts of fixed potassium with increasing K application rates and exhibit a decreasing percentage fixation. Among the twelve soils tested, three profiles were selected based on high, medium and low fixation to study the effect of applied potassium on potassium fixation at different depths. In the high and medium fixing profile, the amount of K fixed in the various depths was comparable to that of surface soils. Results of simple linear regression analyses demonstrated significant correlation of K fixed at the 50 mg Kg^{-1} with exchangeable Ca, % K saturation and CEC of the soil. K fixation in those soils could be clearly explained by Langmuir adsorption isotherms.