

# A study on the transport of natural organic matter (NOM) and phosphorus in gypsum treated soils of the Mt Bold catchment and impacts on water quality.

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## **Abstract**

Losses of nutrient, specifically phosphorus and organic matter, from soil to water are thought to be primary agents of water quality decline in many South Australian (and Australian) drinking water reservoirs. Furthermore agricultural soils of southern Australia are generally nutrient deficient requiring supplementary additions of fertilizer to maintain fertility.

This study investigated the potential of an agriculturally viable soil amendment to enhance the soils' retention of these constituents. This study investigated the effect of gypsum on phosphorus and organic matter mobility in soils, including its effect on soil fertility and water quality. Gypsum was selected following a literature based investigation of potential amendment alternatives and was selected based on its properties including: agricultural viability, availability, cost and physiochemical properties (including solubility and ease of application). While earlier investigations have found gypsum to be effective in reducing P solubility in soils of  $\text{pH} > 6.5$ , the soils of this investigation were of  $\text{pH} < 6.5$ .

Water quality was studied with reference to the Australian Drinking Water Guidelines (NH&MRC and ARMCANZ, 1996) and the treatability of the water under simulated conventional water treatment (coagulation, sedimentation and filtration) conditions and specifically for removal of natural organic matter. Of particular focus was the effect of gypsum on the retention and transport of total and reactive P and on the concentration and character of soluble organic matter in leachate and soils.

In addition to studying the effect of gypsum on the distribution and characters of P and organic matter in soil, changes to physical and chemical fertility were also assessed.

These investigations were conducted at a subcatchment scale at a site within the Mt Bold catchment of the Mt Lofty Ranges, South Australia, described in Chapters 2, 3 and 4. These trials were supported by laboratory based investigations utilizing core leaching and batch trials described in Chapters 5 and 6, respectively.

The subcatchment study investigated the application and effect of gypsum on a typical pasture of the Mt Bold catchment (Chapter 2), on its soil chemistry and fertility (Chapter 3) and on its surface and subsurface water quality (Chapter 4). The study was conducted over a four year period. In the first year, background water quality data for the site were obtained; in the second year, gypsum was applied and over years 2, 3 and 4, surface and groundwater leachate monitoring and sampling was conducted. Parameters analysed included P content (total and dissolved reactive P), total and dissolved organic matter, total ion concentration, total dissolved solids and pH. Solution chemistry modeling was utilized to establish chemical

phases and the organic content was characterized by techniques including pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and  $^{13}\text{C}$  NMR.

Following 3 years of leachate monitoring and study, the soils of the catchments were analysed for its physico-chemical properties including total exchangeable cations and the distribution of organic matter and P in silt and clay fractions.

Both physical and chemical properties of the soil were markedly different between treated and untreated soils. Increases in total exchangeable cations in the treated soil provided an increased sorption capacity for both P and NOM, and therefore potentially reducing the transfer of these constituents to surface and subsurface water.

Calcium ions released from gypsum at the surface exchanged with Al (and other cations) that subsequently were released into the soil solution, and were transferred deeper into the soil profile. The anion sorption capacity at depths  $>20$  cm increased as a consequence of increased exchangeable cations, itself the result of adsorption of these released cations as well as Ca. The sorption capacity may have been further enhanced through the precipitation of new mineral phases (e.g. Al sulphates). The enhanced anion sorption capacity of the soils at depth ( $>20$  cm) enabled the formation of micro-aggregates (size  $\approx 50\text{-}100\ \mu\text{m}$ ) by the incorporation of organic matter, in a manner similar to podzolisation. These micro-aggregates appear to be significant repositories of NOM and P. Importantly the formation of these micro-aggregates (proportionally rich in P and NOM) would reduce the potential of their loss from soil via mobilisation by water and if exposed, by wind.

The retention of these constituents combined with the higher exchangeable Ca, reduced exchangeable Al and with no reduction in exchangeable Mg (in the short term), suggests that gypsum had improved the chemical fertility of the pasture soils. Additional potential benefits to soil physical fertility, as found in this study, are: improved soil structure (particularly aggregate stability) and a small reduction in plant available water (PAW) leading to a complementary increase in air filled porosity AFP.

The effect on the leachates from applying gypsum to field soils is analogous to the outcomes of conventional water treatment using coagulation (*viz* reduced DOC, specific UV absorbance (SUVA), colour and P concentrations). The reduction in the high molecular weight hydrophobic component of NOM having a relatively high level of aromaticity (as indicated by SUVA and specific colour), was supported by both  $^{13}\text{C}$ -NMR and Py-GC/MS.

Reductions in total P were accompanied with reduced proportions of molybdenum reactive phosphorus (MRP), ( $<0.45\ \mu\text{m}$ ) compared with particulate P ( $>0.45\ \mu\text{m}$ ). These observations are further supported by the changes observed in organic matter and P distribution within the soil (Chapter 3).

Overall the results indicate that the mechanisms operating in soils accompanying gypsum treatment are similar to those that occur in conventional water treatment (i.e. coagulation and flocculation). Elevated ionic strength as well as the activity of polyvalent cations (Ca, Mg, Al, Mn and Fe) in the soil solution supports this analogy. In the case of the gypsum amended soils of this study, the final floc was composed not only of Al complexes (as in water treatment) but of high P and NOM- clay aggregates (see Chapter 3). Furthermore this treatment appears to have no deleterious effect on subsequent conventional water treatment of the soil leachates, based upon the jar tests conducted. The remaining, lower concentration

of organics present in the leachate from the gypsum treated soil were found to be relatively more recalcitrant to removal with alum treatment under conventional water treatment conditions, as was expected.

The core leaching trials simulated the field environment under controlled laboratory conditions and was used to study the effects of varying gypsum application rates on leachate quality.

Comparison of the results of the core leaching study and the field investigation outlined above show very similar trends, i.e. reduced pH, P, DOC, SUVA, Specific Colour, Al and Fe and increases in Mn, Mg and Na. Furthermore, the results of this study indicated that a minimum application rate of gypsum required to effect a measurable reduction of P and DOC was between 3 and 10 T/ha for these soils.

Given that P is an important plant nutrient, understanding the precise mechanism of its adsorption in soils is significant for understanding soil fertility. Batch trials were also conducted to develop a greater theoretical understanding of the mechanism of its retention in soils associated with gypsum application.

This study showed that competition between NOM and P existed, however gypsum enhanced the retention of both constituents between pH 5 and pH 9. Defining the precise mechanism of enhancement of P sorption is complicated by the similarity in effect (i.e. inhibition) that both increasing ionic strength and the presence of NOM have on both cooperative adsorption and Ca-P precipitation. Observations in this study reinforce the concept of a continuum between adsorption and precipitation. The results indicate that below pH 7, cooperative adsorption mechanisms are most likely dominate while above pH 7, precipitation of P as calcium phosphate most likely accounts for the removal P from suspension.

Gypsum has several established benefits in agricultural application and this study has demonstrated further potential benefits for agriculture, soils in general and in water quality. Results from this study show that gypsum can enhance the soil's ability to retain some of the primary agents of water quality decline, P and NOM. Potential benefits of using gypsum for this purpose were observed both on-site through improved nutrient retention and fertility in soils and off-site in water runoff (surface and subsurface) through improved water quality.