ASSESSING THE PERFORMANCE AND ENVIRONMENTAL ACCEPTABILITY OF PHOSPHORUS-SATURATED OCHRE AS A FERTILISER

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Summary: Treatment of mine drainage discharges results in the formation of ochre for which no end use has been identified. Ochre adsorbs phosphorus (P) from solution so it could be used for removing P from wastewater. This would produce P-saturated ochre, which could then be recycled as a P fertiliser. Experiments were set up to assess the performance and environmental acceptability of P-saturated ochre as a P fertiliser. Results showed that applying P-saturated ochre improved soil fertility, increased soil pH and did not pose a significant toxic hazard while maintaining the same crop yields as conventional P fertiliser. Furthermore, the insolubility of P bound to ochre in water means that P loss in run off is less likely than when conventional fertiliser is used, reducing the possibility of P polluting adjacent watercourses and thus helping to combat eutrophication.

INTRODUCTION

Phosphorus (P) is an essential nutrient for both plants and animals, but in excess it can be a serious threat to aquatic ecosystems. The input of P to rivers and lakes can contribute to eutrophication, and current EU legislation requires P to be removed (to specified limits) from sewage effluent before it is discharged into sensitive areas.

Flooding of abandoned coal mines often causes mine water discharge into the environment. Treatment of these discharges can result in the accumulation of large quantities of iron hydroxides, known as ochre. At present, no suitable end use for ochre has been identified, but previous research has shown that it effectively adsorbs P from solution (Heal et al., 2003), therefore one possible use would be to utilise it to remove P from sewage. However, such an application raises the question of how to dispose of the ochre when it ceases to be effective for P removal. Subsequent recycling by applying the P-rich ochre as a slow-release fertiliser to agricultural land would be one step towards a more sustainable system. To assess whether P-saturated ochre would be a useful P source for crops without compromising soil quality, experiments were set up to compare the performance of this material with that of conventional P fertiliser.

Initially, grass and barley were grown in pots in soils amended with varying amounts of P-saturated ochre, as well as with conventional P fertiliser and a control with no added P. This was followed by a field trial growing the same crops but with fewer treatments.

MATERIALS AND METHODS

Ochre was obtained from a drying bed at the mine water treatment plant at Polkemmet, West Lothian. P-saturated ochre was prepared for the experiments by repeatedly mixing air-dried material with KH₂PO₄ solution (3 g P l⁻¹) until no further P was removed from solution. The
resulting total and available P concentrations in the ochre were 22.8 and 0.9 g P kg\(^{-1}\) dry weight, respectively.

**Pot Experiment (May - October 2002)**

Soil was collected from the Ap horizon of a P-deficient clay loam soil. The soil was air-dried, sieved (4 mm) and mixed with enough sand to give it a sandy loam texture. The soil was analysed for available P and K by SAC and fertiliser application rates of 85 kg P\(_2\)O\(_5\) ha\(^{-1}\) and 90 kg K\(_2\)O ha\(^{-1}\) recommended.

Sixty 5-l pots were each filled with 4 l of the soil/sand mix. Five replicates of six treatments with varying P contents were prepared for each crop (grass and barley): a control with no added P (CO), a conventional P treatment (CP) with the recommended amount of P added as KH\(_2\)PO\(_4\), and four treatments with P-saturated ochre added giving half, once, twice and five times the recommended amount of P (O(0.5), O(1), O(2) and O(5) respectively). All pots had 0.29 g K and 0.2 g N added, in the form of K\(_2\)SO\(_4\) and NH\(_4\)NO\(_3\). A further 0.06 g of N as NH\(_4\)NO\(_3\) was added after three weeks.

Grass (cv. Parcour) and barley (cv. Chalice) seeds were sown at standard application rates. The pots were distributed randomly over 5 tables in an unheated greenhouse and moved around every 2 weeks. Soil water content was maintained at approximately 80% of field capacity with tap water. When the barley heads had ripened, both barley and grass (including roots) were harvested. All vegetation samples were dried in an oven at 60 °C, weighed then milled in a vertical rotary mill (mesh size 0.5 mm).

Soil samples taken at the start and end of the experiment were analysed for total and available P, total metals (Al, As (at end only), Cd (at start only), Cr, Cu, Fe, Mn, Ni, Pb and Zn) and pH using standard methods (Allen *et al.*, 1974). The vegetation samples were also analysed for total P using standard methods (Allen *et al.*, 1974).

All data were analysed in Minitab v.13 using ANOVA followed by Tukey tests. Significance levels throughout are for P < 0.05 unless otherwise stated.

**Field Trial (March – August 2003)**

Field trials using P-saturated ochre as a fertiliser were then conducted, also with barley and grass. Barley was grown at Glencorse Mains Farm near Edinburgh, while an acid grassland site of low P status was selected at Castlelaw Farm nearby. At both sites, four replicates of three treatments were set out in a randomised block design. The treatments were: a control with no added P (CO), a conventional P treatment (CP) (P application recommended by SAC as triplesuperphosphate (TSP)) and an ochre treatment O(1), which had the same amount of available P added as the conventional P treatment.

At the barley site, P-saturated ochre and TSP were applied to each of the appropriate experimental plots by hand (85 kg P\(_2\)O\(_5\) ha\(^{-1}\)) before the seeds (cv. Golden Promise) were sown. The whole field then received 60 kg N ha\(^{-1}\) and 60 kg K\(_2\)O ha\(^{-1}\). A further 60 kg N ha\(^{-1}\) was applied 3 weeks later. The grass plots were set out on an existing sward. P-saturated ochre and TSP (30 kg P\(_2\)O\(_5\) ha\(^{-1}\)) were applied by hand. 62 kg N ha\(^{-1}\) of NH\(_4\)NO\(_3\) was similarly applied. The plots were covered by cages to protect the grass from grazing animals.
Soil samples were taken from each plot at the start and end of the trial. Available soil P and pH were immediately determined in a portion of the fresh soil. The remainder of the soil was dried and milled for determination of total P and metals. The same analytical techniques were used as in the pot experiment. Grass samples were collected by harvesting a section of each plot by hand in March before treatments were applied, and again in June and August. Barley was similarly harvested in August. Vegetation samples were treated as in the pot experiment.

RESULTS

In the pot experiment, total soil P concentration increased as expected with increasing amounts of added P-saturated ochre. Similarly, in the field experiment, the soil with ochre applied contained significantly more total P than either the conventional P treatment or the control. About 4% of the P in the ochre was determined to be immediately plant-available, and the available P in the soil at the start and end of the pot experiment increased with increasing ochre concentration (Figure 1). The CP treatment was not significantly different in terms of available P from the equivalent ochre treatment (O(1)) at the start of the experiment, but by the end, the O(1) treatment contained significantly more available P than the CP treatment for the barley soil, but not for the grass soil. Similar results were obtained at the end of the field trial.

![Figure 1](attachment:image.png)

Available soil P concentrations at the start and end of the barley pot experiment (bars with the same letter are not significantly different)

Soil pH was increased by adding ochre in both the pot and field experiments. In the former, ochre treatment O(1) had a pH significantly higher than the CP treatment: 6.0 ± 0.2 compared with 5.5 ± 0.1. Similar results were found in the field experiment.

There were no significant differences in soil metal concentrations at the end of either the pot experiment or the field trials between the CP and the O(1) treatments for any of the metals measured. This applied to both barley and grass soils.
In the pot experiment, there was no significant difference in either grass or barley biomass between the CP and the O(1) treatments. In the field trials, there was no difference in the grass yield between treatments, but barley yield was higher from the plots to which ochre had been added than from the plots to which conventional P was added, although not significantly so.

There was no significant difference in the amount of P found in the plants grown in conventional fertiliser and those grown in the equivalent ochre treatment in the pot experiment, whereas in the field trial, there was significantly more P in the barley stems grown in plots treated with ochre. There was no difference between treatments in the amount of P in the harvested biomass in the grass trial.

**DISCUSSION**

The results from both the pot and field experiments showed that adding P-saturated ochre to soil increased both plant-available and total P concentrations in the soil. The plant-available P concentration decreased in all soils between the start and end of the experiments, primarily due to uptake by plants. At the end of both experiments there was significantly more available P in the ochre-treated barley soil than in soil treated with conventional P fertiliser.

In the pot experiment, the amount of P taken up by the plants substantially exceeded the depletion of available P in the soils treated with ochre and in the control (Figure 2). This difference is attributed to the gradual conversion of initially unavailable P in the ochre (and also the soil minerals) into plant-available forms. Possible mechanisms include the action of organic acids from root exudates, which can dissolve unavailable soil Ca, Fe and Al phosphates (Dakora and Phillips, 2002) and increase the concentration of P in soil solution (Hinsinger, 2001).

![Figure 2. Mean P uptake in plant material vs. mean depletion of available P in soil during the experiment for each treatment](image-url)

It is important in assessing the potential supply of P to take into account not only the amount that is immediately available to plants, but also the amount that can be released by desorption from solid surfaces through the growing season. In this context, P-saturated ochre appears to
have the desirable property of acting as a slow-release fertiliser, making P available when required by the roots over the season. The greater amounts of available P left in the ochre-treated soils at the end of the experiments indicates an advantage for future crops, and reduces the need for future applications of P fertiliser.

The moderate liming effect of ochre is also beneficial in agronomic terms. Loss of plant-available P in soils occurs by phosphate fixation, which is especially strong in acid mineral soils. Such losses can be dramatically reduced by liming soils to a pH of 6-7 (Mengel, 1997). The liming effect of the ochre would therefore be expected to counteract, at least in part, any propensity for the P released from the ochre to become fixed by natural soil minerals.

Far from there being any adverse affect on crop yield by using ochre instead of conventional fertiliser, in both the pot and field experiments, crop yields from the ochre-amended soils were higher than from the conventionally fertilised soils, although not significantly.

The regulations governing the application of non-agricultural wastes to agricultural land in the U.K. permit such applications providing they do not contaminate the soil or plants growing on that soil (Waste Management Licensing Regulations, 1994). A possible concern about applying ochre to soils would be the accumulation of potentially toxic metals in the soil. In this context, the most relevant soil quality guidelines are those relating to the application of sewage sludge to agricultural land, as included in the Code of Good Agricultural Practice for the Protection of Soil (MAFF, 1998).

Average soil metal concentrations at the end of the field trial, together with the maximum permissible concentrations and application rates, are given in Table 1. The results from both the pot and field experiments show that soil metal concentrations were well below the guideline values, with the exception of Ni. However, the Ni concentration of the ochre-treated soils was not significantly different from the unfertilised control, so this element was already present in the soil and not due to contamination by ochre.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Max. permissible soil metal conc.† (mg kg⁻¹ dry soil)</th>
<th>Max. annual application over 10 y. (kg ha⁻¹ y⁻¹)</th>
<th>Average soil conc. in ochre treated plots (mg kg⁻¹ dry soil)</th>
<th>Addition in 40 t ha⁻¹ dry ochre* (kg ha⁻¹ y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>200</td>
<td>15</td>
<td>85 ± 21</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>7.5</td>
<td>16 ± 2</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>3</td>
<td>70 ± 11</td>
<td>4.2</td>
</tr>
<tr>
<td>Cd</td>
<td>3</td>
<td>0.15</td>
<td>&lt; 1.6</td>
<td>&lt; 0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>300</td>
<td>15</td>
<td>52 ± 10</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>400</td>
<td>15</td>
<td>156 ± 70</td>
<td>9</td>
</tr>
<tr>
<td>As</td>
<td>50</td>
<td>0.7</td>
<td>0.13 in P-sat ochre</td>
<td>0.01</td>
</tr>
</tbody>
</table>

† For soil pH 5.5-6.0, *equivalent to a P application of 85 kg P₂O₅ ha⁻¹
Table 1 also shows the annual additions of metals associated with an annual application of 40 t P-saturated ochre ha\(^{-1}\) (containing c. 85 kg P\(_2\)O\(_5\) ha\(^{-1}\)). All metals, with the exception of Ni, are well within the limits for sewage sludge. Furthermore, since P-saturated ochre acts as a slow release P fertiliser, annual application would not be necessary in normal agricultural practice to maintain soil P concentrations, thus providing a further safety margin.

Finally, there is an environmental benefit associated with the insolubility of ochre-bound P in water. This means that P loss in run off is less likely than when conventional fertiliser is used, reducing the possibility of P polluting adjacent watercourses and thus helping to combat eutrophication.

**CONCLUSIONS**

Results from pot experiments and field trials with barley and grass show that applying P-saturated ochre improved soil fertility and increased soil pH. The addition of P-saturated ochre, while maintaining the same crop yields as conventional P fertiliser, would not pose a significant toxic hazard in soil or vegetation. Furthermore, the slow release of P from P-saturated ochre means that less frequent applications would be required than when conventional P fertilisers are used.

The use of ochre-bound P should result in less P run off to watercourses than when conventional P fertilisers are used.

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**REFERENCES**