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# ALUMINIUM INTERACTION WITH ORGANIC MATTER AND FLUORIDE DURING SOIL DEVELOPMENT IN OXIDISED MINE WASTE

A thesis presented in partial fulfilment of the requirements for the degree of Master of Science in Soil Science
Massey University

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## ABSTRACT

Significant differences in plant growth response between unmodified waste rock (UWR) and modified (treated with lime and phosphate fertilizers) waste rock (MWR) with topsoil treatments during the first two years of a field trial conducted by Gregg & Stewart (1986; 1987) indicated that Al toxicity was affecting root growth in the UWR. By the end of three years of field trial there was no significant difference in dry matter yield between the MWR and UWR with topsoil treatments indicating possible amelioration of Al toxicity (Gregg et al., 1990). The objective of this study was to measure different forms of Al and F in the soil and waste rock at the end of the third year of field trial and to determine the mechanism of amelioration of Al toxicity in these soils.

Results of this study revealed that there was a significant 2-fold increase in organic-Al (Al-OM) at the UWR interface (B) compared with the waste rock at depth (C) by the end of three year period of soil development. Organic matter decomposition in the topsoil during three years and movement of the soluble organic ligands to UWR interface (B) resulted in conversion of phytotoxic soil solution Al into non-toxic Al-OM forms by complexation with organic ligands in leachates accumulated in the UWR interface.

Total soluble F was consistently high in the UWR profile with a mean value ranging from 1.0 to 1.9 $\mu g\ g^{-1}$. Liming has reduced the F level to 0.3-0.4 $\mu g\ g^{-1}$ in the MWR interface (B) and 0.4-0.5 $\mu g\ g^{-1}$ in the topsoil (A). The waste rock at depth (C) had mean

F values in the range 1.2-1.9 $\mu g\ g^{-1}$. High levels of F in the waste rocks could have also ameliorated Al toxicity in the UWR by formation of non-phytotoxic soluble AlF complexes. This was considered to be another possible reason for no significant differences in the pasture yields between UWR and MWR plots at the end of the third year of trial.

The mean soil pH($H_2O$) for the UWR was 5.1 and liming has raised it by about 1 unit in the MWR. The corresponding pH(0.01 M $CaCl_2$) values were 0.4-0.8 units less than the pH in water. The 0.02 M $CaCl_2$-extractable solution Al (Al-Ca) and 1 M KCl-extractable exchangeable + solution Al (Al-K) have remained high in UWR soil solution irrespective of different depths of topsoil treatments. The Al-Ca and Al-K ranged from 16.7 to 20.5 $\mu g\ g^{-1}$ and 261 to 339 $\mu g\ g^{-1}$ respectively in the UWR interface (B). The Al-Ca and Al-K in waste rock at depth (C) remained at 16.8-22.9 $\mu g\ g^{-1}$ and 238-369 $\mu g\ g^{-1}$ respectively. Modifications have lowered both Al-Ca and Al-K to 0.8-2.7 $\mu g\ g^{-1}$ and 35-66 $\mu g\ g^{-1}$ respectively in the MWR interface (B). Topsoil Al-Ca and Al-K were not significantly different between UWR and MWR and the values for these two forms of Al ranged from 0.6 to 6.0 $\mu g\ g^{-1}$ and 32-87 $\mu g\ g^{-1}$ respectively at the end of the field trial. Normal plant growth response in the UWR in spite of high levels of Al-Ca and Al-K indicated that 0.02 M $CaCl_2$ and 1 M KCl extractants are not good indicators of phytotoxicity as reported in literature because these extractants may be extracting a substantial proportion of non-phytotoxic species of Al.

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To Kesherie & Ishka

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# CHAPTER I

# 1. INTRODUCTION

## 1.1 Background

The Waihi Gold Mining Company is currently mining gold and silver from the Martha Hill Deposit. When mining is completed it is estimated that approximately 22 million tonnes of mine waste and 11 million tonnes of tailings from ore processing will be created from the site. The Waihi Gold Mining Company was required to submit an acceptable plan for the disposal and rehabilitation of the mine waste materials. Thus a conceptual mine plan incorporated the disposal of mine waste materials at the Baxter Road location and progressive restoration of the disposal area to the original land use i.e. pasture farming was developed.

Glasshouse and field trials were required to assess the suitability of the mine waste materials as plant growth media. Glasshouse pot trials carried out by Widdowson et al. (1984) characterised the oxidised mine waste material as having good potential as a plant growth medium. Table 1.1 summarises relevant chemical and physical properties of the oxidised waste material from their data. Their studies showed that the oxidised waste material contained toxic levels of exchangeable Al (8.5 me.%) and was deficient in some major (N, P & Ca) and micro-nutrients (Fe, Cu, Zn). Thus high levels of Al in the oxidised waste was indicated as one of the possible constraints to plant growth. However, the waste material supported good plant growth after adequate chemical modifications

Table 1.1. Selected chemical and physical properties of the oxidised waste rock and topsoil (Martha Hill, Waihi).

| **CHEMICAL PROPERTIES** | Oxidised Waste | Topsoil |
|---|---|---|
| pH(H2O), 1:2.5 soil to water | 5.2 | 5.3 |
| CEC, me.% | 14.4 | 29.0 |
| BS, % | 26.0 | 25.0 |
| Ca, me.% | 0.2 | 2.9 |
| Mg, me.% | 3.0 | 0.7 |
| K, me.% | 0.4 | 0.3 |
| **Al (KCl-extractable), me.%** | **8.5** | **2.1** |
| P (Olsen), ppm | 0.1 | 9.0 |
| S (CaHPO4-extractable), ppm | 35.0 | 22.0 |
| P-retention, % | 28.0 | 91.0 |
| Organic Matter, % | 0.2 | 10.4 |

| **PHYSICAL PROPERTIES** | Oxidised Waste | Topsoil |
|---|---|---|
| Bulk density, (T/cu.m) | 1.4 | 0.6 |
| Total porosity, % | 47.5 | 79.3 |
| Macroporosity, % | 17.0 | 6.5 |
| Water content, % | 33.4 | |
| Plant Available Water, % | 27.6 | 38.3 |
| % < 2 mm fraction | 71.0 | |
| Texture | gritty clay loam | silt loam |

Data from Widdowson et al. (1984) and
Gregg & Stewart (1986)

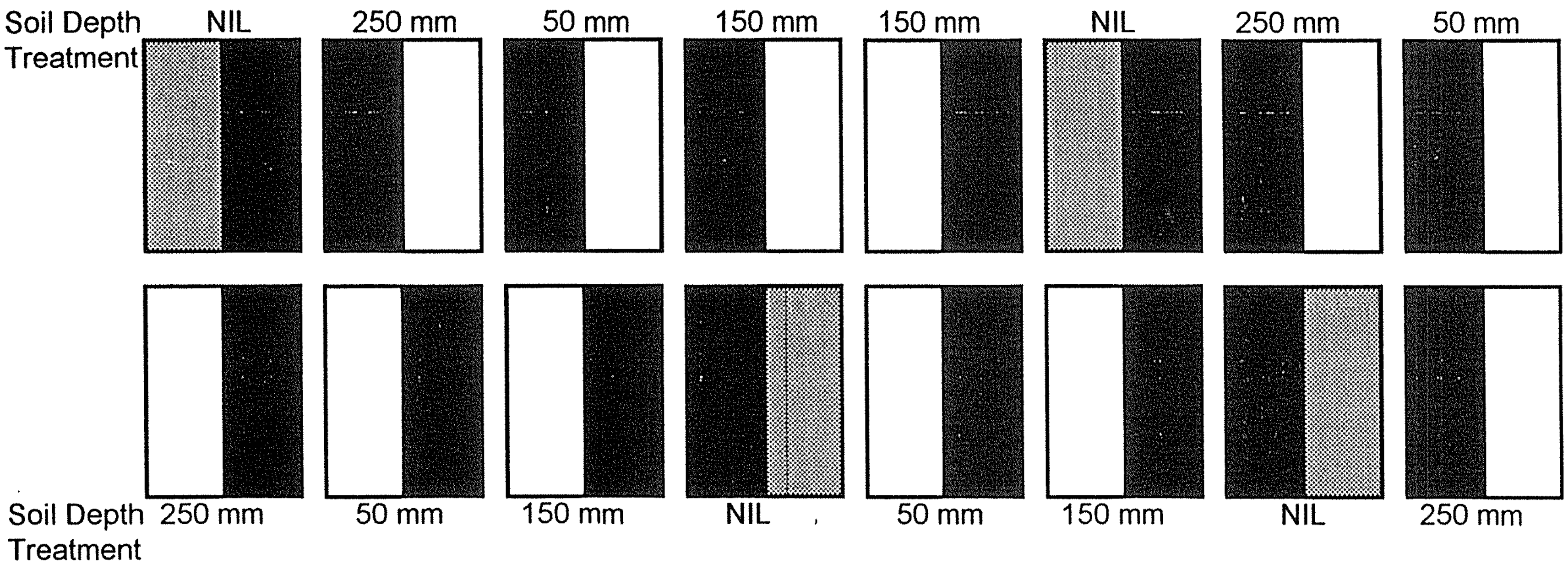
were made (Widdowson et al., 1984; Gregg et al., 1988). The oxidised waste material was also prone to compaction and low aeration during rehabilitation. This finding was confirmed by Horne et al. (1990).

One of the recommendations made by Widdowson et al. (1984) was that it was necessary to carry out field trials to determine the depth of soil cover required for optimum plant growth on oxidised waste rock. Further work was also suggested for studying the inhibitory effects of the mine waste materials on plant growth.

Based on their recommendations and in consultation with the Waihi Gold Mining Company, a three year field trial (1985-88) to assess the plant growth medium potential of the oxidised mine waste was carried out at the Martha Hill site (Gregg & Stewart, 1990). The major treatment studied was topsoil depth requirement for restoration of the oxidised mine waste. The plot design and treatments used are shown in Figure 1.1. The opportunity was also taken to examine the effect of modifying the oxidised waste with lime (6T/ha) and potassic superphosphate (100 kgP/ha) prior to topsoil placement (modified plots) as this was a viable rehabilitation option.

Results from the field trial (Gregg et al., 1990) showed that dry matter yield on the modified waste rock (MWR) plots was significantly (almost 2-fold) higher when compared with unmodified waste rock (UWR) plots during the first year (1985-86) of pasture growth. However at the end of the three year trial period (1985-88) there was no difference in yield between the UWR and

Figure 1.1 Martha Hill trial site (adapted from Gregg & Stewart, 1986)




Plot size = 6 m x 5 m

**WASTE ROCK MODIFICATION**

**Modified waste rock (MWR)** — **(6T Lime + 100 kgP)/ha. incorporated to a depth of 150 mm**

**Modified waste rock (MWR)** — **(6T Lime + 50 kgP)/ha. incorporated to a depth of 150 mm**

**Unmodified waste rock (UWR)** — **No lime or phosphate applied**

*** Urea @ 30 kgN/ha was applied to all plots during pasture growth and after each harvest**

MWR plots, irrespective of topsoil treatments. Moreover, relative yield on the MWR with nil soil treatment was comparatively high throughout the trial period. Thus, although adequate lime application could have ameliorated Al toxicity in the MWR interface (B), some other agents must be responsible for inactivating reactive Al at the UWR interface (B). Speculative possibilities were that the good plant growth response on soils placed over UWR was either due to a "swamping" effect of P from the phosphatic fertilizer or that the Al may have been detoxified by organic and other leachates produced from topsoil placed over UWR.

Wright (1991) attempted to identify possible mechanisms of conversion of toxic Al in the UWR into nontoxic forms. He observed that there was no significant difference in KCl and $CuCl_2$-extractable Al in the shallow and deep samples of the waste rock and concluded that Al may not be toxic component. Mechanisms such as polymerisation of Al-hydroxides, Al binding by organic matter and complexing with available P to form Al-phosphate complexes were likely possibilities suggested by him. However, his findings were inconclusive because of the limitations of data from KCl and $CuCl_2$-extractable Al which measures exchangeable and organic bound Al, respectively.

Recent studies have shown that F in soil solution can exert a strong influence in detoxifying Al (Manoharan et al., 1994). The suspected high concentration of F in the mine waste could have detoxified Al in the UWR at Martha Hill site, thus giving another explanation for obtaining no differences in yield between UWR and MWR in the third year of plant growth.

## 1.2 Objective

The objective of this study was to investigate possible interactions of Al with organic matter and F during soil development in the oxidised mine waste. Quantitative determination of the different fractions of Al present in the soil extracts and F concentrations were therefore carried out to investigate if Al-organic matter or Al-F complexing was responsible for decreasing the toxic effects of Al in the unmodified waste rock (UWR) plots.