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EFFECTS OF CADMIUM APPLICATION AS A HEAVY METAL ON MINERAL CONTENT OF SOIL-PLANT AND YIELD OF PLANT *

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ABSTRACT

An experiment was carried out to investigate the effect of cadmium application on mineral content of soil and plant and cadmium effect on grass yield. This study was aimed to examine some of the complicated relationships that govern cadmium availability to the plants.

The results of the research showed that cadmium application had a significant effect on the mineral content of grass and cadmium (Cd) tended to significantly (P <0.05) depress magnesium and potassium uptake by plants. The plants that had received cadmium had significantly (P <0.05) lower content of magnesium and potassium. The calcium and potassium contents of grass in both treatments were lower than the minimum value recommended for the mineral content of pasture in the literature, while magnesium being within the limit. Cadmium application did not significantly (P >0.05) affect the grass yield.

Key Words : Heavy metals, cadmium, minerals, soil, plant, plant yield.

ÖZET

AĞIR METAL OLARAK KADMİYUMUN TOPRAK VE BİTKİ MİNERAL İÇERİĞİNE VE BİTKİ VERİMİNE OLAN ETKİLERİ

Kadmiyum uygulamasının toprak ve bitki mineral içeriğine ve çayır otu verimi üzerine olan etkilerini araştırmak için yürütülen bu denemede, kadmiyumun bitkiler tarafından alımını etkileyen karmaşık ilişkilerin incelenmesi amaçlanmıştır.

Araştırmada, kadmiyum uygulamasının çayır otunun mineral içeriğinin ve bitkinin Mg ve K' alımı üzerine önemli (P <0.05) etkileri olduğu bulunmuştur. Kadmiyum verilen bitkilerin Mg ve K içeriğinin verilmeyenlere göre önemli derecede daha düşük (P <0.05) olduğu belirlenmiştir. Her iki muameledeki çayır otunun kalsiyum ve potasyum içerikleri literatürlerde önerilen minimum değerden daha düşük; fakat magnezyum içeriği normal sınırlar içinde bulunmuştur. Ayrıca kadmiyum uygulaması çayır otu verimini önemli derecede (P >0.05) etkilememiştir.

Anahtar Kelimeler : Ağır metaller, kadmiyum, toprak, bitki, bitki verimi.

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INTRODUCTION

Heavy metals are hazardous to human life, even in small quantities. These metals include such elements copper, cadmium, lead, selenium, arsenic, mercury and chromium. Heavy metals have significant implications in widely different fields such as human and animal nutrition, environmental protection, human and veterinary medicine, ecology and related sciences.

Cadmium (Cd) is a non-essential trace element and is considered as a pollutant. Cadmium pollution in the environment occurs from smelting industries, attrition of automobile tyres, and burning of diesel and heating oil. Cadmium is added to soils with phosphorous fertilisers and with sewage sludge application to agricultural land. Soil and the above-ground parts of plants also receive additions through the atmosphere, particularly in areas near metal smelters (Bozkurt and Zachou, 1999a).

Several factors affect the activity of cadmium in soils and its availability for plant uptake such as soil pH; the amount of Cd present; the cation sorption capacity of the soil; the presence of micro-elements and of macro-nutrients; soil temperature, moisture content and soil aeration (Bozkurt and Zachou, 1999a).

Cadmium accumulation in pasture becomes increasingly a problem because of its potential transfer into higher food chains. Increased Cd levels in grass means potential cadmium accumulation in animals and health hazards for the consumer.

It is important to take measures to rehabilitate soils contaminated with heavy metals in accordance with the degree of cultivation, and physical and chemical properties of the soils. Soil resistance to contamination by metals depends on the content of organic matter, pH, absroption capacity etc. and also the chemical properties of the metals themselves. Crop selection is also important. Soil slightly contaminated can be improved by applying lime and organic fertilisers. However, the heavily contaminated soils should be excluded from agricultural usage. The concentration of cadmium in foods is controlled by its level in the soil, its availability for plants, and by the physical and chemical properties of the growing substrate.

Therefore, an experiment was conducted to examine the absorption rate and the effects of cadmium on mineral content of soil and plant and cadmium effrect on the yield of grass.

The study was included production of grass following foliar application of hydrous cadmium nitrate [$Cd(NO_3)_2.4H_2O$]. The trial was carried out at the University farm of University of Wales, Bangor, UK between June and November 1994.

METHODS AND MATERIALS

Herbage production

The experiment was conducted in 22 concrete lysimeters of a green house. The dimensions of these were 1.25m length and 1.1m width (1.375 m^2). They were full of sand due to previous experiments. The top 10 cm of sand was cleared and 5-7.5 cm of top soil was added. The added soil had been used for other trials. The last experiment involved a cereal crop which is a very demanding crop in terms of nutrients. Thus, the soil used (mixture of sand and top soil) in the experiment was of low fertility.

Phosphorus and potassium fertiliser (0:24:24, P and K compound fertiliser) was applied at the rate of 40 kg/ha. The pots were sown with 30 kg/ha of perennial ryegrass (*Lolium perenne spp.*) in mid-June 1994.

Due to sunny dry days that followed sowing the plots were covered with top soil and netting to reduce drying of soil. Germination started a week later. The germination rate was low due to the dry conditions and disturbance by birds. Empty patches of soil were resown with no big improvement of the germination rate due to unfavourable weather conditions. The grass was weeded regularly to avoid competition for nutrients.

Grass growth was encouraged with two nitrogen dressings applied at the rate of 40 kg/ha early and late July 1994.

Experimental design

The experiment consisted of two treatments. Cadmium was applied in two levels: zero (0) and 100 mg of Cd/plot. Cd was applied as hydrous cadmium nitrate $[Cd(NO_3)_2.4H_2O]$. The lysimeters were lying in each side of a main passageway. The number of lysimeters (11) was equal for each side. There was no known source of variation between the lysimeters so the treatments were allocated at random.

The nitrogen input was not balanced. The lysimeters with the cadmium treatment received 9 mg of N more than the controls because of the hydrous cadmium nitrate solution applied. This amount of nitrogen was not applicable due to the granulate form of the fertiliser. Each granule weighed more than the amount of N (9 mg) that should be applied in order to balance the nitrogen input.

Cadmium application took place on three successive days in late July (28, 29, 30/7/94). The Cd solution was diluted to concentration of 10, 20, 20 ppm respectively for the three applications in order to avoid foliar damage of the grass. The lysimeters were also watered both before and after the treatment application for the same reason. No foliar damage was observed after the first application of cadmium so the concentration of the cadmium solution was increased to 20 ppm for the second and the third application.

Each lysimeter had a small plastic pipe coming out from the bottom. Each pipe was fitted with an elbow. Collapsible plastic containers were used to collect any water leaching from the draining system of the plots.

The concentration of cadmium in the soil samples was below the limit of detection (0.2 mg/kg of Cd) of the atomic absorption spectrophotometer. A reason for this might be due to the the sampling depth which should have been greater than that of sampling depth actually carried out.

Without knowing the availability of Cd to the plants none of the above mentioned relationships could be tested. The effect of calcium, magnesium and potassium content of soil to the Cd availability could not be tested as well as the effect of pH, Cation Exchange Capacity and Organic Matter.

The calcium content of soil at the beginning of the experiment was significantly different (P=0.001) between the treatments. The lysimeters that subsequently received cadmium, had higher calcium content. There was no significantly difference in the calcium content of the soil after the end of the experiment.

Analysis of variance was performed to examine the effect of treatment on the Mg and K content of the soil at the end of the experiment. Calcium content of the soil in the beginning was used as a covariate in the statistical analysis to balance the differences in the calcium content of the soil. Table 1 shows the effect of treatment on the Mg and P content of soil.

Table 1. Effect of cadmium application on Mg and K content of soil.

		Cadmium				
Minerals (mg/kg DM)	**n**	**With**	s.e	**Without**	s.e	P
Mg	11	37.95	0.971	26.57	0.971	0.04
K	11	48.21	0.976	33.57	0.976	0.01

The Mg and K content of the soil at the beginning of the trial were not significantly different but afterwards both Mg and K level in the soil (P=0.04 and P=0.01, respectively) were significantly affected by the treatment. Magnesium and potassium contents of the soil were higher in the cadmium treatment compared with the control. This suggests that cadmium uptake by plants was increased acting antagonistingly to Mg and K uptake.

Soil pH (mean 5.3), Organic Matter (mean 4.7%) and Cation Exchange Capacity (mean 8.7 meq/100g) were favourable for the Cd availability according to previous reports but this could not be checked in this experiment for the above mentioned reasons. Table 2 shows the pH, Organic Matter and Cation Exchange Capacity content of the soil in the cadmium-treated lysimeters.

No measurements were made on the grass roots which could give some indications of how much of the applied cadmium was available to the plants. The grass was left to regrow so that it could be used in another experiment (Bozkurt and Zachou, 1999b).

It must be noticed the main aim of the experiment was to produce grass with cadmium so that the absorption rate of two different sources of cadmium in sheep could be examined (Bozkurt and Zachou, 1999b).

Table 2. pH, OM and C.E.C content of cadmium-treated lysimeters

Cadmium treated lysimeters	PH	OM (%)	C.E.C (meq/100 g)
1	5.40	3.57	7.67
2	5.50	4.05	7.59
3	4.42	4.00	8.80
4	5.40	5.90	12.10
5	5.32	4.35	8.30
6	5.30	3.30	5.33
7	5.20	6.40	10.47
8	5.30	5.85	9.30
9	5.35	6.10	10.90
10	5.45	3.87	6.93
11	5.35	4.35	8.37
MEAN	**5.3 ±0.20**	**4.70 ±0.75**	**8.70 ±1.30**

Cadmium, potassium, calcium and magnesium content of grass

The grass was digested by wet ashing to avoid cadmium which can be high in dry ashing (Gordon *et al.*, 1971). Wet digestion of grass samples (two from each lysimeter) took place after the feeding trial in sheep.

The cadmium level of grass was tested twice (five and twenty four days after the last cadmium application) employing dry ashing and a recovery rate test. Cd-free grass samples were weighed acurately. Known concentration of cadium solution was added to these samples in order to test the recovery rate after dry ashing. The cadmium concentration of grass was 11 mg/kg with a recovery rate varying from 45 to 63%.

Taking into account previous reports (Gordon *et al.*, 1971) that the concentration of Cd in plants is higher after two weeks than after eight weeks, it was assumed that the cadmium concentration of grass would be approximately 16 mg/kg.

After analysing the grass with the wet digestion method it was discovered that the grass contained on average only 5.93 mg/kg of Cd resulting in an unbalanced experiment. All samples were analysed by an Atomic Absorption Spectrophotometry without background correction for interferences and thus putting the reliability of the results in doubt. Knowing that the sodium level of plants is low (0.26% of the dry weight of ryegrass shoots, Marschner, 1986) the interference of Na with Cd, giving higher values, was minimised.

The Cd concentration of grass was significantly different ($P<0.01$) from zero. This was tested by performing a t-test. No cadmium was detected for the control 2treatment. This was expected as there was no Cd in the soil and Cd application was done very carefully to avoid Cd contamination of the control lysimeters. The effect of cd application on mineral content of grass is shown in Table 3, together with the mineral composition of grassland herbage recommended by Whitehead (1966).

Table 3. Effect of cadmium application on Ca, Mg and K content of grass *

MINERALS (mg/kg DM)	n	Cadmium With	s.e	Without	s.e	P	Recommended Composition**
Ca	11	1.336	0.046	1.755	0.046	0.070	2-10
Mg	11	1.988	0.026	2.263	0.026	0.036	1-4
K	11	7.511	0.177	13.800	0.177	0.000	20-30

*The values presented in the table are not arithmetic means. They are obtained by GLM analysis.
** Recommended by Whitehead (1966).

Cadmium application had a significant effect on the mineral content of grass (Table 3). The mean Ca content of Cd-free grass was 1.76 mg/kg of DM, varying from 0.4 to 2.72 mg Ca/kg of dry matter. Cadmium application decreased the Ca content of grass to 1.34 mg Ca/kg of DM, varying from as low as 0.40 mg/kg to 1.92 mg Ca/kg of DM. There was a tendency (P=0.07) for Cd to replace Ca in the grass that almost achieved statistical significance. All Ca values observed were lower than the recommended levels (Table 3).

Magnesium and potassium content of the Cd-grass was significantly affected by the Cd applicaton (P=0.036 and P=0.00, respectively) The mean Mg content of the control grass was 2.26 mg/kg compared with 1.98 mg/kg of DM for the grass with cadmium application. The Mg concentration varied from 1.67 to 2.91 mg/kg of DM and from 1.60 to 2.27 mg/kg of DM for the control and Cd-grass, respectively. In contrast to Ca and K values, the Mg contents of grass in both treatments were found to be within the limits of the recommended levels (Table 3).

The potassium content for the control treatment varied from 8.06 to 17.70 mg/kg of dry matter giving a mean value of 13.8 mg/kg of K. The Cd-treated grass gave a mean concentration of 7.51 mg K/kg of DM varying from 5.81 to 8.67 mg K/kg of DM. These results suggest that cadmium replaces magnesium and potassium in grass. Furthermore, the K contents of grass in both treatments were found to be lower than the recommended levels (Table 3).

Cadmium effect on grass yield

Cadmium had no significant (P> 0.05) effect on grass yield. The yield (on the basis of both fresh and dry matter yield) and the dry matter percentage (DM%) of the grass was unaffected by the treatment. The effect of cadmium application on yield and dry matter content of grass is shown in Table 4.

Table 4. Effect of cadmium application on yield and dry matter content of grass*.

		Cadmium				
	n	With	s.e	Without	s.e	P
Fresh yield (kg)	11	3.504	0.064	3.821	0.064	0.30
DM yield (kg)	11	0.607	0.006	0.624	0.006	0.61
DM (%)	11	17.820	0.172	16.400	0.172	0.09

*The values presented in the table are not arithmetic means. They are obtained by GLM analysis.

The fresh yield varied from 3.04 to 4.7 kg and from 2.7 to 5.1 kg for the control and the Cd-treatment, respectively. The mean fresh weight of the Cd-free grass was 3.8 kg. The mean fresh weight of the Cd-treated grass was 3.5 kg.

The dry matter content of the grass varied from 15.4 to 18.9% and from 14.9 to 20.5% for the Cd-free and the Cd-grass, respectively. The mean DM content was 16.4 and 17.8% for the control and the Cd treatment respectively.

The dry matter of the yield for the Cd-free grass varied from 0.47 to 0.72 kg giving a mean value of 0.62 kg. The dry weight of the yield for the Cd-treated grass varied from 0.52 to 0.76 kg with a mean value of 0.61 kg. These results are in accordance with previous reports (Sadana *et al.*, 1989; Strnad *et al.*, ; 1991) using low levels of cadmium.

DISCUSSION

Increased pH reduces the cadmium content of plants by affecting Cd solubility (John *et al.*, 1972; Takijima and Katsumi, 1973; Andersson and Nilsson, 1974). The soil pH measurements in this experiment showed values favourable for Cd-availability. The acid soil conditions (mean pH=5.3) would increase the Cd absorption by plants due to increased solubility although such a low pH was not favourable for grass growth. It is generally agreed (Mislin and Ravera, 1986) that a decrease in soil pH will increase the solubility of cadmium which in turn increases crop uptake of the element.

The soil used in this experiment could be characterised as sandy loam with an average OM content of 4.7% and C.E.C of 8.7 meq/100 g of soil. These values of organic matter and cation exchange capacity are characteristic for the type of soil used and the pH. Low C.E.C accomplished with low OM content of the soil increases the exchangeable cadmium from the soil to the grass. It has been reported previously

(Haghiri, 1974) that the retaining power of the organic matter for cadmium is not permanent and that it is predominately through its C.E.C property. Increased C.E.C and OM content of soil increases the soil's ability to absorb Cd and thus decreases cadmium availability.

Soil pH, OM content and C.E.C were advantageous for Cd-availability but as it has already been mentioned in previous sections, this could not be tested.

Jarvis *et al.* (1976) found restricted transport of Cd from the roots of ryegrass even at high levels of uptake. The cadmium content of plants roots grown with added cadmium (10-250 μg/l) was a constant proportion (88%) of the total uptake. Most Cd is retained in roots and little translocated to shoots (Narwal *et al.*, 1990). Based on the results of Jarvis *et al.* (1976) for Cd retention, on Cd content (5.92 mg Cd/kg of DM) of the grass and the mean dry matter yield of the lysimeters (0.607 kg) in this experiment we reached in the conclusion that indeed pH, OM and C.E.C of the soil were favourable for the cadmium availability. 100 mg of cadmium were applied to the lysimeters. If we assume that 88% of that was retained in the roots then only 2.25% of the applied Cd was unavailable as soon as the Cd content of the grass shoots was in average 5.92 mg/kg of DM (9.75%).

Calcium, potassium and magnesium content of the soil was measured both before and after Cd application. The calcium content of the soil was significantly lower in the control lysimeters compared with the Cd-treatment before the cadmium application. No significant difference existed after the end of the experiment. It is not known why the Ca content of the soil differed between the treatments at the beginning. Most probably it was due to the treatments of previous experiments that used the same soil as in this one.

Jarvis *et al.* (1976) found that increased concentration of added Ca^{++} (100-200 μM) with Mn^{++} or Zn^{++} significantly depressed the Cd uptake in short term while there was no significant difference in cadmium uptake when Ca^{++} was added only.

They concluded that the short-term uptake of cadmium by living roots of ryegrass was considerably depressed by high concentrations (100-200μM) of calcium, manganese and zinc when low concentration (2.23 μM $CdCl_2$) of Cd was added.

Magnesium and potassium content of the soil after the end of the experiment was significantly higher in the Cd-applied lysimeters when Ca content of the soil at the beginning was used as a covariate. This suggests that cadmium may depress uptake of magnesium and potassium by competing for exchange sites at the root surface. Previous reports (Gordon *et al.*, 1971) support these results.

Two different methods were employed to assess the cadmium content of the soil at the beginning and at the end of the experiment. In the beginning, the aim was to determine any background cadmium level in the soil although the soil used in the experiment had not been exposed to any known source of cadmium contamination. The Nitric-Perchloric acid method was not established at that time and it also gives the total Cd in the soil. Ammonium acetate extraction has been used previously (Haghiri, 1974) for soil-Cd analysis. At the end of the experiment, the soil samples were analysed for their total Cd content (Nitric-Perchloric acid). The intention was to assess the available cadmium to the plants taking in account the total Cd applied, the total Cd in the soil and the Cd content of the grass.

Calcium and potassium content of both Cd-treated and Cd-free grass was low while their magnesium content was within recommended limits (Whitehead, 1966) (Table 3). Calcium tended to be replaced by cadmium. Cadmium significantly depressed both the potassium and magnesium content of grass. The effect of cadmium on the potassium content of grass was remarkable. Cadmium treated grass had almost half as much potassium as the Cd-free grass. These results were in agreement with the results of the mineral analysis of soil generally found in the literature. Soil concentration of potassium and magnesium was higher in the lysimeters where cadmium was applied. This means that Cd depressed the Mg and K uptake of plants and at the same time replaced them in the grass (Gordon *et al.*, 1971).

Cadmium application did not affect grass yield. This is in accordance with previous experiments when low concentrations of cadmium were used. Strnad *et al.* (1991) reported no yield reduction of clover (*Medicago sativa*) when 0.2 mg Cd/kg of soil were applied in combination with 10 mg Pb and 10 mg Cu/kg of soil. It is generally observed that low cadmium application (mg of Cd/kg of soil) can affect crop yields while DM yield decreases remarkably at higher rates of cadmium application.

There is a widespread concern for contamination of agricultural land with heavy metals. Cadmium is translocated through the food chain of soil, roots, vegetation and animals to man and is present in environmental air in ever-increasing amounts. Concern has been expressed over long periods to low concentrations of the metal. Because, cadmium is an accumulative poison and large populations of animals and man are exposed to low levels of Cd in the environment and in food.

This demonstrates the need for control of heavy metals. Even if the immense repercussions to the environment caused by heavy metals are not of concern to some countries, these countries should recognise the environmental danger they are in. Therefore, every country should take the necessary technical measures to preserve the surrounding environment against being polluted.

REFERENCES

Andersson, A. and Nilsson, K.O. (1974). Influence of lime and soil pH on cadmium availability to plants. Ambio, 3: pp. 198-200.

Anonymous. (1987). Soil analysis. University of Wales, Bangor, UK.

Bozkurt, Y. and Zachou, E. (1999a). Circulation of heavy metals in soil-plant-animal metabolic system with special reference to Cadmium. The Journal of Agricultural Faculty, Selçuk University, (in press).

Bozkurt, Y. and Zachou, E. (1999b). Effect of cadmium application as a heavy metal on digestibility of feeds and its absorption by animals. The Journal of Agricultural Faculty, Selçuk University, (in press).

Chaney, R.L., Stoewsand, G.S., Bache, C.A. and Lisk, D.J. (1978). Cadmium deposition and hepatic microsomal induction in mice fed lettuce grown on municipal sludge-amended soil. Journal of Agriculture and Food Chemistry, 26: pp. 992-994.

Furr, A.K., Stoewsand, G.S., Bache, C.A. and Lisk, D.J. (1976). Study of guinea pigs fed Swiss chard grown on municipal sludge-amended soil Archives of Environment and Health, 31: pp. 87-91.

Gordon, T., Goodman, G.J. and Roberts, T.M. (1971). Plants and soils as indicators of metals in the air. Nature, 231: pp. 287-290.

Haghiri, F. (1974). Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc and soil temperature. Journal of Environmental Quality, 3: 2, pp. 180-183.

Hanson, L.G. and Hinesly, T.D. (1979). Cadmium from soil amended with sewage sludge: Effects of residues in swine. Environmental Health Perspectives, 28: pp. 51-57.

Jarvis, S.C., Jones, L.H.P. and Hopper, M.J. (1976). Cadmium uptake from solution by plants and its transport from roots to shoots. Plant and Soil, 44: pp. 179-191.

John, M.K., Van Laelhoven, C.J. and Chuah, H.H. (1972). Factors affecting plant uptake and phytotoxicity of cadmium added to soils. Environmental Science and Toxicology, 6: pp. 1005-1009.

Marschner, H. (1986). Mineral nutrition in higher plants. Academic Press, London.

Ministry Of Agriculture, Fisheries and Food (M.A.F.F) (1986). The Analysis of Agricultural Materials, Method 11: Cadmium, Cobalt, Copper, Lead, Nickel and Zinc, Nitric-Perchloric acid soluble in soil, HMSO, London.

Ministry Of Agriculture, Fisheries and Food (M.A.F.F) (1986). The Analysis of Agricultural Materials, Method 9: Cadmium, Cobalt, Copper, Lead, Nickel and Zinc in plant material, HMSO, London.

Ministry Of Agriculture, Fisheries and Food (M.A.F.F) (1986). The Analysis of Agricultural Materials, Method 16: Cation Exchange Capacity and Exchangeable cations in soil, HMSO, London.

Ministry Of Agriculture, Fisheries and Food (M.A.F.F) (1986). The Analysis of Agricultural Materials, Method 32: pH and lime requirement of mineral soil, HMSO, London.

Minitab (1992). Statistical package. Release 10. Minitab Inc., Pennsylvania.

Mislin, H. and Ravera, O. (1986). Cadmium in the Environment. Birkhäuser AG, Basel.

Narwal, R.P., Singh, M. and Dahiya, D.J. (1990). Effect of cadmium on plant growth and heavy metals content of corn (Zea mays l.). Crop Research Hisar, 3: 3, pp. 13-20.

Noguchi, A., Fukami, M. and Tsutsumi, M. (1991). The synergetic effect of macronutrient cations on uptake of cadmium in rice plants. Japanese Journal of Soil Science and Plant Nutrition. Rice abstacts (CAB).

Sadana, U.S., Singh, B. and Singh, B. (1989). Effect of cadmium-zinc interaction on yield and cadmium and zinc content of maize (Zea mays L.). Current Science, 58: p. 194-196.

Strnad, V., Zolotareva, B.N. and Lisovskii, A.E. (1991). Effect of application of water-soluble salts of lead, cadmium and copper on their uptake by plants and the productivity of some agricultural crops. Agrokhimiya, 4: pp. 76-83.

Takijima, Y. and Katsumi, F. (1973). Cadmium contamination of soils and rice plants caused by zinc mining. Soil Science and Plant Nutrition, 19: pp. 235-244.

Whitehead, D.C. (1966). Nutrient minerals in grassland herbage. Mimeographed Publication, No. 1/1966. Commonwealth Bureau of Pastures and Field Crops, Hurley