# EFFECT OF FERTILIZER TYPE ON CADMIUM AND FLUORINE CONCENTRATIONS IN CLOVER HERBAGE

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## Abstract

This study investigated whether changing phosphatic fertilizer type affects the accumulation of cadmium (Cd) and fluorine (F) in pasture herbage. North Carolina phosphate rock and partially acidulated fertilizers derived from this rock generally have higher Cd and F concentrations compared to single superphosphate currently manufactured in Australia.

Clover herbage from sites of the National Reactive Phosphate Rock (RPR) trial was collected and analysed for concentrations of Cd (11 sites) and F (4 sites). A comparison was made between pastures fertilized with 4 rates of single superphosphate, North Carolina phosphate rock, and partially acidulated phosphate rock having Cd concentrations of 283, 481, and 420 mg Cd/kg P respectively, and 170, 271, and 274 g F/kg P respectively. One site used Hemrawein (Egypt) phosphate rock (HRP) having a Cd and F concentration of 78 mg Cd/kg P and 256 g F/kg P respectively. To help identify differences in herbage Cd concentrations between sites, unfertilised soils from each site were analyzed for total and extractable Cd contents. At one site Cd concentrations in bulk herbage (clover, grasses and weeds) were related to infestation of the pasture by capeweed (*Arctotheca calendula* L. Levyns).

There were no significant differences between F in herbage from plots fertilized with single superphosphate, partially acidulated phosphate rock or North Carolina phosphate rock, or between sites. Concentrations of F in herbage were low, generally less than 10 mg F /kg. However, there were large differences in Cd concentrations in herbage between sites, while differences between fertilizer treatments were small in comparison. The site differences were only weakly related to total or extractable (0.01 mol/L $CaCl_2$) Cd concentrations in soil.

Significant differences in Cd concentrations in clover due to fertilizer type were found at 5 sites. North Carolina phosphate rock treatments had significantly higher Cd concentrations in clover compared to single superphosphate at 2 sites. Partially acidulated phosphate rock treatments had significantly higher Cd concentrations in clover compared to single superphosphate at 4 sites. At the site where Hemrawein was tested, this treatment had significantly lower Cd concentrations in clover compared to both single superphosphate and North Carolina phosphate rock treatments.

## 1. INTRODUCTION

The use of phosphatic fertilizers on pastures has been demonstrated to increase Cd concentrations in soil [1-3]. In a national survey of “native” (non-agricultural) and pastoral (fertilised) soils in New Zealand, Roberts et al. [3] found that Cd concentrations were 0.20 mg/kg in the native soils and 0.44 mg/kg in the pastoral soils. They attributed the increase in soil Cd concentrations to the use of phosphatic fertilizers, principally single superphosphate (SSP), which contains high concentrations of Cd as an impurity. The elevated Cd concentrations in soil were not clearly reflected in herbage Cd concentrations, except in weed species.

Cadmium concentrations in SSP, reactive phosphate rock (RPR) and partially acidulated phosphate rock (PAPR) are primarily a function of the Cd concentration in the feed rock used in manufacture [4], with generally little Cd contributed from the sulfuric acid used for acidulation. Cadmium concentrations in RPRs may be different to that of the parent rock material, depending on the degree of physical treatment (washing, size sorting, etc.) prior to dispatch. Cadmium concentrations in SSP in Australia have declined over the last 20 years [4, 5], due presumably to changes in the source of rock raw materials used in manufacturing. Furthermore, limits on Cd concentrations in phosphatic fertilizers are being introduced in Australia. The State of Victoria recently adopted a limit of 350 mg Cd/kg P in phosphatic fertilizers [6], while other countries have already imposed much stricter limits [7].

This paper has been modified from the original article “Effect of fertilizer type on cadmium and fluorine concentrations in clover herbage” by McLaughlin, M.J., Simpson, P., Fleming, N., Stevens, D.P., Cozens, G. and Smart, M.K. in Aust. J. Expt. Agric. 37 7 (1997) 1017-1026 by permission of CSIRO Publishing.

This Australian limit could prohibit the use of some RPRs, which have Cd concentrations exceeding this value.

Most RPRs also have high concentrations of F, often exceeding 3% by weight (250g F/kg P), while concentrations of F in SSP are lower due to losses of F during acidulation in the manufacturing plant [7]. Fluorine is a strongly sorbed element in most soils [8]. However, in extremely sandy or acidic soils F is more soluble [8, 9], and would potentially be available for plant uptake in conditions where RPR use is often regarded to be agronomically beneficial compared to soluble P fertilizers. Fluorine has been implicated in a number of incidents of injury to grazing stock through fluorosis [10].

Few data are available to determine if phosphatic fertilizer type plays any role in moderating or enhancing Cd or F uptake by herbage in grazed pastures. The aim of this study therefore, was to determine if use of SSP, RPR or PAPR has any significant effect on Cd and F concentrations in herbage.

## 2. MATERIALS AND METHODS

Eleven sites were used from the national RPR project evaluating RPRs in the high rainfall Mediterranean pasture environment of Australia [11]. These covered a wide range of soil/pasture/climate environments in 5 states across Australia; NSW (Armidale-N4 and N6, Yass-N7, Tarago-N8), Victoria (Benalla-V12, Warnambool-V13), Tasmania (Smithton-T16), South Australia (Wattle Range-S22, Nangwarry-S23, Kangaroo Island-S25) and Western Australia (Nornalup-W30). These sites were chosen on the basis that they represented the lighter-textured and more acidic soils, characteristics known to enhance Cd transfer from soil to plants [12]. Soils (0-100 mm) were acidic with pH (water) varying from 5.0 to 6.1, extractable P concentrations [13] varied from 7 to 19 mg/kg, organic C ranged from 1.6 to 3.8%. Fertilizers were applied to the trial sites from 1992 to 1995 at rates, which varied from site to site, being determined on the basis of plant response to P at each site. A scaling factor (X), was used, on the basis that a rate of 4X at each site should achieve 90% of maximum yield response to water-soluble P fertilizer under optimum conditions with a good clover component in the pasture sward. The scaling factor varied from 5 to 10 kg P/ha per annum across the sites. Treatments sampled were control (unfertilized) plots, and from plots treated with SSP, NCPR and PAPR at P rates of 2X, 4X and 8X, with total P applied to these plots varying from 40 to 320 kg/ha between 1992 and 1995. A more detailed description of soil characteristics, trial treatments and experimental design is given in Simpson *et al.* [11].

### 2.1. Fertilizer analyses

Samples of SSP, North Carolina phosphate rock (NCPR), PAPR (an experimental batch manufactured by 50% acidulation of NCPR with sulfuric acid) and Hemrawein PR (Egypt) (used at site W30) were analysed for total Cd concentration by X-ray fluoresence spectroscopy [14]. Full chemical characteristics of the fertilizers are presented in Simpson *et al.* [11].

Fluorine concentrations were determined by boiling 1 g fertilizer for 10 min with 140 ml of 2.5 M HCl in the presence of 5% (w/v) aluminium potassium sulfate. The solution was then made to volume and the $F^-$concentration in an aliquot determined by ion selective potentiometry using neutral (pH 7.0) ammonium citrate buffer.

### 2.2. Herbage sampling and preparation

Preliminary analysis of Cd concentrations in mixed herbage from four sites indicated a large variability in Cd concentrations between replicate plots (data not shown). This was assumed to be due to a mixed composition of pasture between plots, with varying weed composition leading to variable Cd data. Hence, a single species was chosen for comparisons between fertilizer treatments.

Clover herbage was sampled from selected treatments at sites N4, N6, N7, N8, S22, S23, S25, T16, V12, V13 and W30.

Clover plants were sampled by collecting the terminal and last 2 to 3 sets of leaflets of a stolon from approximately 40 to 50 stolons in the sward. Collection was carried out wearing rubber or surgical gloves to prevent contamination of the plant surfaces by dust or soil. Plants with any noticeable soil contamination were avoided. All plant material was washed in deionized water after collection. Plant material was dried at 40-60°C before dispatch to the laboratory for analysis.

Mixed samples of herbage (grasses, legumes and weeds) were also collected from one site (S25) as part of the normal herbage harvest for dry matter determinations as described by Simpson *et al.* [11]. This herbage was also analyzed for Cd as described below. A visual rating of the degree of infestation of the pasture on each plot by capeweed (*Arctotheca calendula* L. Levyns) was also taken.

All herbage samples were transported in sealed plastic bags and analyzed at the laboratories of the CSIRO Division of Soils in Adelaide. Dried clover material was ground to pass a 250μm stainless steel sieve prior to Cd and F analyses.

### 2.3. Cadmium analysis

A subsample (0.5g) of the ground dried herbage material was digested by boiling for 2 hours at 130°C with 7 mL concentrated Aristar® $HNO_3$ acid. The solution was then made up to volume with dilute (1% w/v) $HNO_3$ acid and Cd concentration in the solution determined by graphite furnace atomic absorption spectrophotometry (GFAAS). Analysis of standard reference materials gave Cd concentrations not significantly different from certified values [6]. All herbage Cd concentrations are expressed on a dry weight basis. The limit of reporting for Cd in herbage material was 0.004 mg/kg.

### 2.4. Fluorine analysis

Concentrations of acid-labile F in herbage were determined as described by Stevens *et al* [15]. Briefly, dried herbage material (0.1g) was digested with concentrated $HNO_3$ acid in sealed containers using microwave heating. Fluoride concentrations in the digest solutions were determined using ion selective potentiometry. This method does not solubilize all F in plant material, particularly F retained in crystalline silicates [15] that is unlikely to be solubilized in the rumen after ingestion by grazing animals.

### 2.5. Soil analyses

Simpson *et al.* determined the general chemical characteristics of the sites [11]. Total Cd concentrations in soil were determined by digesting 0.5 g sample with 8 mL concentrated nitric and hydrochloric acids (3:1) on a steam bath for 2 h. Cadmium was also extracted from soils using 0.01 mol/L $CaCl_2$ solution. Soil (5 g) was shaken for 4 h with 25 mL extracting solution at 20°C. In preliminary experiments, 4 h was found to be a sufficiently long extraction time to allow all desorbable Cd to be released to solution. The suspensions were then centrifuged (20 min at 4000 RCF) and filtered through a 0.45 μm filter. Concentrations of Cd in extracts or digest solutions were determined using GFAAS.

### 2.6. Data analysis

To examine differences between fertilizers, the relationship between the concentration of Cd or F in the clover tops and fertilizer type and rate was analysed using a factorial design ANOVA for each individual site, excluding data for control (unfertilized plots). To examine the effect of fertilization on Cd concentrations, a separate completely randomized design ANOVA was performed for each fertilizer type at each site, including data for control plots. Differences in Cd concentrations between sites were determined by examining the relationship between Cd concentrations in clover from control (unfertilized) plots and soil (0-100mm) characteristics using a factorial ANOVA and step-wise forward multiple regression analyses. To normalize the skewed distribution of the data sets, data were transformed (square root or logarithm) where appropriate.

## 3. RESULTS

Cadmium and F concentrations in the fertilizers are shown in Table I. Hamrawein PR had the lowest Cd concentration and Cd/P ratio, while NCPR and PAPR (manufactured with NCPR) had the highest.

TABLE I. CONCENTRATIONS OF Cd AND F IN THE FERTILIZERS USED. SSP, SINGLE SUPERPHOSPHATE; NCPR, NORTH CAROLINA PHOSPHATE ROCK; PAPR, PARTIALLY ACIDULATED PHOSPHATE ROCK; HPR, HEMRAWEIN PHOSPHATE ROCK (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

| Fertilizer | Cd (mg/kg) | F (%) | P (%) | Cd/P (mg Cd/kg P) | F/P (g F/kg P) |
|---|---|---|---|---|---|
| SSP | 15.1 | 1.7 | 10.0 | 151 | 170 |
| NCPR | 40.3 | 3.5 | 12.9 | 312 | 271 |
| PAPR | 32.0 | 2.9 | 10.8 | 296 | 274 |
| HPR | 5.3 | 3.2 | 12.5 | 42 | 256 |

### 3.1 Herbage Cd concentrations

Data for treatment means are shown in Table II. Cadmium concentrations (treatment means) in the clover herbage ranged from 0.019 (site T16) to 0.405 mg/kg (site V13), with overall mean and median values of 0.189 and 0.187 mg/kg, respectively. Site mean Cd concentrations ranged from 0.027 mg/kg at T16 to 0.372 mg/kg at V13.

There was considerable variation between replicate plots for mean Cd concentrations in clover at most of the sites (data not shown), with the coefficient of variation (CV) for treatment mean values varying from 0.3% to 107%, with an overall mean CV across all sites and treatments of 20%. Site V13 had the least variability (mean CV 9%) and T16 the greatest (mean CV 35%).

Results from the ANOVA examining fertilizers and rate effects at each site are shown in Table III. At 4 of the 11 sites, rate of fertilizer applied had a significant effect on clover Cd concentrations, although variability between replicate plots was often high (>20%) (Fig. 1).

While higher rates of fertilizer addition resulted in higher Cd concentrations in clover at 3 sites (N6, N8, V12), at site N4 higher rates of fertilizer addition reduced clover Cd concentrations (Table III). Significant differences in Cd concentrations in clover due to fertilizer type were found at 5 sites. NCPR treatments had significantly higher Cd concentrations in clover compared to SSP at sites N6 and S25. PAPR treatments had significantly higher Cd concentrations in clover compared to SSP at sites N6, N7, S23, and S25. At site W30, Hemrawein PR treatments had significantly lower Cd concentrations in clover compared to both SSP and NCPR treatments (Table III).

Effects due to site accounted for the most variation in herbage Cd concentrations (Table IV). The relationship between the visual assessment of capeweed infestation and herbage Cd concentrations is shown in Fig. 2.

### 3.2. Herbage F concentrations

A National Instiitute of Standards Testing (NIST) certified reference material (NIST SRM 2695h) analysed by the acid digestion technique used here gave a value of 181±7 mg/kg, while the certified value is 277±27 mg/kg. The low recovery using acid digestion is similar to the result found by [15], and is probably due to the presence of insoluble fluorosilicates in the NIST standard. We preferred the acid digestion technique for this study as the acid-labile fraction is likely to be the fraction most readily bioavailable for grazing animals.

Herbage F concentrations were extremely low (<10 mg/kg), often near the detection limit for the analysis technique (1 mg/kg). There were no consistent effects due to either fertilizer type or rate (data not shown).

### 3.3. Relationships between herbage Cd concentrations and soil characteristics

Total and extractable Cd concentrations are shown in Table V. Clover Cd concentrations were unrelated to all soil chemical characteristics, except total (data not shown) and extractable Cd concentrations (Fig. 3), but this relationship was poor ($R^2<0.31$, $P = 0.12$).

## 4. DISCUSSION

The concentrations of Cd in the NCPR and PAPR fertilizers were high in comparison to the SSP and Hemrawein PR fertilizers. The Cd/P ratio in these fertilizers approached the current regulatory standard of 350 mg Cd/kg P in Victoria for phosphatic fertilizers [6]. The Cd concentration for NCPR found here is slightly lower than those found previously [5] and those reported in the literature [17]. Further Cd and P analyses for NCPR were undertaken at 1 and 2 other commercial laboratories, respectively, yielding Cd and P concentrations of 40.6 mg/kg and 11.9 and 10.2%, respectively. These data result in calculated Cd/P ratios for NCPR of 312 to 545 mg Cd/kg P. Some standardization of laboratory methods is needed to ensure Cd and P concentrations in fertilizers are accurately determined since legislation may prohibit certain products from the market based on Cd/P ratios. It is evident that the Cd/P ratio of NCPR falls close to the current Victorian regulations. Other States are in the process of adopting regulations for Cd in fertilizers, which are likely to be similar to the Victorian levels.

Fertilizer type had a significant effect on clover Cd concentrations at 5 sites, with SSP-treated plots (or Hemrawein PR-treated plots at site W30) having lower Cd concentrations in clover than NCPR- and PAPR-treated plots. However, the significant differences between fertilizers were small and variability between replicate plots was high. Where present, differences between treatments were generally in line with Cd concentrations in the fertilizers, SSP treatments having lower Cd concentrations in clover than PAPR or NCPR treatments.

The treatments sampled represented the upper end of the fertilizer rates commonly used by most grazers (up to 8 times maintenance), yet only small differences in Cd concentrations in clover herbage resulted. Hence it can be concluded that a switch from SSP, containing approximately 150 mg Cd/kg P, to NCPR or PAPR (which contain twice this Cd concentration), will only have a small impact on clover Cd concentrations in the short and medium term. In the long-term however, the higher Cd fertilizers will obviously allow Cd concentrations in soil to increase more rapidly with time with an associated greater risk of increasing Cd concentrations in the herbage and in grazing animals.

As fertilizer type was not independent of fertilizer Cd concentration, no conclusions can be drawn regarding the effect of fertilizer type *per se* on Cd uptake by clover. For example, the availability of Cd present in NCPR or PAPR cannot be assessed relative to Cd present in SSP in these experiments. There are few other data to assess the effect of fertilizer type on plant Cd concentrations. McLaughlin *et al.* [18] examined the effect of 4 types of phosphatic fertilizer (SSP, RPR, diammonium phosphate and monoammonium phosphate) having similar Cd/P ratios on Cd uptake by irrigated potatoes, and found no significant effects. The chemical form of Cd in SSP, RPRs or PAPRs has not yet been clearly identified. Williams and David [1] found granules of SSP in moist soil lost all of their water-soluble P content and still retained 60% of their original Cd content. Williams and David [1] found that concentrations of Cd in the water extracts of the soil were approximately proportional to the soil Ca concentrations, indicating Cd was associated with Ca in both the phosphate and sulfate components of the fertilizer. While there is no evidence to indicate the form of Cd in RPRs, Cd in the rock is presumably substituted for Ca in the crystal lattice (Cd has a similar ionic radius and charge to Ca). The alkaline nature of RPRs [19] may reduce Cd dissolution from the crystal lattice and increase Cd sorption close to the dissolving RPR granule, as Cd sorption to soil is strongly increased as solution pH increases [20]. Further experimentation is needed to determine if Cd in RPR fertilizers is less available to crops than Cd in water-soluble fertilizers.

Fluorine concentrations in all herbage samples were within the range (2-20 mg F/kg) generally considered as background for non-accumulator plants grown in soil free from anthropogenic F

TABLE II. CONCENTRATIONS OF CADMIUM (mg/KG DRY WEIGHT) IN CLOVER SHOOT MATERIAL AT THE SITES. N4, N6, ARMIDALE; N7, YASS; N7, TARAGO; V12, BENALLA; V13, WARNAMBOOL; T16, SMITHTON; S22, WATTLE RANGE; S23, NANGWARRY; S25, KANGAROO ISLAND; W30, NORNALUP. VALUES ARE TREATMENT MEANS (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16]).

| Treatment | Rate | N4 | N6 | N7 | N8 | S22 | S23 | S25 | T16 | V12 | V13 | W30 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | | 0.124 | 0.074 | 0.215 | 0.158 | 0.253 | 0.281 | 0.237 | | 0.257 | 0.404 | 0.061 |
| SSP | 2X | 0.154 | 0.066 | 0.190 | 0.096 | 0.186 | 0.271 | 0.187 | 0.024 | 0.232 | 0.330 | 0.084 |
| SSP | 4X | 0.165 | 0.068 | 0.214 | 0.103 | 0.154 | 0.221 | 0.177 | 0.020 | 0.273 | 0.346 | 0.123 |
| SSP | 8X | 0.172 | 0.081 | 0.255 | 0.112 | 0.187 | 0.256 | 0.188 | 0.057 | 0.291 | 0.393 | 0.148 |
| NCPR | 2X | 0.185 | 0.084 | 0.195 | 0.108 | 0.194 | 0.264 | 0.313 | 0.021 | 0.240 | 0.400 | 0.112 |
| NCPR | 4X | 0.167 | 0.084 | 0.214 | 0.076 | 0.207 | 0.225 | 0.266 | 0.020 | 0.217 | 0.405 | 0.111 |
| NCPR | 8X | 0.143 | 0.109 | 0.208 | 0.126 | 0.262 | 0.240 | 0.303 | 0.021 | 0.304 | 0.356 | 0.146 |
| PAPR | 2X | 0.174 | 0.078 | 0.271 | 0.091 | 0.170 | 0.277 | 0.303 | 0.019 | 0.239 | 0.381 | 0.079 |
| PAPR | 4X | 0.207 | 0.092 | 0.240 | 0.127 | 0.176 | 0.296 | 0.241 | 0.031 | 0.271 | 0.356 | 0.078 |
| PAPR | 8X | 0.129 | 0.078 | 0.288 | 0.151 | 0.192 | 0.329 | 0.222 | 0.035 | 0.302 | 0.352 | 0.072 |
| Site means | | 0.162 | 0.081 | 0.229 | 0.115 | 0.198 | 0.266 | 0.244 | 0.027 | 0.263 | 0.372 | 0.101 |

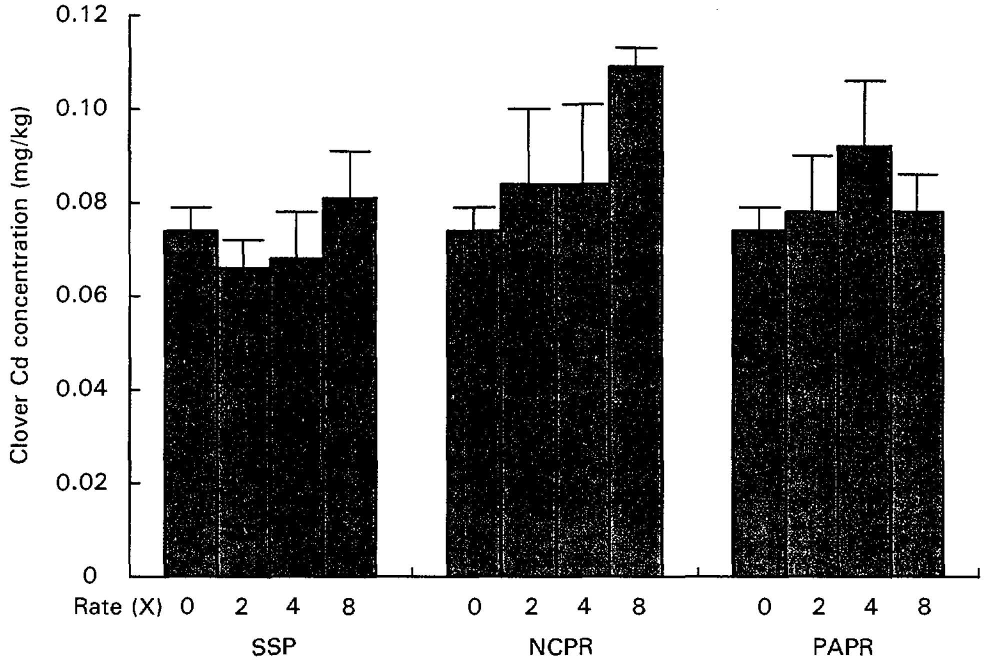

*Fig. 1. Effect of addition of SSP, NCPR, and HPR on Cd concentrations in clover shoots at site N6 (Reprinted with the permission of CSIRO Publishing, [16]).*

TABLE III. SUMMARY OF ANOVA RESULTS FOR EACH SITE ANALYSED USING A FACTORIAL DESIGN (RATE*FERTILIZER) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

| | ANOVA[1] | | |
|---|---|---|---|
| Site | Rate | Fertilizer | Rate*Fert. |
| N4 | ** | n.s. | n.s. |
| N6 | * | *** | * |
| N7 | n.s. | ** | n.s. |
| N8 | * | n.s. | n.s. |
| V12 | ** | n.s. | n.s. |
| V13 | n.s | n.s. | n.s. |
| T16 | n.s. | n.s. | n.s. |
| S22 | n.s. | n.s. | n.s. |
| S23 | n.s. | * | n.s. |
| S25 | n.s. | ** | n.s. |
| W30[2] | n.s. | * | n.s. |

[1] n.s., not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.
[2] no PAPR at site W30, data for Hemrawein used.

TABLE IV. RELATIONSHIP OF SOIL CHARACTERISTICS (0-100 mm STRATUM) TO CLOVER Cd CONCENTRATIONS ACROSS ALL SITES (CONTROL TREATMENTS ONLY) (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

| Source | Degrees of Freedom | Sum of Squares | Mean Square | F value | Probability[1] |
|---|---|---|---|---|---|
| Rate (A) | 2 | 0.047 | 0.023 | 2.12 | ns |
| Fertilizer (B) | 2 | 0.134 | 0.067 | 6.09 | ** |
| Site (C) | 7 | 23.683 | 3.383 | 306.95 | *** |
| Block (D) | 2 | 0.033 | 0.017 | 1.51 | ns |
| A*B | 4 | 0.070 | 0.018 | 1.59 | ns |
| A*C | 14 | 0.198 | 0.014 | 1.59 | ns |
| B*C | 14 | 0.264 | 0.019 | 1.28 | ns |
| A*B*C | 28 | 0.240 | 0.009 | 1.71 | ns |
| Residual | 134 | 1.477 | 0.011 | 0.78 | |
| Total | 207 | 26.147 | | | |

[1] n.s., not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$.

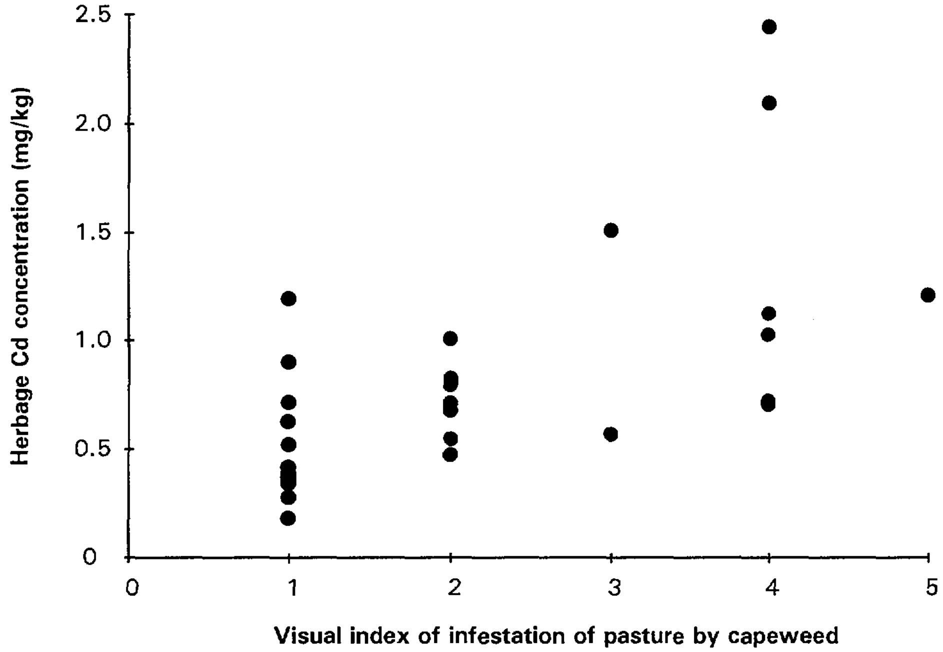

*Fig. 2. Relationship between herbage Cd concentration and visual index of infestation of pasture by capeweed (Arctotheca calendula L. Levyns) at site S25 (Reprinted with the permission of CSIRO Publishing [16]).*

TABLE V. TOTAL AND EXTRACTABLE ($0.01$ mol/L $CaCl_2$) Cd CONCENTRATIONS IN UNFERTILIZED SOILS (REPRODUCED WITH PERMISSION OF CSIRO PUBLISHING [16])

| Site | Extractable-Cd (μg/kg) | Total-Cd (μg/kg) |
|---|---|---|
| N4 | 5.3 | 59 |
| N6 | 2.8 | 65 |
| N7 | 10.7 | 46 |
| N8 | 10.5 | 42 |
| S22 | 13.5 | n.d.[1] |
| S23 | 12.5 | 58 |
| S25 | 4.0 | 52 |
| T16 | 1.2 | n.d. |
| V12 | 15.0 | 96 |
| V13 | 10.2 | 227 |
| W30 | n.d. | n.d. |

[1] n.d., not determined.

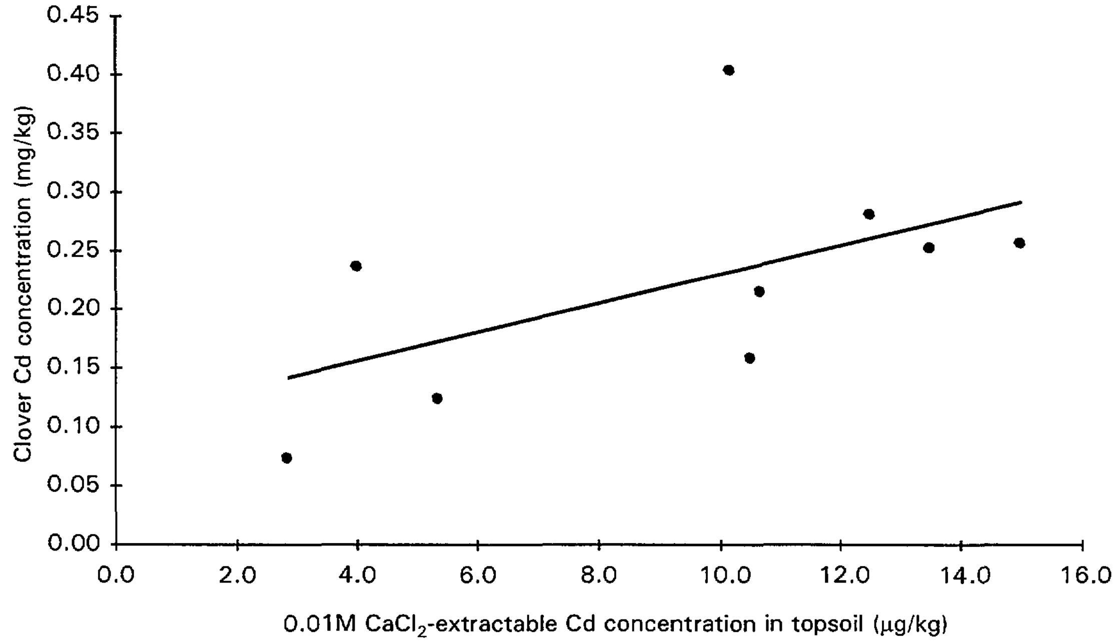

*Fig. 3. Relationship between herbage Cd concentration and visual index of infestation of pasture by capeweed (Arctotheca calendula L. Levyns) at site S25 (Reprinted with the permission of CSIRO Publishing [16]).*

contamination [21], and were unaffected by fertilizer type or rate. Plant uptake of this element is unlikely to lead to problems for grazing animals in most soils [22]. It has been suggested that the maximum level for F in herbage to protect livestock health should be 35 mg/kg or less [23], with the concentrations found in this study being well below this level. However, ingestion of soil by animals or ingestion of fertilizer material remaining on herbage after heavy topdressing could affect animal health depending on soil and fertilizer F concentrations [24], so that F in fertilizers may require more careful management in the long term. For every kg P applied up to 250 g F are applied per hectare in phosphatic fertilizers [8], with RPRs generally having higher F concentrations than SSP or high analysis P fertilizers. This F does not readily leach and, like Cd, is therefore slowly accumulating in all fertilized agricultural soils [25]. Ingestion of soil may not be a problem currently in terms of F intake by grazing animals, but as F concentrations in the top few centimetres of soil increase due to fertilization, this could pose problems in the future. With a fertilization regime of 10 kg P/ha every 2 years, a F content in fertilizer of 250 g F/kg P, a F concentration in soil of 200 mg/kg [25], and a soil bulk density (0-2 cm) of 1000 kg/m$^3$, F concentrations would double in 30 years in the top 2 cm of soil. Negative impacts on animal health are difficult to predict and depend to a large extent on patterns of soil ingestion, which is affected by ground cover. Soil ingestion may be significant over dry summer periods in southern Australia, at high stocking rates, and where drought or other stresses (e.g. acidity, salinity, nutrient deficiencies) reduce ground cover. As far as we are aware, there are no data on soil ingestion in southern Australia under field conditions representative of commercial properties. However, data from New Zealand [26] indicate soil ingestion by sheep grazing perennial pastures ranged from 11 to 275 g/day, peaking in winter, presumably due to soil splash, while soil ingestion by dairy cattle may be over 600 g/day [27]. In the Mediterranean climate of southern Australia, it soil ingestion is most likely during summer and autumn when pasture cover is at a minimum, and amounts of soil ingestion may be greater than those reported by [26]. Using a soil intake figure for 1 year old sheep of 250 g/day [26], F concentrations in herbage and soil of 10 and 300 mg/kg, and a DM intake of 1000 g/day [26], ingestion of soil and pasture would provide 75 and 10 mg F/day, respectively. Soil F concentrations are therefore critical in determining F intake by grazing animals, and the continued accumulation of F in grazing soils may pose some concern from an animal health viewpoint where significant ingestion of soil is likely to occur.

It is unknown if the solubility of F in RPR and SSP differs, but it is likely that the F present in SSP is present as $CaF_2$, which is likely to be more soluble in soil than the F in phosphate rocks. It is therefore possible that with continued use of RPRs the amount of (water-insoluble) F remaining on herbage or at the soil surface may be greater than with SSP, where F may more readily penetrate into the soil. If undissolved RPR remaining on the soil surface is ingested in significant quantities by animals, fluorosis problems could result. However, there is little information available on the bioavailability of F compounds found in SSP and phosphate rock once ingested. Zipkins and Likins [28] and Tsunoda *et al.* [29] found that gastrointestinal absorption of F by rats and humans depended on the forms of F ingested (i.e. $CaF_2$, NaF, $KPF_6$).

Clover was chosen as the indicator species in this study as clover is the most desirable component of a mixed pasture sward and grazers generally manage their pastures to maximize (within limits) the percentage clover component in the pasture. The clover Cd concentrations found in this study fall within the range reported by Roberts *et al.* [3] for Cd in mixed legume herbage at 398 sites in New Zealand. Grasses tend to have lower Cd concentrations than legumes, while weed species usually have higher Cd concentrations than both grasses or legumes [2, 3]. As expected, there appeared to be some relationship between the visual assessment of capeweed infestation of the pasture and herbage Cd concentrations at site S25 (Fig. 2), which confirms earlier findings with this weed species [2,30]. Hence, infestation of pastures by capeweed will also lead to higher concentrations of Cd in the herbage ingested by the grazing animals. Thus, the impact of fertilizer type and grazing management on pasture composition is likely to have a much greater effect, in the short and medium term (up to 10 years), on Cd ingested by grazing animals rather than the Cd concentration in the fertilizer. Hence, management of Cd accumulation in grazing systems in Australia needs to be a combination of measures, which includes control of pasture composition to reduce Cd uptake by animals in the short-term, and use of low Cd fertilizers to control Cd accumulation in the long term.

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