PT423
A national strategy to reduce cadmium in potatoes

M McLaughlin
CSIRO Land and Water

Know-how for Horticulture™

PT423
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Level 6
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Telephone: (02) 9418 2200
Fax: (02) 9418 1352
E-Mail: hrdc@hrdc.gov.au

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A national strategy to reduce cadmium in potatoes

Dr M.J. McLaughlin

CSIRO Land and Water / CRC for Soil & Land Management,
Glen Osmond, South Australia, 5064

FINAL REPORT

HORTICULTURAL RESEARCH AND DEVELOPMENT CORPORATION
PROJECT PT423, January 1999

CSIRO LAND and WATER

HRDC Project PT423

Dr M. J. McLaughlin
CSIRO Land and Water
PMB 2, Glen Osmond
SA 5064

Tel: 08 8303 8433
Fax: 08 8303 8565
Mike.McLaughlin@adl.clw.csiro.au

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1. INDUSTRY SUMMARY

A Project funded by the **Horticultural Research and Development Corporation (HRDC)** was conducted between July 1994 to June 1998, to devise techniques to control cadmium accumulation in potato tubers. The specific objectives of the study were to investigate the following:

- To undertake an industry extension program, to increase grower awareness of the cadmium issue and communicate research findings to date,
- to develop a predictive test for growers to identify high risk soils and environments in relation to cadmium quality of tubers,
- identify, test and evaluate amelioration strategies to overcome the problem of high cadmium concentrations in potato tubers in certain regions of southern Australia identified previously as most likely to produce potato tubers exceeding the maximum permissible concentration of 0.05 mg cadmium kg^{-1} fresh weight,
- to investigate the residual value of fertilizer cadmium in soils and determine the long-term availability of cadmium in soils.

Both field and glasshouse experiments were conducted, with all State Departments of Agriculture in southern Australia being involved at various stages of the investigation. Work focussed in southern Australia as this region has the greatest incidence of high cadmium concentrations in potato tubers. The original objective of studying residual value of fertilizer cadmium in soils, to be studied by Agriculture WA, was dropped when this organisation withdrew from the project as a result of an internal reorganisation.

INDUSTRY EXTENSION

- A glossy 8-page brochure entitled "Managing Cadmium in Potatoes for Quality Produce" was released through the CRC for Soil and Land Management in September 1996 (Appendix 11).

- Six thousand copies of the brochure were distributed nationally to growers, advisers, State Departmental representatives and other interested groups. Feedback from the brochure has been excellent, with several requests from FIFA and State Departments for a second print run.

- Several meetings were held with the Australian Potato Industry Council (APIC) and the Australia New Zealand Food Authority (ANZFA). The result was that APIC's submission to ANZFA to have the maximum permitted concentration for cadmium in potatoes revised upwards to 0.1 mg kg^{-1} was successful. A general review of all food cadmium regulations by ANZFA followed, with submissions also being made to these.

- A total of nine (9) presentations to grower/industry groups and sixteen (16) presentations to scientific/regulatory groups were made during the course of the project.

- The principal investigator assisted the Fertilizer Industry Federation of Australia (FIFA) with a training video "Heavy Metals in Fertilizers" released in November 1996. This is being used to train fertilizer industry distributors and representatives and raise awareness within the industry of heavy metal issues.

- A glossy 4-page brochure entitled "Cadmium in potatoes – managing the risk from saline irrigation water" will be released as an insert in "Eyes on Potatoes" in March 1999 (Appendix 12).

PRE-PLANT AND POST-PLANT TESTING TO DETERMINE CADMIUM RISK

- Soils and irrigation waters were analysed at one hundred and thirty four sites in the major potato production areas in Western Australia, South Australia, Tasmania, Victoria and New South Wales.

- A range of pre-plant soil and irrigation water tests were assessed for their ability to predict tuber cadmium concentrations at harvest, with a simple measure of irrigation water electrical conductivity (EC, a measure of water salinity) prior to planting being the best test. For predictive purposes, concentrations of cadmium in soil were less important than a measure of water salinity.

- When irrigation water EC exceeded 3.0 dS m^{-1}, there was a 50% probability that tubers grown with this water would exceed the new Cd MPC (0.1 mg cadmium kg^{-1} fresh weight).

- Testing of the crop after planting is a valid way to determine tuber cadmium concentrations at harvest. Plant top material should not be sampled, as cadmium concentrations vary markedly with stage of growth in shoots, but not in tubers. Small tubers, 10-20 mm length, should be sampled from 60 days onwards to estimate harvested crop quality.

- Sulfate salinity in irrigation water was found unlikely to have the same effect as chloride in increasing tuber cadmium concentrations.

SOIL TREATMENTS TO REDUCE TUBER CADMIUM CONCENTRATIONS

- A wide range of potential ameliorants were tested for their ability to reduce tuber cadmium concentrations. Materials were low-cost and many were sourced from urban and industrial waste streams.

- In glasshouse experiments, several promising ameliorants were identified, with large reductions in tuber cadmium concentrations found using copper-rich water treatment residuals (solid waste materials produced after treatment of water to potable standard) as a soil ameliorant.

- Field validation trials of ameliorants confirmed that liming is ineffective in reducing tuber cadmium concentrations. Several ameliorants were able to reduce tuber cadmium concentrations under commercial conditions, including copper and zinc salts, a natural clay, magnesite (magnesium carbonate) plus zinc, and ferrous smelter waste.

- Disappointingly, while reductions in tuber Cd concentration due to soil amelioration were statistically significant, the magnitude of the changes were not large enough to prove agronomically useful.

- Liming is still not recommended as a pre-plant soil treatment to reduce tuber cadmium concentrations. There are some indications that liming should be performed several years prior to potato growth to ensure reductions, rather than increases, in tuber cadmium concentrations.

- Given the difficulty in modifying crop cadmium uptake under field conditions, and the poor performance of all ameliorants, detection and avoidance of saline soils and irrigation waters is imperative if crop cadmium quality is to be assured.

2. TECHNICAL SUMMARY

PRE-PLANT AND POST-PLANT TESTING TO DETERMINE CADMIUM RISK

- Soils and irrigation waters were analysed at one hundred and thirty four sites in the major potato production areas in Western Australia, South Australia, Tasmania, Victoria and New South Wales.

- Irrigation waters were analysed for electrical conductivity (EC), major cations and anions. Cadmium was extracted from soil using aqua regia (1:3 HNO_3:HCl), EDTA (ethylenediamine-N,N,N',N'-tetraacetate), DTPA (diethylene-triamine-pentaacetate), 0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$, 0.1 M $CaCl_2$ and 1.0 M NH_4NO_3. The preferred test procedure was validated in a subsequent sampling and analysis program at 39 sites.

- Irrigation water quality (EC or Cl concentration), measured prior to planting, explained the greatest variation in tuber Cd concentrations. Of the soil test procedures, only Cd extracted by 0.01 M $CaCl_2$ significantly improved the predictive capacity of water EC. These two measures explained over 55% of the variance in tuber Cd concentrations.

- The data set were transformed to generate a probability curve for exceeding Cd concentrations of either 0.05 or 0.1 mg kg^{-1} FW, the latter being the current maximum permitted concentration (MPC) in Australia for potato tubers.

- The observation that soil Cd concentration had little influence on predicted tuber Cd concentrations can be attributed to a number of possible factors. Potatoes are grown on mostly light textured soils, with reasonable fertilizer (and hence Cd) histories. Hence soil and management variability, normally addressed by a soil test, was not fully expressed. Furthermore, the number of data points representing high Cd concentrations in tubers (around 0.1 mg kg^{-1} fresh weight) was not large, so that these soils could have had similar chemical characteristics. In this situation, soil Cd would be unrelated to tuber Cd concentrations.

- Investigations of Cd, and other element, uptake by potatoes in relation to stage of plant growth confirmed that plant shoot material is a poor indicator of tuber Cd concentrations. Cadmium concentrations in plant shoots increased with plant age, while tuber Cd concentrations remained fairly constant with growth stage.

- Cadmium concentrations in potato shoot material was approximately ten times higher than in tubers.

- Investigations of uptake of Cd complexed by sulfate indicated that while this ion complexes Cd in the soil solution and appears to be equally available as the free aquo Cd ion, addition of sulfate to soils in irrigation does not increase plant uptake of Cd. This is hypothesised to be due to the effect of sulfate in increasing Cd retention by soil particles.

- Investigations of the uptake of Cd complexed by model organic compounds indicated that plants do not only take up the free aquo ion from solution. Large molecular weight Cd-organic complexes appear to cross the root membrane and are translocated to plant shoots. This contradicts the free ion activity model for metal uptake by plants, which states that only free (uncomplexed) metal ions are biologically active.

SOIL TREATMENTS TO REDUCE TUBER CADMIUM CONCENTRATIONS

- A range of soil ameliorants was tested to assess if tuber Cd concentrations could be markedly reduced in saline water/soil areas. The basis for the amelioration treatments was to either increase the sorption of Cd by soil (using clay materials), or to block Cd uptake by the plant (using copper and zinc treatments). Magnesite ($MgCO_3$) was also included as a low-calcium liming agent, with the aim to determine if lime-induced increases in crop Cd concentrations, observed in this and previous projects, was due to calcium effects on Cd desorption.

- The clay materials were a mixture of industrial and urban by-product materials (coal-washing clays, water treatment residuals (WTRs), industrial clays (bentonites and zeolite), natural mined clays, by-products slags, dusts and muds from the ferrous- and alumina-smelting industries, sewage biosolids and sand-washing clays. The WTRs were derived from both Fe and Al-based chemical flocculation processes for drinking water treatment, as well as one material incorporating activated carbon (Alum+C WTR).

- All the clay materials markedly increased the sorption capacity of soil for Cd, but in glasshouse experiments the greatest reductions in Cd uptake were obtained with copper-rich WTRs. It was hypothesised that copper in these materials was blocking Cd uptake by the potato roots. Copper phytotoxicity also occurred concomitant with the large (>80%) reductions in tuber Cd concentrations.

- Assessment of these materials under field conditions, as well as assessement of the ability of low rates of copper sulfate alone to reduce Cd uptake, was carried out at three field sites in the Upper South East and Adelaide Hills regions of South Australia.

- None of the ameliorants adversely affected tuber yield, nor did they produce tubers of unacceptable chemical quality (excepting Cd).

- Copper and zinc treatments reduced Cd concentrations at all sites, as did magnesite plus Zn, a natural subsoil clay and a by-product dust from the ferrous smelter industry. Reductions were not sufficient to lower tuber Cd concentrations to below the MPC at the two sites in the Upper South East.

- Salinity effects again dominated differences between sites in terms of Cd accumulation by tubers, indicating the importance of accurate and timely predictive testing of soil and irrigation water quality.

3. CONCLUSIONS/RECOMMENDATIONS

- A widespread system of testing of irrigation waters and soils should be adopted by growers prior to planting of potato crops. In this way, salinity hazards can be identified early, and crops grown in areas having better quality water, and lower concentrations of extractable cadmium in soil.

- Post-plant testing of small early tubers (60 day) for cadmium should be adopted where cadmium problems are identified. Analysis of shoot material should not be used as a diagnostic tool.

- If cadmium is suspected as a problem, lime should not be applied to soils at planting, but several years earlier in the crop rotation. Low calcium materials should be used e.g. dolomitic lime or magnesite.

- Where cadmium is suspected to be a problem, low rates of zinc as zinc sulfate, or copper as copper sulfate, could be applied to the soil and incorporated prior to planting. Care needs to be exercised to avoid crop damage by use of high copper/zinc application rates.

4. DIRECTIONS FOR FUTURE RESEARCH

- Given the difficulty in modifying cadmium concentrations in tubers through amelioration of the soil, research should focus on a more fundamental understanding of cadmium uptake by the potato plant (currently under way in HRDC PhD studentship project 96020). This should allow development of new strategies to block cadmium uptake at the root surface.

- Molecular techniques to modify cadmium uptake by the potato plant should be investigated, either to block cadmium transport in the phloem to the developing tuber, or to sequester cadmium in the shoots.

- The long-term availability of cadmium in soils, an objective not addressed by this project as Agriculture WA withdrew their participation, still requires investigation. Cadmium is continually being added to soils, so that knowledge of the eventual fate of this cadmium is essential.

5. GRANT DETAILS 1994-98

1. PROJECT TITLE A national strategy to reduce cadmium accumulation in potato crops

Project Number PT(96)423

2. Organisation

CSIRO Land and Water (formerly Division of Soils)
PMB 2
Glen Osmond
SA 5054

Administration contact

Name	Ms Kathy Heinze
Title	Business Development Manager
Salutation	Kathy
Phone	08 8303 8696
Fax	08 8303 8590
Email	Kathy.Heinze@adl.clw.csiro.au

3. Project Chief Investigator

Name	Dr Mike McLaughlin
Title	Principal Research Scientist
Salutation	Mike
Phone	08 8303 8433
Fax	08 8303 8565
Email	Mike.McLaughlin@adl.clw.csiro.au

4. Project Start 01 July 1994
Project Completion 30 June 1998

5. Project Cost

Year	Amount($)
1994/95	139,938
1995/96	140,818
1996/97	129,730
1997/98	93,277
Total	503,763

6. Keywords Potatoes, cadmium, soil testing, ameliorant

7. Objectives for each year of the project

The objectives of the project were;

Year 1

To commence grower education programs to ensure the industry is aware of the current research findings. To commence development of a robust and reliable predictive test to allow growers to avoid soils/environments where potato production is likely to produce tubers exceeding the MPC for cadmium. To commence research on residual value of fertilizer cadmium in soils. To determine why lime is ineffective in reducing tuber cadmium

Year 2

To complete development of the predictive test for cadmium to allow identification and avoidance of environments posing a cadmium "hazard" and commence research on ameliorative options where cadmium is identified as a problem.

Year 3

To complete research of residual value of fertilizer cadmium in soils, identify soils where cadmium is likely to pose hazards in the future given current fertilizer cadmium inputs and complete studies of new ameliorative strategies to reduce cadmium uptake by crops in problem areas. To ensure cadmium issues are incorporated in decision support software assisting growers with crop nutrition.

Year 4

Field testing of promising new ameliorants. The most promising ameliorants from Year 3 be investigated at 3 field sites in 1997/98 - two sites in the Upper South East of South Australia and one in the Adelaide Hills.

8. Milestones

Task	Task Description	Start	End
1	Appoint staff	01/07/94	30/09/94
2	Organise structure of soil/water/plant sampling program	01/07/94	30/09/94
3	Define sampling strategy for predictive test	01/07/94	30/09/94
4	Pre-plant sampling of all sites for cadmium test	01/08/94	31/03/96
5	Produce grower information sheet on cadmium in potatoes	01/10/94	31/12/95
6	Field/glasshouse experiments to assess liming effectiveness	01/10/94	31/12/95
7	Analysise soils/tubers/waters for predictive test	01/01/95	30/06/96
8	Incorp. cadmium information into decision support system	01/07/95	30/06/96
9	Prepare reports and publications - review meeting	01/01/96	30/06/96
10	Field experiments with new amelioration technology	01/08/96	31/03/97
11	Prepare reports, cadmium update brochure and publications	01/10/96	30/06/97
Additional milestones for proposed extension of project			
12	Glasshouse expts. - effect of sludge Cu on crop/soil quality	01/07/97	31/03/98
13	Field trials (3) to evaluate new amelioration technology	01/10/97	30/04/98
14	Assessment of commercial applicability of new technology	01/05/98	30/06/98

9. Industry Financial Support

Levy paying industries	Total Contribution
Potato	$251,822

6. DETAILS OF PROJECT

The Problem

(i) Nature of problem

There is worldwide concern for health issues related to food purity. Many countries are legislating both to limit the level of potentially toxic elements in foodstuffs, and to limit the concentration of these elements in soil amendments such as fertilizers, liming materials and organic wastes. In Australia the NFA had legislated to restrict the cadmium concentration in vegetables to less than 0.05 mg kg^{-1} wet weight (in 1994). Potatoes and other vegetables, notably the root and leafy vegetables, constitute an important part of the Australian diet (about 100 kg $person^{-1}$ $year^{-1}$) and all have cadmium concentrations well above the norm of most Australian foods (excepting animal offal products).

(ii) Circumstances giving rise to the problem.

The problem has arisen in two ways, one practical and the other perceptual. Firstly, the high requirement of many potato crops for phosphorus, combined with the high content of cadmium in phosphates from our traditional island phosphate rock sources, and the need of potatoes in particular for soils of moderately light texture coupled with irrigation with poor quality water, have created conditions allowing elevated cadmium levels in those crops. Secondly, world-wide concern for environmental purity has encouraged governments to impose stricter controls on soil amendments containing toxic metals.

Strict controls by means of MPC values have been introduced into the legal framework to guard against a perceived risk to public health but do provide a possible constraint on some commercial production if enforced strictly.

(iii) Procedure

The project was a national project involving CSIRO Land and Water (formerly Divisions of Soils) and Division of Horticulture and the CRC for Soil and Land Management, State Departments of Agriculture in Western Australia and South Australia, and liaison with State Departments in Tasmania, Victoria and New South Wales. The project was an extension of current work on cadmium accumulation in potatoes funded under HRDC projects VG 006 (CSIRO), PT212 (National), PT102 (WADA) and PT107 (SARDI) which were due for completion in 1994. At the request of HRDC a combined project proposal was developed which coordinated activity in various organisations into one umbrella project. Work in the above projects and project V/001 l/Rl (Tas. DPI) indicated that;

l) High cadmium concentrations in potato tubers are a regional phenomenon, with tubers cadmium concentrations exceeding the current maximum permissible concentration (MPC) of 0.05 mg kg-1. Violations of the MPC generally occur in WA, SA, Victoria and to a lesser extent in Tasmania, New South Wales and Queensland. The levels of cadmium found in tubers are over 4 times the MPC in certain areas of SA and up to double the MPC in WA and Victoria.

2) High tuber cadmium concentrations tend to be related to (in order of importance) soil chloride concentrations, potato cultivar, soll zinc status and possibly soil acidity.

3) The major ameliorative measure to reduce cadmium uptake by crops traditionally suggested overseas (i.e. liming of soil to reduce soil acidity) has met with limited success in the field in Australia to date, despite encouraging results from glasshouse liming trials.

4) Potato variety has been found to have a marked influence on cadmium concentrations in tubers and some advanced breeding material shows further potential to reduce cadmium uptake.

5) The only fertilizer management strategies to show minimal success in reducing tuber cadmium concentrations (at that time) were zinc applications and changing potassium fertilizer to the sulfate form where water quality was already good.

From a review of current research opportunities discussed at the recent HRDC-sponsored cadmium workshop for the Australian Potato Industry, the following questions were identified as requiring investigation and the proposed project was structured around these identified priority components;

(iv) Components

1) A need was highlighted for Industry extension/education, in collaboration with Industry.

2) Can a predictive soil test be developed to identify problem situations prior to crop planting so that farmers can avoid problem soils/environments?

3) How quickly does the plant-availability of cadmium decline with time? As most soils receive more cadmium in fertilizer than is taken off in produce, it is critical that we determine how long the cadmium added to soil in fertilizer remains in a plant available form. This question is critical in the discussion of future limits for both cadmium in plants, soils and fertilizers.

4) Why has the use of lime in reducing tuber cadmium concentrations been unsuccessful to date in Australia and can other soil ameliorants or amelioration technology be used?

(v) Modification to work plan during project

A number of factors led to changes in the original workplan of the project over the duration of the project.

1) Reorganisation of the administration and structure of Agriculture WA resulted in Component 3 being dropped from the project and unused funds from Agriculture WA returned to the project. This objective was pursued under collaboration with the CRC for Soil and Land Management (Dr Rebecca Hamon).

2) A lack of suitable sites for liming trials in South Australia (due to an extensive program of liming of pastures in the Adelaide Hills region in 1995 and 1996) necessitated refocussing of this component to identifying new ameliorative measures, other than liming, for reducing tuber cadmium concentrations. This was felt to be more focussed to grower needs, rather than determining why liming is ineffective.

3) As a result of work under (2) above, the project was extended for a fourth year to test in the field under commercial conditions the promising ameliorants identified by glasshouse experimentation.

4) Additonal experiments were performed to examine the timing of cadmium uptake by potatoes, in relation to other nutrients (Section 10, Appendix 2). This was needed to determine if plant tests could be used as an indicator of tuber cadmium uptake, and also to determine if management measures to control cadmium uptake needed to be pre-plant or could be during the growth cycle. This component of the project also simultaneously provided significant amounts of data for the CROPTEST nutritional decision support software developed by SARDI.

5) With assistance from visiting scientists and students from overseas institutions, several experiments were conducted to investigate the impact of sulfate salinity on cadmium uptake by plants. Similarly, experiments were performed on how organic molcules affect cadmium uptake by plants as part of a study tour to the Catholic Univeristy, Leuven, Belgium, by the Principal Investigator in 1996 (Section 10, Appendices 3 and 5).

7. CSIRO AND COLLABORATING PERSONNEL INVOLVED IN THE PROJECT

CSIRO

Dr M.J.McLaughlin
Dr R. Correll
Ms M.K.Smart
Ms G. Cozens
Mr S. Andrew
Ms K.T.Sellar

SA Research and Development Institute/Primary Industries SA

Mr Norbert Maier
Mr Chris Korczynski

Dept. Soil Science, The University of Adelaide

Dr Cameron Grant
Ms Suzanne Macks

WADA

Mr Alan McKay

Victorian Dept. Agriculture

Mr Rene de Jong

Tasmanian Dept. Primary Industries and Fisheries

Dr Leigh Sparrow

NSW Agriculture

Mr Stephen Wade

8. SCIENTIFIC OUTCOMES

To date 13 papers have been published in internationally refereed books, journals or conference proceedings during the course of the project. A further 4 journal papers are currently in preparation.

Six conference papers/abstracts have been presented during the course of the project.

Furthermore, a book titled "Cadmium in Soils and Plants" will be published by Kluwer Academic Press in 1999 and forms part of the outcomes of this project.

Book chapters/journal papers published/conference papers submitted during the course of the project

Some of the papers below have part of their data derived from the preceding project, Project VG006 "Effect of soil conditions and fertilizers on cadmium in vegetables - a national approach", but were written and publisheed during the period of this project.

Book chapters

1) McLaughlin, M.J., Smolders, E. and Merckx, R. 1998. Soil:root interface: Physicochemical processes. Pp. 233-277 In "Soil Chemistry and Ecosystem Health." Ed. P.M. Huang. Soil Science Society of America, Madison, WI.

2) McLaughlin, M.J., Parker, D.R. and Clarke, J.M. 1998. Metals and micronutrients: food safety issues. In Special Book Publication of Field Crops Research, Eds. R. Welch and R. D. Graham. (in press). Elsevier Scientific Pubications Ltd., Ireland.

3) Grant, C.A., Bailey, L.D., McLaughlin, M.J. and Singh, B.R. 1999. Management techniques to reduce cadmium transfer from soils to plants. A review. In "cadmium in Soils and Plants" Eds. M.J.McLaughlin and B.R. Singh. Kluwer Academic Publishers, Dordrecht, The Netherlands (in press).

Journal papers

4) Maier, N.A., McLaughlin, M.J., Heap, M., Butt, M., Smart, M.K., and Williams C.M.J. 1997. Effect of current season applications of calcitic lime on pH, yield and cadmium concentration of potato (Solanum tuberosum L.) tubers. Nutr. Cycl. Agroecosys. 47: 1-12.

5) McLaughlin, M.J., the late Tiller, K.G. and Smart, M.K. 1997. Speciation of cadmium in soil solutions of saline/sodic soils and relationship with cadmium concentrations in potato tubers. Aust. J. Soil. Res. 35: 1-16.

6) McLaughlin, M.J., Maier, N.A., Rayment, G.E., Sparrow, L.A., Berg, G., McKay, A., Milham, P., Merry R.H. and Smart, M.K. 1997. Cadmium in Australian potato tubers and soils. J. Environ. Qual. 26: 1644-1649.

7) McLaughlin, M.J., Andrew, S.J., Smart, M.K. and Smolders, E. 1998. Effects of sulfate on cadmium uptake by Swiss chard: I. Effects on complexation and calcium competition in nutrient solutions. Plant Soil 202: 211-216.

8) McLaughlin, M.J., Lambrechts, R.-M., Smolders, E. and Smart, M.K. 1998. Effects of sulfate on cadmium uptake by Swiss chard: II. Effects due to sulfate addition to soil. Plant Soil 202: 217-222.

9) McLaughlin, M.J., Maier, N.A., Correll, R., Smart, M.K., Sparrow, L.A. and McKay, A. 1999. Prediction of cadmium concentrations in potato tubers (*Solanum tuberosum* L.) by pre-plant soil and irrigation water testing. Aust. J. Soil Res. (in press).

Conference papers

10) McLaughlin, M.J., Smolders, E., Merckx, R. and Maes, A. 1997. Plant uptake of cadmium and zinc in chelator-buffered nutrient solution depends on ligand type. pp. 113-118, *In* Plant Nutrition for Sustainable Food Production and Environment, XIIIth International Plant Nutrition Colloquium, T, Ando, K. Fujita, T. Mae, H. Matsumoto, S. Mori and J. Sekija (Eds.), Kluwer Academic Publishers, Dordrecht, Holland.

11) McLaughlin, M.J., Hamon, R.E., Maier, N.A., Correll, R., Smart, M.K. and Grant, C.D. 1998. Screening of phytoremediation and *in-situ* immobilisation techniques to remediate cadmium-contaminated agricultural soils. pp. 229-236 In "Proceedings National Soils Conference - Environmental Benefits of Soil Management", Brisbane, Australia, April 1998. Aust. Soil Sci. Soc. Inc., Sydney.

12) McLaughlin, M.J., Maier, N.A., Correll, R.L., Smart, M.K. and Grant, C.D. 1998. In-situ immobilisation techniques to remediate cadmium-contaminated agricultural soils. pp. 453-460 In "Contaminated Soil '98. Proceedings of the Sixth International FZK/TNO Conference on Contaminated Soil, 17-21 May 1998, Edinburgh, UK." Thomas Telford Ltd, London.

13) McLaughlin, M.J., Maier, N.A. and Smart, M.K. 1998. Use of industrial by-products to remediate saline cadmium-contaminated soils to protect the food chain. In Proc. 16th World Congress Soil Science, Montpellier, France, August 1998.

Conference abstracts

1) McLaughlin, M.J. and Tiller, K.G. 1994. Chloro-complexation of cadmium in soil solutions of saline-sodic soils increases phyto-availability of cadmium. pp.195-196. In Proc 15th Int. Congr. Soil Sci., Acapulco, Mexico, July 1994.

2) McLaughlin, M.J., Kookana, R. and Naidu, R. 1995. Complexation of Cd in the soil-plant system and impact on soil and food quality. Invited presentation to the 10th National Convention of the Royal Australian Chemical Institute, September 1995.

3) Andrew, S.J., Hamon, R.E., and McLaughlin, M.J. 1997. Uptake of cadmium and zinc by Australian wheat cultivars. pp. 325-326 In "Proceedings Fourth International Conference on the Biogeochemistry of Trace Elements", Berkeley, June 1997.

4) McLaughlin, M.J., Andrew, S.J., Smart, M.K. and Smolders, E. 1997. Effect of sulfate complexation in solution on uptake of cadmium by plants. pp. 121-122 In "Proceedings Fourth International Conference on the Biogeochemistry of Trace Elements", Berkeley, June 1997.

5) McLaughlin, M.J., Smolders, E., Merckx, R. and Maes, A. 1997. Effect of organic ligands on uptake of cadmium and zinc by plants in chelator-buffered nutrient solution. pp. 115-116 In "Proceedings Fourth International Conference on the Biogeochemistry of Trace Elements", Berkeley, June 1997.

6) McLaughlin, M.J., Maier, N.A., Correll, R., Smart, M.K., Sparrow, L.A. and McKay, A. 1997. Prediction of cadmium concentrations in potato tubers (*Solanum tuberosum* L.) by pre-plant soil and irrigation water testing. pp. 153-154 In "Moving Towards Precision With Soil and Plant Analysis. Australian Soil and Plant Analysis Council 2nd National Conference", Launceston, Tasmania, November 1997.

9. TECHNOLOGY TRANSFER/INDUSTRY LIAISON

During the course of the project, the Principal Investigator held several meetings with growers, scientists and industry to review the issues, determine research and management priorities and to pass information and research outcomes to industry.

1) Industry meetings

The main industry presentation was to the Australian Potato Industry Council (APIC)/HRDC meeting, held on 12th November 1996 in Melbourne. Data from the project was presented and distribution and feedback from the cadmium information brochure was reviewed.

In addition, several meetings were held with representatives from APIC and the (then) National Food Authority, regarding the application by APIC to have the maximum permitted concentration for cadmium in potatoes revised upwards, using data from this and previous CSIRO cadmium projects. These were successful as judged by the revision of the potato (and all food) MPCs for cadmium in August 1997.

2) Grower/Scientific presentations (unpublished)

A number of talks were given to growers/scientists as part of the project.

1) "Fertilization and cadmium uptake by agricultural crops" to the International Fertilizer Development Centre, Muscle Shoals, Alabama, USA, July 1994.

2) "Impact of salinity on agricultural crop quality - mechanisms and implications" to USDA Environmental Chemistry Labs., Beltsville, Maryland, July 1994.

3) "Impact of salinity on agricultural crop quality - mechanisms and implications" to Department of Crop and Soil Sciences, University of Georgia, Athens, Georgia, USA, July 1994.

4) "Impact of salinity on cadmium uptake by potatoes" to Institute for Sustainable Irrigation Management, Tatura, August 1994.

5) "Cadmium update" Tatiara Potato Growers meeting, Bordertown, SA, October 1994.

6) "Cadmium update" Koo-wee-rup/Thorpedale crisping growers meeting, Coralyn, Victoria, October 1994.

7) "Cadmium speciation and cadmium uptake by plants" to the University of Adelaide Plant Membrane Biology Group, November 1994.

8) "Cadmium uptake by plants as affected by chloride - speciation and plant uptake in field soils and in nutrient solutions" to Department of Agriculture, University of Queensland, November 1994.

9) "Managing cadmium accumulation in irrigated potato crops" to Agriculture WA, Baron Hay Court, South Perth, WA, May 1995.

10) "Cadmium Update", to Tatiara Potato Grower's Association, Bordertown, SA, August 1995.

11) "Cadmium", to The Crisping Group of South Australia, Hahndorf, SA, September 1995.

12) "Cadmium Speciation in Relation to cadmium Availability to Plants" to Institute of Environmental Science and Engineering, Technical University of Denmark, October 1995.

13) "Regulating soils for minimising risks due to cadmium", invited presentation to New South Wales Environment Protection Agency, Sydney, March 1996.

14) "Impact of salinity on cadmium uptake by crops" to Catholic University Leuven, Belgium, June 1996.

15) "Impact of salinity on cadmium uptake by crops" to Netherlands National Institute for Public Health, Utrecht, Netherlands, September 1996.

16) "Cadmium speciation in soils and uptake by plants" to Department of Soil Science, University of Reading, UK, September 1996.

17) "Cadmium speciation in soils and uptake by plants" to Rothamsted Experimental Station, Harpenden, UK, September 1996.

18) "Cadmium uptake by plants - impact of speciation" invited presentation to Agricultural University Norway, As, Norway, September 1996.

19) "Effect of organic ligands on cadmium uptake by plants" to Department of Soil Science, University of Adelaide, Adelaide, October 1996.

20) "Managing agricultural land contaminated by metals in fertilizers and wastes". Invited Plenary Lecture to International Conference on Remediation of Degraded Lands, Hong Kong, December 1996.

21) "Cadmium update" Tatiara Potato Growers meeting, Bordertown, SA, February 1997.

22) "Can water treatment sludges improve food quality?" to Australian Water Quality Centre, Bolivar, March 1997.

23) "Soil salinity and Cd uptake by plants" to USDA Soil Salinity Research Laboratory, Riverside, USA, June 1997.

24) "Cadmium update" Tatiara Potato Growers Annual General Meeting, Bordertown, SA, August 1997.

3) Industry liaison

Throughout the project, close contact has been maintained with the fertilizer industry through the Fertilizer Industry Federation of Australia (FIFA), Ltd. Through one of the member companies, Incitec Pty Ltd, the Principal Investigator participated in a Fertilizer Industry training video "Heavy Metals in Fertilizers" released in November 1996. In addition, assistance was provided to FIFA in review of a chapter on "Heavy Metals in Fertilizers and Agriculture" in their "Australian Soil Fertility Manual", and to Incitec Pty Ltd, for review of their "Agri-Topic – Heavy Metals in Fertilizers and Agriculture" released in October 1996.

Close contact was also been kept with the Australia New Zealand National Food Authority (ANZFA, formerly NFA) and several discussions were held with them regarding the review of the food cadmium regulations. During July-August 1994, technical assistance was provided to the Australian Potato Industry Council to lodge a submission to the NFA to have reviewed upwards the maximum permitted concentration for cadmium in potatoes.

4) Articles/leaflets/media

A glossy 8-page brochure entitled "Managing Cadmium in Potatoes for Quality Produce" was released through the CRC for Soil and Land Management in September 1996 (Appendix 11). Six thousand copies of this were distributed nationally to growers, advisers, State Departmental representatives and other interested groups. Feedback from the brochure has been excellent, with several requests from FIFA and State Departmennts for a second print run.

A second brochure entitiled "Cadmium in potatoes – managing the risk from saline irrigation water", with the same format as the first brochure, is almost complete and should be released in February 1999 as an insert in "Eyes on Potatoes". This summarises results from the predictive test component of this project (Component B, Section 6.iv above). A copy is enclosed at the end of this report (Appendix 12).

5) Decision support software

The findings of this and previous projects have now been included in the "CROPTEST" decision support software for growers and technical advisers released by SARDI in December 1998. A hypertext information library is part of this software, so that fertilization options and nutritional management are linked to cadmium management. This will enhance awareness of cadmium issues by consultants and growers, and will influence crop and fertilizer management decisions to minimise cadmium accumulation in crops.

10. TECHNICAL PAPERS

APPENDIX 1 Prediction of cadmium concentrations in potato tubers (*Solanum tuberosum* L.) by pre-plant soil and irrigation water analyses

Introduction

Potatoes have been identified as a major component of human dietary intake of cadmium (Cd) in Australia (Anon. 1992), and Australian regulations governing maximum permitted concentrations (MPCs) for Cd in root and tuber vegetables have recently been set at 0.1 mg kg^{-1} on a FW basis (Anon. 1997). A number of areas in Australia have the potential to produce potato tubers in excess of the new MPC, due to particular combinations of soil and environmental factors (McLaughlin *et al.* 1997a). It is therefore important that growers are able to identify soils and environments where tubers are likely to exceed the MPC, preferably prior to soil preparation and crop planting, so that site selection can be effectively used as a management tool to minimise Cd in fresh and processed produce.

There have been a number of investigations of the use of chemical extractants to predict Cd concentrations (or uptake) into plants in both glasshouse and field studies, with varying degrees of success (Symeonides and McRae 1977; Sauerbeck and Styperek 1985; Whitten and Ritchie 1991; He and Singh 1991; Mench *et al.* 1994; Andrewes *et al.* 1996). However, none of the above studies satisfy the criteria necessary for the development of a predictive test capable of being used under all commercial conditions. We contend that these test criteria are that:

1) it should account for the major environmental factors known to affect crop Cd concentrations (McLaughlin *et al.* 1994a; 1996);

2) it should be relatively simple, inexpensive and robust;

3) it should be calibrated under field conditions across a wide range of soil types;

4) it should be independently validated; and

5) it must be truly predictive i.e. measurements prior to planting of the crop must be correlated against plant Cd measurements at harvest, and not a correlation between measurements on soil and plant samples at the same point in time. This is particularly important in irrigated crops where soil properties, such as pH, EC and Cl concentrations, can change markedly throughout the growth season (Maier *et al.* 1997).

This paper reports the development of a pre-plant test for Cd risk in irrigated potato soils which was designed to satisfy the above criteria. The results have been expressed in a graphical format to enable an estimate of the probability that a crop will exceed the MPC of Cd.

Materials and methods

Sampling of soils and irrigation waters before planting

One hundred and thirty four sites were chosen in spring 1994, prior to soil preparation for the summer cropping season. The sites include representatives from the major potato production areas in Western Australia, South Australia, Tasmania, Victoria and New South Wales. The possibility that spatial variability would confuse the relationships between pre-plant measurements and tuber Cd concentrations was minimised by sampling tubers and soils from the exact same location at each site. Soils at the sites were sampled by taking 5 cores to 150 mm depth within an area 1 m in diameter using a stainless steel corer in September 1994 to February 1995, prior to cultivation and soil preparation by growers. Soil cores from each sampling point were bulked, thoroughly mixed and a one kilogram sample taken. The area was then permanently marked by placing a Scothmark™ Ball Marker (which contains an electronic transponder) at 70 cm depth in the centre of the sampling area. This depth was assessed as being sufficient to prevent disturbance of the transponder by cultivation practices.

The soils were chosen on the basis that they represented the main potato production soils in southern Australia. Soil Orders (Isbell 1996) sampled were predominantly Ferrosols, Podosols, Sodosols and Chromosols with a wide range of chemical characteristics (Table 1). Soils were air-dried and crushed to pass a 2 mm sieve, prior to mixing and subsampling for chemical analysis.

Table 1. Selected chemical characteristics of soils and irrigation waters prior to planting (n=134)

Characteristic	Range	Median	Mean
	Soil		
pH (water)[A]	4.8-8.1	5.8	5.8
EC (dS m^{-1})[A]	0.02-1.07	0.11	0.15
Extractable Cl (mg kg^{-1})[A]	5-660	25	56
Extractable P (mg kg^{-1})[B]	5-459	53	69
Total Cd (mg kg^{-1})[C]	0.01-0.60	0.11	0.18
Total Zn (mg kg^{-1})[C]	1-130	15	28
	Irrigation water		
pH	6.4-9.2	7.7	7.7
EC (dS m^{-1})	<0.01-4.1	0.43	0.90
Ca (mg L^{-1})	1-245	13	32
Mg (mg L^{-1})	1-105	13	23
Na (mg L^{-1})	3-501	58	118
S (mg L^{-1})	<1-72	4	12
Cl (mg L^{-1})	1-1118	170	270

A 1:5 soil:water ratio
B Colwell (1963)
C Aqua regia digest

Irrigation water samples were also taken prior to crop planting by placing 250 mL water from the irrigation supply line into a polypropylene bottle. Waters were stored at 4°C prior to analyses.

Sampling of soils, waters and tubers at crop maturity

At crop maturity sampling points were located at each site using a EMS II Marker Locator™ tuned to the frequency of the buried transponder. Potato crops were sampled by hand digging tubers from a 1 m square area above the transponder. Twelve to 15 tubers in the size range 80-450 g were collected, with any severely diseased or damaged tubers discarded. Tuber cultivar was noted and tubers were brushed free of soil and transported to the laboratory for analysis.

Soil in the row down to the furrow depth was thoroughly mixed and a one kilogram sample taken by compositing four subsamples. Soils were air-dried and crushed to pass a 2 mm sieve.

Irrigation water was sampled at crop maturity as outlined previously.

Soil and water analyses

Soil pH and electrical conductivity (EC) were determined in a water suspension of soil using a 1:5 soil:solution ratio (Rayment and Higginson 1992). Chloride (Cl) was extracted from soil using water at a soil:solution ratio of 1:5 (Rayment and Higginson 1992). Chloride in the filtered (Whatman No. 42) solution was determined using an automated ferricyanide method (APHA 1992). Phosphorus (P) was extracted from soils using the method of Colwell (1963).

Total and extractable Cd concentrations in soils were determined using the following methods:

(1) Total Cd: total Cd concentrations in soil were determined by boiling 2 g soil with 8 mL aqua regia (HNO_3:HCl, 1:3 ratio) at 110°C for 2 h. The mixture was cooled, diluted to volume with 0.08 M HNO_3 spiked with indium as an internal standard and filtered through a 0.22 µm filter.

(2) EDTA-extractable Cd: Cd was extracted by shaking soils for seven days with 0.05 M sodium EDTA (disodium ethylenediamine-N,N,N',N'-tetraacetate) at pH 6.0 using a soil:solution ratio of 1:2.5 (Clayton and Tiller 1979).

(3) 0.01 M $CaCl_2$-extractable Cd: 5 g soil was shaken for 4 h with 25 mL extracting solution. In preliminary experiments, 4 h was found to be a sufficiently long extraction time to allow equilibrium between soil and solution to occur. The suspensions were then centrifuged (10 min. at 4000 RCF), filtered through a 0.22 µm filter and diluted 5-fold with 0.08 M HNO_3 spiked with indium as an internal standard.

(4) 0.01 M $Ca(NO_3)_2$-extractable Cd: as above only Cd was extracted from soils using 0.01 M $Ca(NO_3)_2$ solution. Activity of Cd^{2+} ion in these solutions was determined by the ligand desorption method of Fujii *et al.* (1983), as outlined previously (McLaughlin *et al.* 1997b).

5) 0.1 M $CaCl_2$-extractable Cd: as for method 3 except 0.1 M $CaCl_2$ was used as the extraction solution (modification of the method of Sauerbeck and Styperek 1985).

6) NH_4NO_3-extractable Cd: 4 g soil was extracted with 40 ml 1.0 M NH_4NO_3 for 1 h (Symeonides and McRae 1977). Samples were centrifuged at 4000 RCF for 20 min and filtered through a 0.22 µm filter. The solution was diluted 5-fold with 0.08 M HNO_3 spiked with indium as an internal standard.

7) DTPA-extractable Cd: soils were extracted using DTPA (diethylenetriaminepentaacetic acid plus buffer in $CaCl_2$) according to the method of Lindsay and Norvell (1969).

Zinc was also extracted from soils using methods 1 and 2.

Concentrations of Cd and Zn in solutions were determined using either a flame or graphite furnace Varian Spectra AA-400 atomic absorption spectrophotometer (GFAAS) equipped with deuterium background correction. Orthophosphoric acid (methods 2, 3, and 7) and palladium (method 4) were used as modifiers. Inductively-coupled plasma mass spectrometry (ICP-MS) using indium as an internal standard (methods 1, 3, 5 and 6) was also used. Due to the very low Cd concentrations in dilute Ca solutions, a comparison was made between ICP-MS and GFAAS analysis of Cd concentrations in extracts from method 3.

Measurement of pH and EC of irrigation waters was according to the methods of Rayment and Higginson (1992). Waters were filtered through a 0.45 µm filter and cations, sulfur, boron and P in irrigation water were determined by ICP atomic emission spectroscopy. Concentrations of chloride (Cl) were determined using an automated ferricyanide method (APHA 1992).

Tuber analysis

Tubers were first cleaned in deionised water and a 10-20 mm longitudinal slice taken from the stem end to the bud end of each tuber. Tuber material was then oven dried and ground < 250 µm. A subsample of the ground dried material (0.5 g) was digested by boiling under convection heating with 7 mL concentrated HNO_3 acid and Cd concentration in the solution was determined by GFAAS (McLaughlin *et al.* 1997a). Analysis of NBS rice flour (Ref.No.1568A) by the above method gave a Cd concentration of 0.023 ± 0.001 mg kg^{-1}, compared to the certified value of 0.022 ± 0.002 mg kg^{-1}. All tuber Cd concentrations are expressed on a fresh weight basis (FW).

Statistical analysis

Relationships between soil and irrigation water test procedures and tuber Cd concentrations were determined using Pearson's correlations. Prediction of the concentration of tuber Cd concentration was assessed using multiple regression against pairs of the soil and water measurements described above. A logarithmic transformation of the tuber Cd concentration was required to give normality and homoscedasticity of the residuals from the regression.

Analyses of probabilities of exceedence of MPCs were performed using a generalised linear model (GLM) with a binomial error and logistic link (McCullagh and Nelder 1989). Because the water quality and soil Cd are unique for each site, there is only a single realisation of the binomial process for each set of predictors. This analysis provided a linear model of λ, where $\lambda = \log\frac{p}{1-p}$ where p is the probability of exceeding a pre-determined tuber Cd concentration. This was considered preferable to modeling p directly because λ was found to

be approximately linearly related to the important soil or water parameters whereas p was not. The predictions of p were obtained from the fitted λ s using the inverse logistic transform

$$p = \frac{\exp(\lambda)}{1+\exp(\lambda)}.$$

All analyses were performed in GENSTAT (Rothamsted Experimental Station 1995).

Test validation

The preferred method for assessing Cd risk was tested in the 1995/96 season by sampling 39 sites in South Australia, Victoria and Tasmania prior to crop planting as outlined previously. At crop maturity tubers were sampled and the Cd concentrations in tubers compared to those predicted by the preferred methodology.

Ability of the preferred method to accurately predict exceedance of the MPC of 0.1 mg kg^{-1} FW was determined using a Chi square (χ^2) comparison.

Results

Soil and water analyses

The soils had a wide range of pH values, Cd concentrations and extractable P concentrations (Table 1). Irrigation waters ranged from high quality, having low concentrations of soluble salts, to very poor quality where soluble salt concentrations were high (ECs >3.0 dS m^{-1}). Sodium and Cl were the dominant ions in the irrigation waters (Table 1). For all States there was a good relationship between irrigation water EC (R^2=0.95, P<0.001) or Cl (R^2=0.95, P<0.001) concentrations at planting and those at harvest, with the slope of the relationship close to 1 for all States (Fig. 1).

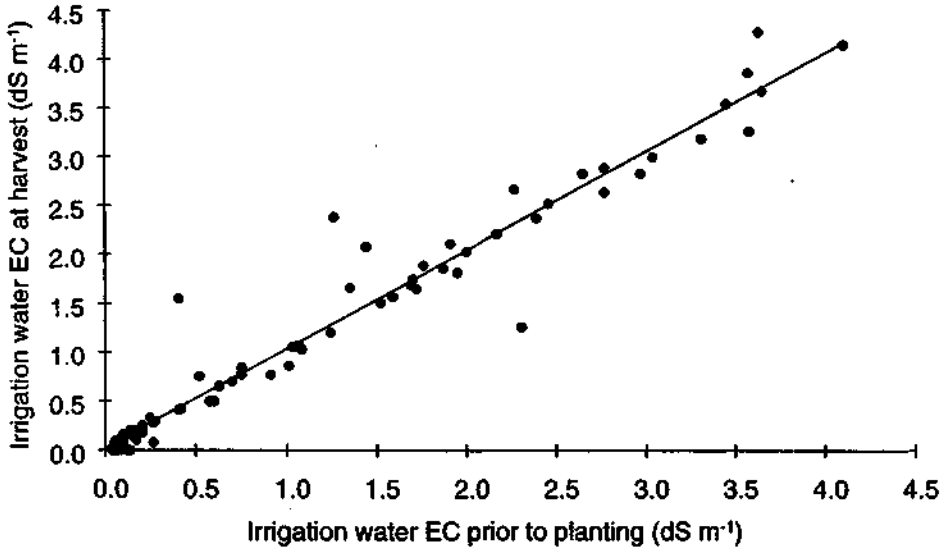

Fig. 1. Relationship between EC of irrigation water measured at planting and at harvest. Fitted line is Y = 0.02+1.01X (R^2=0.95; P<0.001).

Soil characteristics also changed markedly between planting and harvest. Soil pH changes between planting and harvest varied from a drop of 2.2 units to an increase of 1.3 units (data

not shown), while changes in soil EC varied from +0.7 to -0.7 dS m^{-1}. Overall, soil salinity tended to increase due to irrigation and was positively correlated (R^2=0.46, P<0.001) to irrigation water EC measured prior to planting (Fig. 2).

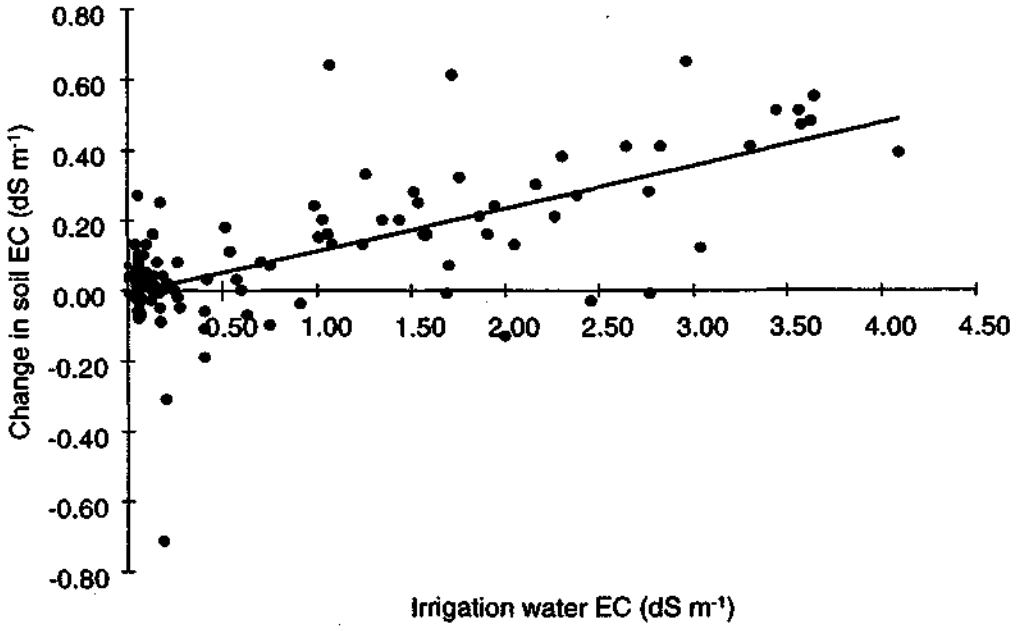

Fig. 2. Relationship between irrigation water quality and change in soil EC between planting and harvest. Fitted line is Y=-0.008+0.121X (R^2=0.46; P<0.001).

Concentrations of Cd extracted from soils using the various reagents are shown in Table 2.

Table 2. Concentrations of Cd (µg kg^{-1}) extracted from soils by the various reagents (n=134).

	Cd concentration		
Soil test method	Range	Median	Mean
		µg kg^{-1}	
EDTA	20-406	85	126
DTPA	10-361	54	61
0.1 M $CaCl_2$	1-225	47	54
1.0 M NH_4NO_3	1-111	13	17
0.01 M $CaCl_2$	1-60	8	12
0.01 M $Ca(NO_3)_2$	0-55	6	9
Cd^{2+} activity (nM)[A]	<0.01-6.9	0.9	1.4

[A] Activity of the free Cd^{2+} ion in the 0.01 M $CaCl_2$ and 0.01 M $Ca(NO_3)_2$ extracts calculated according to the method of Fujii *et al* (1983).

EDTA, DTPA and 0.1 M $CaCl_2$ extracted the greatest amount of Cd from the soils, followed by the 1.0 M NH_4NO_3 solution and the dilute Ca salts. There was excellent agreement between Cd concentrations determined by GFAAS and ICP-MS for the 0.01 M $CaCl_2$

extractant (R^2=0.98, P<0.001, Fig. 3). Concentrations of Cd extracted by the weaker Ca salts and the NH_4NO_3 solutions were low in comparison to the other procedures, but well within the detection limits of the instrumental analysis. The limits of reporting (LOR) using the GFAAS and ICP-MS procedures for soil Cd determined by extraction with 0.01 M $CaCl_2$ and $Ca(NO_3)_2$, calculated as 5 times the detection limit, were 1.25 and 0.5 μg kg^{-1}, respectively. The LOR for extractable Cd using the 1.0 M NH_4NO_3 procedure was 1 μg kg^{-1}.

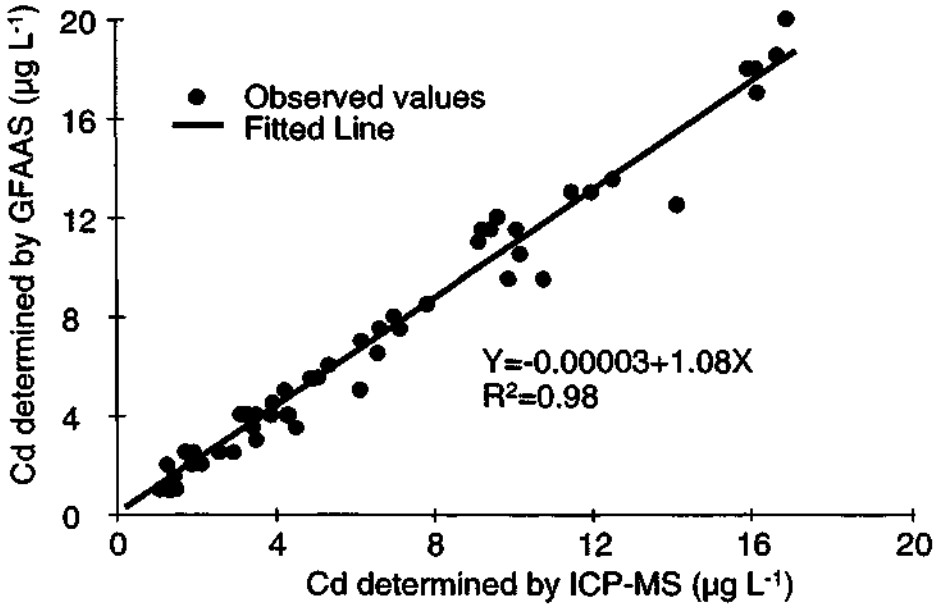

Figure 3. Relationship between Cd in 0.01 M $CaCl_2$ extracts of soil determined by GFAAS and ICP-MS. Fitted line is Y=-0.00003+1.08X : R^2=0.98 (P<0.001).

As expected, there was also a close correlation between amounts of Cd extracted by the various reagents, with total, EDTA- and DTPA-extractable Cd being closely correlated, and Cd concentrations extracted by the salt solutions (0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$, 0.1 M $CaCl_2$ and 1.0 M NH_4NO_3) also highly correlated (Table 3). Cadmium was generally positively correlated to extractable P concentrations, and in the all the salt extracts increased exponentially as soil pH decreased below about 5.5, as shown in Fig. 4 for NH_4NO_3.

Tuber cadmium concentrations

The range, median and mean tuber Cd concentrations (mg kg^{-1} FW) were 0.006-0.296, 0.039 and 0.052, respectively. Eleven of the 134 tuber samples had Cd concentrations exceeding the MPC of 0.1 mg kg^{-1} FW, and 41 samples had Cd concentrations between 0.05 and 0.1 mg kg^{-1} FW. There was a significant effect (P<0.05) of tuber cultivar on tuber Cd concentrations, with cultivars Russet Burbank and Sebago having lower Cd concentrations than Kennebec and Pontiac, in line with previous findings (McLaughlin *et al.* 1994b).

Tuber Cd concentrations were not strongly correlated with soil pH, EC, Cl nor with any soil Cd (or Zn) test procedure performed on soil samples taken prior to planting (R^2<0.1). The greatest amount of variation in tuber Cd concentrations was accounted for by a measure of pre-plant irrigation water quality (either EC or Cl concentration) and this could be slightly improved by including a measure of extractable Cd. Similar fits were obtained from various

combinations of these measures, the best being with irrigation water Cl concentration and Cd extracted by 0.01 M $CaCl_2$ (Table 4). High Cl concentrations in irrigation waters prior to planting led to tubers having high Cd concentrations (Fig. 5). The equation for prediction tuber Cd (mg kg^{-1} FW) was;

Log(Tuber Cd) = -1.793 (±0.039) + 0.00099 (±0.00008) Cl + 0.0130 (±0.0022) Cd (Eq.1)

where Cl is the Cl concentration in the irrigation water (mg L^{-1}) and Cd is the concentration of soil Cd extracted by 0.01M $CaCl_2$ (µg kg^{-1}). The standard error of the parameter estimates are shown in parentheses.

Table 3. Simple linear correlation matrix between amounts of Cd and Zn extracted from soils, soil pH and extractable P (n=134). Values for correlation coefficient (r) numerically greater than 0.17, 0.22, and 0.28 are significant at P= 0.05, 0.01 and 0.001 level respectively

Factor	Values for correlation coefficient (r)									
	pH	Ext. P	EDTA Cd	EDTA Zn	DTPA Cd	0.01M $CaCl_2$ Cd	0.01M $Ca(NO_3)_2$ Cd	Total Zn	Total Cd	NH_4NO_3 Cd
pH										
Ext. P	-0.21									
EDTA-Cd	-0.02	0.40								
EDTA-Zn	0.09	0.13	0.19							
DTPA-Cd	0.02	0.39	0.81	0.21						
0.01 M$CaCl_2$-Cd	-0.64	0.40	0.17	0.04	0.21					
$Ca(NO_3)_2$-Cd	-0.62	0.32	0.15	0.00	0.16	0.97				
Total Zn	-0.08	0.16	0.43	0.42	0.19	-0.18	-0.17			
Total Cd	-0.10	0.50	0.96	0.21	0.75	0.20	0.17	0.52		
NH_4NO_3-Cd	-0.63	0.53	0.35	0.05	0.27	0.88	0.87	0.02	0.41	
0.1M $CaCl_2$-Cd	-0.48	0.65	0.61	0.20	0.62	0.70	0.63	0.16	0.64	0.81

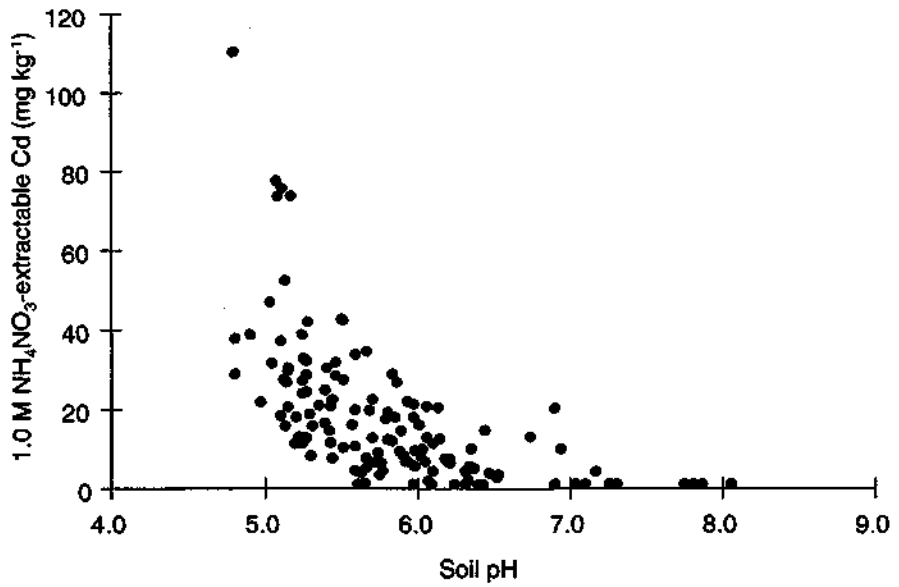

Fig. 4. Relationship between soil pH and Cd extracted from soil using 1.0 M NH_4NO_3.

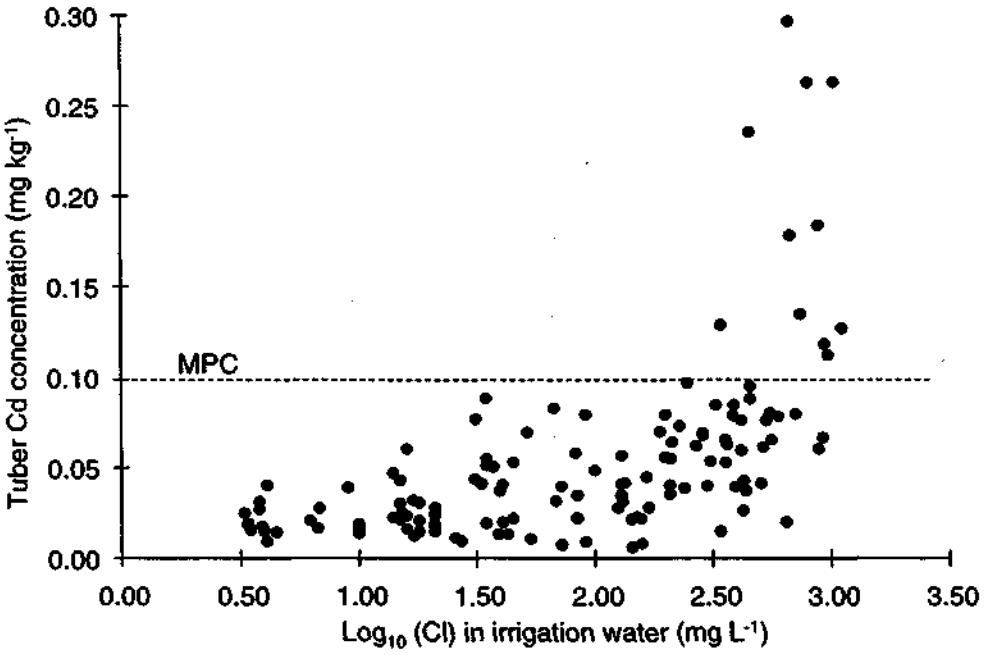

Fig. 5. Relationship between tuber Cd concentration and Cl concentration in irrigation water measured prior to planting.

Table 4. Analysis of variance table for multiple regression of tuber Cd concentration (mg kg^{-1} FW, log transformed) on irrigation water Cl concentration and 0.01 M $CaCl_2$-extractable Cd in soil

Change in model	d.f.	Sum of squares	Mean Square	Variance ratio	% Variation
+ Cl	1	7.084	7.084	127.08***	43.2
+ $CaCl_2$-Cd	1	1.981	1.981	35.54***	12.2
Residual	131	7.302	0.056		44.6
Total	133	16.367	0.123		100.0

*** $P<0.001$

The equation for the probability predictions for tuber Cd concentrations exceeding 0.05 mg kg^{-1} FW based on the EC of the irrigation water (dS m^{-1}) was,

$$\lambda = -1.82\ (\pm 0.32) + 1.53\ (\pm\ 0.29)\ EC \qquad \text{(Eq.2)}$$

For tuber Cd concentrations exceeding 0.1 mg kg^{-1} FW the equation was

$$\lambda = -7.14\ (\pm 1.58) + 2.465\ (\pm\ 0.599)\ EC \qquad \text{(Eq.3)}$$

The backtransformed probabilities are shown in Figure 6. A similar equation was obtained using irrigation water Cl. A lower deviance was obtained with irrigation water Cl for predicting tuber Cd concentrations above 0.05 compared to EC, but EC gave better predictions for concentrations exceeding 0.1 mg kg^{-1} FW (Table 5). The equation based on EC was preferred because of the ease of EC determinations.

Table 5. Analyses of deviance for prediction of tuber Cd exceeding 0.05 mg kg^{-1} FW. The measure of soil Cd is extraction using 0.01M $CaCl_2$

Model	d.f.	Deviance
	Tuber Cd<0.05	
Cl	132	124.3
Cl + Soil Cd	131	109.9
EC	131	130.7
EC+ Soil Cd	130	117.9
	Tuber Cd<0.10	
Cl	132	32.57
EC	131	30.60

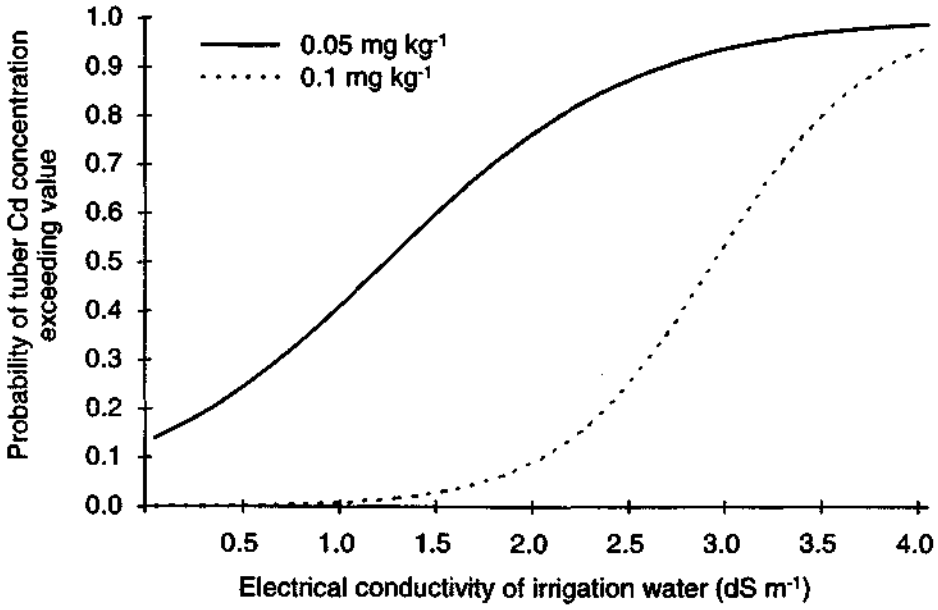

Fig. 6. Probability of tuber Cd exceeding values of 0.05 and 0.1 mg kg^{-1} FW at different irrigation water ECs.

Levels of Cd extracted by 0.01 M $CaCl_2$ (Method 5) affected the probability of tuber Cd exceeding 0.05 mg kg^{-1} FW (P<0.001). However, whereas irrigation water EC decreased the deviance from 178.0 to 130.7, the inclusion of soil Cd reduced the deviance only by a further 12.8 to 117.9. Irrigation water EC was therefore a much better predictor of tuber Cd concentration than was soil Cd. For ease of graphical presentation, the soils were arbitrarily classified as being low Cd if Cd extracted by 0.01 M $CaCl_2$ was <5 µg kg^{-1}, intermediate for concentrations of 5-15 µg kg-1, or high if soil Cd was >15 µg kg^{-1}. The GLMs for each soil class had different intercepts (P<0.05) but similar slopes. A summary of these models is given in Table 6.

Although there was a substantial difference between the soil Cd levels for low and medium groups, the intercepts of the models for these two groups were similar. We included them both because the overall trend of the effect of soil Cd was significant. The probability of tuber

Cd concentration exceeding the 0.05 level is shown for each class in Fig. 7. The 11 cases where Cd exceeded the MPC of 0.1 mg kg^{-1} FW were insufficient to enable similar curves to be constructed for this MPC.

Table 6. Intercept and slope of relationship between λ ($\lambda = \log\frac{p}{1-p}$, where p is the probability of exceeding a tuber Cd concentration 0.05 mg kg^{-1} FW) and irrigation water EC for soils with low, medium and high extractable soil Cd.

Cd Level	Average soil Cd µg kg-1	Intercept	Slope
Low	3.0	-2.66 ± 0.57	1.83 ± 0.34
Medium	9.0	-2.39 ± 0.53	1.83 ± 0.34
High	20.6	-1.24 ± 0.37	1.83 ± 0.34

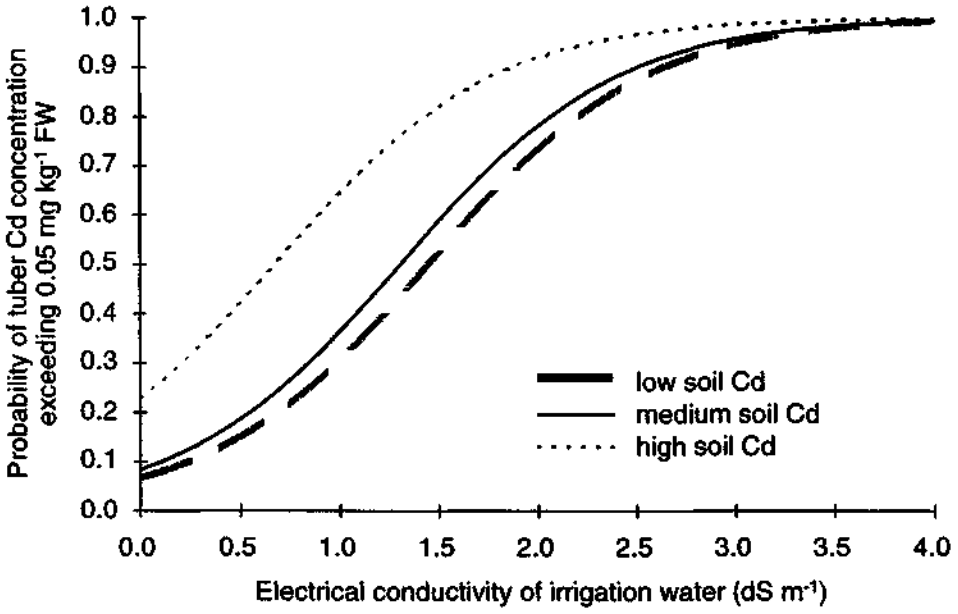

Fig. 7. Probability of tuber Cd exceeding 0.05 mg kg^{-1} FW for soils of low, medium and high levels of 0.01 M $CaCl_2$-extractable Cd.

Test validation

Tuber Cd concentrations in the validation samples varied from 0.007 to 0.145 mg kg^{-1} FW with only five samples exceeding the MPC. Using pre-plant EC as the predictor of tuber Cd concentration, predictions of tuber Cd exceeding the MPC were reasonable, with the predicted probability of MPC violations agreeing well with the observed (Table 7).

There was still considerable variation in the data however, with one tuber Cd value being low when violation of the MPC was predicted to be highly probable (point A in Figure 8) and others in excess of the MPC but only having a low probability of violation predicted by the model (e.g. points B and C in Fig. 8).

On further investigation, it was found that point A had an extremely low (<1 μg kg^{-1}) $CaCl_2$-extractable Cd concentration in soil, and soil Cd was not included in the model for predicting probabilities of violating the 0.1 mg kg^{-1} FW Cd level. For point B it was found that irrigation water EC at this site prior to planting was 0.23 dS m^{-1}, which by harvest had risen to 2.48 dS m^{-1}. There was no ready explanation for why the tuber Cd concentration was high for point C yet the predicted probability of exceeding the MPC was very low.

Table 7. Observed and expected frequency of incidences of tuber Cd exceeding or meeting the MPC of 0.10 mg kg^{-1} FW

Tuber Cd (mg kg^{-1} FW)	Observed (O)	Expected (E)	$(O-E)^2/E$
>0.10	5	4.15	0.174
<0.10	34	34.85	0.021
Total	39	39	0.194[A]

[A] χ^2 value not significant at P=0.05.

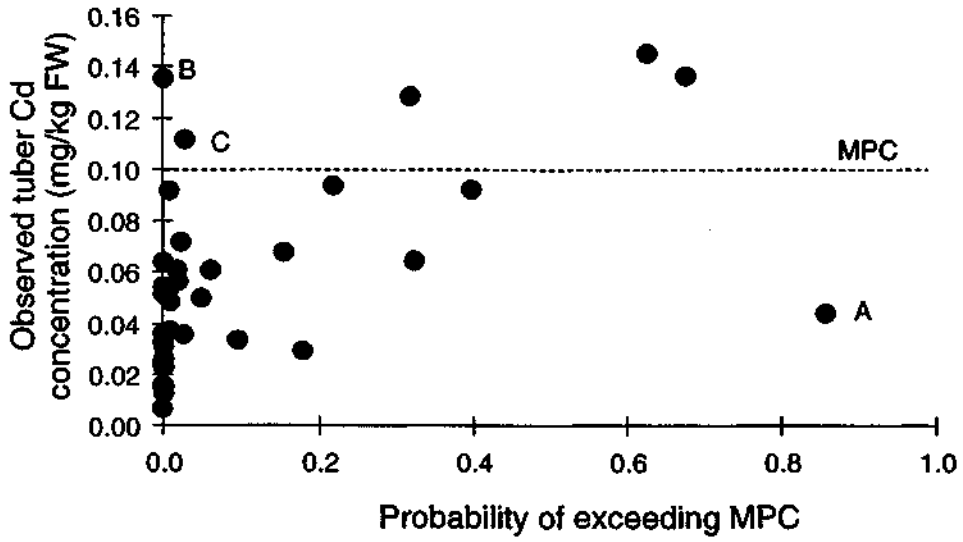

Fig. 8. Predicted probability of tuber Cd exceeding MPC (0.1 mg kg^{-1} FW) in relation to observed tuber Cd concentrations for validation samples. Points A, B and C are discussed in text.

Discussion

Compared to soil testing for prediction of crop response to macronutrient element concentrations in soils, testing to predict concentrations of trace metals in crops has been problematic. Not least of these problems are the analytical difficulties of determining trace concentrations of elements in soil extracts. For this reason, and to mimic the mechanisms which plant roots utilise to access micronutrients in soil, micronutrient elements have traditionally been extracted from soils with strong chelating agents such as DTPA and EDTA (Brown *et al.* 1960; Lindsay and Norvell 1969), which provided concentrations of trace metals in solution easily measurable by flame atomic absorption techniques. With improvements in

analytical methodology over the last 2 decades, ultra-trace concentrations of metals can now be routinely detected in solution using GFAAS, ICP-MS or voltammetric and potentiometric techniques, allowing the investigation of the utility of less aggressive extractants for determining the amount of "plant-available" metals in soil. Examples of this class of extractant are 0.01 M $CaCl_2$ and 1.0 M NH_4NO_3 (Symeonides and McRae 1977; Whitten and Ritchie 1991; Andrewes *et al.* 1996). GFAAS is equally effective as ICP-MS in determining trace concentrations of Cd in neutral salt extracts of soil, with the former instrumentation being more widely available and less expensive. Limits of reporting for Cd (5 times the detection limit) using GFAAS were 0.25 $\mu g\ L^{-1}$ in solution, or 1.25 $\mu g\ kg^{-1}$ soil, which was sufficient for the amounts of Cd extracted by 0.01 M $CaCl_2$ from these agricultural soils.

Only a small fraction of the total Cd in soil was solubilised by the weak salt solutions at moderate to high pH values (>6.0), but this fraction increased considerably as soil pH fell below 6.0. In weak Ca salts the fractional increase was from 0.002 to 0.373, and in NH_4NO_3 from 0.003 to 0.855 (data not shown). Whitten and Ritchie (1991) also found soil pH markedly affected solubility of Cd in 0.01 M $CaCl_2$ solution, and more recently Prüess (1995) showed the marked effect of pH on metal solubility in 1.0 M NH_4NO_3. Cadmium retention to soils is highly pH dependent, and it has been widely observed that as soil pH falls, Cd retention decreases markedly (Garcia-Miragaya and Page 1978; Tiller *et al.* 1979). However, this increasing solubility of Cd at lower soil pH values did not translate into increased availability of Cd to the potato plants, as soil pH (at either planting or harvest) was unrelated to tuber Cd concentrations. It is unclear why soil pH and pH changes associated with liming have not been found to have a significant effect on tuber Cd concentrations in this and related studies (McLaughlin *et al.* 1994a, 1997a; Maier *et al.* 1997), although there are several other reports indicating soil pH and liming may have little effect on plant Cd concentrations under field conditions (Pepper *et al.* 1983; Andersson and Siman 1991; Sparrow *et al.* 1993; Li *et al.* 1996).

Few soil tests procedures for Cd have been calibrated or tested under commercial conditions. Indeed, early experiments (Symeonides and McRae 1977) investigating soil extractants to estimate plant-available Cd used soils that had been amended to high levels (100 mg kg^{-1}) with Cd salts, well outside the range of concentrations found in most agricultural or even urban contaminated soils. Furthermore, Symeonides and McRrae (1977) used 3 levels of Cd addition (0, 50 and 100 mg kg^{-1}), so that strong relationships between soil and plant Cd measurements were likely as the resulting regression relationships were highly leveraged. Rayment (1994) compared a range of Cd extractants for their relationship with potato Cd concentrations from a survey of 21 locations in Queensland (7 properties with 3 sampling locations at each site and 3 depths of sampling). For surface soils (0-10 cm), only Cd extracted by EDTA was significantly related (R^2 = 0.27) to tuber Cd concentrations. Surprisingly, other extractants were either inversely related to tuber Cd, or the relationship was quadratic. Lee *et al.* (1996) found good correlation between soil and plant Cd measurements due to the soils being amended with Cd salts. Other workers who used unamended soils generally used only a small number of soils, mostly in glasshouse trials. For example, Andrewes *et al.* (1996) used 5 soils, with 3 of these having additional Cd added as fertiliser, Krishnamurti *et al.* (1995) used 11 soils and Whitten and Ritchie (1991) used only 3 soils with Cd availability varied by lime treatment. Most of the above studies reported strong relationships (R^2>0.8) between extractable Cd in soil and Cd levels in plants. On the other hand, studies conducted on field soils unamended with salts often find much poorer relationships. He and Singh (1993) used a wide range of soils (133) and found that Cd concentrations in oats and grasses were significantly but not strongly related (R^2 = 0.21,

$P<0.001$) to Cd extracted from soils using 1.0 M NH_4NO_3. Garrett *et al.* (1998) compared 1 M NH_4Cl and 0.1 M $Na_4P_2O_7$ as extractants for soil Cd in a series of 34 soils in Canada to predict Cd in durum wheat grain, and found Cd extracted by both procedures could explain greater than 70% of the variation in grain Cd concentration. However, even these tests were not truly predictive in that the relationships between plant and soil Cd concentrations were determined on soil and plant samples taken at the same time (usually crop maturity). This may only lead to significant errors if soil properties controlling Cd uptake vary between the time of sampling (prior to cultivation) and the time of Cd uptake by the crop e.g. salinity introduced through irrigation, cultivation and profile mixing after sampling, pH shifts due to fertilization, etc.

In our studies, soil and irrigation water samples were taken at harvest as well as prior to planting, as we were concerned that irrigation water quality could change throughout the growing season and therefore affect the relationship between any pre-plant soil or water measurement and final tuber Cd concentration. Water quality may change due to growers changing source of supply e.g. from bore to farm dam, or due to changes in the storage itself e.g. increasing salinity in farm dams over summer due to evaporation. Soil ECs may also vary due to fertiliser management, rainfall and evapotranspiration through the crop growth cycle. Fortunately irrigation water quality did not markedly change during the season at most sites, as evidenced by the data in Fig. 1. The importance of considering potential increasing (or decreasing) salinity in irrigation water between planting and harvest is seen in the validation test, where one poor prediction (using the pre-plant water quality as a predictor) was due to a 10-fold increase in water salinity over the season.

Despite a wide range of soil test procedures being evaluated, tuber Cd concentrations were best predicted prior to planting by measuring irrigation water EC. This is a simple and inexpensive determination, yet was able to explain almost half of the variation in tuber Cd concentrations at harvest. The dominant effect of EC is through the effect of Cl in the water (McLaughlin *et al.* 1994a), increasing the mobility of Cd in the soil/root zone (Smolders and McLaughlin 1996). The only soil test which significantly improved the prediction of tuber Cd concentrations was 0.01 M $CaCl_2$, accounting for a further 12% of the variation in tuber Cd concentrations, with the effect more evident at lower levels of irrigation water salinity. This extractant has been used before at various strengths for extracting Cd from soils (Sauerbeck and Styperek 1985; Whitten and Ritchie 1991; Fujii *et al.* 1983; Rayment 1994). The advantage of this extractant over the other extractants for the soils studied here is that the Cl in the extracting solution assists desorption of Cd from soil surfaces by the accompanying cation (Ca), probably mimicking the action of Cl in the irrigation waters. Consideration of the ionic activity of Cd^{2+} in the extraction solution (McLaughlin *et al.* 1997b) using the technique of Fujii *et al.* (1983) did not improve the predictive capacity of the method. Despite the significant additional variance in tuber Cd accounted for by Cd extracted by 0.01 M $CaCl_2$, a measure of irrigation water EC was four times more effective in predicting tuber Cd concentration. It is surprising that soil Cd was not related more strongly to tuber Cd concentrations, as salinity can only have a marked effect on Cd uptake if Cd is present in the soil and available to be mobilised by Cl. Most of these soils had had prior P fertilisation over a number of years, so that enough Cd had probably already accumulated in the soil to allow the effect of salinity to be well expressed.

Despite the ability of the proposed procedure to predict the probability of exceeding tuber Cd concentrations at either the 0.05 or 0.1 mg kg^{-1} FW level, a significant amount (>40%) of the variation in tuber Cd concentrations remained unexplained. This may be due to other factors

not included in the test, such as soil texture, soil organic matter content, tuber variety or due to grower management practices not reflected by the pre-plant measurements e.g. tactical N, P or micronutrient fertilizer applications, which can all affect Cd availability to plants (McLaughlin *et al.* 1996). Tuber variety could be included in an assessment of Cd risk, using the rankings for Cd accumulation by commercial varieties currently available (McLaughlin *et al.* 1994b). However, given the very wide range of growing conditions, soils and varieties studied here, it is perhaps not surprising that a significant percentage of the variation remains unexplained, as has been found in other studies covering a similarly wide range of soils (He and Singh 1993). Nevertheless, the proposed procedure provides growers with useful information with which to select sites for potato cropping in order to minimise the risks of producing crops exceeding the chosen target values.

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APPENDIX 2 Uptake and partitioning of cadmium and macro- and micro-nutrients in potato (*Solanum tuberosum* L.).

Introduction

Knowledge of nutrient and cadmium uptake and partitioning between different plant parts, nutrient and cadmium removal in the harvested portion, rate of growth and total dry matter production, is useful to develop efficient and sustainable nutrient and cadmium management strategies.

The concentration of nutrients and cadmium in plants is affected by many factors, including nutrient mobility, which need to be understood to develop an effective plant sampling procedures, and to ensure that interpretations and recommendations, based on plant test data, are valid.

The objective of this experiment was to determine the uptake and partitioning of cadmium and macro- and micro- nutrients in potato.

Materials and Methods

A glasshouse experiment was conducted at the SARDI Plant Research Centre during August - November, 1995. The experimental design was a randomized block, with 12 sampling times replicated 5 times. The cultivar grown was Pontiac.

The experimental procedure was as follows:

I. A siliceous sand from a site in the Mt Lofty Ranges (Mt Compass) was used in the experiment. The soil was air dried and sieved to <5 mm before use. To characterise the soil, a sub-sample was collected for chemical and physical analysis. For each experiment 300 mm diameter, free draining pots and 15 kg of air dry soil were used.

II. The soil from each pot was spread on a plastic sheet to <10-15 mm in depth. Basal N, P, K fertilisers, supplying equivalent to 150 kg N ha^{-1} (as ammonium nitrate), 100 kg P ha^{-1} (as single superphosphate) and 150 kg K ha^{-1} (as potassium sulfate), were broadcast evenly over the soil and then thoroughly mixed into the soil. Approximately two thirds of the soil was replaced into the pot.

III. Immediately prior to planting, a subsample of soil was collected from each pot for chemical analysis.

IV. Tuber seed pieces of the cv. Pontiac (one per pot) were planted on the 21st of August and covered with 2-3 cm of soil, after which the pots were placed in a glasshouse. For each pot, the remaining soil was added when the plants were 25-30 cm tall to minimize the risk of tubers developing above the soil surface.

V. Depending on stage of growth, the plants were watered 1-6 times a week using mains water. On the 8th, 18th and 29th of September and the 6th of October the plants were fertilised with Aquasol, and on the 13th, 16th and 27th of October, with potassium nitrate. The side-dressings were applied to ensure these nutrients did not limit growth or tuber yield. During growth, each plant was supported by a trellis.

VI. Twelve times during the growing season a plant was randomly selected from each replicate for fractionation. Plants were harvested on the 15th (first harvest), 21st and 28th of September, 5th, 12th, 19th and 26th of October and 2nd, 9th 17th, 24th and 30th (final harvest) of October.

VII. The plants were separated into tubers, stolons, stems, younger leaves (leaves 1-6) and older leaves (leaves > 6). Each fraction was rinsed in 0.1% Decon, deionised reverse osmosis water and blotted dry. Fresh and dry weights were determined prior to chemical analysis.

Chemical analysis of plant materials

Cadmium. Sub-samples (0.1 g) of the dried ground plant materials were digested with concentrated nitric acid until the digest mixture was clear. The digest solution was diluted to 10 ml using 0.016M nitric acid. All samples were digested in duplicate with blanks and internal reference materials in each batch. Cadmium concentrations in the digest solutions were determined using an atomic absorption spectrophotometer with graphite furnace atomisation and deuterium background correction. Orthophosphoric acid was used as a modifier.

Other elements. Concentrations of B, Ca, Cu, Fe, K, Mg, Mn, S and Zn in the digest solutions were determined using Inductively-Coupled Plasma Atomic Emission Spectroscopy.

Results and Discussion

1. Cadmium

1.1. Accumulation of cadmium in the plant

Cadmium accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting (See Figure 1.1).

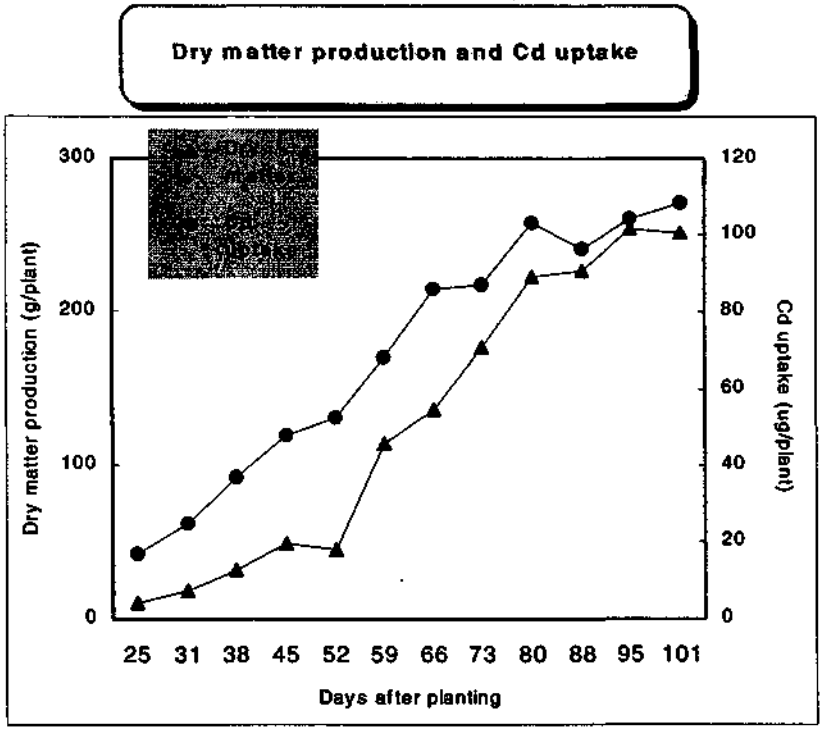

Figure 1.1. Total dry matter production and cadmium uptake. Data are for the cv. Pontiac grown in pots in a glasshouse

Cadmium uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of cadmium was relatively constant during the period 25-80 days after planting (Figure 1.1).

1.2 Accumulation of cadmium by different plant parts

The distribution of cadmium among the different plant parts, varied during the growing season. Data for the cv. Pontiac, show that during the period 40-50 days after planting cadmium uptake was in the order, older leaves > tubers, stems and younger leaves > stolons (see Figure 1.2). In contrast at > 80 days after planting, the order was tubers >> older leaves > younger leaves > stems > stolons (Figure 1.2).

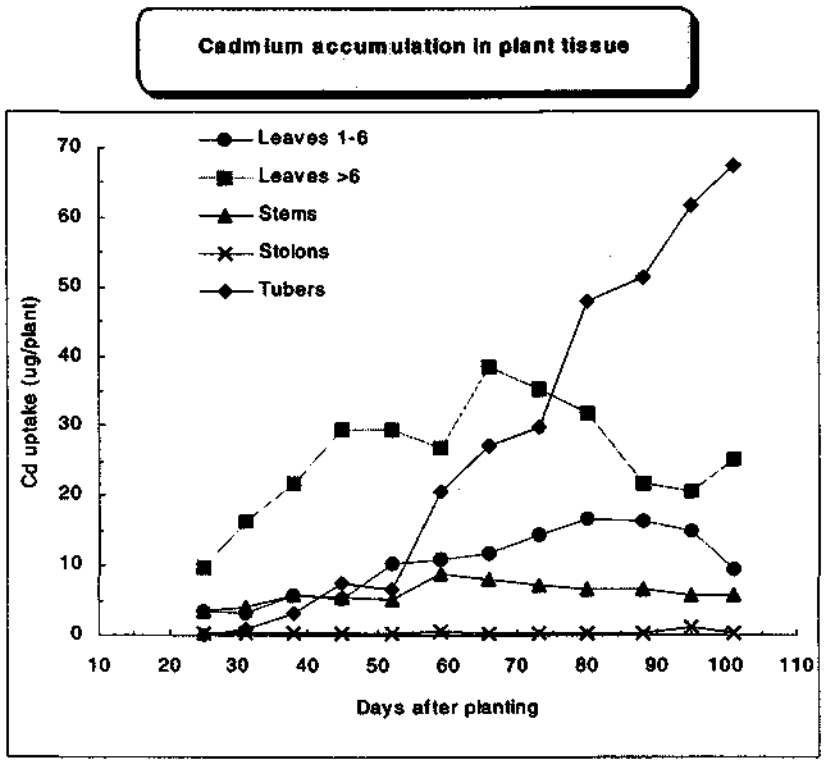

Figure 1.2. Cadmium uptake by different plant fractions. Data are for the cv. Pontiac grown in pots in a glasshouse

At the final harvest, 62.2% of the total cadmium accounted for was removed in tubers compared with only 23.3% in older leaves (leaves >6), 8.8% in younger leaves, 5.2% in stems and 0.5% in stolons. During the period 66-95 days after planting, older leaves lost 34.4% of the cadmium contained at day 66 (See Figure 1.2).

1.3 Cadmium in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 1.3, show cadmium concentrations for different plant parts, and how they change relative to one another, during the growing season.

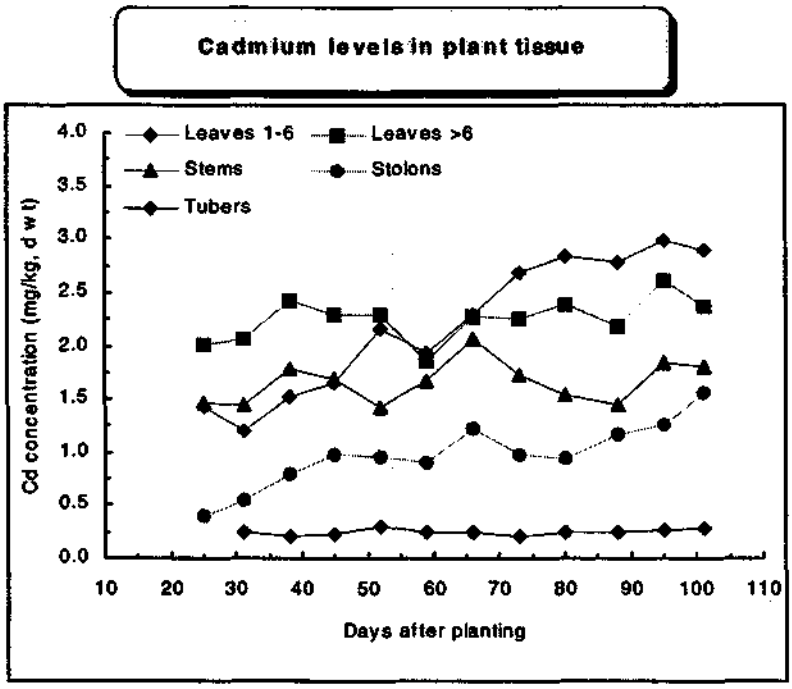

Figure 1.3. Cadmium concentrations in different plant parts during the growing season. Data are for the cv. Pontiac, grown in pots in a glasshouse.

During tuber bulking cadmium concentrations in the different plant parts were generally in the order: leaves > stems > stolons > tubers. (See Figure 1.3). Cadmium levels in tubers were relatively stable during the growing season. In contrast, levels in younger leaves (younger leaves) showed a consistent increase.

2. Phosphorus

2.1. Accumulation of phosphorus in the plant

Phosphorus accumulation was positive during the vegetative and tuber bulking periods (see Figure 2.1).

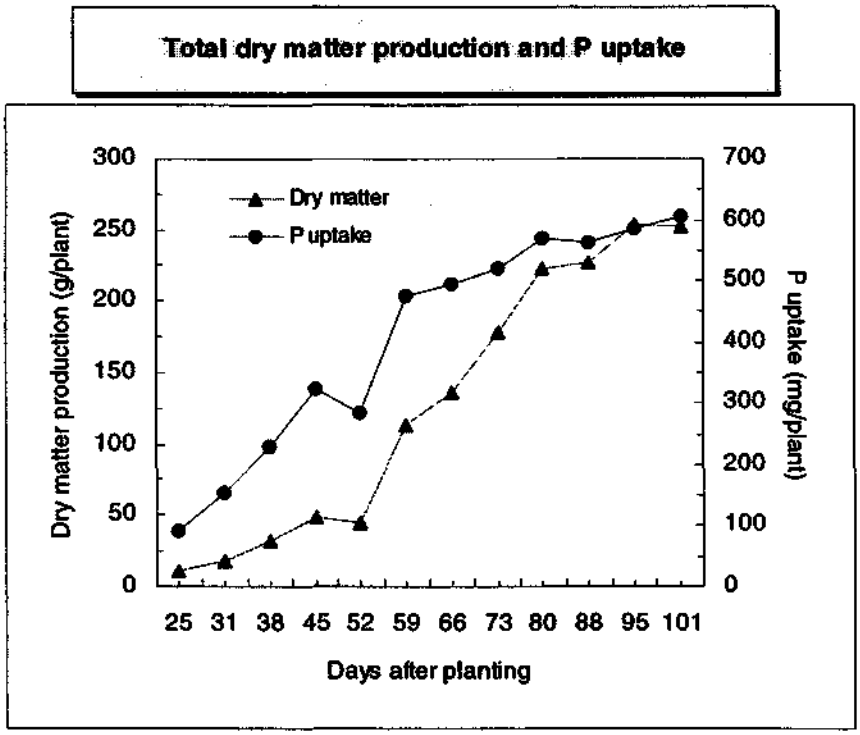

Figure 2.1. Total dry matter production and phosphorus uptake. Plants were grown under an adequate phosphorus fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

The data presented in Figure 2.1 for the cv. Pontiac, grown with adequate phosphorus supply, show that during the vegetative-early tuber set period (< 52 days after planting) phosphorus accumulation was more rapid than dry matter production (ie. growth). In contrast, 59-95 days after planting when rapid tuber bulking occurred, the rate of dry matter production, was greater than phosphorus accumulation. McCollum (1978) reported similar patterns of phosphorus accumulation, which was positive until at least 72 days after emergence, and the P-uptake curve lay above, but essentially parallel to, the growth curve until the plants approached maturity. Our data showed similar trends.

2.2 Accumulation of phosphorus by different plant parts

The distribution of phosphorus among the different plant parts, varied during the growing season. Data for the cv. Pontiac presented in Figure 2.2 show that 40-50 days after planting phosphorus uptake was in the order, older leaves > tubers >> younger leaves (young leaves) > stems > stolons. In contrast, at > 80 days after planting, the order was tubers >>> leaves, stems and stolons.

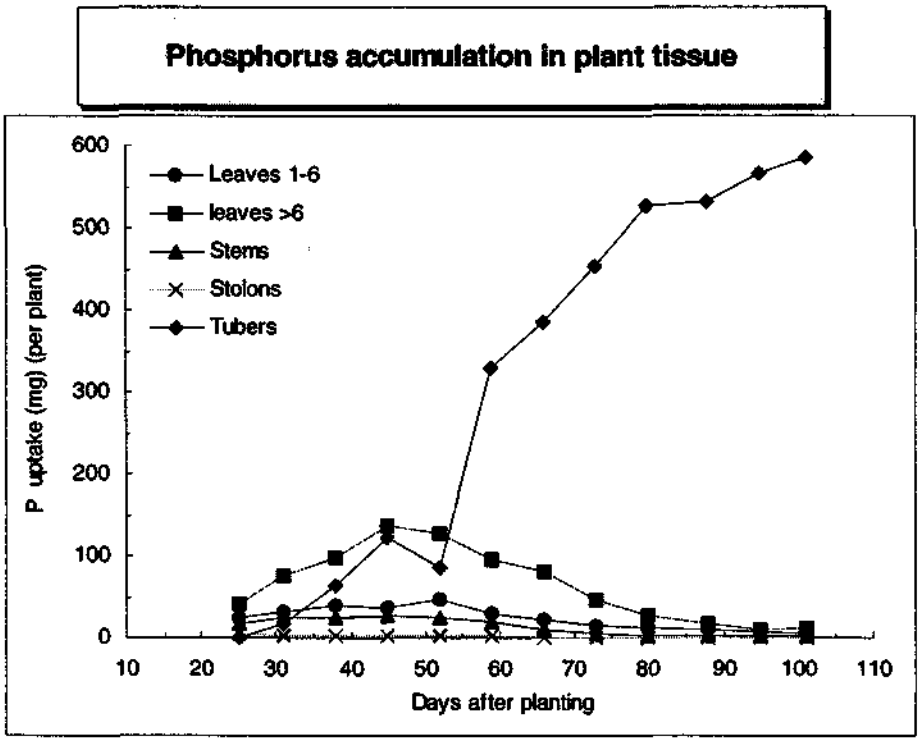

Figure 2.2. Phosphorus uptake by different plant fractions. Plants were grown under an adequate phosphorus fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Older leaves (during the vegetative-early tuber bulking period) and tubers (during tuber bulking) are major sinks for phosphorus (See Figure 2.2). For example, at 101 days after planting (final harvest), 96.7% of the total phosphorus accounted for was translocated to tubers, compared with only 2.8% in leaves, 0.4% in stems and 0.1% in stolons. Christensen and Jackson (1981) for the cv. Russet Burbank, reported that the uptake of phosphorus by whole tops, leaves and roots increased as phosphorus supply increased. For 31 day old plants with adequate P supply, phosphorus uptake was in the order, whole tops > leaves >>> roots. Jackson and Haddock (1959) for the cv. Russet Burbank, and Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported similar trends for phosphorus accumulation in tops and tubers. Jackson and Haddock (1959) found that tops accumulated phosphorus until 95 days after planting. Thereafter (95-152 days after planting), tops lost 45% of the phosphorus contained at 95 days. In our study with the cv. Pontiac, tops accumulated phosphorus until 45-52 days after planting and during this period, older leaves were the main sink for phosphorus. However, during the period 52-95 days after planting, older leaves (leaves >6) lost 91.7% of the phosphorus contained at day 52 (See Figure 2.2). Loss of phosphorus from vegetative tissue may be due to retranslocation from tops to tubers and leaf senescence. McCollum (1978) reported that 82% of the total phosphorus accounted for was located in tubers. Jackson and Haddock (1959) found that at the end of the season, tubers of the cv. Russet Burbank accounted for approximately 83% of the phosphorus taken up by the plant

2.3 Phosphorus uptake rates

Nutrient uptake rates by tubers depend on bulking rates and duration of the tuber bulking period. Based on data presented in phosphorus accumulation and removal for the cv. Pontiac,

growing tubers may accumulate phosphorus at a rate of 0.52 kg ha^{-1} day^{-1} when averaged over the tuber bulking period. Westermann (1993) presented uptake data for a range of cvv. grown in America, including: Russet Burbank, 0.41-0.59 kg ha^{-1} day^{-1}; Norchip 0.34-0.48 kg ha^{-1} day^{-1}; and Kennebec, 0.63-0.90 kg ha^{-1} day^{-1}. Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported that tubers accumulated phosphorus at approximately 0.32 kg ha^{-1} day^{-1}. Jackson and Haddock (1959) reported that for the cv. Russet Burbank, maximum absorption of phosphorus occurred 88-95 days after planting, and during this period, tubers absorbed phosphorus at 0.25 kg ha^{-1} day^{-1}.

Ezeta and McCollum (1972) and Harris (1992, p. 166) have tabulated phosphorus uptake rates for different cultivars and countries.

2.4 Phosphorus in leaf, stem, stolon, tuber and root

Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), presented concentrations in different plant fractions, and at 116 days after planting (total growth period was 195 days) the order was, leaves > stems ~ roots+stolons+below ground stems; at 172 days the order was, leaves >> tubers > roots+stolons+below ground > stems. Data for the cv. Pontiac, presented in Figure 2.4, show phosphorus concentrations for different plant parts, and how they change relative to one another, during the growing season.

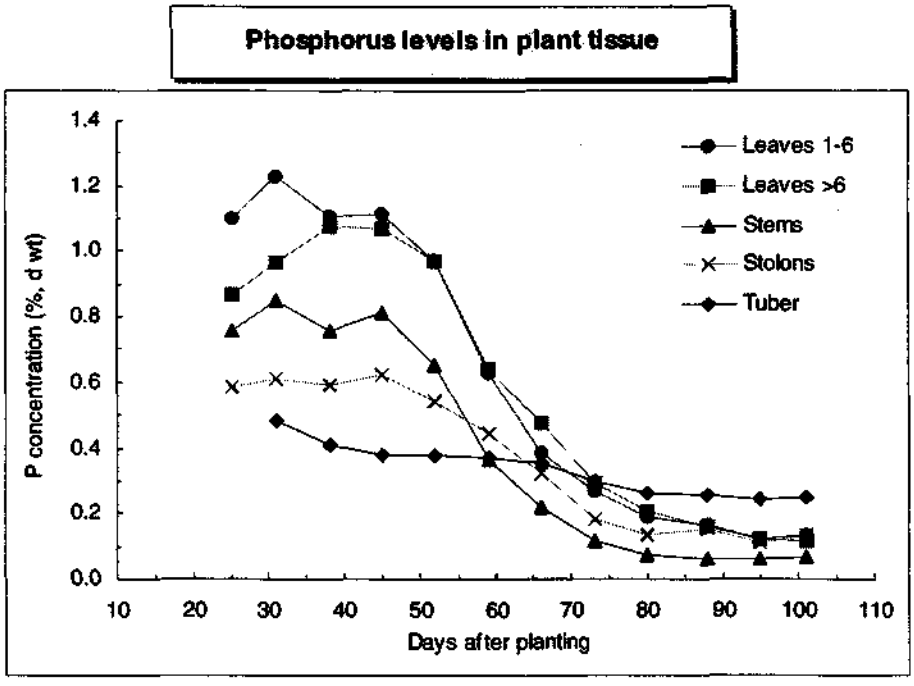

Figure 2.4. Phosphorus concentrations in different plant parts during the growing season. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate phosphorus fertiliser regime

During tuber initiation (25-38 days after planting), phosphorus concentration in the different plant parts were in the order: older leaves > younger leaves > stems > stolons > tubers. In contrast, 80 - 100 days after planting, concentrations were in the order, tubers > leaves and stolon > stems. Jackson and Haddock (1959) presented data showing that 74 days after planting, phosphorus concentrations in tubers were greater than in tops, particularly late in the season (116-152 days after planting). Painter (1979) also presented data showing that, late in

the season, phosphorus concentrations in tubers (0.29%) were greater than levels in tops (0.21%).

3. Potassium

3.1. Accumulation of potassium in the plant

Potassium accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting. (See Figure 3.1).

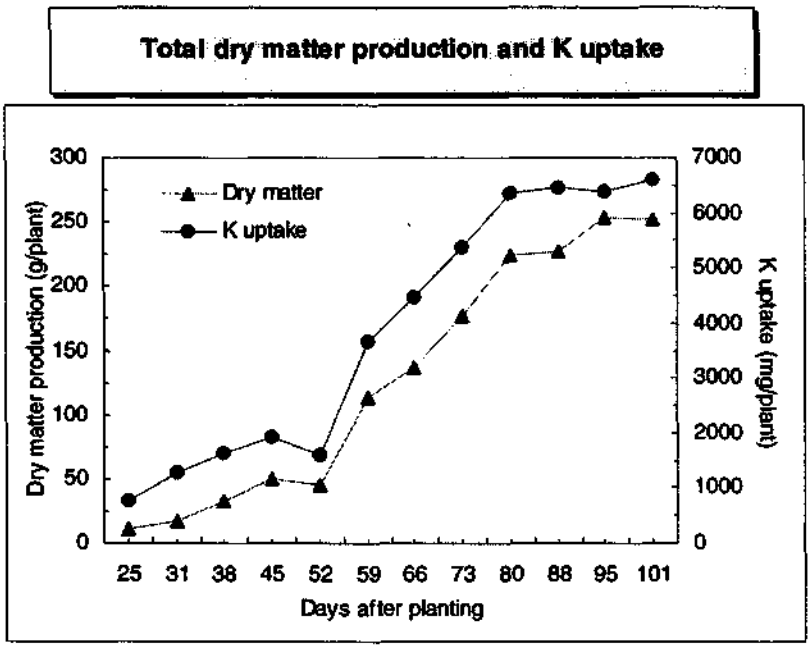

Figure 3.1. Dry matter production and potassium uptake by tops+stolons+tubers. Plants were grown under an adequate potassium fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Potassium uptake by tops+stolons+tubers closely paralleled growth or dry matter production for tops+stolons+tubers. The steepest portion of both curves occurred between 52 and 80 days after planting (Figure 3.1). Jackson and Haddock (1959) and Ezeta and McCollum (1972) presented similar curves for potassium uptake by tops+tubers.

3.2. Accumulation of potassium by different plant parts

The distribution of potassium among the different plant parts, varied during the growing season. Data for the cv. Pontiac, show that 40 days after planting potassium uptake was in the order, older leaves > tubers • younger leaves • stems > stolons. In contrast at > 60 days after planting, the order was tubers >>> older leaves > younger leaves > stems > stolons (See Figure 3.2).

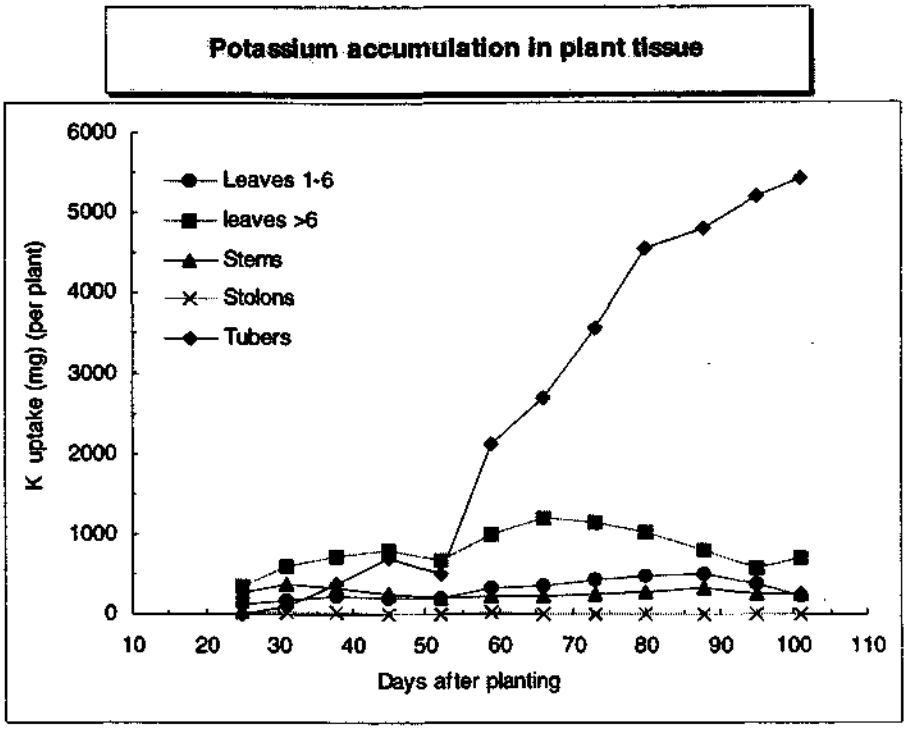

Figure 3.2. Potassium uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate potassium fertiliser regime

At the final harvest, 82.1% of the total potassium accounted for was removed in tubers, compared with only 14.0% in leaves; 3.8% in stems and 0.1% in stolons. Jackson and Haddock (1959) found that at the end of the season, tubers of the cv. Russet Burbank accounted for approximately 89% of the potassium taken up by the plant. Jackson and Haddock (1959) for the cv. Russet Burbank, and Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported similar trends for potassium accumulation in tops and tubers. Jackson and Haddock (1959) found that tops accumulated potassium until 95 days after planting. Thereafter (95-152 days after planting), tops lost 80% of the potassium contained at 95 days. In our study, during the period 66-95 days after planting, older leaves (leaves >6) lost 52.4% of the potassium contained at day 66 (See Figure 3.2).

3.3. Potassium uptake rates

Nutrient uptake rates by tubers depend on bulking rates and duration of the tuber bulking period. Based on data presented in potassium accumulation and removal for the cv. Pontiac, developing tubers may accumulate potassium at a rate of 4.8 kg ha^{-1} day^{-1} when averaged over the tuber bulking period. Westermann (1993) presented uptake data for a range of cultivars grown in America, including: Russet Burbank, 3.1-4.0 kg ha^{-1} day^{-1}; Norchip 2.5-3.2 kg ha^{-1} day^{-1}; and Kennebec, 4.6-6.1 kg ha^{-1} day^{-1}. Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported that tubers accumulated potassium at approximately 5.6 kg ha^{-1} day^{-1}. The maximum rate was 6.6 kg K ha^{-1} day^{-1}.

Ezeta and McCollum (1972) and Harris (1992, p. 166) have tabulated potassium uptake rates for different cultivars and countries.

3.4. Potassium in leaf, stem, stolon, tuber and root

Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento) presented potassium concentrations in different plant fractions. At 137 days after planting (total growth period was 195 days) the order was, leaves > stems > tubers > roots+stolons+below ground stems. Data for the cv. Pontiac, presented in Figure 3.4, show potassium concentrations for different plant parts and how they change relative to one another during the growing season.

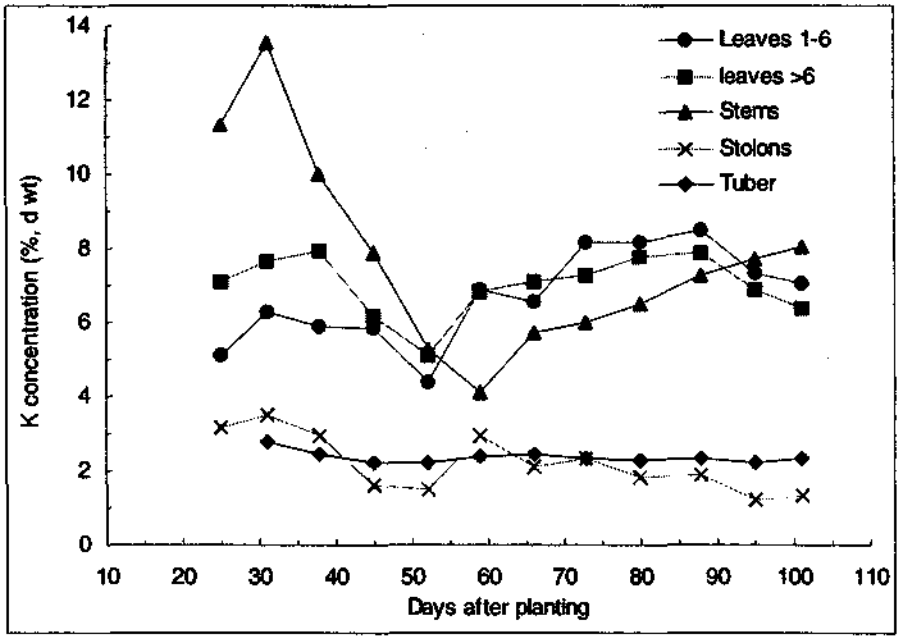

Figure 3.4. Potassium concentrations in different plant parts during the growing season. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate potassium fertiliser regime

During tuber initiation and early tuber bulking stages (25-45 days after planting), potassium concentration in the different plant parts were in the order: stems >> older leaves > younger leaves >> stolons • tubers. In contrast, 55-90 days after planting, concentrations were higher in leaves compared with stems. Ward (1959) presented data showing that potassium concentrations in different tissues of one month old plants were in the order, stem > leaf > tuber > root. The differences were greater in plants at adequate to high plane of potassium nutrition, compared with deficient plants. Data presented by Tiwari et al. (1982) for the cv. 'Kufri Chandramkhi' grown with deficient and adequate potassium supply, show that potassium concentrations at maturity were in the order: top > tuber > root.

4. Calcium

4.1. Accumulation of calcium in the plant

Calcium accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting. (See Figure 4.1).

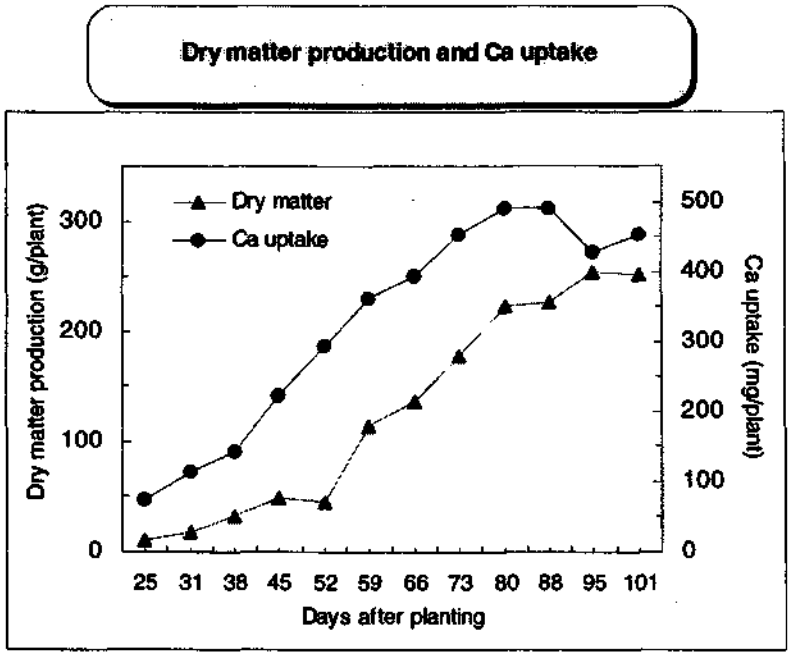

Figure 4.1. Dry matter production and calcium uptake by tops+stolons+tubers. Plants were grown under an adequate calcium fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Calcium uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The steepest portion of the calcium uptake curve occurred 39-58 days after planting (Figure 4.1). Ezeta and McCollum (1972) presented similar curves for calcium uptake by tops+tubers and dry matter production. Uptake of calcium reached a maximum of 60 kg ha^{-1} at 137 days after planting. After this date calcium accumulation decreased, which may have been due to leaf drop. Data presented in Figure 4.1, show that for the cv. Pontiac maximum uptake of 30.3 kg ha^{-1} occurred 80 days after planting.

4.2. Accumulation of calcium by different plant parts

The distribution of calcium among the different plant parts, varied during the growing season. Data for the cv. Pontiac, show that 30 days after planting calcium uptake was in the order, older leaves > stems > younger leaves • stolons • tubers. In contrast at > 70 days after planting, the order was older leaves >> younger leaves >> stems • tubers > stolons (See Figure 4.2).

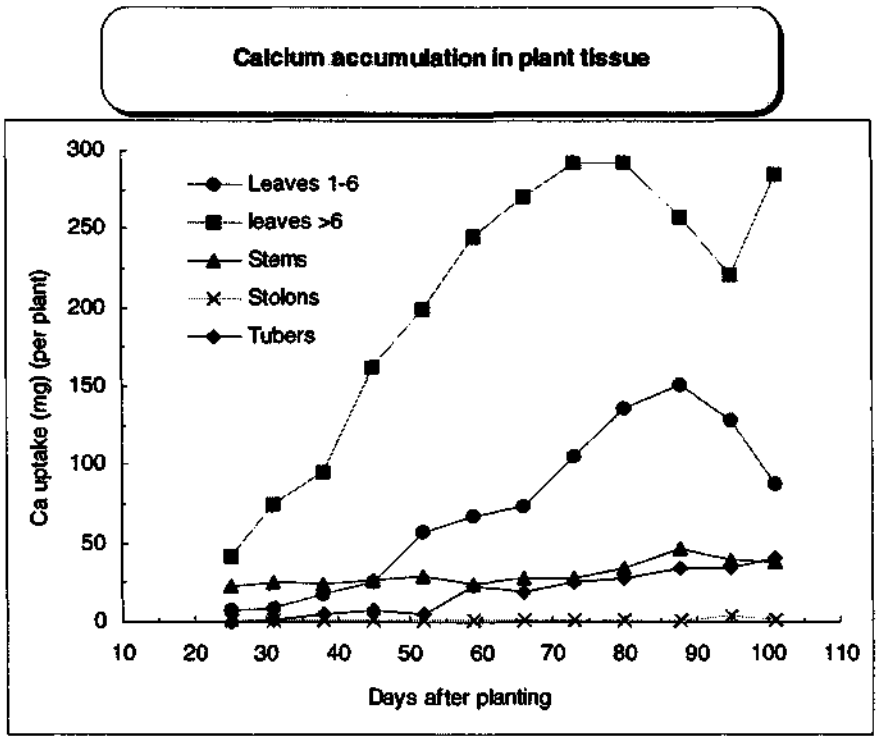

Figure 4.2. Calcium uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate calcium fertiliser regime

At the final harvest, 63.0% of the total calcium accounted for was removed in older leaves, compared with only 19.3% in younger leaves, 8.9% in tubers, 8.5% in stems and 0.3% in stolons. Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported similar trends for calcium accumulation in tops and tubers.

4.3. Calcium in leaf, stem, stolon, tuber and root

Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), presented concentrations in different plant fractions, the order at 137 days after planting (total growth period was 195 days) was, leaves (1.51%) > roots+stolons+below ground stems (0.92%) > stems (0.84%) >> tubers (0.09%). Data for the cv. Pontiac, presented in Figure 4.3, show calcium concentrations for different plant parts, and how they change relative to one another, during the growing season.

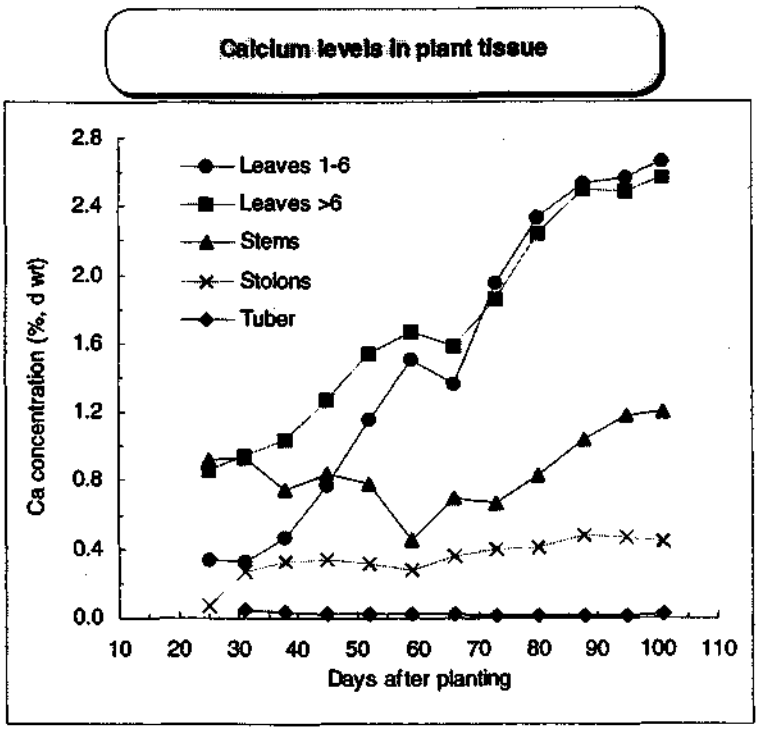

Figure 4.3. Calcium concentrations in different plant parts during the growing season. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate calcium fertiliser regime

During tuber initiation and early tuber bulking stages (25-40 days after planting), calcium concentrations in the different plant parts were in the order: older leaves • stems > younger leaves • stolons > tubers. In contrast, 55-90 days after planting, the order was: leaves >> stems > stolons > tubers (See Figure 4.3). Painter (1979) also presented data showing that, late in the season, calcium concentrations in tubers (0.074%) were much lower than concentrations in tops (0.92%). Locascio and Rhue (1990) showed that calcium concentrations in whole tops (0.69-0.96%) sampled at early flowering were higher than concentrations in recently matured leaves (0.38-0.63%).

5. Magnesium

5.1. Accumulation of magnesium in the plant

Magnesium accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting. (See Figure 5.1).

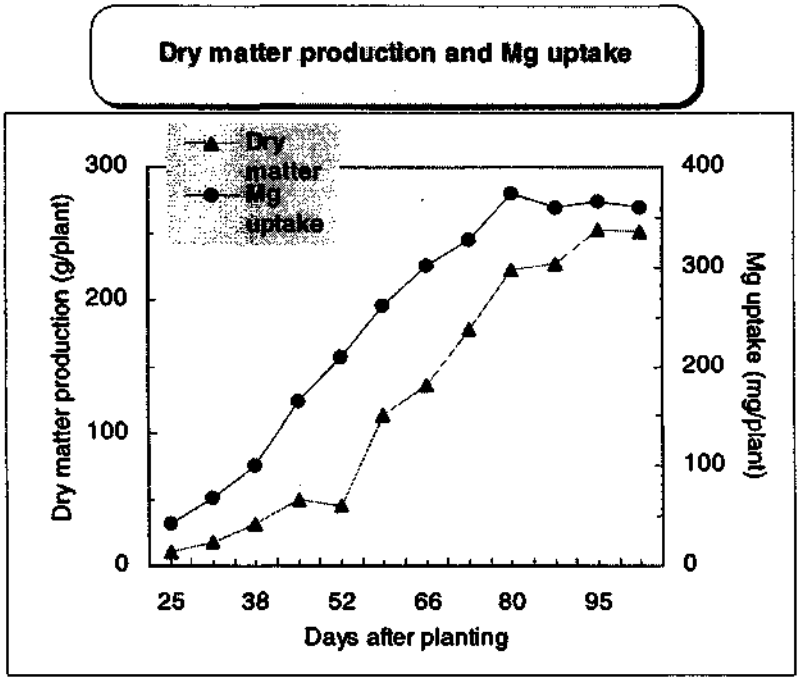

Figure 5.1. Dry matter production and magnesium uptake by tops+stolons+tubers. Plants were grown under an adequate magnesium fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Magnesium uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of magnesium was relatively constant during the period 25-80 days after planting (Figure 5.1). Ezeta and McCollum (1972) presented similar curves for magnesium uptake by tops+tubers and dry matter production. Uptake of magnesium reached a maximum of 31 kg ha^{-1} at 137 days after planting. After this date magnesium accumulation decreased, which may have been due to leaf drop. Data presented in Figure 5.1, show that for the cv. Pontiac maximum uptake of 23.0 kg ha^{-1} occurred 80 days after planting.

5.2. Accumulation of magnesium by different plant parts

The distribution of magnesium among the different plant parts, varied during the growing season.

Data for the cv. Pontiac, show that during the period 31-66 days after planting magnesium uptake was in the order, older leaves > stems ≈ younger leaves • tubers > stolons. In contrast at > 73 days after planting, the order was tubers >> older leaves > younger leaves ≈ stems > stolons (See Figure 5.2).

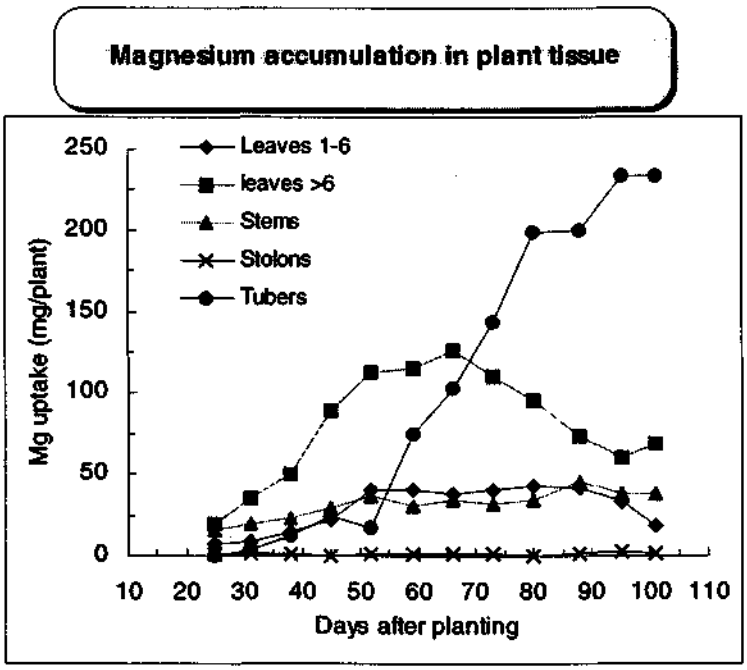

Figure 5.2. Magnesium uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate magnesium fertiliser regime

At the final harvest, 64.9% of the total magnesium accounted for was removed in tubers compared with only 19.9% in older leaves, 10.7% in stems, 5.1% in younger leaves and 0.2% in stolons. During the period 66-101 days after planting, older leaves lost 45.6% of the magnesium contained at day 66 (See Figure 5.2). Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), reported similar trends for magnesium accumulation in tops and tubers.

5.3. Magnesium in leaf, stem, stolon, tuber and root

Ezeta and McCollum (1972) for Solanum andigena (cv. Renacimiento), presented concentrations in different plant fractions, the order at 137 days after planting (total growth period was 195 days) was, leaves (0.70%) > stems (0.49%) > roots+stolons+below ground stems (0.40%) >> tubers (0.12%).

Data for the cv. Pontiac, presented in Figure 5.3, show magnesium concentrations for different plant parts, and how they change relative to one another, during the growing season.

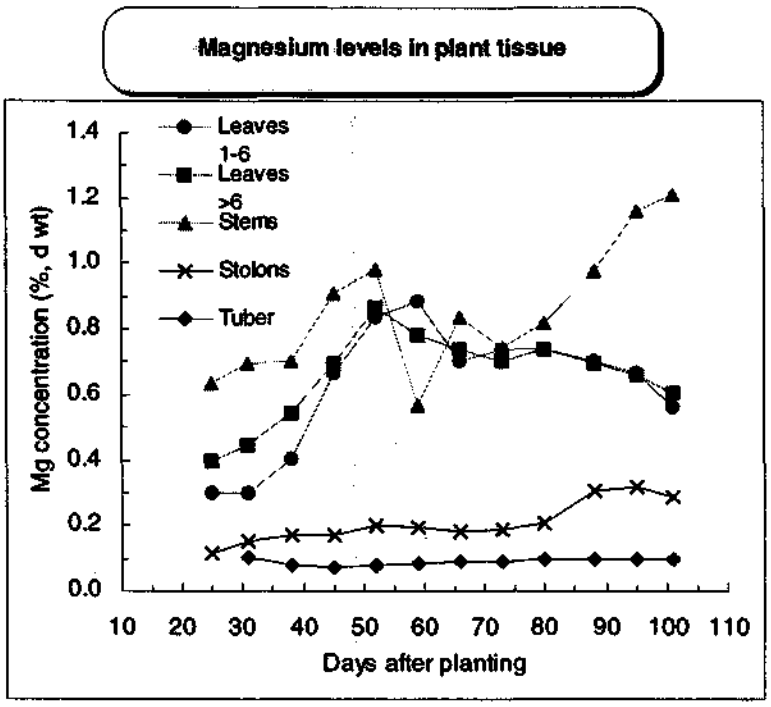

Figure 5.3. Magnesium concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate magnesium fertiliser regime

During tuber initiation and early tuber bulking stages (25-40 days after planting), magnesium concentrations in the different plant parts were in the order: stems > leaves > stolons > tubers. In contrast, 59-80 days after planting, concentrations in stems and leaves were similar (See Figure 5.3). Painter (1979) also presented data showing that, late in the season, magnesium concentrations in tubers (0.15%) were lower than concentrations in tops (0.48%). Similarly, Carpenter (1963) found that concentrations in tubers were less than in tops, for example, 62 days after planting concentrations in tubers were in the range 0.29-0.31% compared with 1.19-1.37% in tops. Yuan (1985) reported that magnesium concentrations in vegetative tissue of the cv. Atlantic sampled one day before harvest, were higher than concentrations in tubers (1.9-2.0 vs 0.09%). Locascio and Rhue (1990) showed that magnesium concentrations in whole tops sampled at early flowering were higher than concentrations in recently matured leaves, however, the magnitude of the difference varied between years. In 1980, concentrations in whole tops were in the range 1.11-1.22% and were consistently higher than concentrations in recently matured leaves, which ranged from 0.71-0.74%. In contrast, in 1981 magnesium concentrations in whole tops (0.92-1.03%) were similar to concentrations in leaf tissue (0.85-1.08%).

6. Sulfur

6.1. Accumulation of sulfur in the plant

Sulfur accumulation was positive during the vegetative and tuber bulking periods, up to 88 days after planting (See Figure 6.1).

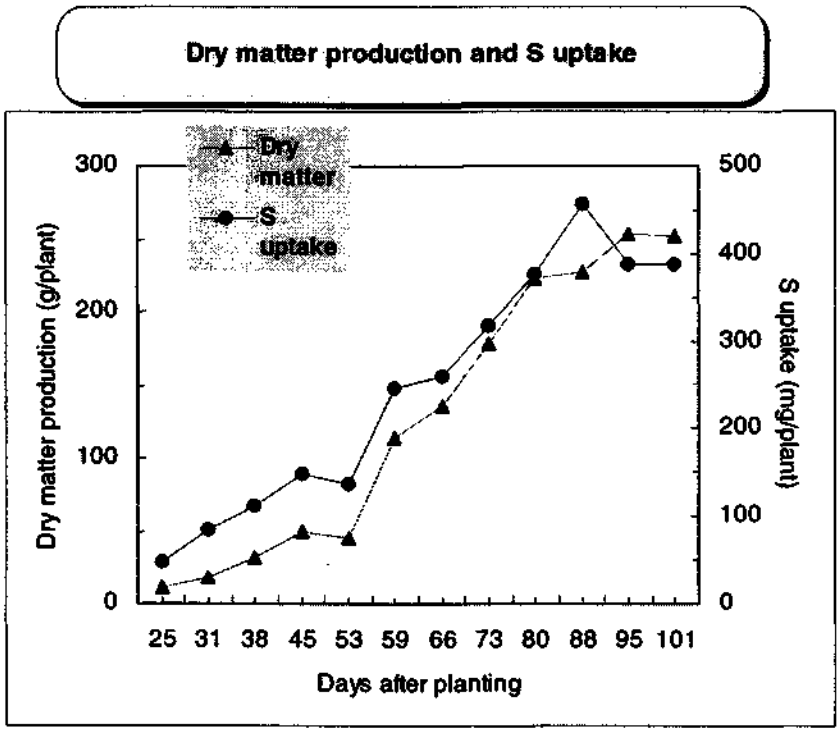

Figure 6.1. Dry matter production and sulfur uptake by tops+stolons+tubers. Plants were grown under an adequate sulfur fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Sulfur uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of sulfur was relatively constant during the period 53-88 days after planting (Figure 6.1).

6.2. Accumulation of sulfur by different plant parts

The distribution of sulfur among the different plant parts, varies during the growing season. Data for the cv. Pontiac, show that during the period 25-53 days after planting sulfur uptake was in the order, older leaves (leaves >6) >stems, tubers and younger leaves > stolons. In contrast, during the period 59 to 88 days after planting, the order was tubers >> older leaves > younger leaves > stems ≈ stolons (See Figure 6.2).

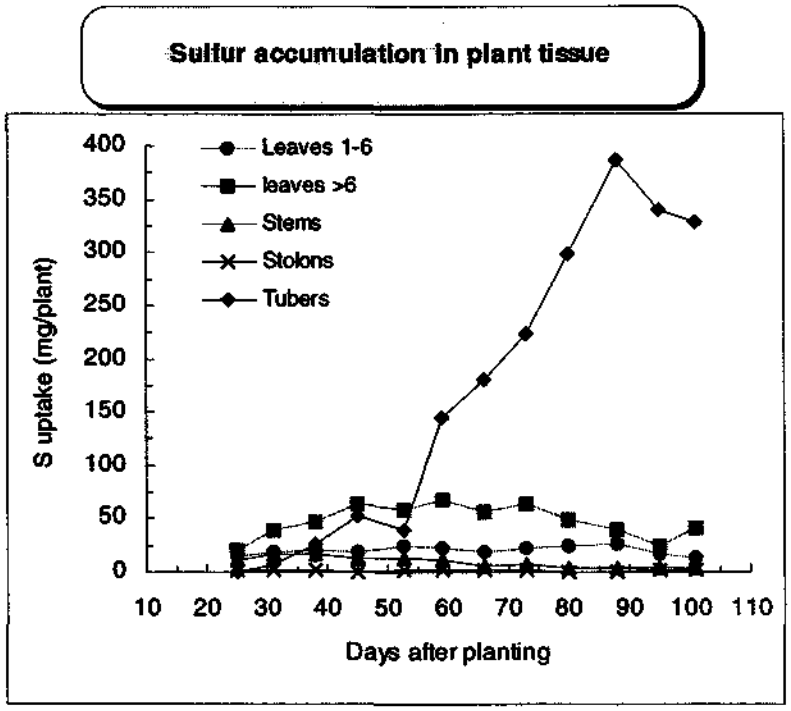

Figure 6.2. Sulfur uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate sulfur fertiliser regime

At the final harvest, 84.6% of the total sulfur accounted for was removed in tubers compared with only 10.6% in older leaves (leaves >6), 3.6% in younger leaves, 0.9% in stems, and 0.3% in stolons. During the period 59-95 days after planting, older leaves lost 62.6% of the sulfur contained at day 59 (See Figure 6.2).

6.3. Sulfur in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 6.3, show sulfur concentrations for different plant parts, and how they change relative to one another, during the growing season.

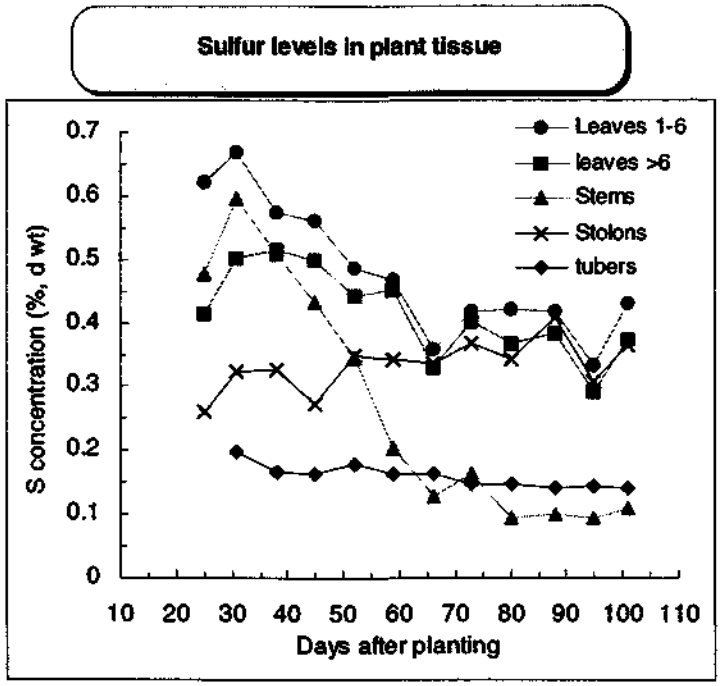

Figure 6.3. Sulfur concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate sulfur fertiliser regime

During tuber initiation and early tuber bulking stages (25-45 days after planting), sulfur concentrations in the different plant parts were in the order: younger leaves > older leaves > stolons > tubers. In contrast, > 66 days after planting, concentrations in leaves and stolons were similar and greater than sulfur concentrations in tubers and stems (See Figure 6.3).

7. Boron

7.1. Accumulation of boron in the plant

Boron accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting (See Figure 7.1).

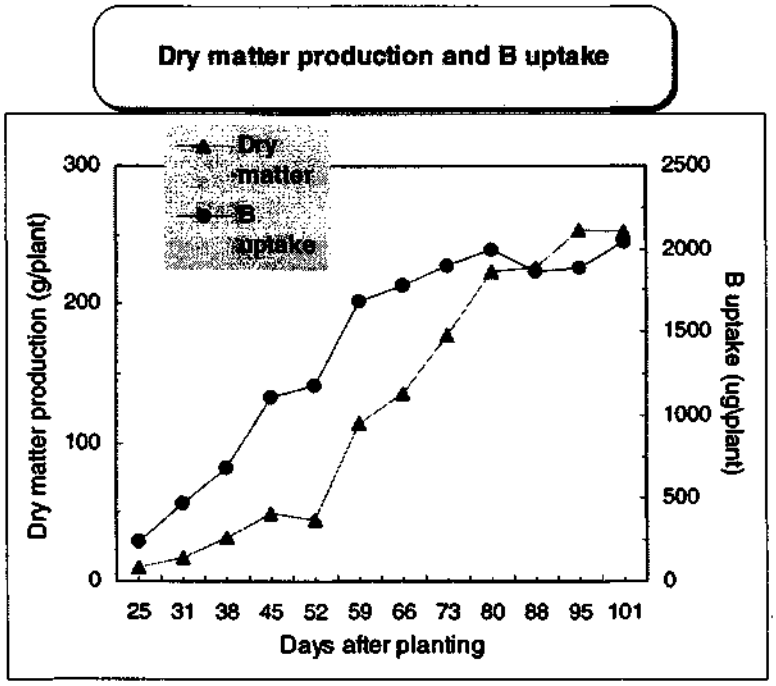

Figure 7.1. Dry matter production and boron uptake by tops+stolons+tubers. Plants were grown under an adequate boron fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Boron uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of boron was relatively constant during the period 25-59 days after planting (Figure 7.1).

7.2. Accumulation of boron by different plant parts

The distribution of boron among the different plant parts, varied during the growing season. Data for the cv. Pontiac, show that during the period 40-60 days after planting boron uptake was in the order, older leaves > tubers and younger leaves > stems > stolons (see Figure 7.2). In contrast at > 66 days after planting, the order was tubers >> older leaves > younger leaves > stems > stolons (Figure 7.2).

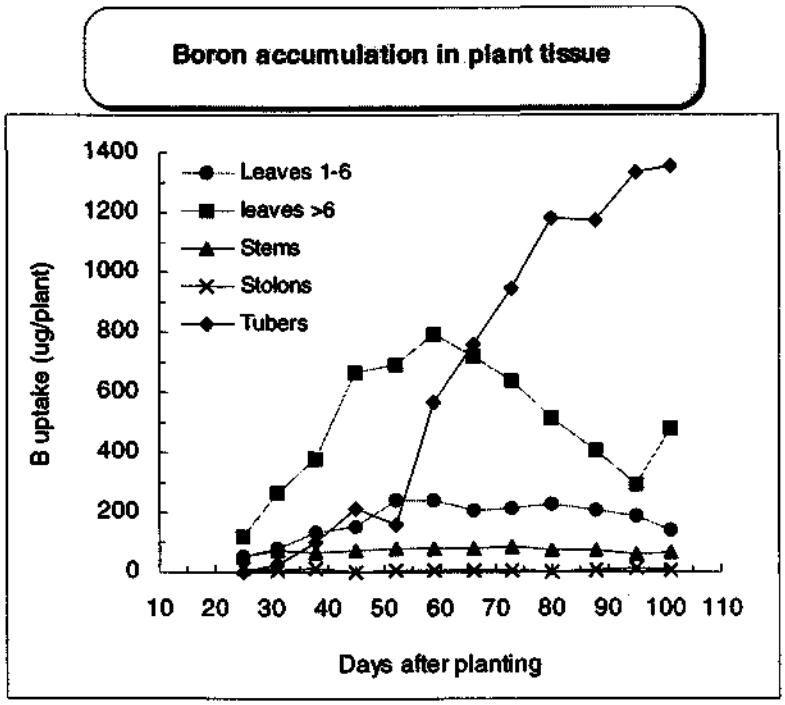

Figure 7.2. Boron uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate boron fertiliser regime

At the final harvest, 66.2% of the total boron accounted for was removed in tubers compared with only 23.7% in older leaves (leaves >6), 6.7% in younger leaves, 3.2% in stems and 0.2% in stolons. During the period 59-95 days after planting, older leaves lost 63.3% of the boron contained at day 59 (See Figure 7.2).

7.3. Boron in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 7.3, show boron concentrations for different plant parts, and how they change relative to one another, during the growing season.

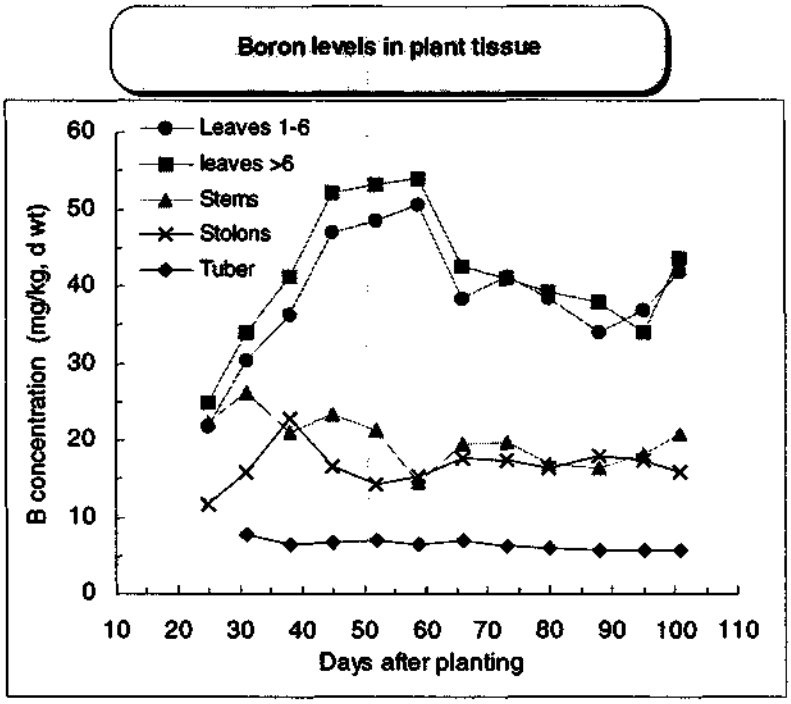

Figure 7.3. Boron concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate boron fertiliser regime

During tuber bulking boron concentrations in the different plant parts were in the order: leaves >> stems and stolons > tubers (See Figure 7.3). Gupta et al. (1985) reported that transpiration, xylem stream and leaf venation affected the accumulation of boron in leaves. They also cited work showing that the distribution of boron was not uniform within plant parts, for example, boron accumulates in the margin of leaves. Vimala et al. (1990) for the cv. Famosa, reported that mean (sem) boron concentrations in leaves (27.1 ± 0.54 mg kg^{-1}) and stems (22.6 ± 0.22 mg kg^{-1}) were greater than in tubers (4.3 ± 0.13 mg kg^{-1}). Painter (1979) also presented data showing that, late in the season, boron concentrations in tubers (6 mg kg^{-1}) were lower than concentrations in tops (26 mg kg^{-1}). Eaton (1944) for the cv. British Queen, reported that boron levels in leaves were greater than in tubers, for example, in plants grown in solution with 1 mg B kg^{-1} contained 98 mg kg^{-1} boron in leaves and 22 mg kg^{-1} in tubers. MacVicar et al. (1946) presented data for the cvv. Triumph, Cobbler, Chippewa and Rural New Yorker which showed that mean boron concentrations in tubers were in the range 7.8-10.7 mg kg^{-1}, depending on soil type. Rosen et al. (1991) showed that boron concentrations in recently matured leaves sampled 74 days after planting (34 or 55 mg kg^{-1}) were greater than concentrations in tubers (5.7 or 6.4 mg kg^{-1}). Roberts and Rhee (1990) found that boron concentrations in tops were greater than in vines, for example, in 1986 concentrations in tops were in the range 32-88 mg kg^{-1}, compared with 4.5-12.2 mg kg^{-1} in tubers. Similarly in another experiment conducted in 1987, concentrations in tops were in the range 27-120 mg kg^{-1}, compared with 4.4-9.9 mg kg^{-1} in tubers.

8. Copper

8.1 Accumulation of copper in the plant

Copper accumulation was positive during the vegetative and tuber bulking periods (See Figure 8.1).

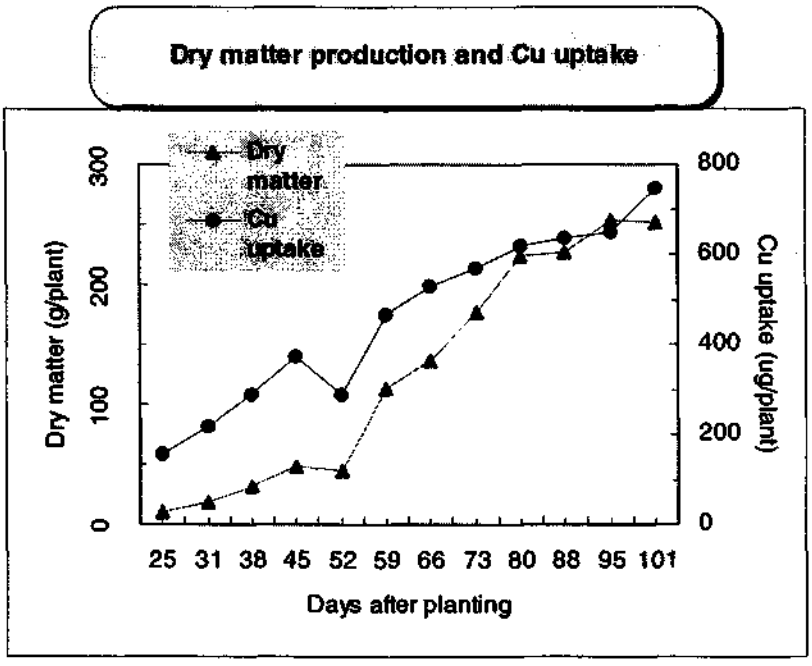

Figure 8.1. Dry matter production and copper uptake by tops+stolons+tubers. Plants were grown under an adequate copper fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

Copper uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of copper was relatively constant during the vegetative and tuber bulking periods. The decrease in uptake during the period 45-52 days after planting corresponded to a rapid increase in tuber bulking rate (Figure 8.1).

8.2. Accumulation of copper by different plant parts

The distribution of copper among the different plant parts, varied during the growing season.

Data for the cv. Pontiac, show that during the vegetative period copper uptake by different tissues was in the order, older leaves > younger leaves > stems and stolons. In contrast during tuber bulking and maturation periods accumulation in different tissues was in the order, tubers>> older leaves > younger leaves > stems and stolons (See Figure 8.2).

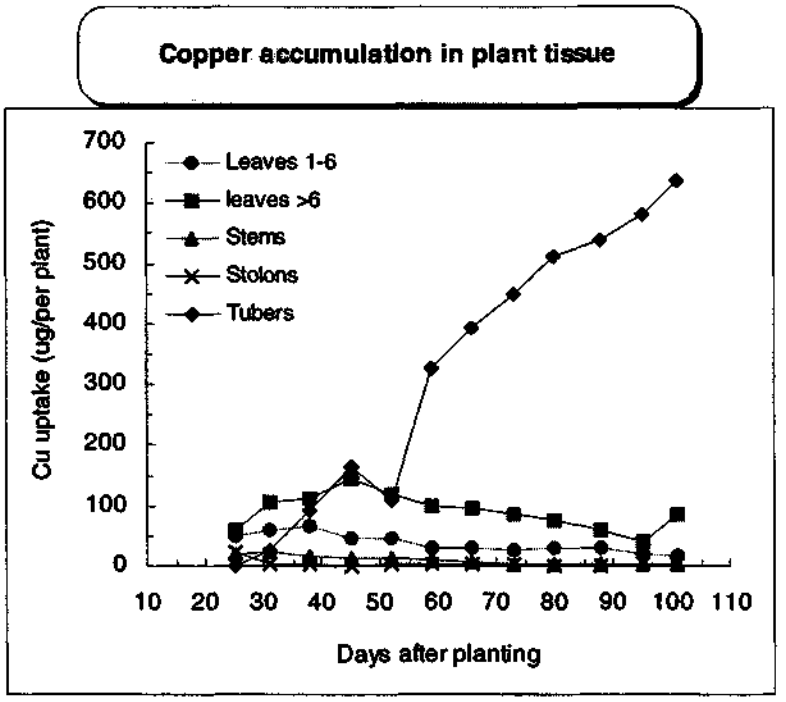

Figure 8.2. Copper uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate copper fertiliser regime

At the final harvest, 85.3% of the total copper accounted for was removed in tubers compared with only 11.5% in older leaves, 0.6% in stems, 2.3% in younger leaves and 0.3% in stolons. During the period 45-95 days after planting, older leaves lost 73.0% of the copper contained at day 45 (See Figure 8.2).

Mathur and Levesque (1983) for the cv. Kennebec grown in pots, reported copper uptake associated with the highest yields were, 0.13-0.20 mg pot^{-1} by tops and 0.14-0.22 mg pot^{-1} by tubers. In the experiment with Pontiac presented in Figure 8.2, copper uptake by tops (leaves+stems) and tubers at the final harvest was 0.11mg pot^{-1} (ie. per plant) or 0.64 mg pot^{-1}, respectively. Sharma and Arodra (1992) also reported that accumulation of copper by tubers (27.8 - 30.9 g ha^{-1}) was greater than by haulms (tops; 15.8 - 18.1 g ha^{-1}).

8.3. Copper in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 8.3, show copper concentrations for different plant parts, and how they change relative to one another, during the growing season.

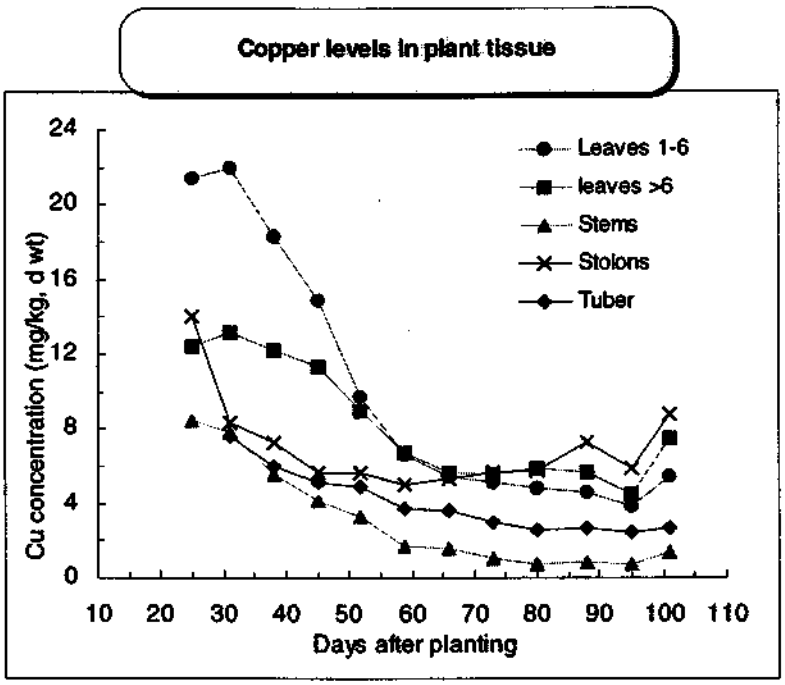

Figure 8.3. Copper concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate copper fertiliser regime

During tuber initiation and early tuber bulking stages (31-52 days after planting), copper concentrations in the different plant parts were in the order: younger leaves > older leaves > stem, stolon and tuber (See Figure 8.3). In contrast, late in the season (> 80 days after planting), concentrations in the different tissues were in the order, stolons > leaves > tubers > stems. Painter (1979) presented data showing that, late in the season, copper concentrations in tubers (10 mg kg^{-1}) were slightly higher than concentrations in tops (7 mg kg^{-1}). Vimala et al. (1990) for the cv. Famosa, reported that mean (sem) copper concentrations in leaves (11.4 ± 0.97 mg kg^{-1}) and stems (12.6 ±1.66 mg kg^{-1}) were greater than in tubers (1.3 ± 0.10 mg kg^{-1}). Locascio and Rhue (1990) showed that copper concentrations in whole tops sampled at early flowering were higher than concentrations in recently matured leaves, however, the magnitude of the difference varied between years. In 1980, concentrations in whole tops were in the range 10-11 mg kg^{-1} and were consistently higher than concentrations in recently matured leaves, which ranged from 4-5 mg kg^{-1}. In contrast, in 1981 copper concentrations in whole tops (5-8 mg kg^{-1}) were not consistently higher than concentrations in leaf tissue (4-10 mg kg^{-1}). Rosen et al. (1991) showed that copper concentrations in recently matured leaves sampled 74 days after planting (eg. 41-162 mg kg^{-1}) were greater than concentrations in tubers (eg. 4.8-5.7 mg kg^{-1}).

9. Zinc

9.1. Accumulation of zinc in the plant

Zinc accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting. (See Figure 9.1).

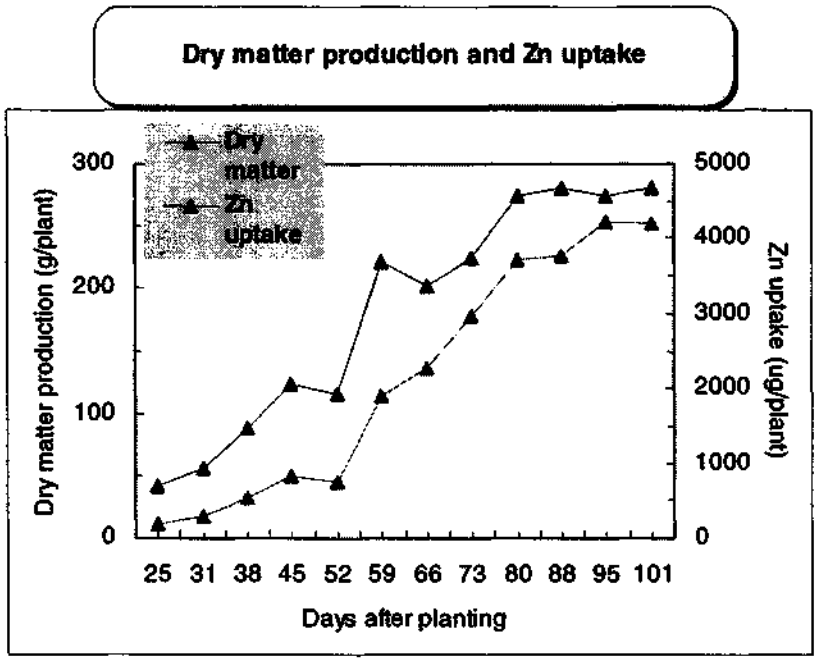

Figure 9.1. Dry matter production and zinc uptake by tops+stolons+tubers. Plants were grown under an adequate zinc fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse.

Zinc uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of zinc was relatively constant during the period 52-80 days after planting (Figure 9.1). Tiwari and Dwivedi (1991) for the cv. Kufri Chandramukhi, concluded that total zinc uptake followed a similar pattern to dry matter production.

9.2. Accumulation of zinc by different plant parts

The distribution of zinc among the different plant parts, varied during the growing season.

Data for the cv. Pontiac, show that during the period 25-52 days after planting, zinc uptake was in the order, older leaves >stems, younger leaves and tubers > stolons. In contrast at > 52 days after planting, the order was tubers >>> older leaves ≈ stems > younger leaves > stolons (See Figure 9.2).

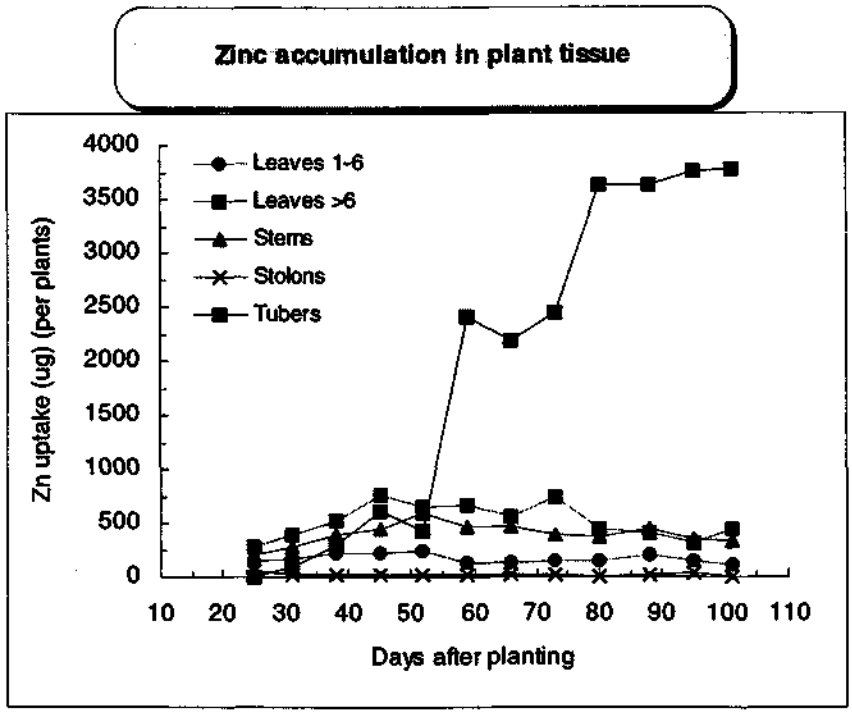

Figure 9.2. Zinc uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate zinc fertiliser regime

At the final harvest, 80.7% of the total zinc accounted for was removed in tubers compared with only 9.7% in older leaves, 6.9% in stems, 2.5% in younger leaves and 0.2% in stolons. During the period 45-101 days after planting, older leaves lost 40.8% of the zinc contained at day 45 (See Figure 9.2). Yuan et al. (1985) for the cv. Atlantic, reported that total zinc uptake by tubers was 120 or 180 g ha^{-1}, compared with uptake by vegetative tissue of 220 or 260 g ha^{-1}. Smith (1977) cited work showing that redistribution of zinc and other trace elements commenced after flowering and at harvest tubers accounted for 48.8-69.8% of the total zinc in the plant. Tiwari et al. (1982) for the cv. 'Kufri Chandramkhi', reported a mean total zinc uptake of 362.4 g ha^{-1}, of this 48, 32 and 20% was accounted for by tuber, top and root. Christensen and Jackson (1981) found that depending on phosphorus and zinc supply, zinc uptake by potato leaves ranged from 13 to 50 µg $plant^{-1}$, and by total tops from 25 to 89 µg $plant^{-1}$. Jackson and Carter (1976) for the cv. Russet Burbank, reported that zinc uptake ranged from 0.15 to 0.69 mg $plant^{-1}$ depending on the fertiliser applied and placement. Trehan and Grewal (1984) used pot experiments to determine zinc deficiency and toxicity limits for the cv. Kufri Chandramukhi. They found that the uptake of zinc was in the range 1.22-3.17 mg pot^{-1} during summer and 0.88-2.43 mg pot^{-1} during winter. Tiwari and Dwivedi (1991) for the cv. Kufri Chandramukhi, showed that zinc uptake by tubers depended on soil zinc status and rate of zinc applied. For soils low in zinc (< 0.6 mg kg^{-1} DTPA-Zn), zinc uptake ranged from 103.6 to 173.5 g ha^{-1} depending on the rate of zinc applied, at medium soil zinc status (0.6-1.0 mg kg^{-1} DTPA-Zn), it ranged from 194.8 to 229.9 g ha^{-1}, and for soils high in zinc (>1.0 mg kg^{-1} DTPA-Zn), from 214.2 to 232.6 g ha^{-1}. Sharma and Grewal (1988) also for the cv. Kufri Chandramukhi, grown on an alluvial sandy loam (Ustochrept; pH7.7-7.9), found that zinc uptake by tubers was in the range 39.7-67.0 g ha^{-1}, depending on the micronutrient applied (Zn, Mn, Fe or Cu) or the method of application (soil, spray or seed soaking). The minimum uptake was 35.8 g Zn ha^{-1} in the control plots. Sharma and Arodra (1992) for the cv. Kufri Chandramukhi, showed that zinc uptake by tubers (77-151 g ha^{-1}) was greater than uptake by haulms (20-28 g ha^{-1}).

9.3. Zinc in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 9.3, show zinc concentrations for different plant parts, and how they change relative to one another, during the growing season.

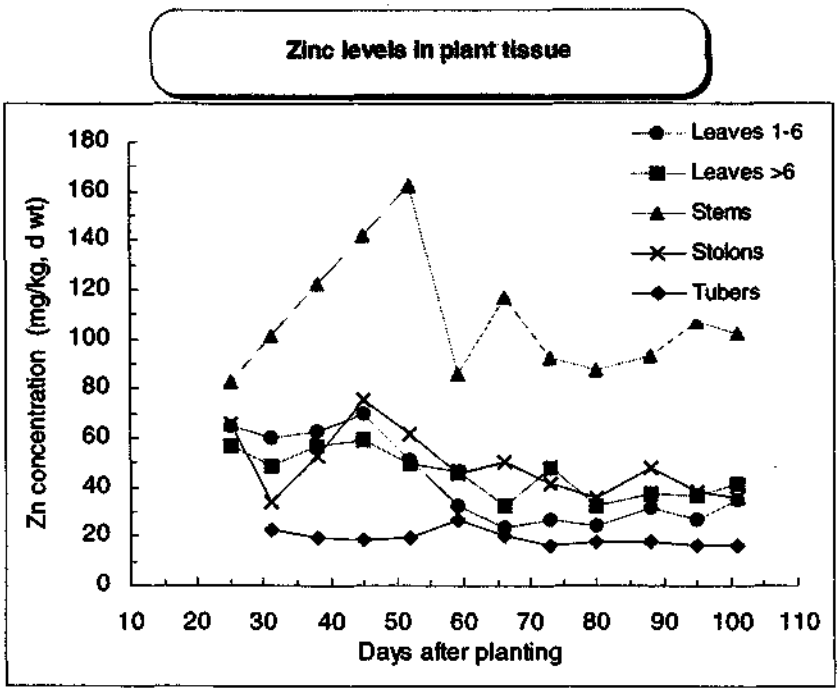

Figure 9.3. Zinc concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate zinc fertiliser regime.

During the vegetative and tuber bulking stages, zinc concentrations in stems were greater than concentrations in leaves and stolons (See Figure 9.3). Overall, concentrations were lowest in tubers. The sudden decrease in stem zinc concentration 52-59 days after planting corresponded with the onset of rapid tuber bulking, see accumulation of zinc in the plant and accumulation of zinc by different plant parts. Vimala et al. (1990) for the cv. Famosa, reported that mean (sem) zinc concentrations in leaves (157.3 ± 3.31 mg kg^{-1}) and stems (84.8 ± 1.79 mg kg^{-1}) were greater than in tubers (12.1 ± 0.32 mg kg^{-1}). Painter (1979) presented data showing that, late in the season, zinc concentrations in tubers (18 mg kg^{-1}) were less than concentrations in tops (24 mg kg^{-1}). Yuan et al. (1985) for the cv. Atlantic, found that zinc concentrations in tops, sampled one day before harvest, (192 or 197 mg kg^{-1}) were greater than concentrations in tubers (22 or 25 mg kg^{-1}). Locascio and Rhue (1990) showed that zinc concentrations in whole tops sampled at early flowering were lower than concentrations in recently matured leaves, however, the magnitude of the difference varied between years. In 1980, concentrations in whole tops were in the range 36-42 mg kg^{-1} and were consistently lower than concentrations in recently matured leaves, which ranged from 49-68 mg kg^{-1}. In contrast, in 1981, zinc concentrations in whole tops (34-50 mg kg^{-1}) were not consistently lower than concentrations in leaf tissue (38-42 mg kg^{-1}). Rosen et al. (1991) showed that zinc concentrations in recently matured leaves sampled 74 days after planting (eg. 17-19 mg kg^{-1}) were greater than concentrations in tubers (eg. 8.8-14.5 mg kg^{-1}). Data presented by Tiwari et al. (1982) for the cv. 'Kufri Chandramkhi' grown with adequate potassium and zinc supply,

show that zinc concentrations at maturity were slightly higher in tubers (50.8-61.0 mg kg^{-1}) compared with tops (45.2-50.0 mg kg^{-1}) and roots (43.7-51.0 mg kg^{-1}). Boawn and Leggett (1964) reported zinc levels in roots, stems and leaves (4th or 5th) of the cv. Russet Burbank. When zinc supply was adequate, the order was roots (41 or 55 mg kg^{-1}) > stems (20 or 21 mg kg^{-1}) > leaves (16 or 17 mg kg^{-1}). In plants showing severe deficiency symptoms, zinc concentration in roots (32 mg kg^{-1}) was greater than concentrations in stems (17 mg kg^{-1}) and leaves (17 mg kg^{-1}).

Trehan and Grewal (1983) for the cv. Kufri Chandramukhi, reported that the distribution of zinc between different plant parts varied with zinc and phosphorus supply. They found that at low P, zinc levels in the plant were highest in the roots (98 mg kg^{-1}), intermediate in stem and leaves (56 mg kg^{-1}) and lowest in nodes (43 mg kg^{-1}). With increasing P supply, zinc concentrations increased in roots, stems and nodes but decreased in leaves.

Soltanpour et al. (1970) for the cv. Russet Burbank, presented zinc levels in leaf (4th and 5th from the top) and stem (3rd to 6th node from the top) tissue. Differences in zinc levels between the two tissues appears to depend on the source and rate of zinc used and method of placement. For example, at location 7 and using ZnEDTA as the source, for the band placement, zinc levels in stems (33-42 mg kg^{-1}) were greater than in leaves (25-28 mg kg^{-1}) For the disc application, the differences in concentrations between stem (24-30 mg kg^{-1}) and leaf (23-28 mg kg^{-1}) tissues was less. Omran et al. (1991) reported zinc levels in leaves (sampled late in the season) and mature tubers of the cv. King Edward. For winter crops, concentrations in leaves were in the range 23-70 mg kg^{-1}, and in tubers, 11-45 mg kg^{-1}. For summer crops, the ranges were 17-40 mg kg^{-1} in leaves and 12-36 mg kg^{-1} in tubers.

10. Manganese

10.1. Accumulation of manganese in the plant

Manganese accumulation was positive during the vegetative and tuber bulking periods, up to 80 days after planting (See Figure 10.1).

Manganese uptake by tops+stolons+tubers parallelled growth or dry matter production for tops+stolons+tubers. The uptake of manganese was relatively constant during the period 25-66 days after planting (Figure 10.1).

10.2. Accumulation of manganese by different plant parts

The distribution of manganese among the different plant parts, varied during the growing season.

Data for the cv. Pontiac, show that during the period 25-38 days after planting, manganese accumulation in the different tissues was in the order, older leaves > younger leaves and stems > tubers and stolons (See Figure 10.2). In contrast, during the period 52-95 days after planting, manganese had accumulated rapidly in the older leaves and the order was, older leaves >> younger leaves > tubers > stems >> stolons (Figure 10.2).

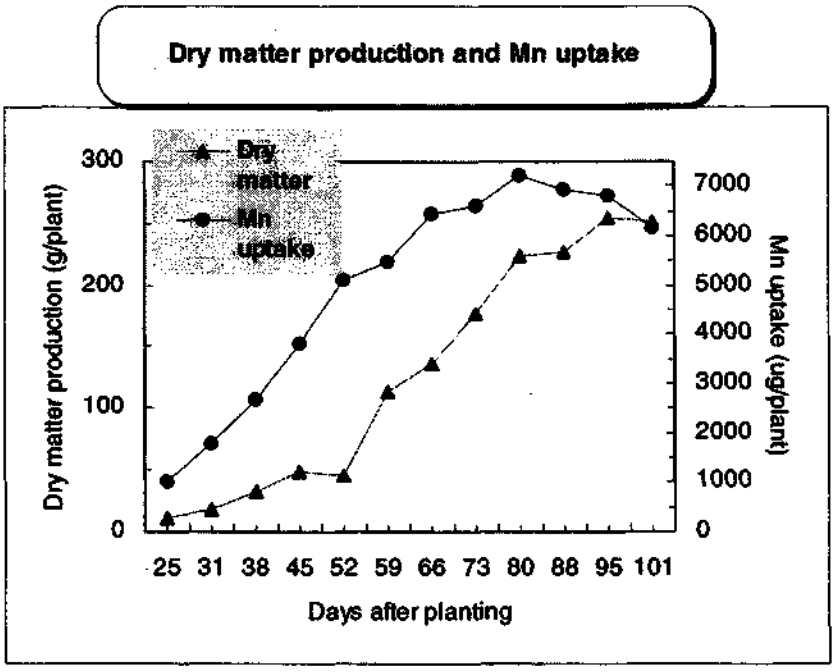

Figure 10.1. Dry matter production and manganese uptake by tops+stolons+tubers. Plants were grown under an adequate manganese fertiliser regime. Data are for the cv. Pontiac grown in pots in a glasshouse

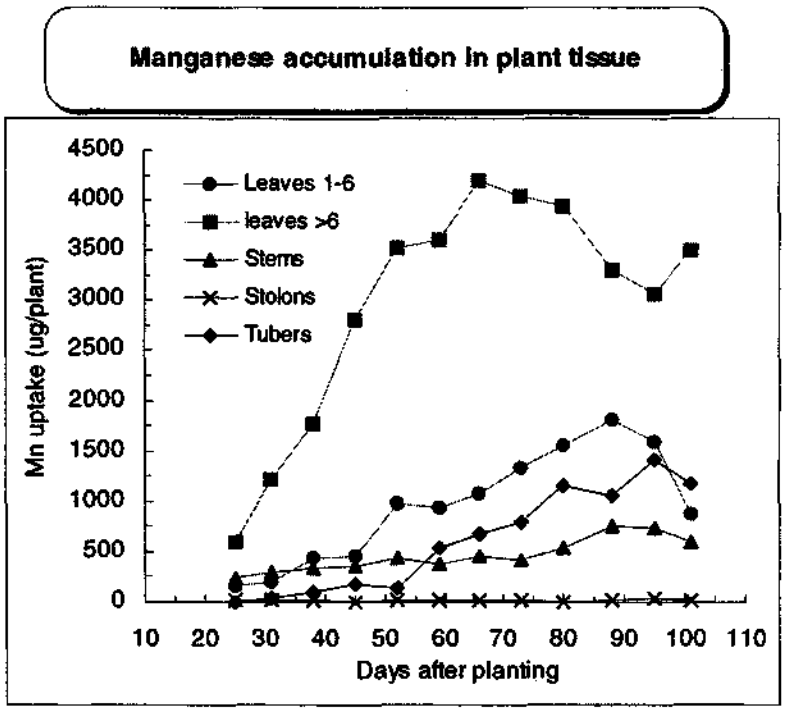

Figure 10.2. Manganese uptake by different plant fractions. Data are for the cv. Pontiac, grown in pots in a glasshouse. Plants were grown under an adequate manganese fertiliser regime

At the final harvest, only 19.1% of the total manganese accounted for was removed in tubers compared with 56.8% in older leaves, 14.3% in younger leaves, 9.7% in stems and 0.1% in stolons. During the period 66-95 days after planting, older leaves lost 27.2% of the manganese contained at day 66 (See Figure 10.2). Yuan et al. (1985) for the cv. Atlantic,

reported that total manganese uptake by tubers was 20 or 40 g ha^{-1}, compared with uptake by vegetative tissue of 620 or 750 g ha^{-1}. Sharma and Grewal (1988) also for the cv. Kufri Chandramukhi, grown on an alluvial sandy loam (Ustochrept; pH 7.7-7.9), found that manganese uptake by tubers was in the range 68.1-89.9 g ha^{-1}, depending on the micronutrient applied (Zn, Mn, Fe or Cu) or the method of application (soil, spray or seed soaking). The minimum uptake was 67.3 g Mn ha^{-1} in the control plots. Vimla et al. (1990) for the cv. Famosa, reported that removal of manganese by different plant parts was in the order leaves (648.2 g ha^{-1}) > stems (205.5 g ha^{-1}) > tubers (25.8 g ha^{-1}).

10.3. Manganese in leaf, stem, stolon, tuber and root

Data for the cv. Pontiac, presented in Figure 10.3, show manganese concentrations for different plant parts, and how they change relative to one another, during the growing season.

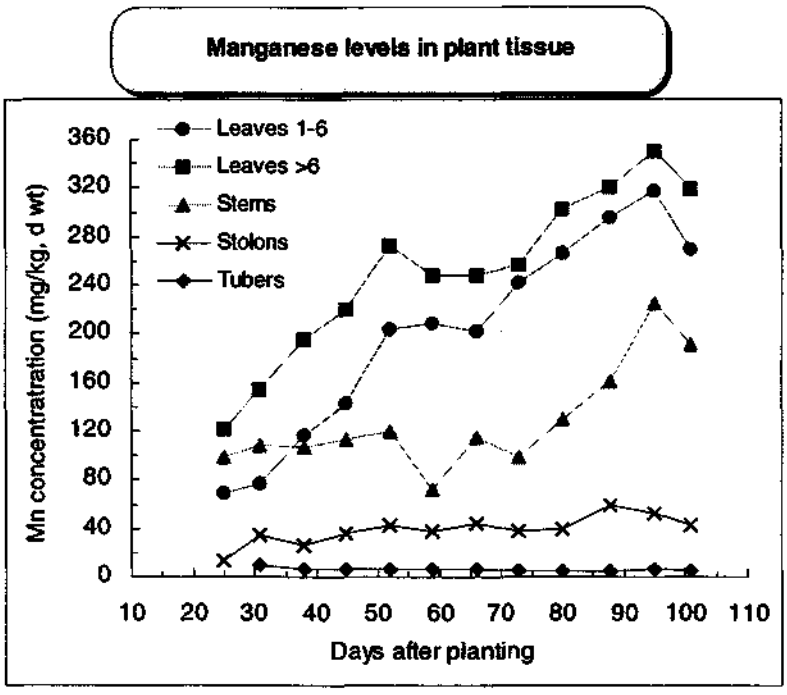

Figure 10.3. Manganese concentrations in different plant parts during the growing season. Data are for the cv. Pontiac grown in pots in a glasshouse. Plants were grown under an adequate manganese fertiliser regime.

During the period 25-31 days after planting, manganese concentrations in the different plant parts were in the order: older leaves > stems> younger leaves > stolons > tubers. In contrast, 45-101 days after planting, concentrations were in the order: older leaves > younger leaves > stems > stolons > tubers (See Figure 10.3). Painter (1979) presented data showing that, late in the season, manganese concentrations in tubers (7 mg kg^{-1}) were lower than concentrations in tops (32 mg kg^{-1}). Vimala et al. (1990) for the cv. Famosa, reported that mean (sem) manganese concentrations in leaves (1216.8 ± 26.4 mg kg^{-1}) and stems (368.3 ± 10.3 mg kg^{-1}) were greater than in tubers (6.8 ± 0.2 mg kg^{-1}). Locascio and Rhue (1990) showed that manganese concentrations in whole tops sampled at early flowering were higher than concentrations in recently matured leaves, however, the magnitude of the difference varied

between years. In 1981, concentrations in whole tops were in the range 37-70 mg kg^{-1} and were consistently higher than concentrations in recently matured leaves, which ranged from 22-37 mg kg^{-1}. In contrast, in 1980, manganese concentrations in whole tops (30-46 mg kg^{-1}) were not consistently higher than concentrations in leaf tissue (24-43 mg kg^{-1}). Rosen et al. (1991) showed that manganese concentrations in recently matured leaves sampled 74 days after planting (eg. 71-85 mg kg^{-1}) were greater than concentrations in tubers (eg. 10.7-12.3 mg kg^{-1}). Yuan et al. (1985) for the cv. Atlantic, found that manganese concentrations in tops, sampled one day before harvest, (472 or 650 mg kg^{-1}) were greater than concentrations in tubers (4 or 5 mg kg^{-1}). Lee (1972) for the cv. Netted Gem, reported manganese levels in upper tops (top of the plant down to and including the third mature leaf), lower plant tops (remaining portion down to the base of the stem) and roots. Concentrations were in the order, roots > lower tops > upper tops. For example, for the 2 mg kg^{-1} Mn treatment, concentrations in the different plant parts were roots, 10,004 mg kg^{-1}, lower tops, 4,173 mg kg^{-1} and upper tops, 2,431 mg kg^{-1}. Bolle-Jones (1955) for the cv. Majestic (1950 experiment), presented mean manganese concentrations for different plant parts namely, laminae, 59 mg kg^{-1}; stems and petioles, 68 mg kg^{-1}; tubers, 11.0 mg kg^{-1}; and roots, 199 mg kg^{-1}.

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APPENDIX 3 Effect of sulfate on cadmium uptake by plants in solution culture

Introduction

Cadmium uptake by potatoes is now known to be enhanced by high chloride (Cl) concentrations in irrigation water. Salinity in irrigation water may also be due to high concentations of sulfate (SO_4^{2-}). A visiting student from Wageningen Agricultural University in the Netherlands, Rose-Marie Lambrechts, and a visiting Postdoctoral Fellow from the Catholic University of Leuven in Belgium, collaborated with this project to investigate if SO_4^{2-} salinity has the same effect on plant Cd uptake as Cl. Swiss chard, was used as an indicator species, to keep minimise experimentation times.

In solution, increasing concentrations of Cl lead to reductions in activity of the free Cd ion (Cd^{2+}), so that increasing Cl^- salinity should reduce Cd uptake by plants, in addition to any effects of increased ionic strength on root function. Recently, solution culture experiments have demonstrated that increasing concentrations of Cl in solution indeed reduce Cd uptake by plants, but not to the extent predicted by reductions in Cd^{2+} activity (Smolders and McLaughlin, 1996a). In experiments where activities of Cd^{2+} were constant across increasing Cl concentrations using organic ligands or chelex resins to buffer Cd^{2+} (Smolders and McLaughlin, 1996a; Smolders and McLaughlin, 1996b), Cd uptake by plants was increased by Cl, suggesting that chloro-complexes of Cd were either transported across the plasma membrane or helped to overcome a diffusional limitation to uptake of Cd^{2+}.

As SO_4 is also a component of irrigation waters and soil solutions, and as SO_4 may also reach concentrations in soil solution sufficient to significantly complex Cd^{2+} (McLaughlin et al., 1997), it is important that the effects of SO_4 complexation on Cd uptake by plants be understood. This paper presents data on the effect of SO_4 on Cd uptake in nutrient solution where interactions with soil are excluded, and Appendix 4 details experiments using soil-grown plants.

Materials and methods

Plant growth - nutrient solution experiments

Seeds of Swiss chard (*Beta vulgaris* L., cv. Fordhook Giant) were moistened with tap water and allowed to germinate in the dark (25 °C). Seedlings were transplanted to 8.3-L pots containing continuously aerated complete nutrient solutions. Solution composition was the same as the basic nutrient solution described by Smolders and McLaughlin (1996a).

During the initial growth period no Cd was added. At 9 days after sowing (DAS), seedlings were thinned to about 12 per pot prior to imposing experimental SO_4 treatments (see below). Activities of Fe^{3+} in solution were buffered using N,N'-bis(2-hydroxybenzyl)-ethylenediamine-N,N'-diacetate (HBED) because of its high selectivity for Fe^{3+} compared to Cd^{2+} (Martell and Smith, 1974). HBED was prepared as an 8 m*M* stock solution according to Chaney (1988) from HBED (acid form) and a 10 % molar excess $FeCl_3$ to ensure that virtually no free HBED was left in solution. The pH of all solutions was adjusted to 6.10 ± 0.1 and maintained at this pH during plant growth using MES buffer to avoid pH effects on Cd uptake

(Hatch et al., 1988). Speciation calculations using GEOCHEM-PC (Parker et al., 1995) predicted no complexation of Cd by MES for all treatments.

Cadmium was added to all solutions at 10 DAS from a stock solution spiked with ^{109}Cd. The final Cd concentration was 50 n*M* in all treatments and the final ^{109}Cd activity in solution was approximately 6 Bq mL^{-1}. Samples of the nutrient solutions were taken at 11 DAS and on a daily basis from 13 DAS. If ^{109}Cd activities were lower than 95 % of the initial value, a readjustment was made using the labelled Cd stock solution.

The pots were randomised in a growth cabinet and re-randomised during the growth period. Air temperature in the growth cabinet was adjusted to obtain a constant solution temperature of 25 °C (± 1 °C) during the 12 h/12 h day/night cycle. Air humidity was not controlled. Pots were regularly topped up with deionised water to compensate for evaporation and transpiration. Plants were harvested at 20 DAS in all treatments.

Experiment 1 - Effect of increasing sulfate concentrations on Cd uptake at constant ionic strength

Sulfate treatments consisted of five levels (i.e. 8, 20.5, 33, 45.5, 58 m*M*) added as Na_2SO_4, while maintaining ionic strength constant at 0.15±0.01 using $NaNO_3$. Concentrations of cations, P and S in solution were checked by analysis using inductively-coupled plasma atomic emission spectroscopy, and these concentrations were used as input data for speciation calculations using GEOCHEM-PC (Parker et al., 1995). In all experiments Cd^{2+} was unbuffered (not complexed by an organic ligand) so that the free Cd concentration ($[Cd^{2+}]$) was reduced as SO_4 concentrations in solution increased, with corresponding increases in the concentration of $CdSO_4^0$ complexes (Table 1).

Table 1. Ionic strength of solutions and concentrations of Cd^{2+} and Ca^{2+} ions and their sulfate complexes calculated using GEOCHEM-PC in Experiment 1.

Ionic strength	$[SO_4^{2-}]$ mM	$[Ca^{2+}]$ mM	$[Cd^{2+}]$ nM	$[CdSO_4^0]$ nM	$[CaSO_4^0]$ mM
0.16	8.0	5.0	37.2	7.0	0.6
0.15	20.5	4.2	30.0	16.2	1.4
0.15	33.0	3.6	25.3	21.9	2.0
0.15	45.5	3.2	22.0	26.0	2.4
0.16	58.0	2.9	19.4	29.1	2.7

Experiment 2 - Effect of increasing sulfate concentrations on Cd uptake at varying free Ca^{2+}

As Ca concentrations in solution may affect Cd uptake by plants (Tyler and McBride, 1982), any effect of SO_4 on Cd uptake may be indirect through reducing free Ca^{2+} concentrations in solution. Additional experiments were performed to test this hypothesis. Treatments were SO_4 concentrations of 8 and 45.5 m*M* at constant ionic strength (using $NaNO_3$ compensation), with three additional treatments of the 45.5 m*M* SO_4 concentration having additional Ca added as $Ca(NO_3)_2$ to give final Ca concentrations in solution of 6.6, 7.6 and 9.4 m*M*. These treatments were used to provide a range of $[Ca^{2+}]$ across the SO_4 treatments (Table 2), while $[Cd^{2+}]$ was constant across these treatments. Plants were harvested at 18 DAS in this experiment.

Table 2. Concentrations of total Ca, free Ca^{2+}, free Cd^{2+} ions and their sulfate complexes calculated using GEOCHEM-PC in Experiment 2.

Ionic strength	$[SO_4^{2-}]$ mM	$[NO_3^-]$ nM	$[Ca_T]^a$ mM	$[Ca^{2+}]$ mM	$[Cd^{2+}]$ nM	$[CdSO_4^0]$ nM	$[CaSO_4^0]$ mM
0.14	8.0	108.0	5.6	4.9	37.0	7.7	0.6
0.15	45.5	33.0	5.6	3.2	22.0	26.0	2.4
0.15	45.5	35.0	6.6	3.8	22.1	25.8	2.8
0.16	45.5	36.9	7.6	4.4	22.1	25.7	3.2
0.16	45.5	40.5	9.4	5.5	22.6	25.2	3.9

[a] Ca_T = total Ca concentration in solution

Analyses

At harvest, plants were divided into shoots and roots. Roots were blotted dry and individual shoot and root fresh weight was recorded. Root samples were washed for 30 min in a 200 mL $CaCl_2$ (10 m*M*) and $Cd(NO_3)_2$ (10 μ*M*) solution prior to oven drying. This wash was included to desorb extracellular (non-absorbed) ^{109}Cd. In a preliminary experiment, ^{109}Cd efflux from roots was measured as a function of washing time and found to be virtually complete after 30 min washing (Smolders and McLaughlin, 1996a).

Shoots and roots of all plants (12) grown in each pot were pooled and oven dried (70 °C). Dried shoot samples were weighed and ground in a mortar. ^{109}Cd activity in duplicate subsamples of the ground material was determined in a Phillips 4800 gamma counter. Dried roots were transferred into counting vials and ^{109}Cd activity determined without prior grinding. Geometry effects on counting efficiency and absorption of the radiation by the plant material were found to be negligible. The average coefficient of variation between these analytical duplicates was about 2 %. Stable Cd was measured in HNO_3 digests of some shoot samples by flameless atomic absorption spectrophotometry to confirm Cd concentrations determined from activities of ^{109}Cd.

Statistical analysis

Treatment effects were analysed by linear regression analyses using solution SO_4 as the independent variable. Cadmium speciation in selected treatment solutions was calculated using GEOCHEM-PC (Parker et al., 1995). As ionic strengths were the same in all treatments, solution ion activities were directly proportional to solution ion concentrations across treatments. The formation constant (log K) used for the $CdSO_4^0$ species was 2.45 (Lindsay, 1979).

Results

Plant root and shoot dry weights were unaffected by sulfate treatments in both experiments (Figure 1).

Similarly, plant dry weights were unaffected by Ca treatments in Experiment 2 (data not shown).

Despite solution concentrations of the free Cd^{2+} ion decreasing almost 50% by increasing solution SO_4 concentrations from 8 to 58 m*M* (Table 1), Cd uptake by plants was unaffected by SO_4 treatments (Figure 2).

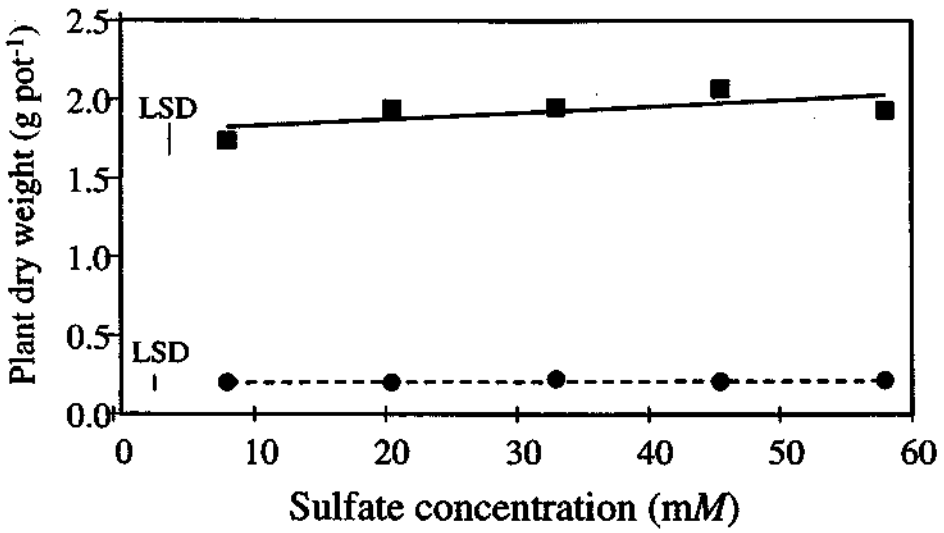

Figure 1. Effect of SO_4 concentration in nutrient solution on shoot (■) and root (●) dry weights at constant solution ionic strength.

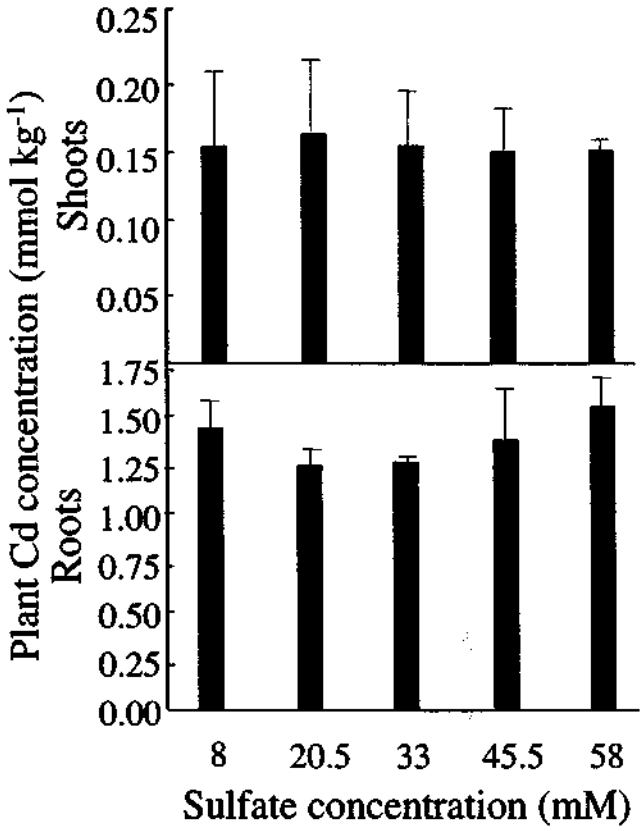

Figure 2. Effect of SO_4 concentration in nutrient solution on shoot and root Cd concentrations (± SD) at constant solution ionic strength.

Concentrations of $CdSO_4^0$ species in solution increased four-fold from 7.0 to 29.1 n*M* across the same range of sulfate concentrations. Concentrations of the free Ca^{2+} ion also decreased across SO_4 treatments, due to ion pairing in solution.

In Experiment 2 where solution SO_4 concentrations were 45.5 mM, addition of Ca to the nutrient solutions to boost the concentration of free Ca^{2+} up to and exceeding the levels found in low SO_4 treatments (Table 2), had no effect on plant Cd concentration (Figure 3). Concentrations of free and complexed Cd were constant across these treatments (Table 1). Cadmium concentrations in plants were slightly lower than in Experiment 1.

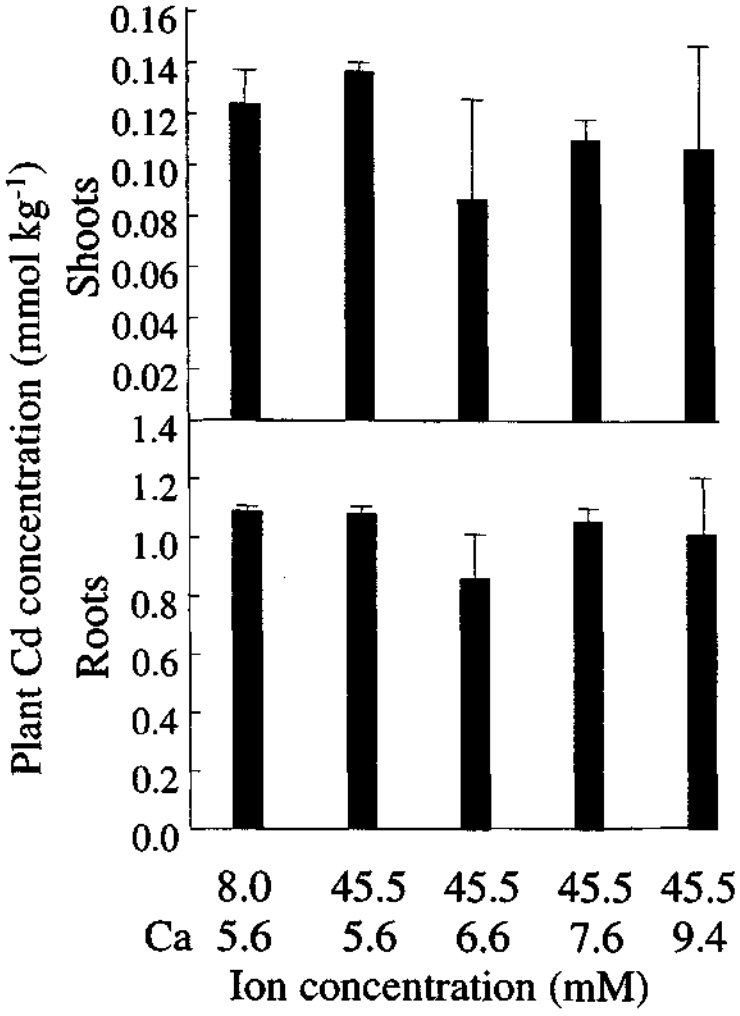

Figure 3. Effect of increasing Ca and SO_4 concentrations (total) on shoot and root Cd concentrations (± SD) at constant solution ionic strength.

Discussion

If the free metal is the only species taken up by plant roots, uptake should be reduced in line with the reduction in free Cd activity ((Cd^{2+})), or with reductions in Cd concentration ($[Cd^{2+}]$) if ionic strength is kept constant. The data presented here show that Cd uptake by plants from solution is unaffected by increasing concentrations of SO_4, despite SO_4 causing a reduction in free Cd^{2+} ion activity due to the formation of $CdSO_4^0$ complexes. The lack of effect of SO_4 was consistent at both constant Ca concentration (Ca^{2+} *activity* decreasing) and at constant

Ca^{2+} activity (Ca *concentration* increasing to compensate for Ca complexation by SO_4). The effects were unrelated to ionic strength effects due to the increasing SO_4 concentrations, as these were maintained constant by compensation with $NaNO_3$. There are three possible explanations for these observations.

The first possible explanation is that the formation constants used for the calculation of Cd complexation by SO_4^{2-} are incorrect. This appears unlikely as the Cd^{2+}-SO_4^{2-} system has been well studied, and Helmke et al. (1997) have recently shown (using Donnan dialysis with a cation exchange membrane) that the concentrations of free Cd^{2+} in SO_4-rich solutions were identical to those calculated with the $CdSO_4^0$ formation constant provided by Lindsay (1979).

The second possible explanation for the data is that the complexed $CdSO_4^0$ species provide an effective buffer for the uptake of Cd^{2+} at the root membrane i.e. alleviating a diffusional limitation of Cd transport through the unstirred layer of solution around the root and in the apoplast. The apoplast is a highly charged zone (due to carboxylic acids and other organic functional groups) forming a barrier to movement of cations to sites of uptake (Grignon and Sentenac, 1991). A similar postulate was made concerning the enhancing effect which Cl has on uptake of Cd by plants from solution even where Cd^{2+} activity is held constant (Smolders and McLaughlin, 1996b).

The third possible explanation for these data is that the $CdSO_4^0$ ion is taken up by plant roots with an efficiency equivalent to Cd^{2+}. Recently, we have demonstrated that Cd^{2+} complexes with Cl^- ($CdCl_n^{2-n}$) also appear to be available to plants (Smolders and McLaughlin, 1996a;b), and current experiments with isolated membranes from giant algal cell (*Chara* sp.) also suggest that $CdCl_n^{2-n}$ complexes may indeed be membrane permeable (Dunbar, Reid, McLaughlin and Hamon, unpublished data). While $CdSO_4^0$ is uncharged, it is still a highly polar ion pair and presumably is labile in the sense that dissociation would be rapid in the presence of a strong sink for Cd^{2+}. While uncharged molcules have the potential to be lipophilic, and hence diffuse freely through the apoplast and across cell membranes, it is unknown if the apparent uptake of $CdSO_4^0$ found in this study can be attributed to this characteristic.

While it has been generally stated that only free metal ions are transported across membranes, there is some evidence, especially in the marine toxicology literature, that some uncharged metal complexes may move freely across biological membranes (Phinney and Bruland, 1994; Vercauteren and Blust, 1996). For example, Phinney and Bruland (1994) found that Cu^{2+} bound to dithiocarbamate or oxine formed an uncharged complex which was freely available to the marine diatom *Thalassiosira weissflogii.* Similarly, Vercauteren and Blust (1996) found that the uptake of divalent Zn by the common mussel *Mytilus edulis* was enhanced through the formation of a lower charged Zn-histidine complex.

We noted no effects of Ca on Cd uptake, even though the range of Ca concentrations was narrow in order to compensate for reductions in free Ca^{2+} activities through the formation of $CaSO_4^0$ complexes. Calcium is known to inhibit uptake of zinc and nickel by plants (Chaudhry and Loneragan, 1972; Gabbrielli and Pandolfini, 1984) and to reduce toxicity of Cd to plants (Hosono et al., 1979; Sadana and Takker, 1983), although the latter studies often failed to account for indirect alleviation of metal toxicity through reduced ion activities by addition of Ca salts. Jarvis et al. (1976) also found Ca inhibited plant Cd uptake. However, in that study the addition of Ca to the solutions as $CaCl_2$ confounds the interpretation of the data, as chloro-complexation of Cd would also have been important. Tyler and McBride (1982) found that adding $CaSO_4$ to solution and increasing Ca concentrations from 1 to 5 *mM* had no

effect on Cd uptake, but decreased the shoot:root ratios of Cd (i.e. reduced translocation). Most of the above studies failed to remove surface-bound Cd from roots in order to distinguish between *absorption* and *adsorption*. Furthermore, most of these studies used solution Cd concentrations in the µM range, concentrations well above those found in the pore water of agricultural soils (Holm et al., 1995; McLaughlin et al., 1997). At high Cd concentrations, the strength of metal binding to charged surfaces is inversely related to surface coverage (Hendrickson and Corey, 1981). While little is known of the competitive Ca/Cd exchange characteristics of the root apoplast , it is unlikely that Ca-Cd competition for root uptake at high solution Cd concentrations is similar to that at low solution Cd concentrations. It is therefore important that the Ca-Cd interaction be investigated at environmentally relevant solution Cd^{2+} activities (<50 n*M*), as done in the present study.

Sulfate is ubiquitous in soil solutions and in irrigation waters, especially in saline irrigation regions, with concentrations in saturation extracts of soil and in soil solution ranging up to 20-50 m*M* (Jurinak and Suarez, 1990; McLaughlin et al., 1997). The data presented here suggest that like Cl, SO_4 may be an important determinant of crop Cd concentrations. Sulfate complexes of Cd predominate in solutions with SO_4 concentrations exceeding about 30 m*M* (Figure 4).

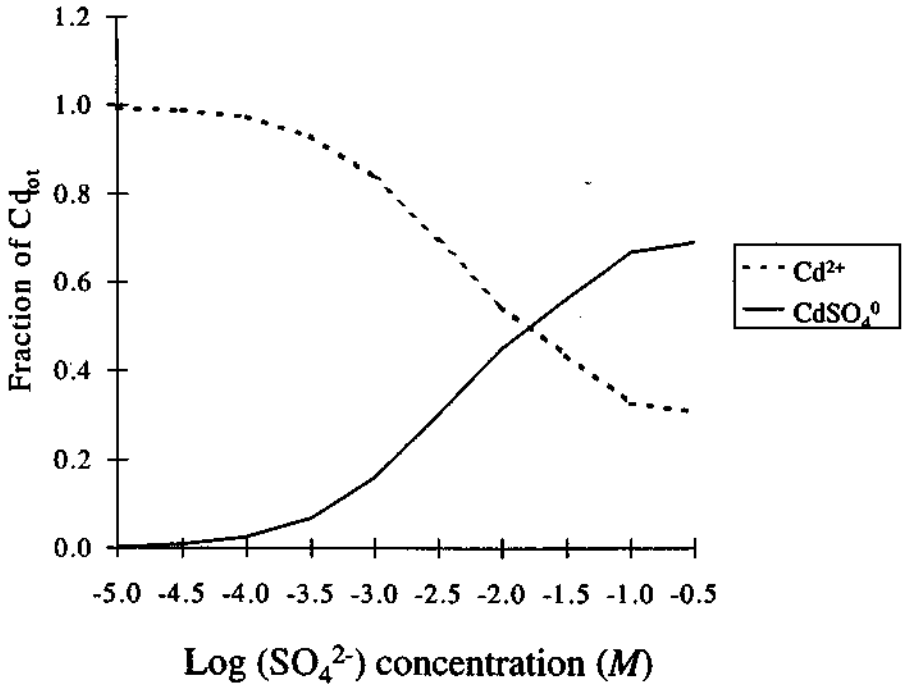

Figure 4. Fraction of total Cd in solution present as the Cd^{2+} ion and $CdSO_4^0$ complexes in relation to solution sulfate concentrations.

If SO_4 increases total Cd concentrations in soil solution as does Cl, sulfate salinity has the potential to significantly increase Cd uptake by plants, as the $CdSO_4^0$ ion is clearly available for plant uptake. The second paper in this series presents data on the effect of increasing SO_4 concentrations in soil solution on Cd uptake by Swiss chard (Appendix 4).

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APPENDIX 4 Effect of sulfate on cadmium uptake by plants in soils

Introduction

Increasing concentrations of chloride (Cl) in soil solution markedly increase Cd concentrations in soil solution due to complexation of Cd by Cl and desorption of Cd from the soil solid phase (McLaughlin et al., 1997). Thus, increased Cd concentrations in field crops in saline areas have been attributed to this chloro-complexation of Cd (McLaughlin et al., 1994; Smolders and McLaughlin, 1996). Soil salinity, however, can also lead to high (>10 m*M*) concentrations of SO_4 in soil solution (McLaughlin et al., 1997). Given data from nutrient solution experiments suggesting that the availability to plants of Cd complexed by SO_4 is equivalent to that of the free Cd^{2+} ion (Appendix 3), sulfate salinity has the potential to markedly increase Cd uptake from soils affected by SO_4 salinity.

The effects of both Cl and SO_4 ions were studied in acidic and limed soil in glasshouse experiments some 14 years ago (Bingham et al., 1984; Bingham et al., 1986) with the conclusion that Cl significantly increased plant Cd concentrations, and that this effect was due to increased activities of free Cd^{2+} ion in soil solution. The authors concluded that chloro-complexed Cd was not available for uptake by plants. In these same series of experiments, there was no effect of added SO_4^{2-} ion on plant Cd uptake, but there were no consistent effects of SO_4 on solution Cd concentrations. Unusually, soil solution Cd concentrations were increased by liming the soil. The interpretation of Bingham et al.'s data is confounded by the significant effect of the complementary cations (Na and Ca) on Cd desorption, due to the high rates (up to 2.5 mg kg^{-1}) of Cd added to the soils (as $CdSO_4$), and the possible effects of salinity on root function through osmotic stress.

In previous plant growth experiments conducted in nutrient solutions, it was found that the $CdSO_4^0$ ion was equally available for uptake by plants as the Cd^{2+} ion (Appendix 3). If SO_4 complexes and desorbs Cd from soil surfaces to the same extent as Cl, SO_4 salinity may have a significant effect on Cd uptake by plants. The aim of these experiments was to investigate the effect of SO_4 salinity in soil on Cd uptake by plants.

Materials and methods

Plant growth

A sandy soil (Alfisol: Soil Survey Staff, 1975) having relatively low EDTA-extractable Cd concentrations (Table 1) was air dried at 40°C, crushed and sieved to <2 mm.

Pots were filled with 1.25 kg of soil and moistened with complete nutrient solution up to -12 kPa (0.20 ml solution g^{-1} dry soil). The nutrient solution contained: 6 m*M* $Ca(NO_3)_2$; 3 m*M* K_2SO_4; 3 m*M* $MgSO_4$; 0.1 m*M* KH_2PO_4; 5 µ*M* $ZnSO_4$; 1 µ*M* $CuSO_4$; 10 µ*M* $MnSO_4$; 30 µ*M* H_3BO_3; 28.5 n*M* $(NH_4)_6Mo_7O_4$. Sulfate treatments were imposed by increasing the concentration of Na_2SO_4 and treatments with equivalent Na salinity were imposed using $NaNO_3$. Both sodium salts were added to the nutrient solution at the following concentrations: 0, 30, 60, 90 and 120 $mmol_c$ L^{-1}. Each treatment was replicated threefold and after addition of nutrient solution, pots were covered and equilibrated for 4 days prior to planting.

Table 1. Soil characteristics.

Characteristic	
pH (water)†	5.4
Clay (%)	9
Silt (%)	10
Sand (%)	81
Total C (%)	1.4
EDTA-extractable Cd (mg kg^{-1})‡	0.31

† 1:5 soil:water ratio.
‡ according to the method of Clayton and Tiller (1975).

Seeds of Swiss chard (*Beta vulgaris* L., cv. Fordhook Giant) were germinated on filter paper moistened with a solution containing 0.2 m*M* $CaSO_4$ and 0.03 m*M* H_3BO_3. Two days after sowing (DAS), 10-15 germinated seeds were transplanted per pot. The soil surface was covered with polyethylene beads to reduce evaporation and the pots were placed in a growth cabinet. Temperature in the growth cabinet was maintained at 25 °C (± 1 °C) during the 12 h/12 h day/night cycle. Photosynthetically active radiation was 300 µmol quanta m^{-2} s^{-1}. Pots were re-randomised daily. Daily evapotranspiration was measured gravimetrically and soil moisture potential maintained at -12 kPa using alternately demineralised water or nutrient solution (without Na_2SO_4 or $NaNO_3$ salts). The number of plants per pot was reduced to 5 at 13 DAS.

Plants (tops only) were harvested at 19 DAS. The shoot of each plant was weighed and all plant tops from the same pot were pooled and oven dried (70 °C). Shoot dry weight was recorded and plant samples were ground in a mortar.

Analyses

Subsamples (50 mg) of the dried and ground plant material were digested with concentrated nitric acid (1.5 mL). The digest solution was diluted to 20 mL using 0.016 *M* nitric acid. All samples were digested in duplicate with blanks and an in-house quality control material in each batch. Every second batch digested included two reference materials (rice flour from the National Institute for Environmental Studies, Japan, and cabbage leaves from the Institute of Physics and Nuclear Techniques, Poland) having certified concentrations of Cd.

Cadmium concentrations in the digest solutions were determined using an atomic absorption spectrophotometer with graphite furnace atomization (GFAAS) and deuterium background correction. Orthophosphoric acid (1% v/v) was used as a matrix modifier.

Concentrations of Ca, Cu, Fe, Mg, Mn, Mo, P, S and Zn in the digest solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Each plant sample was digested in duplicate and the average of each analysis was taken as the observation of one independent replicate (pot).

Soil samples were taken from each pot at harvest by subsampling from the entire pot. Visible roots were removed by handpicking and soil solution was displaced from the soil by centrifugation (4000 RCF, 30 min). Extracted solutions were then centrifuged at 25000 RCF for 60 min and filtered (<0.2 µm). The pH of the solutions was measured immediately. Concentrations of Cl, SO_4^{2-} and NO_3^- in the soil solutions were measured by Ion

Chromatography (Dionex, AS4A-SC column) and cations by ICP-AES. Cadmium concentrations in the soil solution were determined by GFAAS. Any effects of high salt concentrations on measured Cd concentrations were determined using the method of standard addition.

Speciation of Cd in soil solution

Speciation of Cd in the soil solution was estimated with the computer program GEOCHEM-PC (Parker et al., 1995) using the measured total elemental concentrations as input data (averages for each treatment). The formation constant (log K) of $CdSO_4^0$ complex was (corrected to zero ionic strength) 2.5. Carbon dioxide in the solutions was assumed to be ten times greater than atmospheric, although varying this parameter had little effect on computed activities of Cd species. Given the high salt concentrations used and the weak association of Cd with organic ligands (Alloway et al., 1984), complexation of Cd by organic ligands was not considered.

Statistical analysis

Treatment effects were assessed by linear regression analyses or ANOVA using a factorial design with anions (NO_3, SO_4) and salt rate (added 0, 30, 60, 90 and 120 $mmol_c\ L^{-1}$) as the treatments.

Results

Soil solution data

In the NO_3^- treatments, soil solution pH decreased by approximately 0.6 units from 7.7 to 7.1 with increasing rate of NO_3^- addition, while in SO_4 treatments the decrease was greater (1.3 units).

Concentrations of Ca, K, Mg, Mn, and Zn in soil solution were significantly increased by increasing additions of both salts, with small differences between NO_3 and SO_4 treatments (data not shown).

Concentrations of NO_3 and SO_4 measured in soil solution at plant harvest were similar to those added, although it appeared that some SO_4 was lost from solution at higher concentrations (Figure 1).

Concentrations of Cd in soil solution were significantly increased ($P<0.05$) in the SO_4-treated soils, while increases in the NO_3-treated soils were smaller and less consistent (Table 2). Activities of Ca^{2+} in soil solution were unaffected by NO_3 treatments but significantly reduced by SO_4 treatments (Table 3).

Activities of Cd^{2+} (calculated by GEOCHEM-PC) were increased by both NO_3 and SO_4 treatments, but these changes were inconsistent with anion concentrations in soil solution (Table 3). The largest and most consistent effect was that SO_4 treatments significantly increased activities of $CdSO_4^0$ in soil solution.

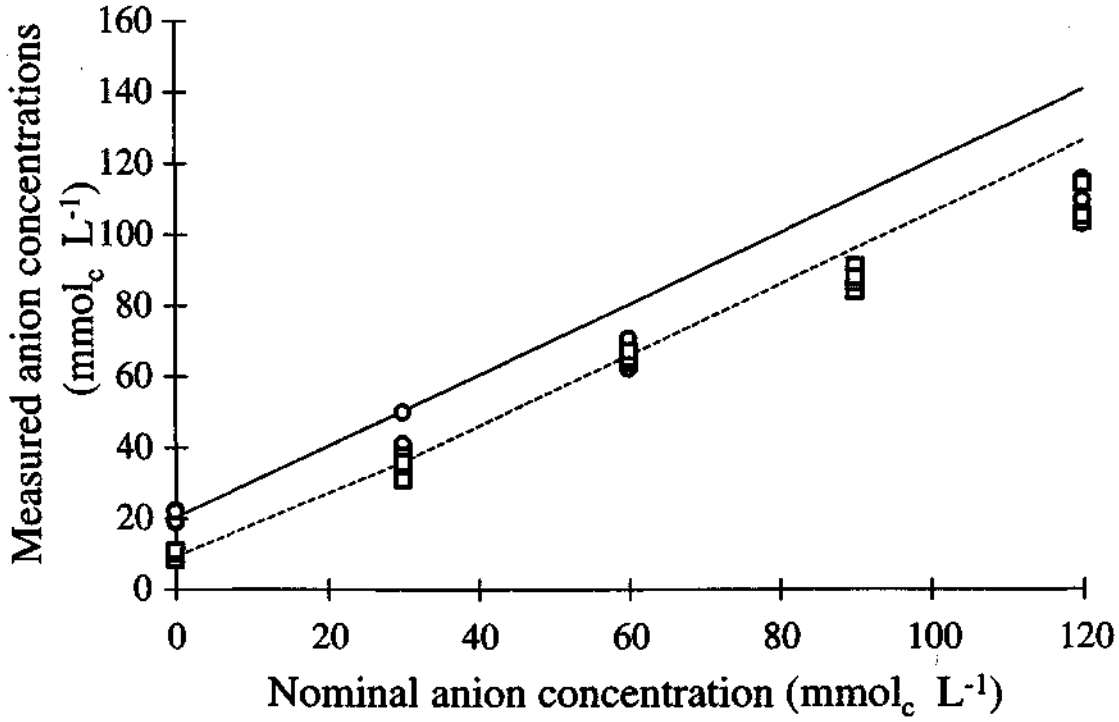

Figure 1. Relationship between measured anion concentrations in soil solution and concentrations predicted after treatment with salt solutions. Symbols are measured concentrations of NO_3 (□, ------) and SO_4 (○, ——) and lines represent 1:1 relationships between measured and nominal anion concentrations.

Table 2. Effect of anion type and anion concentration (mmol$_c$ L^{-1}) on measured total Cd concentrations in soil solution.

Anion conc.	0	30	60	90	120
	Solution Cd (n*M*)				
Anion					
Nitrate	23.4	18.9	75.6	43.4	44.5
Sulfate	23.4	67.8	63.4	63.4	70.1
LSD† (P<0.05)	20.0				

† Interaction LSD for Anion × Concentration

Plant dry weights

Plant dry weights were significantly reduced by increases in both SO_4 and NO_3 concentrations in soil solution. However, at any given salt addition rate there were no significant differences in plant dry weights between these treatments (Figure 2).

Table 3. Effect of anion type and added anion concentration ($mmol_c\ L^{-1}$) on activity of Ca^{2+}, Cd^{2+}, and $CdSO_4^0$ complexes in solution.

Ion	Ca^{2+}		Cd^{2+}		$CdSO_4^0$	
Anion	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}
	Activity of ionic species					
Concn. ($mmol_c\ L$)	(mM)		---------- (n*M*) ----------			
0	2.7	2.7	6.7	6.7	7.8	7.8
30	2.8	2.6	5.3	13.6	4.6	30.9
60	3.2	1.9	19.5	10.8	15.3	32.7
90	3.0	1.6	10.6	9.3	7.8	35.3
120	2.9	1.4	10.6	9.3	7.1	41.1
LSD† (P<0.05)	------ 0.5 ------		------ 5.1 -----		------ 7.0 ------	

† Interaction LSD for Anion × Concentration

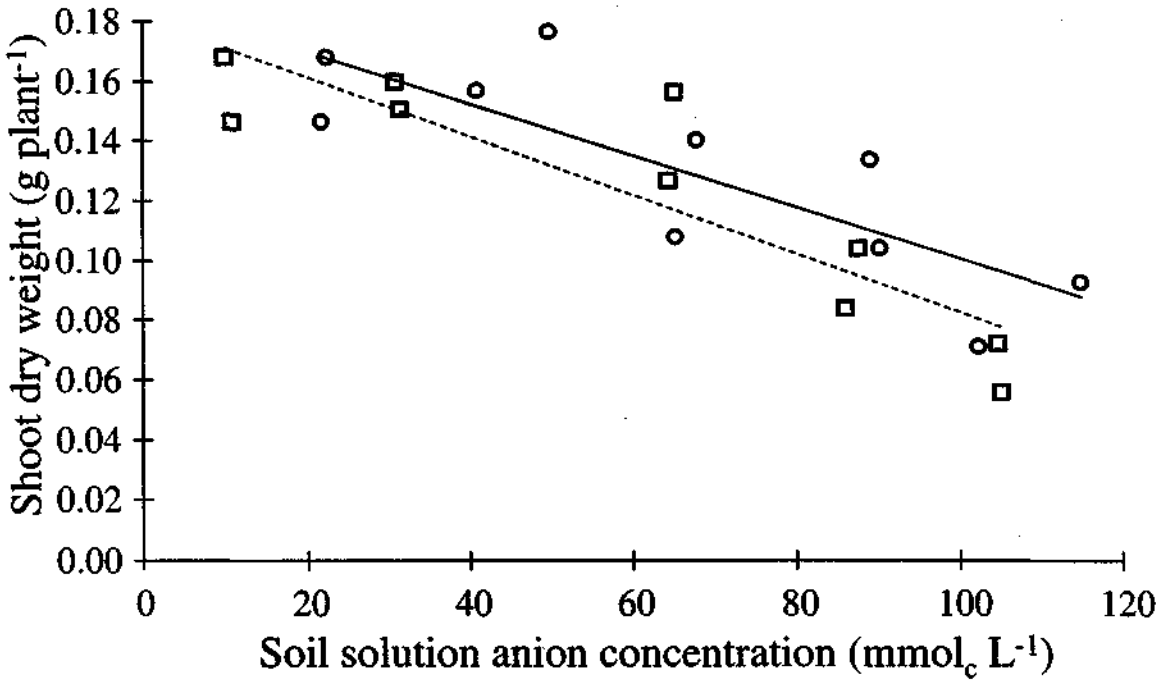

Figure 2. Effect of increasing concentrations of NO_3 (□) and SO_4 (○) in soil solution on shoot dry weights. Fitted lines are linear regression lines:
----- $NaNO_3$ Y=0.181-0.001X: R^2=0.79, P<0.001
—— Na_2SO_4 Y=0.187-0.0009X: R^2=0.67, P<0.001

Uptake of elements by plants

Concentrations of Ca, K, Mg and Mn in plant shoots were decreased as rates of salt application increased, while there was no consistent effect on plant Zn concentrations. Concentrations of Ca in plants in SO_4 treatments were significantly lower than those in NO_3 treatments (data not shown).

Concentrations of Cd in plant shoots were not significantly affected by the NO_3 treatments but were marginally but significantly ($P<0.05$) increased by the SO_4 treatments (Figure 3).

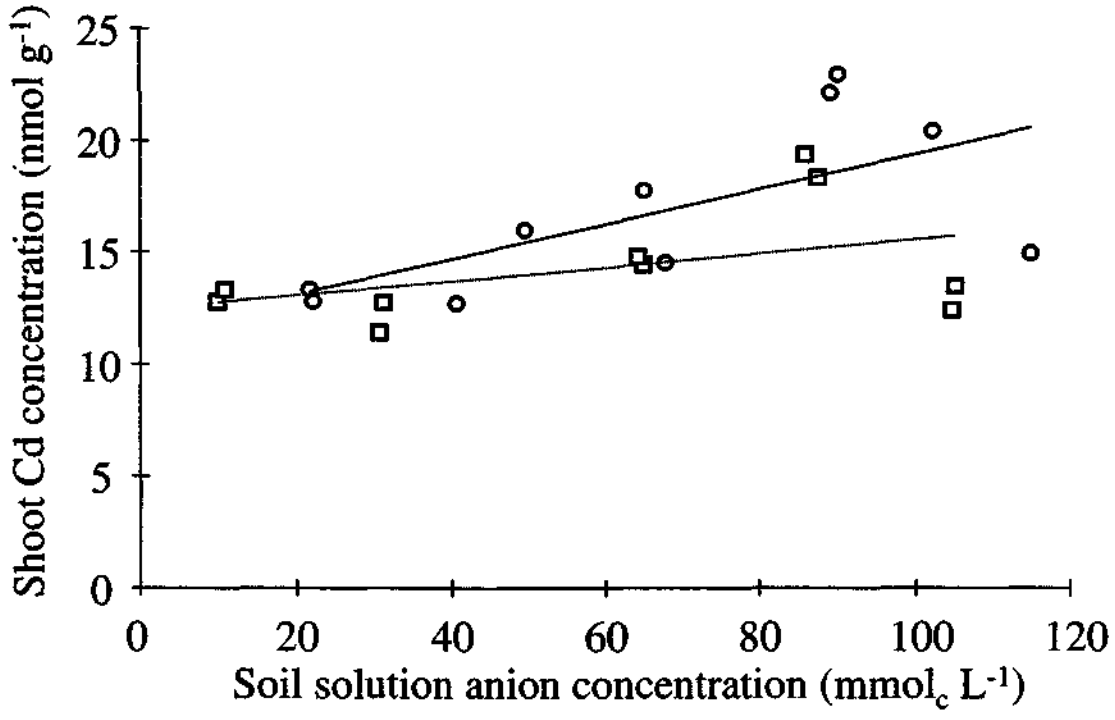

Figure 3. Effect of increasing concentrations of NO_3 (□) and SO_4 (O) in soil solution on shoot cadmium concentrations. Fitted lines are linear regression lines:
----- $NaNO_3$ $Y=12.5+0.031X$: $R^2=0.19$, $P=0.21$
—— Na_2SO_4 $Y=11.6+0.077X$: $R^2=0.44$, $P=0.04$

Cadmium uptake by plants was not consistently affected by either the NO_3 treatments or the SO_4 treatments, until anion concentrations reached 120 $mmol_c\ L^{-1}$ when Cd uptake was decreased in both treatments (Table 4). Cadmium uptake in NO_3 treatments was generally slightly less than in SO_4 treatments.

Discussion

In previous experiments, plant uptake of Cd was unaffected by additions of SO_4 to nutrient solution despite free Cd^{2+} activities decreasing markedly (Appendix 3), suggesting that the $CdSO_4^0$ ion is equally available to plants as the Cd^{2+} ion. In the companion experiments reported here, SO_4 increased Cd concentrations in soil solution but Cd uptake by plants was only marginally increased. This is in contrast to the effect of Cl, which markedly increased both solution Cd concentrations and Cd uptake by plants (Smolders et al., 1998).

Table 4. Effect of anion type and added anion concentration ($mmol_c\ L^{-1}$) on Cd uptake by plants.

Anion conc.	0	30	60	90	120
	Cd uptake ($nmol\ pot^{-1}$)				
Anion					
Nitrate	18.2	16.6	18.4	15.7	7.3
Sulfate	18.2	21.4	17.5	23.8	12.6
LSD† (P•0.05)	4.8				

† Interaction LSD for Anion × Concentration

Previous evidence for additions of sulfate to soil increasing plant Cd concentrations are equivocal and open to conflicting interpretations for a number of reasons (Bingham et al., 1986; Salardini et al., 1993; Sparrow et al., 1994; McLaughlin et al., 1995). Bingham et al. (1986) added varying levels of Na_2SO_4 to a limed and unlimed sandy loam soil (Abruptic Durixeralf) leading to SO_4 concentrations in saturation paste extracts of up to 25 m*M*. Cadmium was also added to the soils as $Cd(NO_3)_2$ to levels reaching 2.5 mg kg^{-1}, and Cd availability was assessed using Swiss chard. The authors did not find an overall significant effect of SO_4 on plant Cd concentrations. It is interesting to note, however, that in the unlimed soil amended with only 0.25 mg Cd kg^{-1}, Cd concentration in Swiss chard increased from 4.7 mg kg^{-1} to 7.4 mg kg^{-1} with increasing rate of SO_4 application. Unusually, liming significantly increased total Cd and Cd^{2+} concentrations in saturation paste extracts. Despite these increases in solution Cd due to liming, plant Cd concentrations were significantly reduced, a result the authors suggested was due to Ca competition effects on Cd uptake. The addition of high amounts of Cd salts led to high solution Cd concentrations (up to 6 μ*M*), so that Cd was likely to be bound much less strongly than in representative agricultural soils (Hendrickson and Corey, 1981), so that ion exchange of Cd with Na or Ca complicated interpretation of liming or SO_4 effects.

Salardini et al. (1993) compared the effect of KCl, KNO_3 and K_2SO_4 on Cd concentrations in seeds of poppies (*Papaver somniferum* L.) grown under leaching and non-leaching situations in pots in the glasshouse. There appeared to be no significant difference between KNO_3 and K_2SO_4 treatments in either leached or unleached pots (despite the authors conclusions to the contrary), while addition of KCl increased seed Cd concentrations in unleached pots and decreased seed Cd in leached pots. In the same experiments, addition of $ZnSO_4$ decreased Cd concentrations compared to $ZnCl_2$, while addition of gypsum generally tended to increase seed Cd concentrations. While it is difficult to draw firm conclusions about effects due to SO_4 from their data, the effects of Cl and gypsum were clear. The latter effect was suggested by the authors to be due to the impact of Ca and increased ionic strength in soil solution decreasing Cd retention by soil surfaces, thereby increasing Cd availability to plants.

Sulfate is a commonly found in high concentrations in soil solutions and in irrigation waters, e.g. Jurinak and Suarez (1980) reported from a survey of well and river waters in USA that median SO_4 concentrations were 3.6 and 4.1 m*M* respectively, while in saturation extracts of a range of salt-affected soils, median SO_4 concentrations were 29.4 m*M*. In a survey of irrigated soils in South Australia, McLaughlin et al. (1997) reported that concentrations of SO_4 in soil

solution ranged from 0.5 to 24.8 m*M*, with mean and median concentrations of 7.9 and 6.9 m*M*. As these solution concentrations were found in soils wetted to -5 kPa in the laboratory, it is likely that concentrations would be higher in soil solution in the field where evaporation and transpiration concentrate salts in the solution, particularly in sodic soils where low Ca concentrations prevent the precipitation of solid phase $CaSO_4$. In soils with these concentrations of SO_4, it is therefore likely that a considerable proportion of the inorganic Cd in soil solution is complexed by SO_4. In our experiments, concentrations of SO_4 found in soil solution were slightly lower than the concentrations added, but we were unable to determine if this was due to anion sorption or precipitation. The latter was unlikely as Ca concentrations in solution did not markedly decrease in line with increasing addition of SO_4.

The concentration of the free Cd^{2+} ion in soil solution is highly buffered by soil components so that if SO_4 were to behave similarly to Cl and have little effect on soil surface charge (except through ionic strength effects), increasing the soil solution SO_4 concentration to approximately 60 $mmol_c\ L^{-1}$ should double the total Cd concentration in solution, through complexation and desorption of Cd from soil surfaces (assuming free Cd^{2+} activity is highly buffered and constant with increasing salt in solution). However, SO_4 is itself adsorbed by soil surfaces to a much greater extent than Cl, so that while SO_4 complexation may tend to increase solution Cd concentrations, the greater negative charge imparted to soil surfaces through SO_4 adsorption may also increase Cd retention and reduce solution concentrations. Thus, effects of SO_4 on Cd retention by soil are less clear than those for Cl. For example, Garcia-Miragaya and Page (1976) found that SO_4 reduced Cd sorption by montmorillonite to a much smaller extent than Cl, while Benjamin and Leckie (1982) found that increasing SO_4 concentrations in solution also reduced Cd sorption by model oxides (amorphous iron oxide, silica and gibbsite) but had no effect on Cd sorption by lepidocrocite. Hoins et al. (1993) found that increasing SO_4 increased Cd retention by goethite.

Given the data in the above studies and those reported here, it would appear that SO_4 will not have the same marked effect on plant Cd uptake as does Cl and therefore SO_4 salinity of irrigation waters will not increase crop Cd concentrations to the same extent as Cl. The effect of gypsum in increasing Cd concentrations in crops, where this occurs (Salardini et al., 1993) is therefore unlikely to be due to SO_4 complexation, but is more likely to be due to Ca displacing Cd from exchange sites on soil into soil solution (Christensen, 1984), or due to increasing ionic strength reducing Cd sorption (Garcia Miragaya and Page, 1976). These effects are evidently dominant (Salardini et al., 1993) over any Ca-Cd competition for uptake at the root membrane (Tyler and McBride, 1982), which raises questions as to the strength of the Ca-Cd competition for uptake at environmentally relevant Cd activities in solution. Tyler and McBride (1982) studied Ca-Cd interactions at Cd^{2+} activities several orders of magnitude in excess of those normally encountered in agricultural soil solutions (<10 nM). Further studies should investigate cationic interactions with Cd uptake at these solution activities.

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APPENDIX 5 Uptake of Cd and Zn in relation to complexation by organic molecules

Introduction

It is well known that cadmium (Cd) uptake by potatoes is enhanced by increasing concentrations of Cl in soil, and that this effect is due to the plant taking up Cd complexed by Cl ions (Smolders and McLaughlin 1996b). Data presented in Appendices 3 and 4 indicate that sulfate in irrigation waters is unlikely to have any adverse impact on crop quality. A further consideration is the effect of organic molecules in waters and soil on uptake of trace metals by plants. This study was performed under a collaborative arrangement with the Catholic University of Leuven, Belgium, to investigate the scientific basis for Cd and zinc (Zn) uptake by plants as affected by organic molecules.

The uptake of Cd and Zn ions by plants from solution has been studied for several decades, with early work using solutions with relatively high solution metal concentrations, particularly for Cd (Haghiri, 1973; Jarvis et al., 1976; John, 1973). Presumably, high metal concentrations were used due to the absence of information regarding Cd concentrations in soil solutions, and/or the difficulty of measuring and maintaining constant activities of Cd in solution at environmentally-relevant levels (sub μM level). Since these early experiments, much information is now available regarding the concentrations of both Cd and Zn in soil solutions (Hirsch and Banin, 1990; Holm et al., 1995; McLaughlin et al., 1997), with concentrations of Cd an Zn typically being in the nM and low μM range, respectively. Design of experimental systems to investigate Cd uptake by plants at such low solution activities for Cd has either focussed on short term (<2 day) kinetic experiments where depletion of solution Cd activity is minimal (Cataldo et al., 1983), on the use of organic chelates to buffer ion activities in solution (see Parker et al., 1995 for a review), or on the use of chelating resins to buffer metal activities (Checkai et al., 1987b).

Chelator-buffering techniques to control metal activities in solution for plant growth studies rely on the assumptions that only the free metal ion in solution is taken up by plants, that the complexed metal pool is much larger then the amount of metal removed from solution by the plant, and that the chelator does not interfere with root ion-transport processes. Chelator-buffering techniques have been used to investigate critical solution activities for trace nutrient metals such as Fe (Bell et al. 1991), Zn (Welch et al. 1993: Yang et al. 1994) and Mn (Webb et al., 1993), and to investigate plant uptake of Cu (Taylor and Foy, 1985) and Cd (Smolders and McLaughlin, 1996a). Checkai et al. (1987b) used resin and chelator buffered systems simultaneously to demonstrate that Cd uptake by plants was unaffected by increasing concentrations of CdEDTA in solution, adding strength to the hypothesis that only the free metal is taken up from solution.

However, the hypothesis that uptake of metals from solution by roots is only controlled by the activity of the free metal in solution is being challenged. A number of workers have found that plant uptake of Fe (Bell et al., 1991; Romheld and Marschner, 1981) and Cu (Taylor and Foy, 1985; Checkai et al., 1987b) are not only related to free metal ion activities in solution. Similar findings in the marine toxicology literature have also raised questions about the free ion hypothesis (Campbell, 1995). If this is indeed the case, then critical activities for trace nutrients determined in chelator-buffered systems may be in error. We therefore examined the

hypothesis that charge/binding strength of metal complexes influence free metal availability for root uptake and translocation.

Materials and methods

Seeds of Lettuce ((*Lactuca sativa* L. Appia) were sown in vermiculite, moistened with tap water and allowed to germinate in the dark (25°C). Eight days after sowing (DAS), 12 uniform seedlings were transplanted to 9 liter culture vessels containing continuously aerated complete nutrient solutions. Solution composition was: Ca (3.55 *mM*); Mg (1.45 *mM*); Na (1.1 *mM*); K (1.2 *mM*); SO_4^{2-} (1.45 *mM*); NO_3^- (8.1 *mM*); $H_2PO_4^-$ (0.2 *mM*); Cl (10 μM); H_3BO_3 (30 μM); Mn (10 μM); Cu (1 μM) and MoO_4^{2-} (0.2 μM). Activities of Fe^{3+} in solution were buffered using FeHBED (Fe-N,N'-bis(2-hydroxybenzyl)-ethylenediamine-N,N'-diacetate, 25 μM) because of its high selectivity for Fe^{3+} compared to Cd^{2+} and Zn^{2+} (Martell and Smith, 1974). It was prepared as a 8 *mM* stock solution according to Chaney (1988) from HBED (acid form) and a 10 % molar excess $FeCl_3$ to ensure that virtually no free HBED was left in solution. pH of all solutions was adjusted to 6.10 ± 0.1 and maintained at this pH during plant growth using MES buffer (2 *mM*) to avoid pH effects on Cd uptake (Hatch et al., 1988). All metal species in solution were calculated using GEOCHEM-PC (Parker et al., 1995).

Treatments were addition of the following organic ligands to the solution to give a final concentration of 50 μM for all ligands (except Tetren, 25 μM) - nitrilotriacetate (NTA), ethylenediamine-N,N,N',N'-tetraacetate (EDTA), trans-1,2-cyclohexyl-diamine-N,N,N',N'-tetraacetate (CDTA), diethylenetriaminepentaacetate (DTPA), N-2-hydroxyethyl-ethylenediamine-N,N',N'-triacetate (HEDTA), ethylene-bis-(oxyethylenenitrilo)-tetraacetate (EGTA), hydroxyethyl-imino-diacetate (HEIDA), N,N-ethylene-diamine-diacetate (EDDA), 1,4,7,10,13-pentaazatridecane (Tetren), 8-hydroxyquinoline-5-sulfonate (Sulfoxine), ortho-phenanthroline (OP) and dithiodicarbamate (DDC).

As Zn is an essential micronutrient, and due to differential complexation of Zn by the different strength ligands, activities of Zn^{2+} in the ligand treatments were modified by addition of $ZnSO_4$ to give activities within the range 10^{-7} *M* to 10^{-9} *M*. The critical activity of Zn^{2+} for plant growth in chelator-buffered solutions has been reported to be below 10^{-9} *M* (Norvell and Welch, 1991; Yang et al. 1994).

A control treatment consisting of rates of Cd^{2+} added to the solution without any ligand was also included. Activities of Cd^{2+} activities in these solutions ranged from $10^{-6.6}$ to $10^{-9.6}$ *M*. In addition, as uptake of Cd is known to be dependent on plant Zn status (Abdel-Sabour et al., 1983), particularly where plants are Zn-deficient (Oliver et al., 1994), a series of Zn control treatments without ligands were formulated, where Cd^{2+} activity in solution was maintained constant at $10^{-8.3}$ M and Zn^{2+} activity was varied from $10^{-5.6}$ to $10^{-8.3}$ *M*. Concentrations of Cd and Zn in these solutions were maintained by radiolabelling with ^{109}Cd and ^{65}Zn, regular radioassay and replenishment as necessary.

All treatments were replicated three times. Dissociation constants for the ligands were obtained from Martell and Smith (1974) and were converted to zero ionic strength and 25°C where necessary.

Cadmium and Zn were added to the solutions to give a final range of activities of the free cadmium (Cd^{2+}) and zinc (Zn^{2+}) ions in solution ranging from 10^{-12} to 10^{-7} *M* and $10^{-9.9}$ to 10^{-7} *M* (Table 1), respectively. Concentrations of Cd and Zn in these solutions were maintained by radiolabelling with ^{109}Cd and ^{65}Zn, regular radioassay and replenishment as necessary.

Table 1. Metal activities maintained in solution for all treatments.

Ligand	$Log(Cd^{2+})$	$Log(Zn^{2+})$	Dominant species
Cd^{2+} control	6.6-9.6	5.6	M^{2+}
Zn^{2+} control	8.3	5.6-8.3	M^{2+}
NTA	7.7	7.8	ML^{-}
EDTA	10.0	9.3	ML^{2-}
CDTA	10.9	9.7	ML^{2-}
DTPA	11.5	9.6	ML^{3-}
HEDTA	10.2	9.9	ML^{-}
EGTA	10.0	7.5	ML^{2-}
HEIDA	6.7	7.0	ML^{0}
EDDA	6.8	7.9	ML^{0}
Tetren	7.3	7.6	ML^{2+}
Sulfoxine	6.8	7.5	ML^{+}
OP	8.0	9.1	ML_2^{2+}
DDC	nd	nd	ML^{0}

nd = not determined

During plant growth, activites of ^{109}Cd and ^{65}Zn were monitored at transplanting (8 DAS) and at 11, 14, 17, 19, 21, and 22 DAS by removing 5 ml solution and counting radioisotope activities by γ-spectroscopy.

Plants were harvested at 23 DAS. Roots and shoots were separated. Shoots were rinsed in deionised water, while roots were washed by immersing for 30 min. in a solution of 5 *mM* $CaCl_2$ and 1 *mM* $LaCl_3$ to desorb extra-cellularly bound metals (Reid et al., 1996). Roots were then rinsed in deionised water. Roots and shoots were blotted dry, weighed and dried for 48 h at 70°C. Plant material was weighed, finely ground in a mortar and ^{109}Cd and ^{65}Zn concentrations determined in a subsample of the material by γ-spectroscopy of the dried powder.

Results

Effects of ligands on root and shoot growth are shown in Figure 1. Plants in OP treatments died due to precipitation of iron and trace metals out of solution (data not shown) and those in EDDA treatments had significantly ($P<0.05$) reduced root and shoot growth. Plants grown in DDC treatments initially had retarded root growth, the solutions developed a brown precipitate which coated the roots, and Cd and Zn activities in solution were markedly reduced. Due to uncertainties in the speciation of metals in the DDC-buffered solutions, data for metal uptake from these treatments were not used. There were no significant ($P=0.05$) differences in root or shoot growth with the other ligands or with the Cd^{2+} control treatment (no ligand). Root growth in the EGTA solutions was very variable, but shoot growth was normal and similar to the other ligand treatments. As there were no differences in plant growth, treatment effects expressed either as plant metal concentrations or as plant metal uptake were not significantly different.

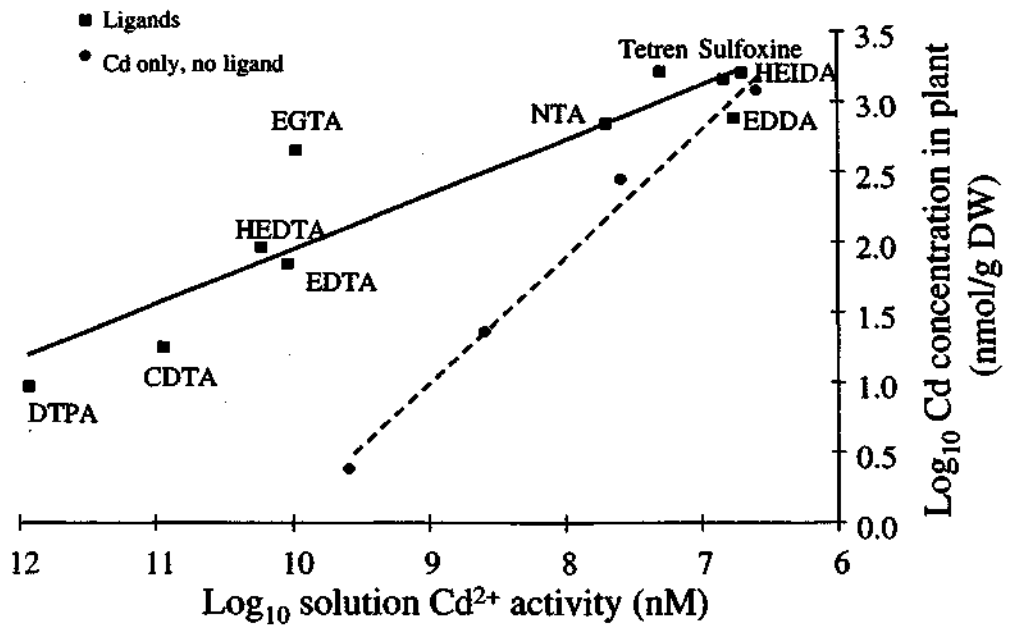

Figure 1. Shoot (a) and root (b) dry weights in the control and ligand treatments. Bars represent standard deviation of mean values (n=3).

Plant Cd concentrations (roots+shoots) were linearly related (R^2=0.99, P<0.001) to solution Cd^{2+} activities in the control (no ligand) treatment, with the slope of this log-log relationship being close to 1.0 (Figure 2).

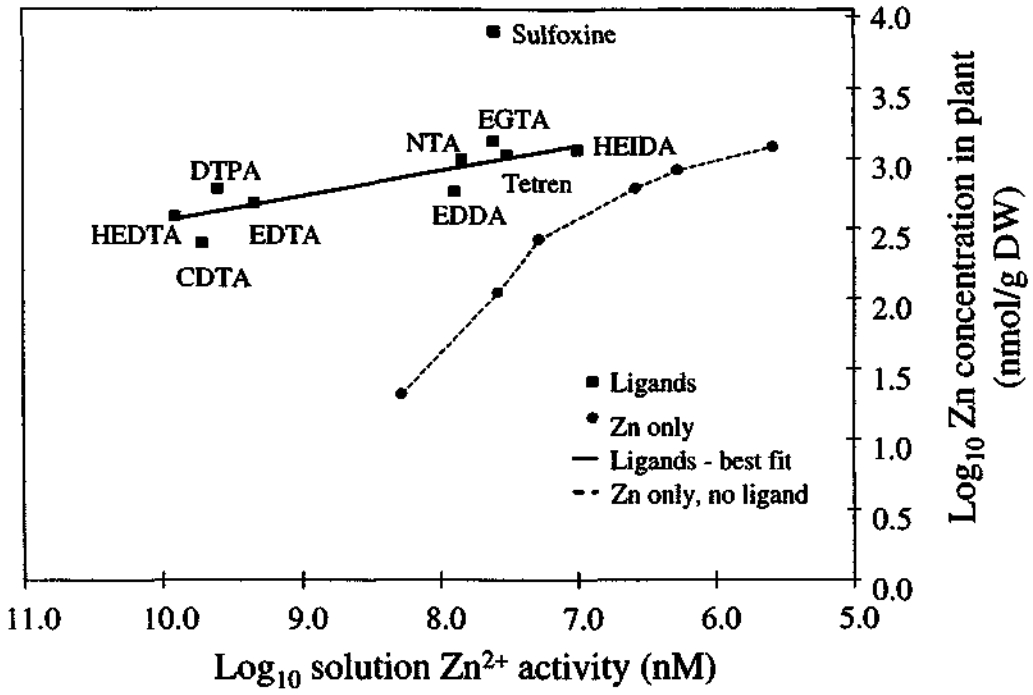

Figure 2. Relationship between plant Cd concentration and the negative logarithm of solution Cd^{2+} activity in molar units (pCd^{2+}) in the absence and presence of ligands. Standard deviations of mean values are within the area of the points on the graph. Fitted lines are y = 5.9 - 0.4x: R^2 = 0.87, P<0.001 (ligands) and y= 9.22 - 0.92x: R^2 = 0.99, P<0.001 (Cd only, no ligand).

In the Zn control treatments, plant Cd concentrations were relatively unaffected by varying solution Zn^{2+} activities from $10^{-8.3}$ to $10^{-6.5}$ *M*. Above $10^{-6.5}$ *M* Zn^{2+}, Cd concentrations in plants were depressed (data not shown).

Ligands which formed weak uncharged complexes (HEIDA), weak positively charged complexes (Tetren) or a combination of weak neutral and positively charged complexes (Sulfoxine) led to much greater Cd concentrations in plant roots and shoots than strong negatively charged ligands, given the same initial solution Cd concentration. This was due to reductions in the activity of the free Cd^{2+} ion (Figure 2). In the ligand treatments, plant Cd concentrations were also linearly related to the free metal ion activities in solution, but in contrast to the control treatment the slope of this relationship (0.39) was significantly lower than 1.0 (Figure 2). EGTA appeared to allow significantly greater Cd concentrations to accumulate in plants compared to EDTA, despite calculated solution Cd^{2+} activities being identical. Plants grown in Tetren-buffered solutions had similar Cd concentrations to those grown in HEIDA, despite solution Cd^{2+} activities being 50 *nM* instead of 200 *nM*, respectively.

In the absence of ligands, plant Zn concentrations were decreased as solution Zn^{2+} activities decreased from $10^{-5.6}$ to $10^{-8.3}$ *M*, but the decline in Zn concentrations was not linearly related to solution Zn^{2+} activity with plant Zn concentrations falling slowly as solution Zn^{2+} activities approached $10^{-7.3}$ *M*, and falling more rapidly thereafter(Figure 3).

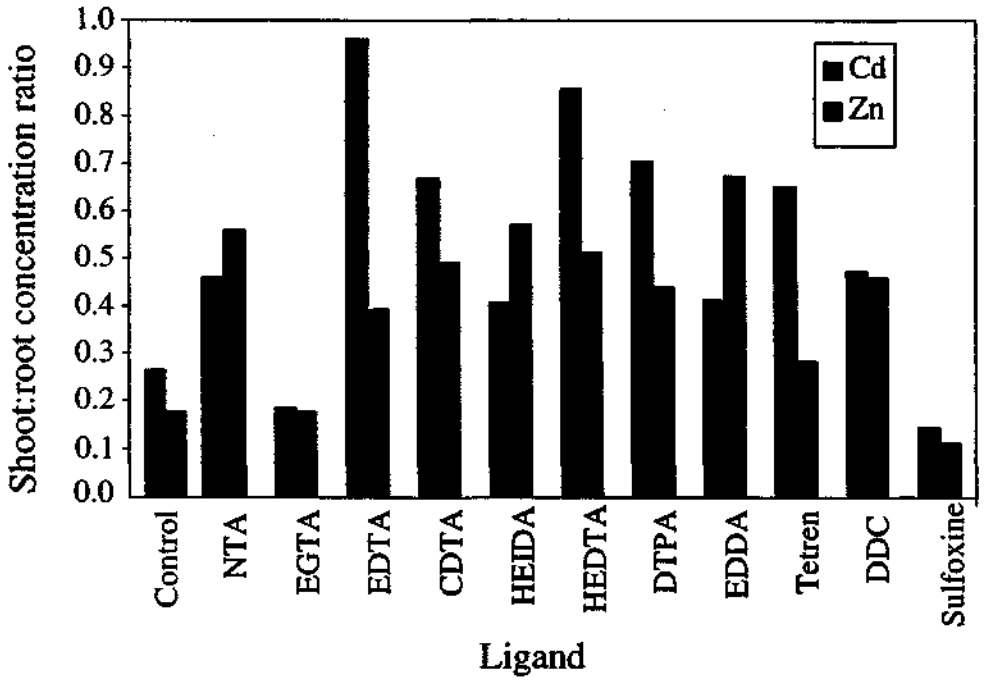

Figure 3. Relationship between plant Zn concentration and solution Zn^{2+} activity (negative logarithm in molar units - pZn^{2+}) in the absence and presence of ligands. Standard deviations of mean values are within the area of the points on the graph. Fitted line is 4.4 -0.19x: $R^2 = 0.75$, $P<0.001$ (ligands) and the Zn only line (no ligand) is hand fitted.

Given the same Zn^{2+} activity in solution, Zn concentrations in plants in the presence of ligands was significantly greater than in the absence of ligand (Figure 3). There appeared to be a

linear relationship between solution Zn^{2+} activity and plant Zn uptake across ligand types, but the slope of the relationship was small (0.19).

Distribution of Cd and Zn between shoots and roots was markedly affected by ligand type (Figure 4). In general, proportionately more metal was translocated to shoots in the presence of ligands compared to the Cd or Zn only treatments, except for EGTA and Sulfoxine treatments which had similar metal shoot:root ratios to control treatments.

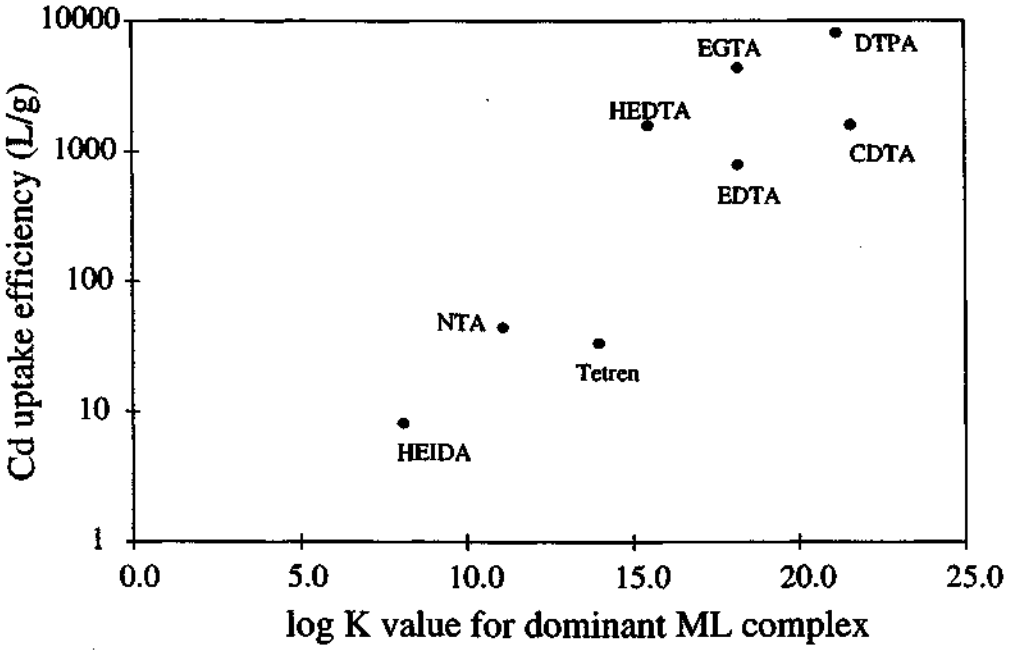

Figure 4. Effect of ligands on shoot:root ratios of metals in plants.

Discussion

The free ion hypothesis for uptake of metals by both plants and biota, has gained much support in both plant nutrition (Parker et al., 1995) and in ecotoxicological studies with aquatic organisms (Campbell, 1995). In experiments to determine the critical free ion activity in solution below which plants suffer micronutrient metal deficiencies, a benchmark assumption in these studies is that the activity of the free hydrated metal ion determines plant uptake of that metal (Bell et al., 1991; Webb et al., 1993; Welch et al., 1993: Yang et al., 1994). As metal uptake is principally governed by activity of the free metal ion, uptake is a negative function of metal-ligand binding constant at constant solution metal *concentration*. Hence plant Cd concentrations are lower in DTPA-buffered solutions than in NTA-buffered solutions, despite solution Cd *concentrations* being equal across treatments (Figure 2).

However, our results here suggest that across a range of chelator-buffered systems, there is no single relationship between metal ion *activities* in solution and metal uptake by plants, but that at any given activity, plant metal uptake will be dependent on the type of ligand in solution. Efficiency of free metal uptake, defined as the plant metal concentration (or uptake) divided by solution metal ion *activity*, was a positive function of the strength of the metal-ligand binding constant and charge (Figure 5).

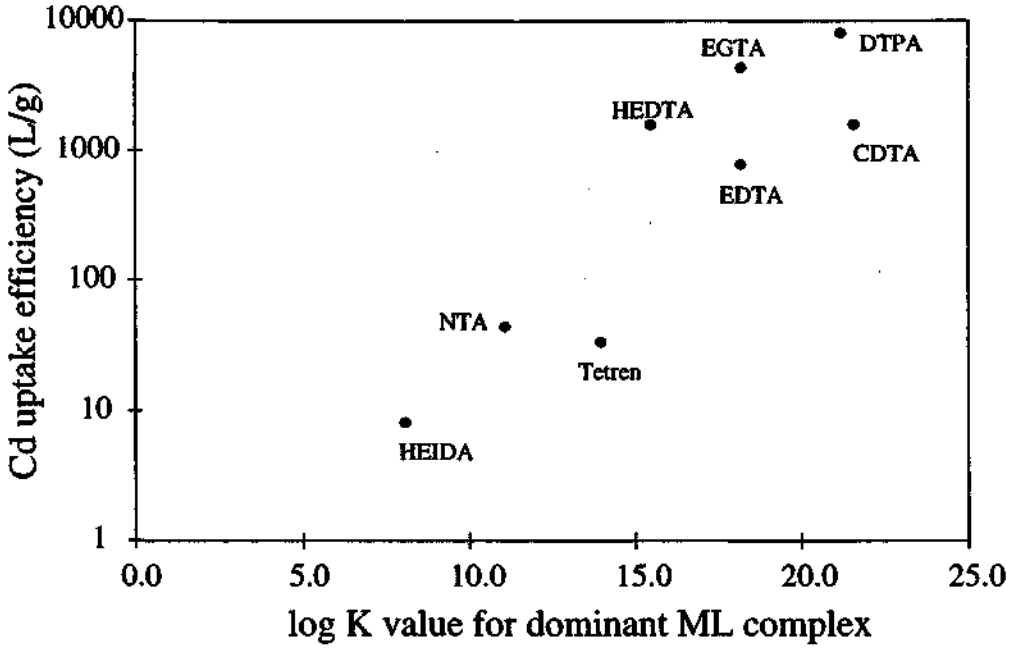

Figure 5. Relationship between Cd^{2+} uptake efficiency, calculated as plant Cd concentration per unit solution Cd^{2+} activity, and binding constant of dominant metal:ligand complex.

Unfortunately, the distinction between effects of charge and binding strength of the metal ligand complex on plant uptake were difficult to separate, due to all the uncharged or positively-charged ligands (HEIDA, Tetren, Sulfoxine) forming weak ligands with Cd, and the highly-negatively charged ligands (EDTA, CDTA, DTPA) forming strong complexes with Cd. However, it is evident from Figure 5 that Tetren, which forms positively-charged Cd complexes, has a similar uptake efficiency to NTA, which forms negatively charged complexes, despite the ML binding constant being 3 orders of magnitude stronger. Similar results have been reported by Iwasaki and Takahashi (1989) for Cu uptake by ryegrass and clover in the presence of Trien, which is related to Tetren, and also forms positively-charged complexes with metal ions. Sinnaeve et al. (1983) also found Tetren increased metal uptake by plants.

Thus for Cd, which compared to Zn appears not to have uptake as strongly regulated (Figures 2 and 3), it can be postulated that for each ligand, or in the absence of a ligand, there is a unique relationship between plant Cd uptake and solution metal activity, which has a slope of 1.0, while at any given solution metal activity, plant uptake will be dependent on the ligand type and strength (Figure 6).

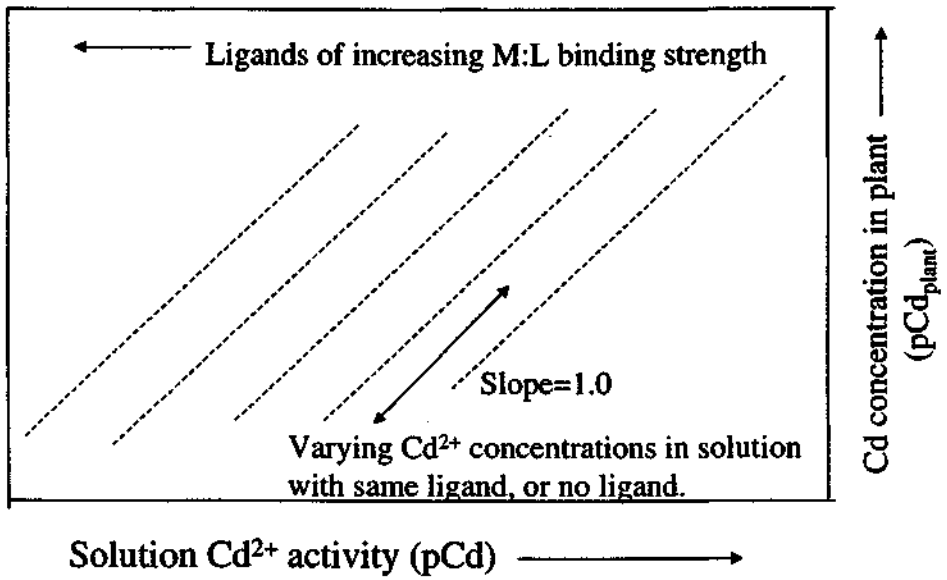

Figure 6. Generalised relationship between plant Cd uptake in relation to changing Cd^{2+} activities in the absence and presence of ligands. Changing Cd^{2+} for any single ligand (or in the absence of ligand) yields a relationshiop with a slope of 1.0, while changing ligand at constant solution Cd^{2+} shifts the relationship to increasing plant Cd concentrations.

We attempted to keep Zn^{2+} activities in solution in the range 10^{-6} *M* to 10^{-10} *M*, the range in which we expected that Zn would have little effect on Cd uptake. Deficiency of Zn has been shown to enhance Cd accumulation (Oliver et al., 1994) and Zn is known to inhibit Cd uptake in short-term uptake experiments (Cataldo et al., 1983). From the Zn control experiment it was evident that Cd uptake was relatively unaffected by solution Zn^{2+} activities between $10^{-8.3}$ *M* and $10^{-6.5}$ *M*. We were unable to attain lower Zn^{2+} activities in these solutions without ligands, due to the presence of small amounts of carrier Zn in the ^{65}Zn stock solutions. In the presence of ligands, where Zn^{2+} activities varied from 10^{-7} *M* to $10^{-9.9}$ *M*, plants did not exhibit any signs of Zn deficiency. These Zn^{2+} activities are above those found to be critical for plant growth ($10^{-10.5}$ *M*) in chelator-buffered solutions (Norvell and Welch, 1993; Yang et al., 1994).

The reasons for differences in plant Cd and Zn concentrations between the different chelator-buffered systems can be postulated to be:

1) Uptake of the intact metal-ligand complex. Evidence for uptake of metal complexes is for example found using double -labelled $^{65}Zn/^{14}C$-labelled metal-ligand complexes suggesting uptake of a Zn phytosiderophore complex in maize plants (von Wiren et al.., 1996). Recent evidence using chelates in phytoremediation studies also suggests that intact metal-chelate complexes are readily taken up by roots and enhance transport to shoots (Huang et al., 1997). The increase in shoot:root ratios of Cd and Zn noted for most ligands in comparison to metal-only controls (Figure 4) suggests that the metals are present within the plant in the complexed form. Uptake of the metal-ligand complex can occur at breaks in the endodermis. For example, Römheld and Marschner (1981) found that maize could absorb intact FeEDDHA

(Fe-ethylenediamine-di(o-hydroxyphenyl acetic acid)) at breaks in the endodermis where lateral roots budded;

2) Uptake of metal from solution is a diffusionally limited process, whereby the unstirred layer adjacent to the root, and the negatively charged apoplastic space provide a barrier to metal movement to carrier sites or channels where metals are membrane transported. Certainly, this hypothesis would explain the relationship between metal-ligand binding constant and charge and efficiency of metal uptake found in this study. Indeed, this was one of the reasons cited by Halvorson and Lindsay (1977) to explain a significantly lower critical Zn^{2+} activity in chelate buffered solution than in previous studies withunbuffered solution culture (Carrol and Loneragan, 1968).

Irrespective of the actual mechanisms, it is apparent that there is no single relationship between metal activities in solution and metal uptake by plants, in the presence of synthetic organic ligands. Similar conclusions were made recently with regard to complexation of Cd by chloride (Smolders and McLaughlin, 1996a,b) and sulfate (McLaughlin et al., 1997). Hence, critical solution activities determined for metal micronutrients (Bell et al., 1991; Webb et al., 1993; Welch et al., 1993: Yang et al., 1994) must be regarded to be ligand-specific, and as noted above are likely to be significantly lower than critical activities determined in chelator-free systems.

An interesting but untested hypothesis, is that complexation of metals by natural organic ligands in soils may also significantly affect plant metal uptake, by mechanisms similar to those postulated here for synthetic ligands. Cabrera et al. (1988) found that uptake and toxicity of high solution concentrations of Cd to barley was reduced by humic acid (HA), in line with reductions in Cd^{2+} activity due to HA addition, as measured by dialysis and ion-selective potentiometry. However, recalculation of the data of Cabrera et al. (1988) indicate that Cd uptake by the plants was actually enhanced by HA addition at constant Cd^{2+} *activity*.

A more concerning outcome from these studies is that plant uptake of metals in chelator-buffered systems may lead to erroneous conclusions regarding critical ion activities for nutrition or phytotoxicity. This may in part explain the large differences observed for critical solution Zn^{2+} activities to avoid plant Zn deficiency determined in flowing solution culture conditions (10^{-7} *M*, Carrol and Loneragan, 1968), compared to those determined in chelator-buffered systems ($10^{-10.5}$ *M*, Halvorson and Lindsay, 1977; Norvell and Welch, 1993; Yang et al., 1994). Furthemore, given that the intact metal-ligand complex may be taken up by the plant, we would recommend that ion competiton effects on metal uptake should not be studied in chelator-buffered systems. It would appear that manually-buffered or resin-buffered solution culture techniques (Checkai et al., 1987a; Smolders and McLaughlin, 1996b) may be more appropriate to study metal ion uptake by plants.

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APPENDIX 6 Reducing cadmium uptake by addition of ameliorants to soil – urban waste materials

Introduction

Cadmium (Cd) is a widely-dispersed pollutant in the environment, accumulating in many agricultural soils and posing a potential hazard to food quality and human health. Many factors affect availability of soil Cd to plants, including pH, soil salinity, soil organic matter content, soil texture, soil micronutrient status, etc. (Chaney and Hornick, 1978; McLaughlin et al., 1996). For both dryland and irrigated potato crops, soil salinity has recently been shown to have a much more significant influence on soil-plant transfer of Cd than was considered previously (Li et al., 1994; McLaughlin et al., 1994). Farmers therefore need management techniques to minimise Cd contamination of food crops grown with saline irrigation waters.

The effect of salinity in increasing plant uptake of Cd is predominantly due to the complexation of Cd by chloride (Cl) in the soil solution. Chloro-Cd complexes are not only more mobile then free Cd^{2+} in the soil-root zone (Doner, 1978), but also may be taken up directly by plant roots (Smolders and McLaughlin, 1996). If high Cd concentrations in crops result from low soil pH, remediation can be performed by the application of liming materials (Chaney and Hornick, 1978), although results are not always predictable (Maier et al., 1997). However, where high crop Cd concentrations are the result of salinity, there are no simple techniques to reduce the Cl content of soil or irrigation water. Techniques are therefore required to reduce the phytoavailability of soil Cd in these systems.

This paper presents the results from a study investigating the use of inexpensive industrial by-products to reduce Cd phytoavailability in saline soils.

Materials and Methods

A glasshouse experiment was performed using potatoes (*Solanum tuberosum* cv. Atlantic) as the test crop. A total of thirteen (13) soil amendments were chosen on the basis that they were inexpensive materials with the potential to significantly reduce availability of Cd to plants, principally through increasing the sorption capacity of the soil for Cd under conditions of high salinity. The materials were a mixture of industrial by-product clay material (coal-washing clays - CW clays), water treatment residuals (WTRs), industrial clays (coarse (c) and fine (f) bentonites and zeolite) and natural mined clays. The WTRs were derived from both Fe and Al-based chemical flocculation processes for drinking water treatment, as well as one material incorporating activated carbon (Alum+C WTR). The soil used was an Alfisol with sandy texture, having a neutral pH, a low cation exchange capacity (CEC), and a Cd concentration typical of horticultural soils in Australia (McLaughlin et al. 1997).

Pots were filled with 15 kg soil and amendments at an application rate equivalent to 25 t ha^{-1}. After 4 weeks incubation at -10kPa moisture potential, basal nutrients were added and one seed potato tuber was planted to a depth of 2-3 cm. Nutrients were applied 2-3 times during the growth period and pots were watered according to plant demand with a solution containing 600 mg Cl L^{-1} as NaCl.

Table 1. Chemical composition of soil and remediation materials used.

	EC	pH_w	Total C	C.E.C	Total Cd	Oxalate Fe	Oxalate Al
	dS/m		%	$cmol^+ kg^{-1}$	mg kg^{-1}		
Soil	0.6	6.3	1.7	7	0.075	600	1000
Water treatment biosolids (WTRs)							
Iron WTR	1.8	7.3	5.7	30	0.044	20700	57300
Alum WTR 1	0.4	7.2	17.2	19	0.363	103800	16900
Alum WTR 2	1.9	7.7	6.7	34	0.069	6800	7300
Alum+C WTR	0.4	7.1	20.0	18	0.358	104600	16900
Industrial and natural clays							
CW clay	0.2	9.6	19.9	7	0.119	800	3700
Bentonite coarse	3.2	5.3	0.1	78	0.005	1300	400
Bentonite fine	2.4	5.4	0.1	68	0.004	1300	400
Wirrega clay	0.9	9.5	3.2	18	0.016	1100	600
WF clay 1	0.3	9.2	0.3	20	0.007	1000	800
WF clay 2	0.2	8.4	0.1	142	0.004	900	400
Mundulla clay	0.4	9.3	1.0	18	0.006	1100	500
Zeolite	0.1	6.3	0.1	132	0.021	1400	200
Lime	0.3	8.6	ND	1	0.227	200	300

ND = not determined.

Plant material was harvested and elemental concentrations in plant shoots and tubers were determined as outlined by McLaughlin et al. (1994). Soil and amendment pH and electrical conductivity (EC) were determined in a water suspension of soil using a 1:5 soil:solution ratio (Rayment and Higginson, 1992). Total carbon (C) was determined using a Leco™ furnace. Cation exchange capacity was determined using NH_4Cl leaching procedure and iron (Fe) and aluminium (Al) were extracted using acidic ammonium oxalate (Rayment and Higginson, 1992).

Total and extractable metal concentrations in soils and amendments were determined using aqua regia with microwave heating, and diethylenetriaminepentaacetate (DTPA - Lindsay and Norvell, 1979). In addition, Cd sorption capacity of the amendments was assessed by shaking 4 g soil for 16 hours with 40 mL of either 0.05 M $Ca(NO_3)_2$ or 0.05 M $CaCl_2$ having graded concentrations of Cd to give final solution concentrations less than 250 nM. Solutions were filtered through a 0.22 µm filter prior to analysis by flameless atomic absorption spectroscopy. Sorption data were converted to either linear ($y = a + bx$) or Freundlich ($\ln y = a + b \times \ln x$) sorption equations with the solid:liquid distribution coefficient (K_d) being the slope term in these equations

Results

The materials had a wide range of capacities to retain Cd (Table 8).

Table 8. Values of the linear models applied to sorption data and ΔK_d values.

Soil/amendment[a]	Electrolyte anion	Adjusted R^2	K_d L kg^{-1}	Intercept nmol L^{-1}	ΔK_d L kg^{-1}
Soil	Cl	0.96	3	0.83	0.19
	NO_3	0.96	16	-1.31	
Iron WTR	Cl	1.00	430	-9.6	0.47
	NO_3	1.00	920	-8.1	
Alum WTR 1	Cl	0.99	180	-1.42	2.25
	NO_3	1.00	80	-1.87	
Alum WTR 2	Cl	0.94	210	-11.72	0.51
	NO_3	0.97	410	-6.04	
Alum+C WTR	Cl	1.00	88	-1.18	0.50
	NO_3	1.00	175	-0.94	
CW clay	Cl	0.98	12	2.28	0.41
	NO_3	0.93	29	6.05	
Bentonite coarse	Cl	0.99	7	0.32	0.64
	NO_3	0.99	11	1.16	
Bentonite fine	Cl	0.97	4	0.09	0.44
	NO_3	0.97	9	1.86	
Wirrega clay	Cl	0.98	460	-12.97	0.31
	NO_3	0.99	1470	-3.18	
WF clay 1	Cl	0.98	80	0.39	0.39
	NO_3	0.97	205	4.09	
WF clay 2	Cl	0.99	37	1.97	0.10
	NO_3	0.98	360	-2.52	
Mundulla clay	Cl	0.97	139	-0.06	0.42
	NO_3	0.93	328	5.72	
Zeolite	Cl	0.99	0.5	-0.06	0.25
	NO_3	0.87	2	1.01	
Lime	Cl	1.00	109	-0.95	0.29
	NO_3	0.96	376	-7.91	

[a]WTR = water treatment biosolid, CW = coal washing

All sorption relationships were highly linear and there was no benefit in a Freundlich transformation (Figure 4). By comparing K_d values determined in equivalent NO_3^- and Cl^- solutions (ΔK_d), it was possible to gain not only an indication of the sorption capacity of the amendments for Cd, but also a measure of the ability of the materials to retain sorbed Cd against high solution Cl^-, simulating irrigation with saline water.

Plant shoot growth was adversely affected by some of the WTRs, notably the Alum WTR 1 and Alum+C WTR treatments (Figure 5). Tuber yield was variable between replicates and treatments effects on tuber yield did not always correspond to effects noted in shoot growth. Cadmium concentrations in tubers and plant tops were also markedly reduced by all WTRs, particularly in the treatments most adversely affected in terms of dry matter yield - Alum WTR 1 and Alum+C WTR treatments. Some of the natural clay materials also markedly reduced tuber Cd concentrations with little or no effect on yield parameters (e.g. Wirrega clay).

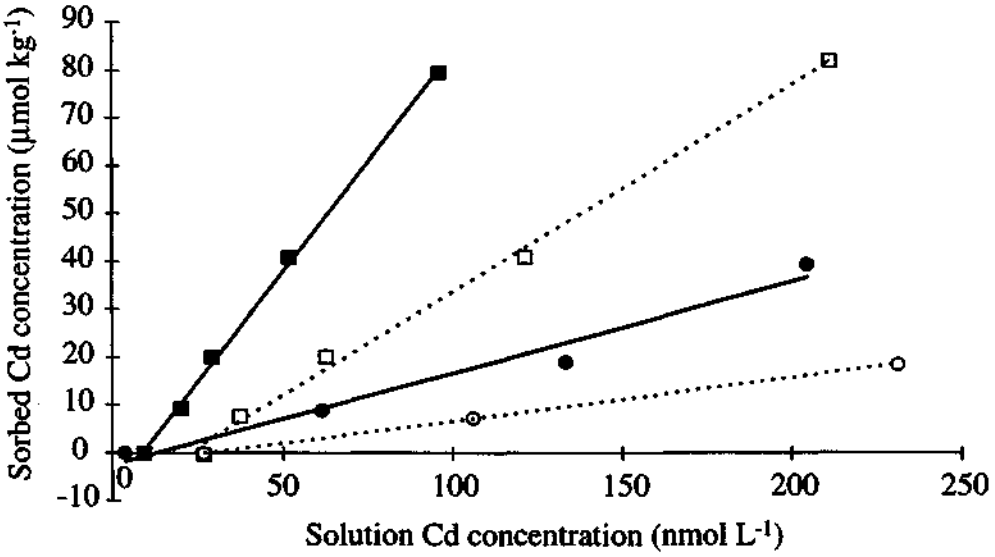

Figure 4. Cadmium sorption relationships for Fe WTR (squares) and Al WTR 1 (circles) determined in a background electrolyte of either 0.05 M $Ca(NO_3)_2$ (solid symbols) or 0.05 M $CaCl_2$ (open symbols). Coefficients for fitted lines are given in Table 2.

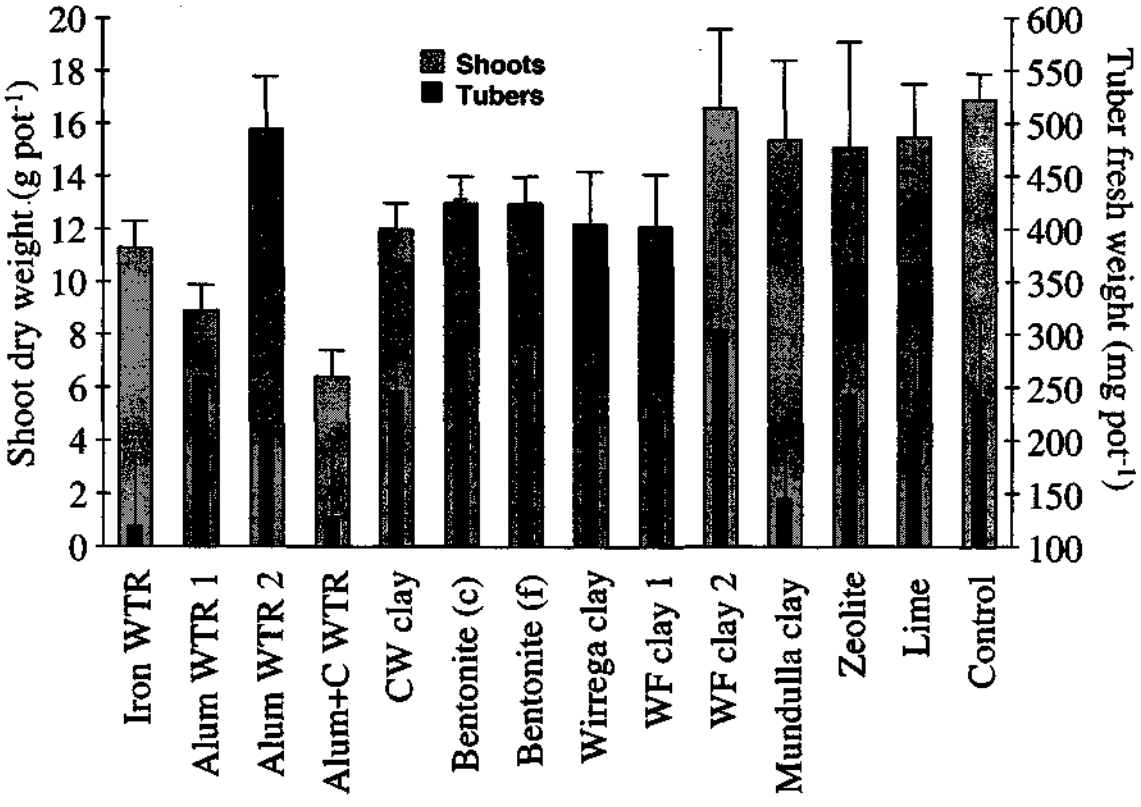

Figure 5. Effect of remediation treatments on shoot and tuber yield.

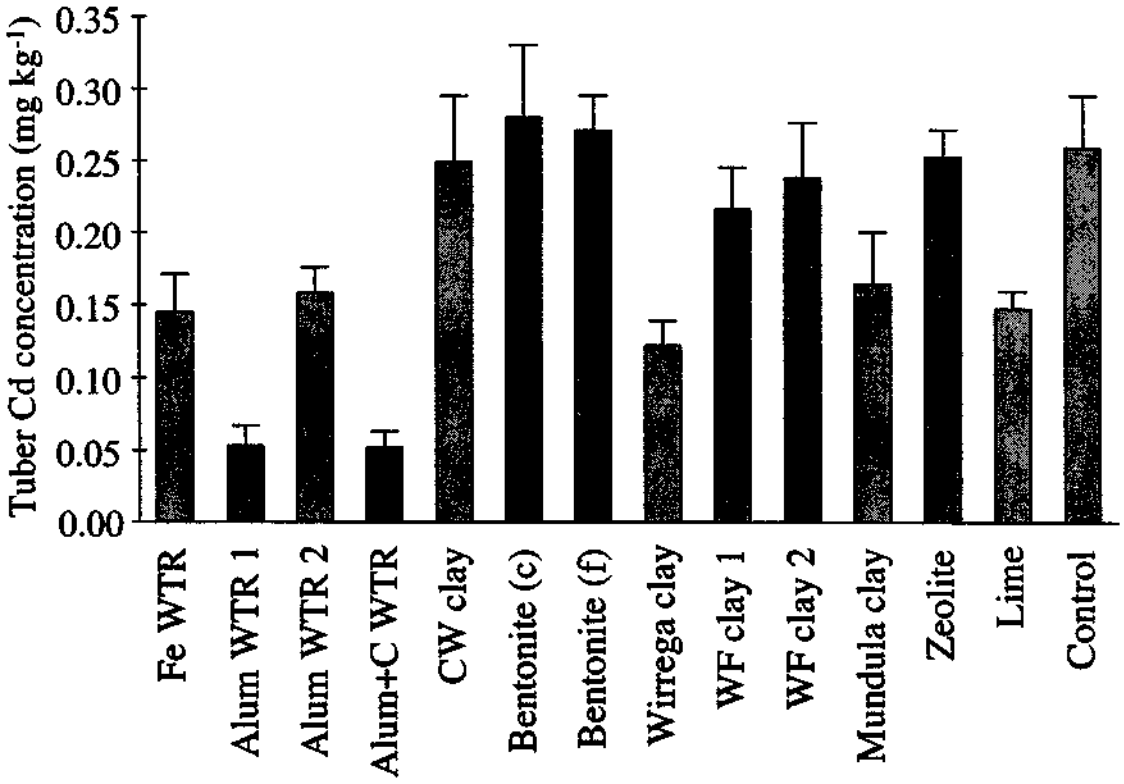

Figure 6. Effect of remediation materials on potato tuber Cd concentrations.

Ability of the amendments to reduce tuber Cd concentrations was not correlated to any sorption measure, or to the increase in soil pH caused by some amendments (data not shown). There were strong positive relationships between Cd in tubers and Zn in both tubers and shoots (R^2 = 0.78, P<0.001 and R^2 = 0.90, P<0.001, respectively). Similarly, there were strong positive correlations between P in shoots or tubers and tuber Cd concentrations (R^2 = 0.82, P<0.001 and R^2 = 0.90, P<0.001, respectively). Reductions in plant Cd concentrations were not related to reductions in plant growth - Cd uptake (mg pot^{-1}) was also significantly affected by the treatments (data not shown). Significant reductions in shoot and tuber growth, and tuber Cd concentrations, in WTR treatments were associated with elevated concentrations of Cu in plant tissue, with up to a tenfold increase in shoot Cu concentrations observed (to 30 mg kg^{-1} dry weight). Analysis of the WTRs for Cu indicated Cu concentrations of up to 0.6% in some of these materials.

Discussion

The adverse effect on plant shoot growth and tuber yield of some of the remediation materials trialed appeared to be principally related to very high Cu concentrations in some of the WTRs. Copper is used as an algicide in many inland water impoundments in Australia, and the Cu added to the water bodies adsorbs strongly to particulate and mineral organic matter in suspension. Water purification processes flocculate these colloids using alum or iron salts, so that the resulting solid waste material precipitated out of solution may have high Cu concentrations. Despite the likelihood that Cu is strongly bound in the WTRs, it appears that there is sufficient phytoavailable Cu to significantly affect plant growth, even at moderate rates of WTR application to soil.

The significant reduction in tuber Cd concentrations and plant Cd uptake associated with Cu may be due to strong competition between Cd and Cu for uptake at the root membrane. There is some evidence in the literature that increasing Cu concentrations in solution reduce plant Cd uptake (Cataldo et al., 1983), but it is unclear if the Cu competition effect noted is merely a response to phytotoxicity. Investigation of the use of Cu-enriched WTRs at lower rates of application, or small application of inorganic Cu, to reduce plant Cd concentrations appears warranted.

The strong relationship between Cd and P concentrations in plants suggests that some of the effect of the remediation treatments was related to P nutrition of the plant. The interaction between P nutrition and Cd is well known (Williams and David, 1977), so that part of the effect of the amendments in reducing Cd may have been to reduce root proliferation through the soil, and hence access to soil Cd, due to reduced P availability. Concentrations of P in shoots and tubers were not at unusually low levels, given that plants were harvested at maturity (most nutrition criteria are for younger tissues). There was no strong relationship between P concentrations in tissues and dry weight, suggesting that P availability was not limiting shoot or tuber yield.

Despite using remediation materials that have high retention capacities for Cd in relation to the original soil, the materials appeared to have little effect based on their ability to sorb Cd. K_d values were up to 2 orders of magnitude greater than the original soil, and were in the upper range of values found in the literature for soils (Christensen, 1989). Part of the reason for this may be due to the low, but agronomically realistic, rates of application used in the experiment. The remediation materials constituted less that 1% by weight in the soil, so that effects on sorption may have been masked by other characteristics of the materials which affected Cd to a greater extent (e.g. Cu).

Conclusions

A number of inexpensive remediation materials were identified which have the potential to significantly reduce Cd uptake by plants. WTRs and some natural clay materials have potential in this regard, but the presence of phytotoxic concentrations of Cu in some WTRs may limit their use for Cd remediation. Further investigation of the Cu-Cd interaction in terms of plant Cd uptake is warranted.

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APPENDIX 7 Reducing cadmium uptake by addition of ameliorants to soil – industrial waste materials

Introduction

Cadmium (Cd) accumulation in agricultural soils is a concern in many countries. The rate of soil contamination is usually slow compared to industrial contamination (usually <30 g ha^{-1} yr^{-1}) and cadmium concentrations in soil are usually not high varying from 0.1-1.0 mg kg^{-1} in agricultural soils not receiving sewage biosolid wastes, up to 3 mg kg^{-1} where sewage wastes are used. While these concentrations are not high by standards used to assess contaminated sites in urban areas, they are sufficiently high to cause concerns due to food chain contamination (McLaughlin *et al.*, 1996; Jinadasa *et al.*, 1997). Furthermore, due to the generally low land values in agricultural areas compared to urban and industrial land, remediation techniques must be low cost and integrated into crop production cycles. In Australia, soil salinisation has increased transfer of Cd through the food chain (McLaughlin *et al.*, 1994) so farmers are seeking remediation techniques to minimise Cd accumulation in crops.

Many urban and industrial wastes must be disposed of to landfill, wasting the value inherent in many of these materials. For example, ferrous and alumina smelter by products have many characteristics which could improve agricultural soil productivity. Light-textured soils can have their nutrient retention capacity improved by addition of iron, manganese or aluminium oxides. These materials also have the ability to bind toxic heavy metals into forms unavailable for plants and microorganisms.

This study investigated low-cost Cd remediation options for saline soils using urban and industrial by-products, particularly those from the ferrous- and alumina-smelting industries.

Materials and methods

A glasshouse experiment was performed using potatoes (*Solanum tuberosum* L.) as the test crop. A total of thirteen (13) soil amendments were chosen on the basis that they were inexpensive materials with the potential to significantly reduce availability of Cd to plants, principally through increasing the sorption capacity of the soil for Cd under conditions of high salinity. The materials were a mixture of by-products slags, dusts and muds from the ferrous- and alumina-smelting industries, a natural clay (palygorskite), sewage biosolids and sand-washing clays (Table 1).

The soil used was an Alfisol with sandy texture, having a neutral pH, a low cation exchange capacity (CEC), and a Cd concentration typical of horticultural soils in Australia (McLaughlin *et al.*, 1997).

The soil was air dried and 15 kg dry soil was sieved (<5 mm) into 300 mm diameter, free draining pots. Treatments were thoroughly mixed with the soil at rates equivalent to 5 and 25 t ha^{-1}. The soil was wetted up to -10kPa moisture potential and incubated for 4 weeks prior to planting. The soil was then removed from the pot and nitrogen (N, as ammonium nitrate), phosphorus (P, as superphosphate) and potassium (K, as potassium sulfate) were thoroughly mixed with the soil at rates equivalent to 100 kg N ha^{-1}, 75 kg P ha^{-1} and 150 kg K ha^{-1}. After basal fertilisation, approximately two thirds of the soil was replaced into the pot.

In each pot, one seed potato tuber (*Solanum tubersosum* cv. Atlantic) was planted to a depth of 2-3 cm, after which the pots were placed in a glasshouse. For each pot, the remaining soil was added when the plants were 20-25 cm tall to minimise the risk of tubers developing above the soil surface. Nitrogen and K were applied as side-dressings 2-3 times during the growth period to ensure these nutrients did not limit growth or yield responses. During growth, each plant was supported by a trellis and pots were watered according to plant demand.

Table 9. Chemical composition of soil and remediation materials used (BF=blast furnace, SWC=sand-washing clay).

	EC	pH_w	Total C	Total P	Oxalate	
					Al	Fe
	dS/m		%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Soil	0.5	6.79	1.25	398	400	3300
Lime	0.21	8.84	nd	1236	nd	nd
Fe fine slag	1.2	11.9	7.5	2085	2800	92400
Fe dust 1	14.4	11.78	8.5	913	1200	180700
Fe dust 2	12.76	12.55	0.71	680	400	267500
Fe slag medium	8.75	12.65	0.38	5671	3700	71800
Fe slag rough	3.3	12.54	0.58	4779	5900	74300
BF Fe dust	3.34	5.77	0.93	549	500	160100
BF Fe flue dust	7.66	7	17.8	358	1900	85300
BF Fe slag 1	1.02	11.3	0.14	104	19000	1900
BF Fe slag 2	6.23	12.4	1.07	3690	3000	46500
Palygorskite	0.23	9.06	0.41	62	900	400
SWC	0.74	8.52	0.24	164	1000	1500
Biosolids	7.89	7.2	22.3	18828	22300	8500
Al-red mud	4.95	11.62	1.04	481	7900	10500

nd = not determined.

After plant maturity and when haulms had senesced, the tubers were harvested and a soil sample was collected for chemical analysis. Plant tops were separated from roots, and shoot material was washed in deionised water prior to drying at 70°C and recording of dry weights. Tubers were also washed and weighed prior to chemical analysis.

Elemental concentrations in plant shoots and tubers were determined as outlined by McLaughlin *et al.* (1994).

Soil and amendment pH and electrical conductivity (EC) were determined in a water suspension of soil using a 1:5 soil:solution ratio (Rayment and Higginson 1992). Total carbon (C) was determined using a Leco™ furnace. Cation exchange capacity was determined using NH_4Cl leaching procedure (Method , Rayment and Higginson 1992). Phosphorus (P) was extracted from soils using the method of Colwell (1963) and concentrations of P in extracts were determined using the method of Murphy and Riley (1962). Iron (Fe) and aluminium (Al) were extracted from amendments using acidic ammonium oxalate to estimate the concentrations of amorphous oxide material (Tamm, 1943).

Total and extractable metal concentrations in soils and amendments were determined using the following methods:

1) Total metals - total Cd concentrations in soil were determined by boiling 2 g soil with 8 ml aqua regia (HNO_3:HCl, 3:1 ratio) at 110°C for 2 hours. The mixture was cooled, diluted to volume with 0.08 M HNO_3 and filtered through a 0.22 µm filter prior to spectroscopic analysis by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) or graphite furnace atomic absorption spectroscopy (GFAAS).

2) DTPA-extractable Cd, Cu and Zn - soils were extracted using DTPA (diethylenetriaminepentaacetate) according to the method of Lindsay and Norvell (1979).

Results and Discussion

The materials contained a range of heavy metals (Table 2).

Table 2. Concentrations of metals in the amendments.

	Al	Fe	Mn	Cd	Cu	Ni	Pb	Zn
	%	%	%	----------		mg kg^{-1}	----------	
Soil	0.9	1.0	0.06	0.1	6	3.8	<9	21
Lime	0.1	0.3	0.04	0.2	10	3.3	<9	25
Fe fine slag	0.7	31.2	1.64	0.0	30	9.9	<9	69
Fe dust 1	0.2	44.8	3.32	32.8	70	23.9	635	10104
Fe dust 2	0.1	58.6	1.00	1.3	64	20.1	101	1959
Fe slag medium	1.0	21.7	4.03	0.2	9	2.7	<9	43
Fe slag rough	1.6	19.3	4.00	0.1	11	2.5	<9	22
BF Fe dust	0.1	59.6	0.16	0.1	55	24.3	105	2225
BF Fe flue dust	0.5	41.9	0.10	1.0	38	8.9	638	5548
BF Fe slag 1	5.1	0.5	0.34	0.0	3	<2.2	15	25
BF Fe slag 2	1.0	15.8	2.74	0.1	9	5.9	<9	67
Palygorskite	4.8	2.3	0.05	0.0	16	31.6	14	18
SWC	9.3	3.2	0.01	0.0	16	21.4	37	30
Biosolids	4.3	1.7	0.02	9.8	1001	70.3	445	1816
Al-red mud	5.3	36.0	0.08	0.0	50	5.4	20	42

As expected, all the alumina and ferrous-smelting by products were very high in iron (Fe) with Fe concentrations up to 60% in the blast furnace dusts. Cadmium concentrations were low in all materials except Fe dust 1, which was a dust derived from air filtration units at a steel smelter, and in sewage biosolids. The biosolids were also very high in copper (Cu) compared to other materials (Table 2).

Plant growth was not significantly affected by the amendments (data not shown). Cadmium uptake was significantly reduced by some of the treatments, particularly Cu-enriched sewage biosolids, and alkaline (non-calcareous) clays (Figure 1).

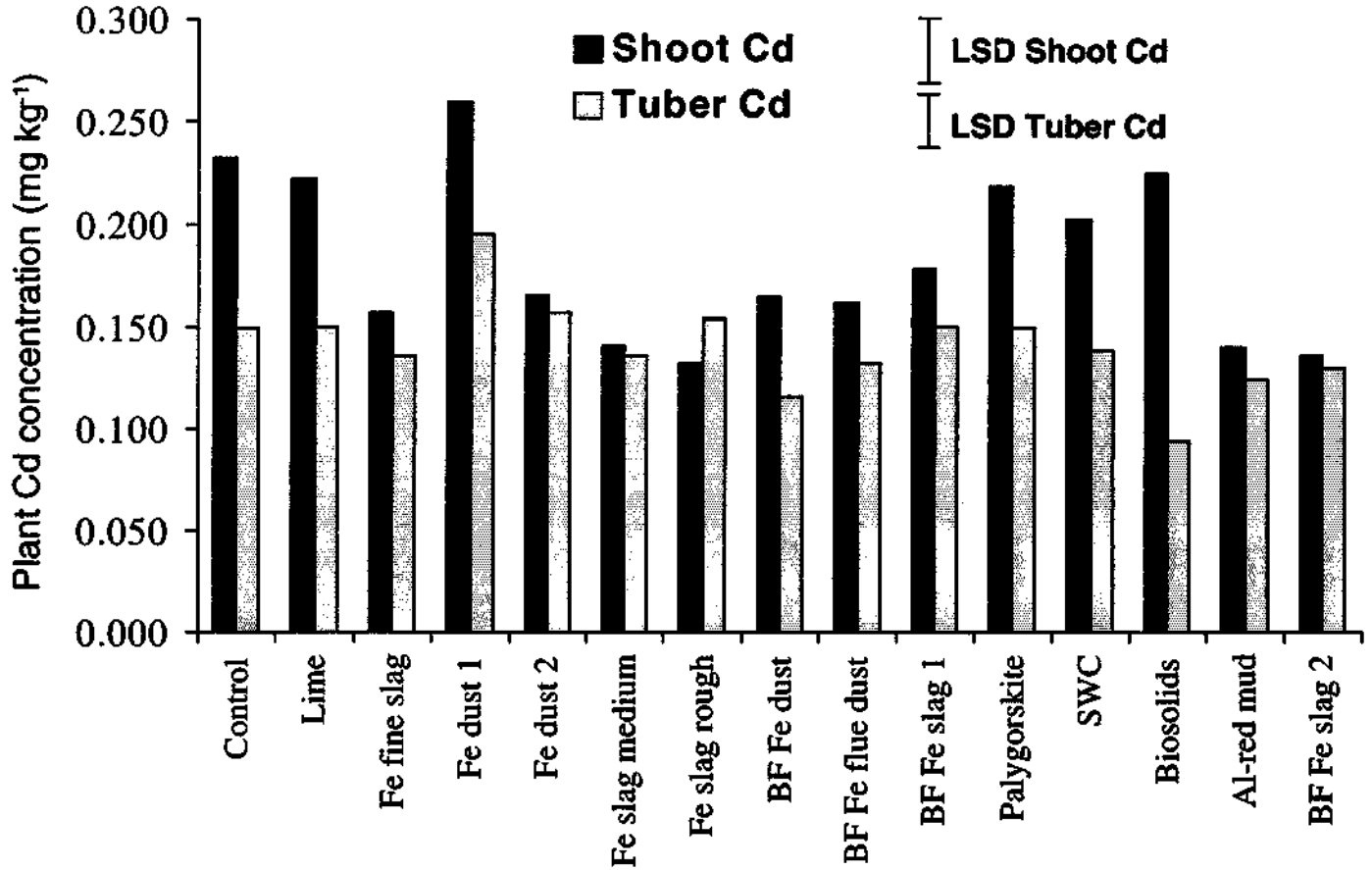

Figure 1. Effect of soil amendments on Cd concentration in potato shoots (dry weight basis) and tubers (fresh weight basis).

Cadmium concentrations in crops treated with Fe dust 1 was actually increased, probably due to the high Cd present in this material. While sewage biosolids had high Cd concentrations, Cd concentrations in crops treated with this material were actually *decreased.* This may have been due to increased retention of Cd by organic matter added in the biosolids, or could have been due to the high Cu present in this material. In recent experiments in our laboratory, Cu has been found to be antagonistic to Cd uptake by potatoes (Appendix 6).

Uptake of Cu, Mn, P and Zn into plant shoots and tubers was also significantly affected by the amendments (Table 3). Concentrations of DTPA-extractable Cd, Cu and Zn in soils are shown in Table 4. Plants growing on soils treated with sewage biosolids took up more Cu (and less Cd) than other plants (Table 3), in line with increased levels of DTPA-Cu and sodium bicarbonate-extractable P (Table 4).

Table 3. Concentrations of copper, manganese, phosphorus and zinc in potato shoots.

	Tuber				Shoot			
	--- mg kg^{-1} ---		%	mg kg^{-1}	--- mg kg^{-1} ---		%	mg kg^{-1}
	Cu	Mn	P	Zn	Cu	Mn	P	Zn
Control	6.6	7.6	0.41	26	5.5	70	0.36	51
Lime	5.9	8.1	0.34	22	5.1	43	0.23	22
Fe fine slag	5.1	8.0	0.32	21	3.8	55	0.19	20
Fe dust 1	9.4	14.8	0.35	33	6.3	186	0.24	103
Fe dust 2	6.6	7.0	0.36	27	4.8	29	0.24	44
Fe slag medium	7.2	10.5	0.37	16	5.7	72	0.27	16
Fe slag rough	5.8	9.6	0.33	13	4.9	75	0.25	15
BF Fe dust	6.5	8.8	0.39	30	5.0	81	0.26	83
BF Fe flue dust	9.4	9.4	0.42	36	5.9	95	0.29	126
BF Fe slag 1	6.3	7.4	0.36	25	5.1	31	0.27	38
BF Fe slag 2	5.2	8.1	0.34	14	4.9	57	0.23	17
Palygorskite	6.6	7.9	0.42	26	4.3	66	0.34	45
SWC	6.7	8.5	0.40	29	4.2	45	0.31	50
Biosolids	13.7	8.3	0.43	29	15.4	81	0.44	82
Al-red mud	7.0	8.1	0.36	25	5.3	28	0.23	33
LSD (P<0.05)	1.7	1.9	0.05	3	1.9	27	0.06	11

Concentrations of Cu in shoots were below levels found to be phytotoxic (Huett *et al.,* 1997). Manganese concentrations were high in plants treated with Fe dust 1 and the medium and coarse Fe slag materials, in line with the high total manganese concentrations in these materials (Table 2). All the smelter-derived materials significantly reduced uptake of P into plant shoots, probably due to increased retention of P by the oxides in these materials, and this was reflected to some extent in reduced concentrations of sodium bicarbonate-extractable P in soils at harvest. Biosolids enhanced P uptake and increased sodium bicarbonate-extractable P in soil. Growth was unaffected by these varying P

concentrations. Concentrations of Zn in shoots of plants treated with Fe dust 1, blast furnace dust (BF Fe dust) blast furnace flue dusts (BF Fe Flue dust) and biosolids were significantly increased over control values. Similar increases were noted in concentrations of DTPA-extractable Zn in these same treatments.

Table 4. Concentrations of DTPA-extractable Cd, Cu and Zn and $NaHCO_3$-extractable P (Bic-P) in soils at harvest.

	pH	DTPA			Bic-P
		Cd	Cu	Zn	
		mg kg^{-1}			
Control	5.9	0.09	1.00	2.3	121
Lime	7.7	0.03	0.76	1.5	129
Fe fine slag	7.4	0.05	0.71	1.5	115
Fe dust 1	6.4	0.34	0.89	36.6	106
Fe dust 2	4.5	0.08	0.81	2.7	111
Fe slag medium	8.1	0.05	0.67	1.3	171
Fe slag rough	8.0	0.05	0.71	1.3	166
BF Fe dust	6.0	0.07	0.96	6.3	108
BF Fe flue dust	6.2	0.09	0.93	22.7	118
BF Fe slag 1	7.0	0.06	0.76	1.5	119
BF Fe slag 2	7.9	0.04	0.72	1.6	154
Palygorskite	5.8	0.08	0.90	2.0	111
SWC	5.9	0.08	0.96	1.9	111
Biosolids	6.2	0.15	4.51	12.7	153
Al-red mud	6.7	0.06	0.84	1.7	103
LSD (P•0.05)	1.1	0.01	0.10	0.51	8

Conclusions

Smelter wastes are possible low-cost ameliorants for reducing Cd concentrations in agricultural crops on saline soils. In association with other agronomic strategies to manage Cd transfer through the food chain (McLaughlin *et al.*, 1996), re-use of these materials on soils presents a low cost disposal option for these industries. However, it appears the water-treatment residuals are more effective in reducing uptake of Cd by potatoes (Appendix 6) and therefore warrant further investigation under field conditions.

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APPENDIX 8 Reducing cadmium uptake by large additions of zinc to soil – glasshouse experimentation

Introduction

In earlier experiments under HRDC Project VG 006 "Effect of soil conditions and fertilizers on cadmium in vegetables - a national approach", field experiments had been carried out to determine the effect on tuber cadmium (Cd) concentrations of additions of zinc sulfate ($ZnSO_4.7H_2O$) to soils. In these experiments, Zn was added to soil by banding at planting (McLaughlin et al., 1995) with reductions found in tuber Cd concentrations of the order of 10-15%. Zinc is known to act antagonistically in relation to Cd uptake by plants (Abdel-Sabour et al., 1988; Honma and Hirata, 1978) and if Zn acts at the root surface to reduce Cd uptake, then banding of Zn fertilizer may be less efficient than broadcast and incorporated Zn. The aim of this experiment therefore, was to determine if additions of high rates of Zn, incorporated into the soil at planting, could significantly reduce Cd uptake by potatoes.

Materials and Methods

A glasshouse experiment was conducted at the SARDI Plant Research Centre during January – May 1996. The experimental design was factorial with 3 replications. Treatments were 4 Zn rates (0 – 250 kg ha^{-1} equivalent), 4 soils and 2 water qualities (mains water and water containing 1200 mg Cl L^{-1}). The cultivar grown was Pontiac.

The experimental procedure was as follows:

I. Four soils were used in the experiment – Mt Compass, Upper South East, Riverland and Victoria (Table 1). The soil was air dried and sieved to <5 mm before use. To characterise the soil, a sub-sample was collected for chemical and physical analysis. For each experiment 300 mm diameter, free draining pots and 15 kg of air dry soil were used.

II. The soil from each pot was spread on a plastic sheet to <10-15 mm in depth. Basal N, P, K fertilisers, supplying equivalent to 150 kg N ha^{-1} (as ammonium nitrate), 100 kg P ha^{-1} (as single superphosphate) and 150 kg K ha^{-1} (as potassium sulfate), were broadcast evenly over the soil and then thoroughly mixed into the soil. Zinc sulfate ($ZnSO_4.7H_2O$) was then broadcast evenly over the soil and then thoroughly mixed into the soil. Rates of application were 0, 50, 100 and 250 kg ha^{-1} equivalent. Approximately two thirds of the soil was replaced into the pot.

III. Immediately prior to planting, a subsample of soil was collected from each pot for chemical and physical analysis (Table 1).

IV. Tuber seed pieces of the cv. Pontiac (one per pot) were planted on the 22nd January 1996 and covered with 2-3 cm of soil, after which the pots were placed in a glasshouse. To minimize the risk of tubers developing above the soil surface, the remaining soil was added to pots when the plants were 25-30 cm tall.

Table 1. Soil chemical and physical characterics.

Soil		Mt.Compass	Upper SE	Riverland	Victoria
EC[a]	dS/m	0.02	0.23	0.02	0.08
pH_w[a]		5.2	5.9	7.0	5.6
pH_{Ca}[b]		4.4	5.4	6.3	5
Cl[a]	mg kg^{-1}	6	59	10	13
Total C[c]	%	0.4	2.4	0.4	3.4
Org.C.	%	0.4	2.4	0.4	3.4
Exchangeable cations and cation exchange capacity ($cmol^+$ kg^{-1})					
Ca		0.92	4.74	2.54	9.46
Mg		0.19	1.55	0.59	1.48
Na		0.10	0.52	0.14	0.16
K		0.05	0.50	0.22	1.29
Total		1.3	7.3	3.5	12.4
CEC[d]		1.8	6.5	3.1	15.9
Particle size analysis					
Clay	%	2	7	4	26
Silt	%	0	1	0	31
F. Sand	%	21	78	36	26
C. Sand	%	77	11	60	13
EDTA-Cd[e]	mg kg^{-1}	<0.01	0.02	<0.01	0.13
EDTA-Zn[e]	mg kg^{-1}	0.58	2.92	0.54	15.86

[a] 1:5 soil:water ratio.
[b] 1:5 soil:0.01M $CaCl_2$ ratio.
[c] LECO combustion method (Rayment and Higginson, 1992).
[d] 1M NH_4Cl, pH 7.0, pretreatment for soluble salts (Rayment and Higginson, 1992).
[e] Clayton and Tiller method (1975).

V. The plants were watered as required, with mains water ("fresh") or with the equivalent volume of NaCl solution (33.8mM) every other watering ("saline"). Plants were sidedressed with potassium nitrate, magnesium sulfatre and calcium nitrate at 18, 31, 38, 51, 53 and 60 days after planting. The side-dressings were applied to ensure these nutrients did not limit growth or tuber yield. During growth, each plant was supported by a trellis.

VI. Plants were harvested 107 days after planting. The plants were separated into tubers, stems and leaves. Tubers were brushed free of soil and washed in tap water and de-ionised water. Each plant part was rinsed in 0.1% Decon, deionised reverse osmosis water and blotted dry. Fresh and dry weights were determined prior to chemical analysis.

Chemical analysis of plant materials

Cadmium. Sub-samples (0.1 g) of the dried ground plant materials were digested with concentrated nitric acid until the digest mixture was clear. The digest solution was diluted to 10 ml using 0.016M nitric acid. All samples were digested in duplicate with blanks and internal reference materials in each batch. Cadmium concentrations in the digest solutions were determined using an atomic absorption spectrophotometer with graphite furnace atomisation and deuterium background correction. Orthophosphoric acid was used as a modifier.

Other elements. Concentrations of P, K, Ca, Mg, Na. S, B, Cu, Zn, Mn and Fe in the digest solutions were determined using Inductively-Coupled Plasma Atomic Emission Spectroscopy.

Results and Discussion

Tuber and plant shoot yield

There were significant differences between soils, Zn and water treatments in terms of tuber fresh weight and leaf+stem dry weight. For tuber fresh weight yield, there were significant interactions between soil×Zn, Zn×water and soil×water treatments. Two-way tables of treatment means are shown in Tables 2-4.

Table 2. Fresh weight of tubers (g pot^{-1}) in relation to soil type and Zn treament.

Soil	Rate of Zn addition (kg ha^{-1} equivalent)			
	0	50	100	250
Mt. Compass	748	639	444	140
Upper SE	722	548	679	172
Riverland	352	312	501	385
Victoria	1007	1013	818	779
		LSD = 369		

As can be seen in Table 2, high rates of Zn addition (250 kg ha^{-1} equivalent) significantly reduced tuber yields in the Mt. Compass and Upper SE soils, mainly due to the poor buffering capacity of these soils for Zn and the resultant high concentrations of Zn in the plants (Zn toxicity - see below). Saline irrigation water significantly reduced yields in the Upper Se and Riverland soils, but had no effect on the other soils (Table 3). The adverse effect of salinity was evident only at the lower rates of Zn addition (100 kg ha^{-1} equivalent and less) i.e. Zn toxicity was not exacerbated by saline irrigation water (Table 4).

Irrigation water salinity had the reverse effect on leaf+stem weights compared to tuber weights, with total stem weights in fresh treatments being 28.8 g pot^{-1}, and in saline treatments was 32.2 g pot^{-1}. Leaf+stem weights were generally unaffect by Zn treatments, except in the Mt. Compass soil where weights decreased from 26.8 g pot^{-1} in the control (0 Zn) to 5.1 g pot^{-1} at 250 kg Zn ha^{-1} equivalent.

Table 3. Fresh weight of tubers (g pot^{-1}) in relation to soil type and water treament.

Soil	Water treatment	
	Saline	Fresh
Mt. Compass	441	544
Upper SE	290	771
Riverland	179	595
Victoria	905	904
	LSD = 185	

Table 4. Fresh weight of tubers (g pot^{-1}) in relation to Zn treatment and water treament.

Zn treatment	Water treatment	
(kg ha^{-1} equiv.)	Saline	Fresh
0	546	868
50	416	840
100	496	725
250	357	380
	LSD = 185	

Tuber cadmium and nutrient composition

Tuber Cd concentrations were increased by saline irrigation water treatments (Figure 1), and the effect was consistent across soils, as found previously (McLaughlin et al., 1994). Tuber Cd concentrations were highest in the Upper SE soil and were similar to Cd concentrations found in tubers grown under field conditions in this soil type. The Riverland soil produced tubers with the lowest Cd concentrations, and again tuber Cd concentrations were in line with field experience on this soil type.

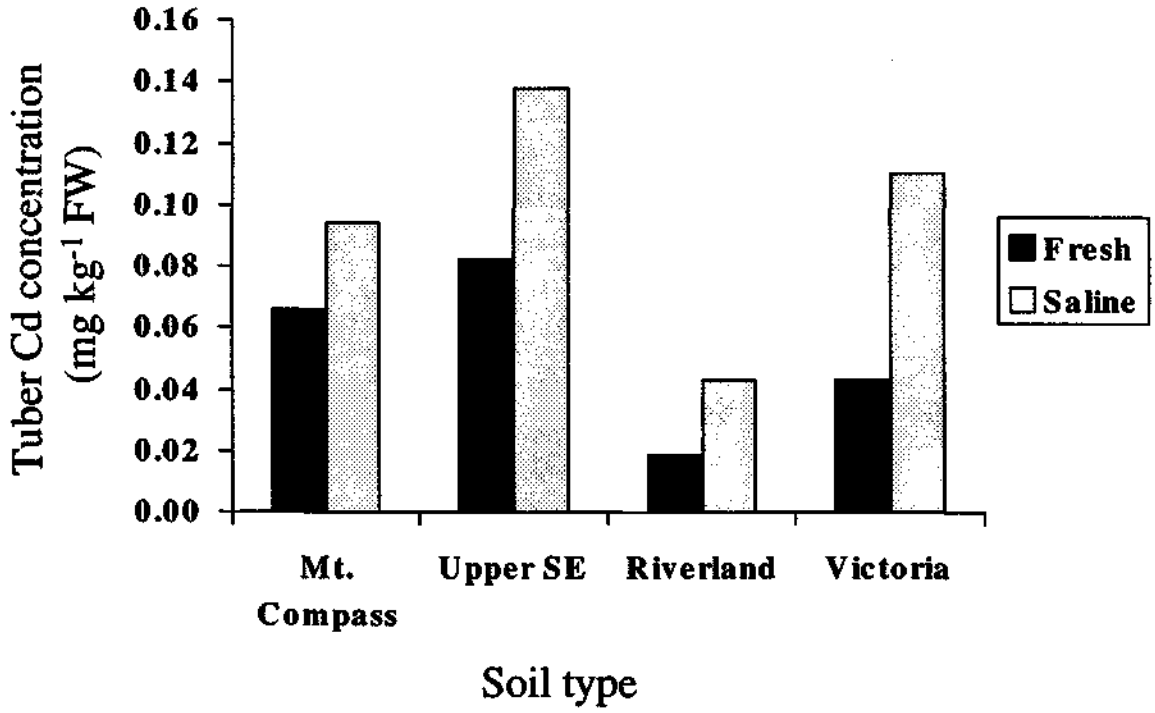

Figure 1. Effect of irrigation water salinity on tuber Cd concentrations (FW = fresh weight).

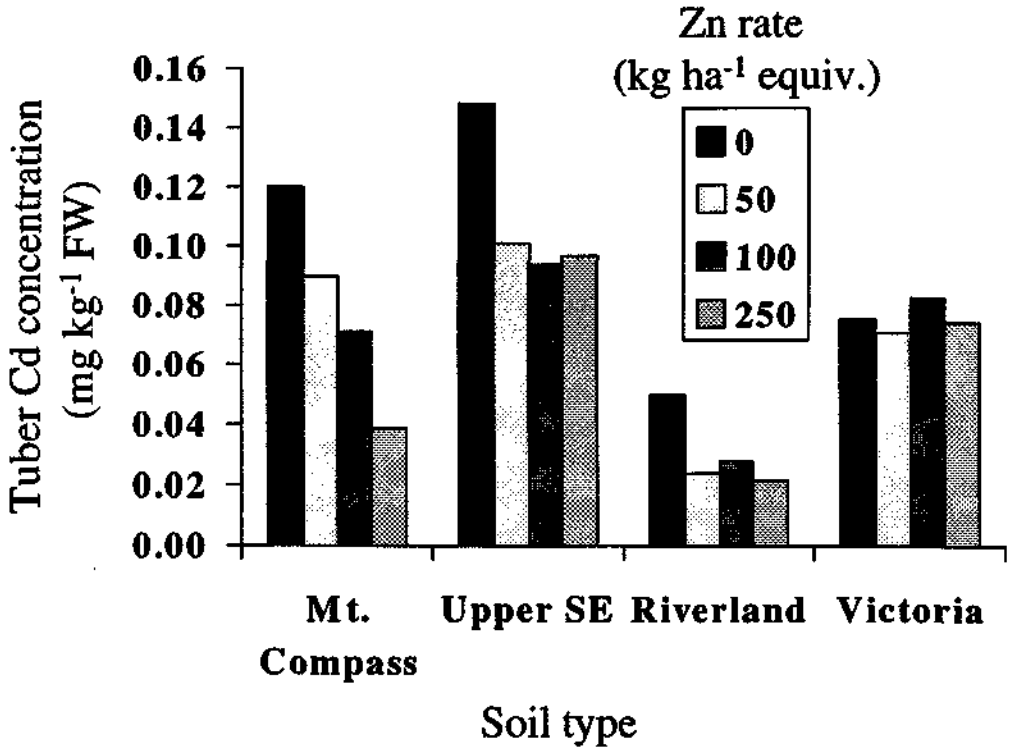

Figure 2. Effect of soil type and Zn treatments on tuber Cd concentrations (FW = fresh weight).

Tuber Cd concentrations were significantly decreased by addition of Zn, although the largest reductions in Cd concentration were accompanied by significant reductions in tuber yield on Mt. Compass and Upper SE soils, indicating Zn toxicity.

Zinc concentrations in leaves confirmed that Zn concentrations were toxic in these soils (Figure 3). Critical leaf Zn concentrations have not been developed for potatoes, but the upper value in the range for concentrations regarded as adequate is approximately 100 mg Zn kg^{-1} DW. In plants related to potatoes (tomatoes) where toxic values of Zn have been reported, critical values for toxicity have been reported as 250-500 mg Zn kg^{-1} DW (Huett et al., 1997). At the highest Zn rate, concentrations of Zn in leaves of plants growing on the Mt. Compass, Upper SE and Riverland soils easily exceeded these critical values. Plants growing on the Victorian soil had lowest Zn concentrations in leaves, likely due to the high clay content of this soil reducing Zn concentrations in soil solution. This soil also had high concentrations of EDTA-extractable Zn prior to any Zn additions. This may be the reason for the lack of any effect of Zn in reducing tuber Cd concentrations on this soil.

Conclusions

There is thus a potential danger in applying high rates of Zn to soil to attempt reductions in tuber Cd concentrations, and the rate of Zn addition must be chosen carefully to avoid phytotoxic symptoms appearing. Zinc on its own did not provide the large reductions in tuber Cd required, but Zn should certainly form part of a soil amendment program for Cd management.

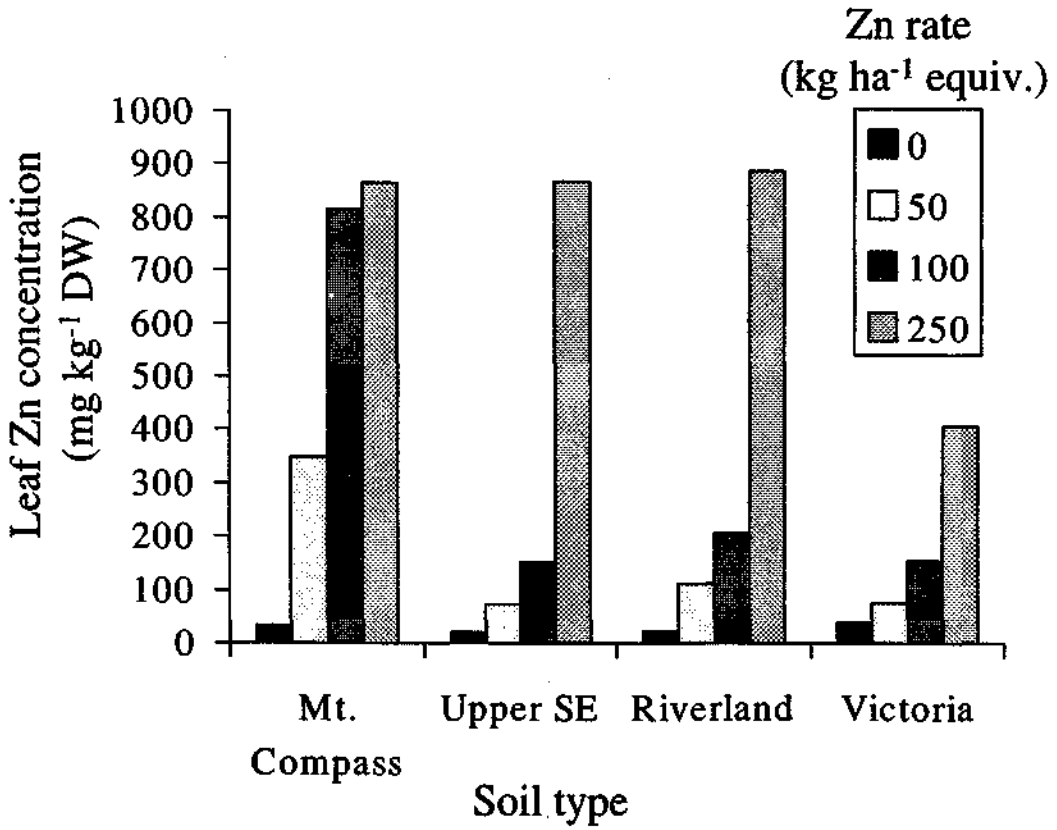

Figure 3. Effect of soil type and Zn treatments on leaf Zn concentrations (DW = dry weight).

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APPENDIX 9 Reducing cadmium uptake by addition of ameliorants to soil – field experimentation

Introduction

Several promising ameliorants to reduce potato tuber Cd concentrations have been identified in glasshouse experiments, detailed in Appendices 6, 7 and 8. This study was designed to field trial some of the more promising ameliorants and ameliorant combinations under field conditions, to determine if significant reductions in tuber Cd concentrations could be realistically achieved.

Materials and Methods

Three field trials were established, two in the Upper South East and one in the Adelaide Hills. Soil characteristics are shown in Table 1.

Table 1. Soil chemical and physical characterics.

Soil		Adelaide Hills	Upper SE 1	Upper SE 2
EC[a]	dS/m	0.17	0.08	0.14
pH_w[a]		5.6	6.2	5.4
Cl[a]	mg kg^{-1}	29	16	75
Total C[b]	%	1.4	1.2	0.8
Exchangeable cations and cation exchange capacity ($cmol^+ kg^{-1}$)				
Ca		3.4	2.4	2.4
Mg		0.8	1.1	0.8
Na		0.2	0.1	0.1
K		0.2	0.4	0.4
Total		4.6	4.1	3.8
CEC[c]		5.5	4.6	4.8
		Particle size analysis		
Clay	%	7	5	5
Silt	%	10	<1	4
F. Sand	%	68	81	81
C. Sand	%	11	11	7

[a] 1:5 soil:water ratio.
[b] LECO combustion method (Rayment and Higginson, 1992).
[c] 1M NH_4Cl, pH 7.0, pretreatment for soluble salts (Rayment and Higginson, 1992).

Trial design was a randomised block with twelve treatments and four replicates. Treatments were a series of "best bet" options for reducing tuber Cd concentrations;

Control
Copper sulfate at 3 rates – 10, 25 and 50 kg ha^{-1} equivalent
Zinc sulfate – 25 kg ha^{-1} equivalent
Copper/zinc – combination of 25 kg Cu ha^{-1} and 25 kg Zn ha^{-1} equivalent

Lime – 15 t ha^{-1} equivalent
Natural clay - 25 t ha^{-1} equivalent
Ferrous smelter dust (FSD) - 25 t ha^{-1} equivalent
Magnesite ($MgCO_3$) - 15 t ha^{-1} equivalent
Magnesite+Zn – as above plus 25 kg ha^{-1} equivalent
Water treatment residuals (WTR) + Zn - 25 t ha^{-1} equivalent and 25 kg Zn ha^{-1} equivalent

Magnesite was introduced as two of the treatments with the hypothesis being that the absence of any effect of liming in past trials (Maier et al., 1997) was due to effects of Ca in the liming materials. Magnesite is a low cost liming material which is low in Ca, and we hypothesised that this material could be a useful ameliorant.

Plot dimensions were 4 m by 4 m with 1 m buffer strips between plots. Amendments were spead by hand and rotary hoed to 15cm to thoroughly incorporate the materials in the soil. The plots were permanently marked by placing a Scothmark™ Ball Marker (which contains an electronic transponder) at 100 cm depth in the corner of the plots. This depth was assessed as being sufficient to prevent disturbance of the transponder by cultivation practices. Further details of experiments are given in Table 2.

Table 2. Experimental details.

Site	Date amendments incorporated	Planting date	Leaf sampling date	Harvest date	Variety
Adelaide Hills	5/11/97	20/11/97	19/1/98	23/2/98	Atlantic
Upper SE 1	13/11/97	4/12/97	29/1/98	25/3/98	Kennebec
Upper SE 2	3/12/97	20/12/97	19/2/98	22/4/98	Crystal

Trial sites were planted by the grower and crop and irrigation water management were identical to the commercial crops. Approximately 60 days after planting, leaf samples were taken from all plots by sampling the 5th leaf (from the apex) of 20 plants from each plot. The whole leaf was used for analysis.

At crop maturity sampling points were located at each site using a EMS II Marker Locator™ tuned to the frequency of the buried transponder. Potato crops were sampled by hand digging tubers from an area 2 m by 3 rows. Ten tubers in the size range 80-450 g were collected, with any severely diseased or damaged tubers discarded. Tubers were brushed free of soil and transported to the laboratory for analysis.

The tubers were rinsed free of soil in tap water, then gently scrubbed in reverse osmosis water using a nylon brush to remove all adhereing soil. Tubers were then rinsed a second time in clean tap water and finally in Cd-free distilled water. Tuber blemishes and eyes were removed and a 1 cm thick slice from the stem end to the bud end was taken from each tuber using a stainless steel knife. Tuber skin was carefully removed from each tuber slice, ensuring as little flesh as possible was removed with the skin. The slices were again rinsed in distilled water, blotted dry and diced into 1 cm cubes on a polypropylene chopping board. The tuber material was weighed, dried at 70°C for 48 h and reweighed. Dried tuber material was ground(<500μm) using a stainless steel mill.

A subsample of the ground dried material (0.5 g) was digested by boiling under convection heating with 5 mL concentrated HNO_3 acid and Cd concentration in the solution was determined by GFAAS (McLaughlin *et al.* 1997). Analysis of reference NIES (medium Cd) rice flour by the above method gave a Cd concentration of 0.323 ± 0.036 mg kg^{-1}, compared to the certified value of 0.32 ± 0.02 mg kg^{-1}. All tuber Cd concentrations are expressed on a fresh weight basis (FW). Concentrations of B, Ca, Cu, Fe, K, Mg, Mn, S and Zn in the digest solutions were determined using Inductively-Coupled Plasma Atomic Emission Spectroscopy and are expressed on a dry-weight basis (DW).

Results and Discussion

Tuber yields were significantly different ($P<0.001$) between sites, with Upper SE 1 having significantly lower tuber yields (21.4 t ha^{-1} equivalent) compared to the other two sites (33.4 and 32.8 t ha^{-1} equivalent). Soil amendments had no significant effect on tuber yields ($P>0.05$), nor was there any significant effect on tuber size distribution.

Both site and amendment treatments significantly affected tuber Cd concentrations, with no interaction between these terms (log transformed data). Site and treatment mean data are therefore presented below by averaging across treatments (for site means) and across sites (for treatment averages – see Figure 1). Tuber Cd values were significantly different between the sites, with the Adelaide Hills site having a mean tuber Cd (across all treatments) of 0.040 mg kg^{-1} FW, and the two sites in the Upper South East having mean tuber Cd values of 0.117 and 0.131 mg kg^{-1} FW. Many of the amendments reduced Cd concentrations compared to control values, while tuber Cd concentrations tended to be higher after liming, confirming previous findings (Maier et al., 1997).

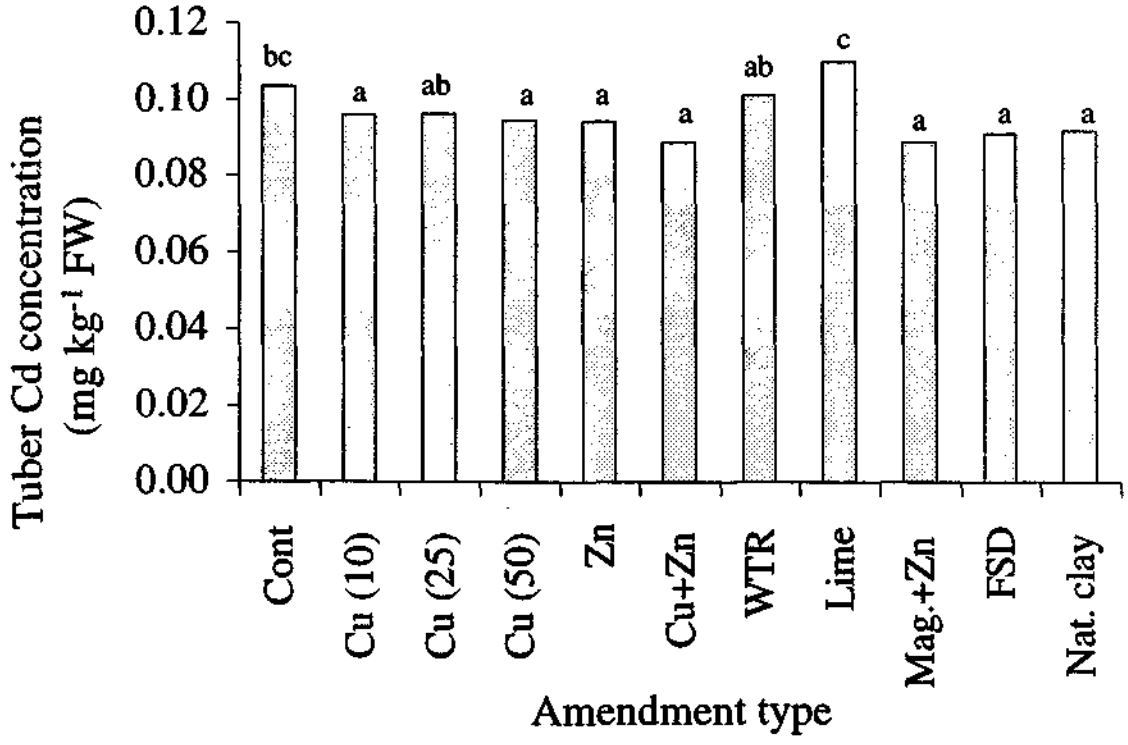

Figure 1. Effect of soil amendments on tuber Cd concentrations at 3 sites in South Australia. Means are averaged across sites and those columns with the same letter above are not significantly different ($P<0.05$).

Disappointingly, while reductions in tuber Cd concentration due to soil amelioration were statistically significant, the magnitude of the changes were not large enough to prove agronomically useful. For example, at Upper SE 2, tuber Cd concentrations were decreased from 0.140 mg kg^{-1} FW in control plots to 0.114 in Cu/Zn-treated plots, not enough to produce tubers meeting the MPC.

Similarly, the WTR material, which had proved successful in glasshouse trials in reducing tuber concentrations (by up to 80%), performed poorly under field conditions.

Treatments incorporating Cu also increased Cu concentrations in tubers ($P<0.001$), from around 3-6 mg kg^{-1} DW in control plots to 6-10 mg kg^{-1} DW in plots receiving 25 kg ha^{-1} equivalent or higher (Table 3). This increase is not considered to be of concern as Cu levels are well within those regarded normal.

Table 3. Concentrations of Cu in tubers (mg kg^{-1} DW).

Treatment	Adelaide Hills	Upper SE 1	Upper SE 2
Control	4.4	5.9	3.7
Cu (10)	5.9	7.9	5.0
Cu (25)	6.1	8.0	5.5
Cu (50)	5.8	9.9	5.8
Zn	4.9	5.1	4.2
Cu/Zn	6.4	9.1	5.2
WTR	5.5	6.9	4.5
Lime	4.5	4.4	3.9
Mag.+Zn	8.5	4.7	4.1
FSD	4.5	5.5	3.9
Nat. Clay	4.9	6.6	5.0
LSD ($P<0.05$)	---------- 2.0 ----------		

Similarly, treatments incorporating Zn increased tuber Zn concentrations from 16-27 mg kg^{-1} DW in control plots to 22-44 mg kg^{-1} DW in plots receiving 25 kg Zn ha^{-1} equivalent or higher (Table 4). Again, these increases are not considered problematic.

Conclusions

From the filed validation trials, it would appear that several treatments (Cu, Zn, FSD and natural clay) have the potential to reduce tuber Cd concentrations under commercial conditions. Reductions will only be of the order of 10-15%, insufficient in some saline areas to produce tubers meeting the MPC, but another management tool to assist growers to reduce Cd accumulation in tubers.

Table 4. Concentrations of Zn in tubers (mg kg^{-1} DW).

Treatment	Adelaide Hills	Upper SE 1	Upper SE 2
Control	16.3	27.6	26.5
Cu (10)	18.5	29.2	25.4
Cu (25)	16.7	35.6	24.6
Cu (50)	16.8	29.7	25.7
Zn	22.5	43.9	30.3
Cu/Zn	28.8	36.8	28.0
WTR	19.6	33.2	30.1
Lime	15.4	26.7	25.1
Mag.+Zn	17.7	28.3	28.0
FSD	18.1	36.8	26.9
Nat. Clay	25.1	36.8	31.8
LSD (P<0.05)	----------	5.6	----------

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APPENDIX 10 Physical properties of field soils treated with Cd-reducing ameliorants

Introduction

Some of the ameliorants used to reduce Cd concentrations described in Appendix 9 (particularly residuals from water-clarification, WTR+Zn), have been shown in other studies to improve soil physical fertility when applied to sandy soils in the field (*eg.* Skene *et al.* 1995). This study was designed in conjunction with the field trials outlined in Appendix 9 (following glasshouse trials described in Appendices 6, 7 and 8) to determine whether the various Cd-reducing ameliorants also improved soil physical properties such as available water, aeration, and soil resistance to penetration.

Materials and Methods

Appendix 9 outlines the details of the field trials established in the Adelaide Hills and the upper Southeast of South Australia.

Undisturbed soil cores were collected in cylindrical rings (5cm high x 4.8cm inside diameter) from the top 10 cm, 60 days after planting. These were packed in plastic bags and returned to the laboratory for placement in pressure chambers on porous ceramic plates to measure:

- water retention (to determine whether available water was influenced by the treatments)
- aeration (air-filled porosity)
- soil resistance to penetration (limitations to root growth due to high strength).

To determine if any changes occurred in the soil during plant growth and irrigation, repeat analyses were performed at harvest time for the Adelaide Hills site.

Results and Discussion

All soils had relatively low bulk densities (< 1.3 g cm^{-3}) with porosities exceeding 0.50 (*ie.* > 50%). This means there is plenty of pore space for root growth and development, though it says nothing about the size of the pores and how much water is held in them for plants. The available water content was critically low (< 0.15 or 15%) in two of the soils 60 days after planting (Table 1), but this did not appear to be influenced significantly by any of the amendments.

Most of the water in the soil at all three field sites was held in macropores (as seen by the large drop in volumetric water content (VWC) between saturation and field capacity, corresponding to suctions 0.1 kPa and 10 kPa respecitively (Figure 1). This is typical of many sandy soils - most water applied to the soil by irrigation drains freely through the surface soil and is largely unavailable to plants. The water retention of the soil at the three sites was not influenced significantly by any of the amendments, so there appears to be no danger they will reduce availability of irrigation water when added to the soil.

Table 1. Bulk density (g cm^{-3}) and plant available water.

	Adel. Hills 60d	**Adel. Hills Hvst**	**Upper SE 1 60d**	**Upper SE 2 60d**
Mean Bulk Density	1.18±0.014	1.19±0.043	1.30±0.018	1.17±0.015
Field Treatments:	Plant Available Water ($VWC_{10kPa-1500kPa}$)			
Control	0.107	0.177	0.078	0.159
WTR	0.123	0.175	0.069	0.144
Mag+Zn	0.085	0.159	0.079	0.177
FSD	0.074	0.173	0.080	0.175
Nat.clay+Zn	0.066	0.179	0.069	0.173
Mean Available Water	0.091±0.023	0.172±0.008	0.075±0.005	0.165±0.014

Soil aeration between field capacity and wilting point at all three sites exceeded the minimum value of 0.10 (*ie.* 10% air-filled pores) required for plant growth (Figure 2). In fact, all soils and all treatments had air-filled porosities > 0.20, which means so long as subsoil drainage is sufficient (so the surface soil reaches field capacity within 48 h after irrigation), no root limitations exist due to anaerobic conditions. The amendments seemed to have no significant impact (positive or negative) on aeration.

Despite the low bulk densities (*ie.* high porosities) and good aeration status (largely due to the sandy texture) soil strength appeared to reach limiting-values (1000 kPa) well within the water content range for irrigation at two of the three sites. This was particularly the case with the soil in the Adelaide Hills at harvest time (Figure 3). Variability in the measurements of soil resistance was large, so that treatment effects were not significant - nevertheless, it can safely be said that none of the amendments caused any significant increase in soil resistance to root growth across the water content range of practical interest in this context.

From analysis of the Adelaide Hills site at 60 days after planting and at harvest, there were no effects of measurement time on any of the above parameters.

Conclusions

Laboratory measurements on soil samples taken from the three field sites where Cd-reducing amendments were trialed indicate that soil physical properties were not altered significantly by any of the amendments at the rates applied (*ie.* < 50 t/ha). This indicates that where positive reductions in Cd-uptake can be achieved by an amendment, its application will not cause significant problems with compaction, strength, aeration and available water. On the contrary, if application rates greater than those trialed here were to be used, it is likely that improvements to physical properties would be experienced, particularly in relation to water-holding capacity.

It is not possible from this work to suggest application rates that might improve physical properties, but the important issue is that within the boundaries of the likely application rates, these properties will not be impacted upon adversely.

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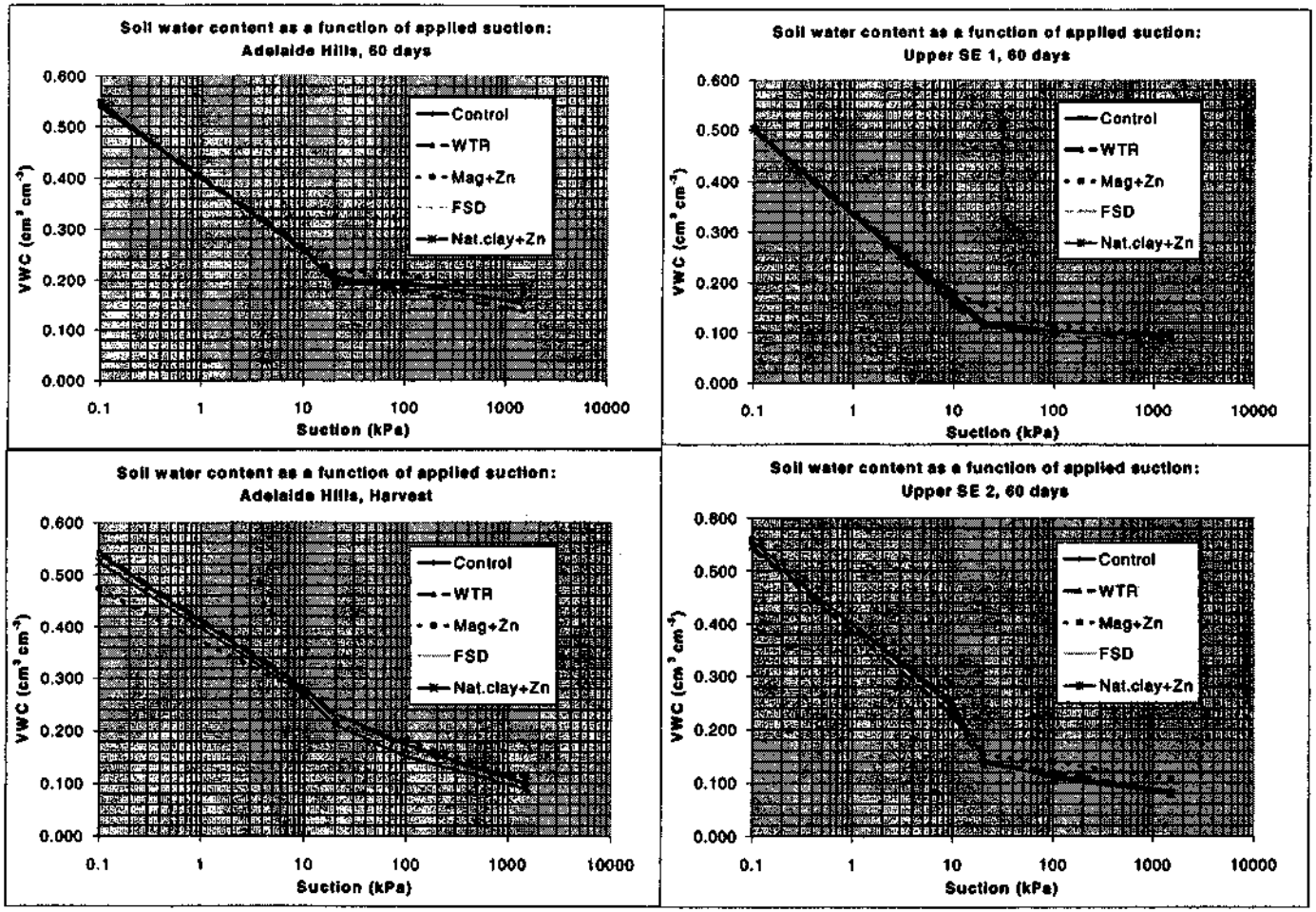


Figure 1. Water retention curves for the 3 sites. The Adelaide Hills site was also checked at crop harvest (see text).

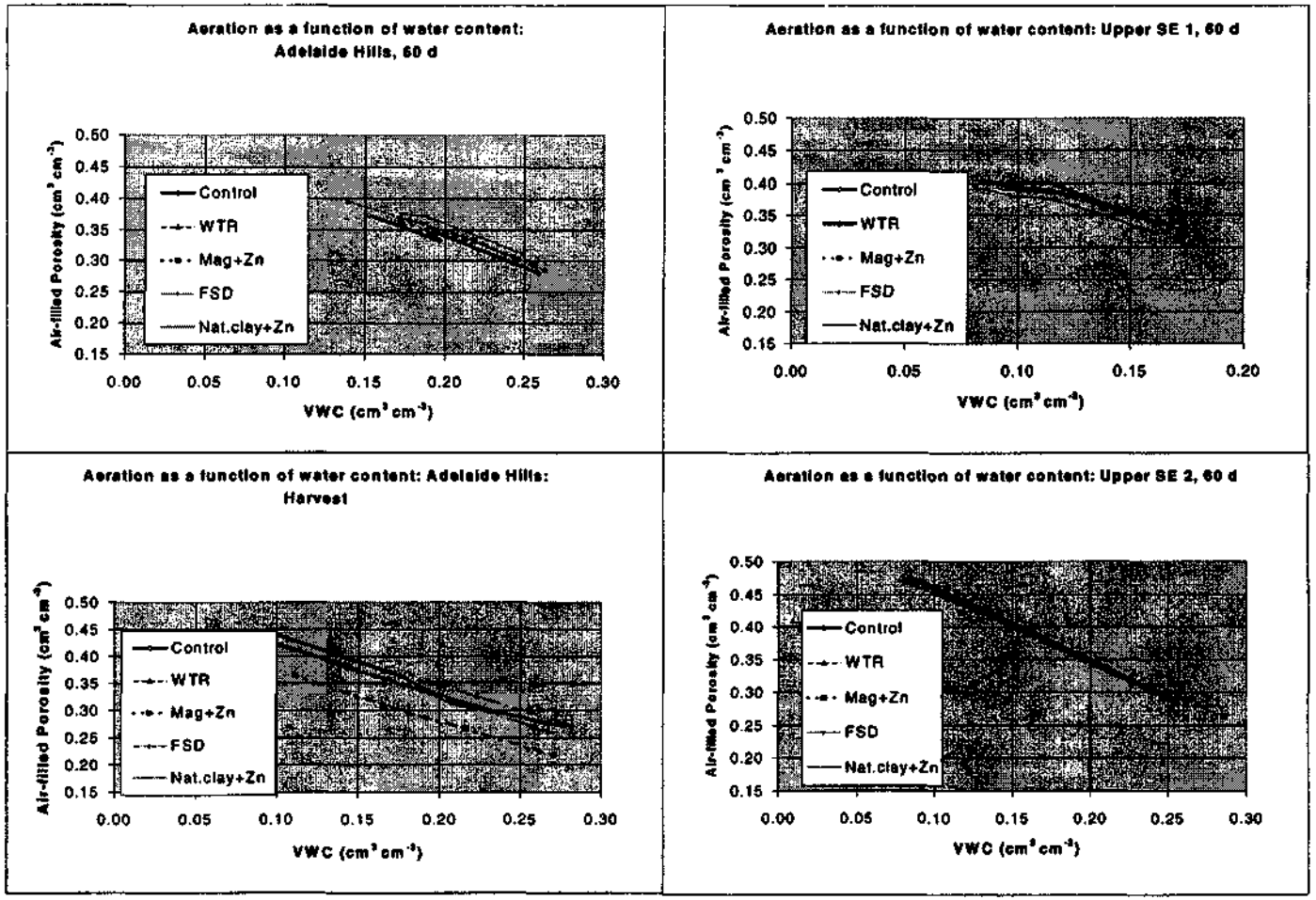


Figure 2. Aeration status curves for the 3 sites. The Adelaide Hills site was also checked at crop harvest (see text).

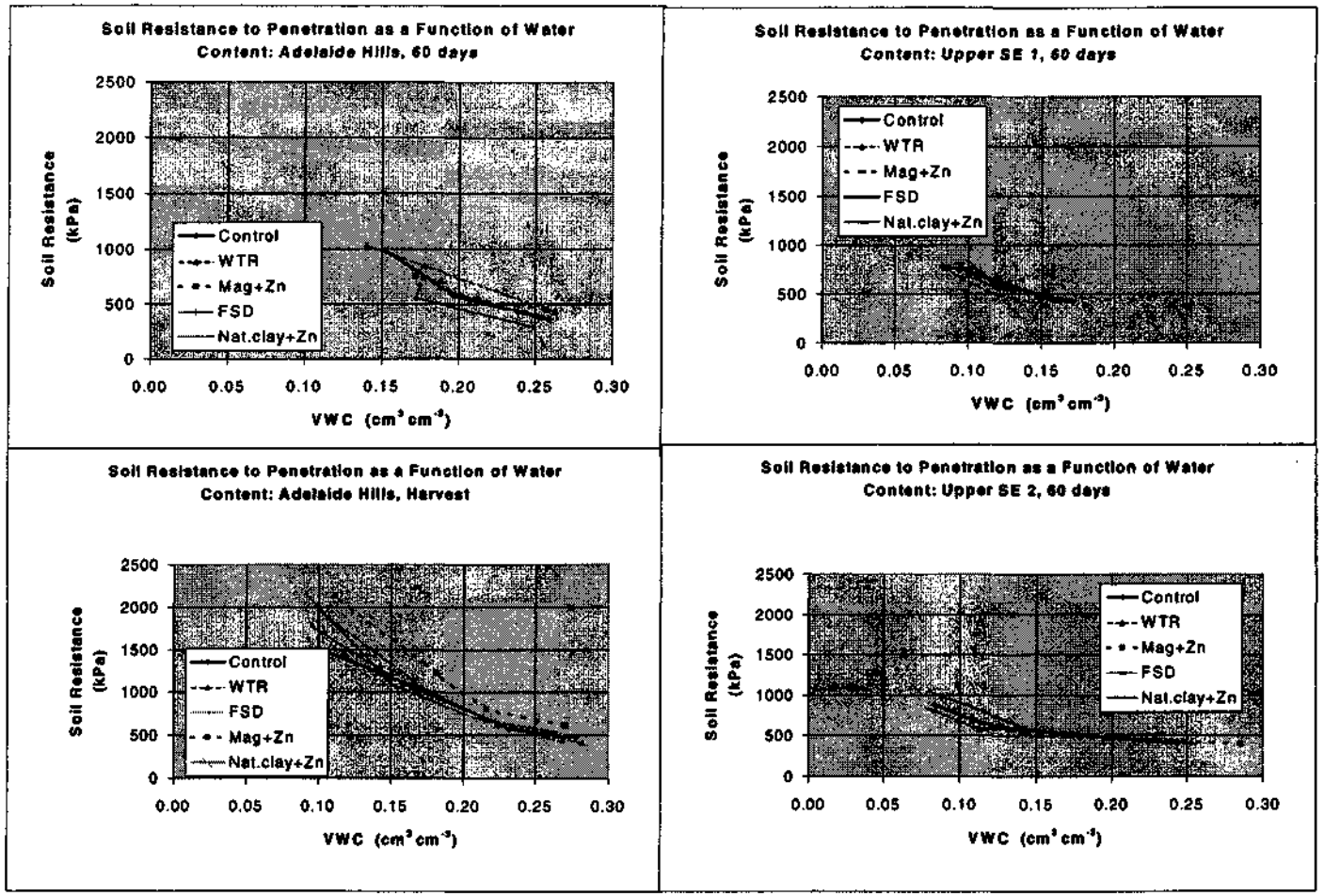


Figure 3. Soil resistance curves for the 3 sites. The Adelaide Hills site was also checked at crop harvest (see text).

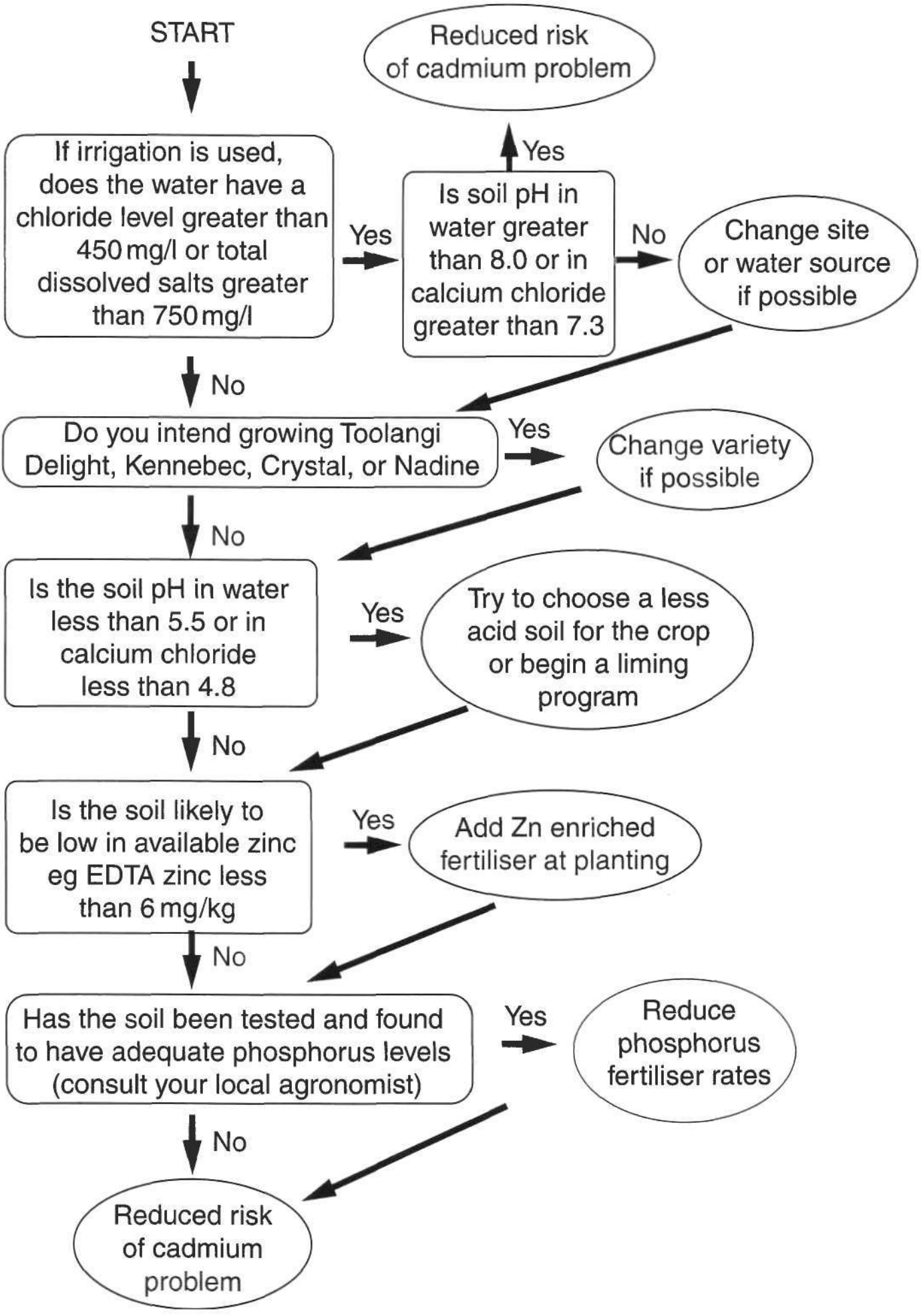
APPENDIX 11 Grower brochures 1 – Managing cadmium in potatoes for quality produce

Managing cadmium in potatoes for quality produce

Consumer demand for quality products is increasing. Concern about the presence of chemical impurities has resulted in monitoring and research into food quality in Australia. Cadmium has been indentified as being of potential concern.

Compiled by Cooperative Research Centre for Soil & Land Management and CSIRO Division of Soils
ISBN 1 876162 12 0 - 6/96CRCSLM

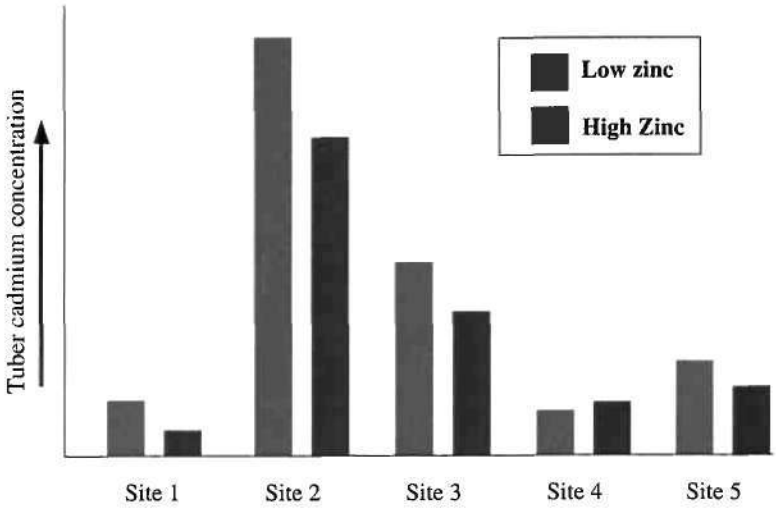
Grower checks if tuber cadmium levels are high



Management practices to minimise cadmium levels

Selection of nitrogen and potassium fertilisers to minimise cadmium uptake

Glasshouse and field experiments have shown that changing nitrogen fertiliser has little impact on tuber cadmium concentrations. Changing from potassium chloride to potassium sulphate has decreased tuber cadmium by up to 30% in areas where chloride in soil and irrigation water is low. However potassium sulphate costs more.



Effect of zinc on tuber cadmium

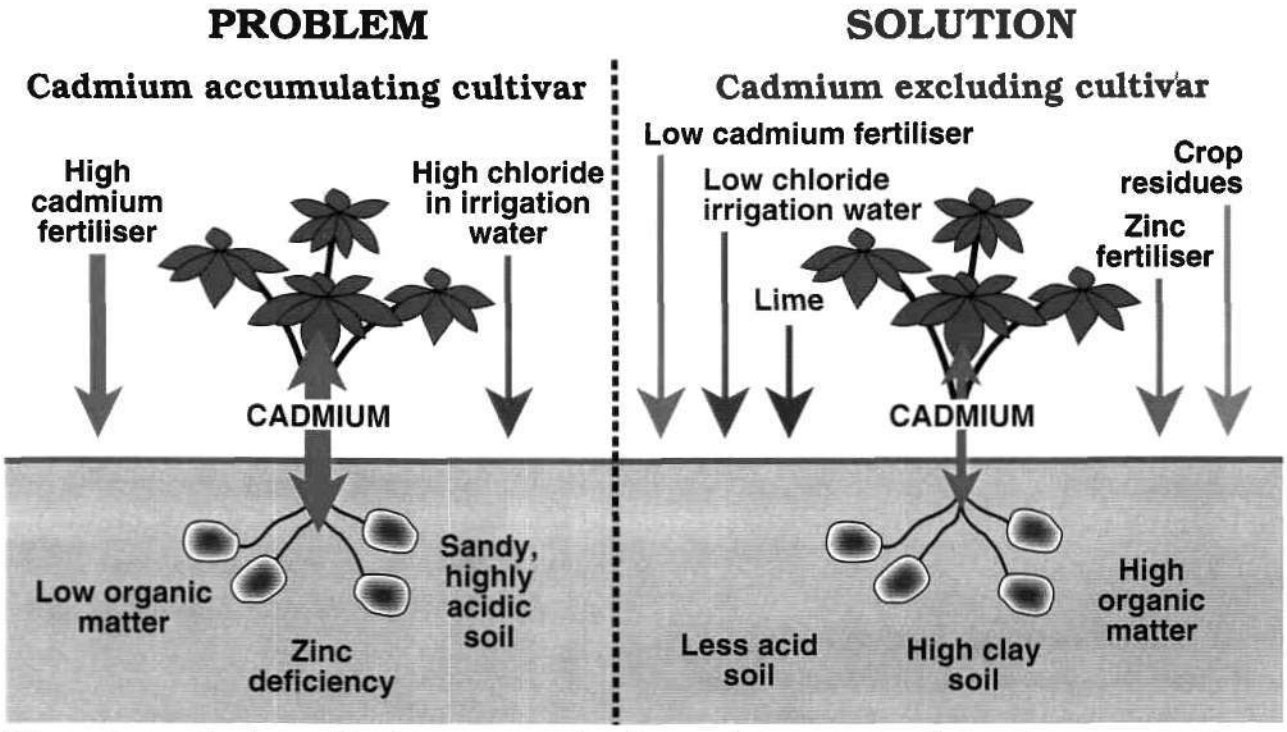
Addition of zinc

Banding 50-100 kg zinc/ha as zinc sulphate at planting has significantly reduced tuber cadmium concentrations at some trial sites. These rates are more than is usually applied to treat zinc deficiency in potatoes.

Zinc broadcast and incorporated into the soil is suggested as a trial where the concentration of EDTA zinc in the soil is less than 6mg/kg. Rates of 30-100 kg zinc sulphate/ha could be used (consult your agronomist).

Zinc deficiency has not been widely observed in Australia, so it is unlikely that the zinc will increase potato yields. Any effect of zinc on tuber cadmium should last several years.

Cadmium content of the zinc fertiliser should be checked before using, as the cadmium content of trace element products is normally higher than standard NPK fertilisers.



Managing cadmium effectively means implementing a range of practices as a total system. In paddocks where tuber cadmium concentrations are already high, the impact may be small in the short term, but sound management will be essential to assist control of long term cadmium levels.

What is cadmium?

Cadmium is a widespread naturally occurring element, present in soils, rocks, waters, plants and animals. It occurs naturally with deposits of lead and zinc, but unlike zinc is not essential to life. Cadmium can accumulate in humans, and high levels can affect human health.

Why is cadmium a problem?

- There is a smaller safety margin in foods, between levels of cadmium and regulatory health limits, compared to other heavy metals such as lead and mercury.
- Cadmium is concentrated in particular parts of plants. Leaves contain the most, followed by storage roots and tubers, seeds or grain and fleshy fruits.
- Human intake of cadmium is through food consumption, smoking and occupational exposure.

Sources of cadmium

- Natural levels in soil range from less than 0.1 mg/kg to 0.5 mg/kg, or about 0.1 to 0.7 kg cadmium/hectare in the top 10 centimetres of soil.
- Rain and irrigation water generally have very low cadmium concentrations. Sewage sludges may contain cadmium as an impurity.
- Cadmium in the atmosphere may be high in the vicinity of industrial activities such as smelting, but in most agricultural regions the amounts added to the soil from the atmosphere are minimal.

Greater use of rock phosphate from the United States, Africa and the Middle East has reduced cadmium inputs to soils.

- Phosphatic fertilisers can contain high levels of cadmium depending upon the source of rock phosphate. Trace element fertilisers and phosphogypsum also may contain high levels. Nitrogen and potassium fertilisers normally have a very low cadmium content.

The Fertiliser Industry Federation of Australia (FIFA) has agreed to progressively reduce the levels of cadmium in phosphate fertilisers by making greater use of rock phosphate with low cadmium content.

The fertiliser industry has adopted a voluntary limit of 250 mg cadmium per kg of phosphorus in horticultural fertilisers, which are generally applied at higher rates than fertilisers for pastures or other crops.

Cadmium levels in Australian food and exports

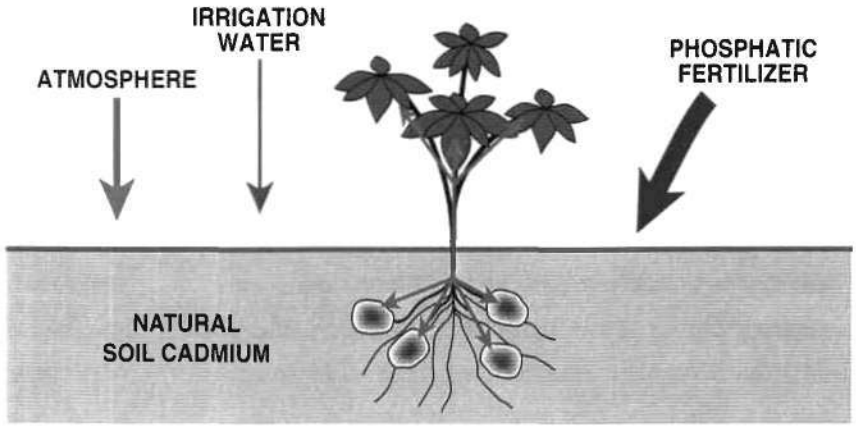
- Dietary intake of cadmium in Australia is low by world standards and our food exports have a "clean" reputation worldwide. To maintain this quality advantage we need to minimise any potential cadmium accumulation in food products.

How is cadmium taken up by plants ?

- Plants absorb most of their cadmium from soil through their roots.
- Cadmium in soil readily attaches to clay particles and organic matter, making it less available for uptake by plants. Sandy soils with low clay content and organic matter are likely to result in a higher uptake.
- The availability of cadmium to plants decreases as soil pH increases, or as soils become more alkaline.
- Zinc and cadmium uptake by plants occurs in a similar way, and it appears that if soil zinc levels are low then more cadmium will be taken up.
- Cadmium in soil tends to remain in the surface layers where it is available to plants. It can be removed by erosion or by leaching from very light sandy acid soils.

A regular testing program of the harvested crop is recommended.

SOURCES OF CADMIUM UPTAKE IN POTATOES



- Higher concentrations of chloride in the soil appear to mobilise cadmium and increase uptake by plants. This could occur from irrigation with saline water, in areas subject to dryland salinisation, or from the intensive use of chloride based fertilisers.
- Uptake varies considerably between different plant species and between varieties or cultivars.
- Cadmium present in farm produce can also be as a result of soil or dust contamination either in the field or during processing, as well as by direct uptake from the soil.

How do you know you have a cadmium problem ?

In most cases you can not tell visually if a plant has high cadmium. The concentration of cadmium needs to be measured. Plant symptoms would only be evident in grossly contaminated soils in industrial or urban areas and not in agricultural soils.

A regular plant testing program is recommended for growers. Tuber samples of the harvested crop should be forwarded to accredited laboratories as cadmium analysis is a specialised service.

The Australia New Zealand National Food Authority currently has set a limit for potatoes in the domestic market of 0.05 mg/kg cadmium on a fresh weight basis. This is lower than many other countries who have initiated similar limits, and is currently under review.

There are no critical levels for cadmium in agricultural soils.

Management practices to minimise cadmium levels

Use of phosphatic fertilisers with low cadmium content

It is recommended that low cadmium fertilisers are used. The impact of this on reducing tuber cadmium levels at sites with a long phosphate fertiliser history is only likely to occur over the medium to long term.

Your supplier will be able to advise you on the cadmium content of fertilisers. Look for products of less than 250 mg cadmium per kg of phosphorus. Such products are commercially available. Where repeated high applications of phosphorus (that is greater than 100kg per crop) are anticipated, fertilisers of less than 150mg cadmium per kg of phosphorus are desirable.

Where a paddock has adequate soil phosphorus levels for potatoes (for critical levels consult your local agronomist) phosphorus rates can be reduced as yield response will be limited, and further cadmium will be added through the fertiliser application.

Maintain or increase soil organic matter

There is good evidence that organic matter helps to reduce cadmium availability to plants.

Soil organic matter is generally built up by:

- the retention of crop residues after harvest
- use of green manure crops
- pasture phases in crop rotations
- significantly reducing the number of crop cultivations

The build-up or breakdown of soil organic matter is a slow process and significant changes only occur in the medium to long term, unless organic matter is introduced from external sources such as manures.

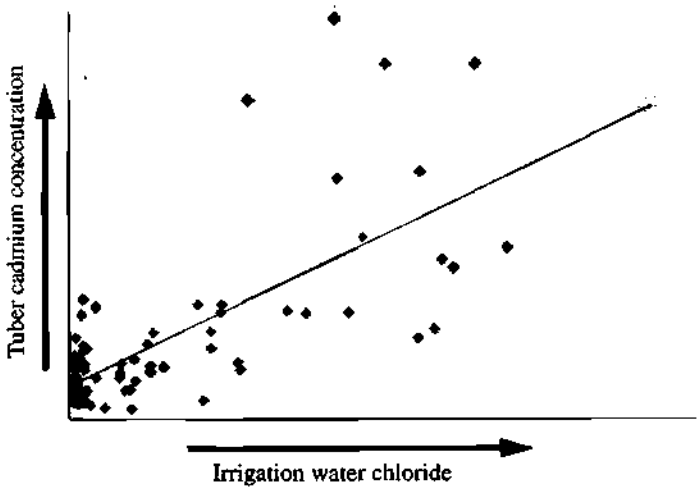
Avoid use of irrigation water with high chloride levels

Field experiments have shown that increased chloride content in the topsoil will increase tuber cadmium levels.

A major source of chloride is likely to be saline irrigation water. Experiments have confirmed increases in tuber cadmium levels with increasing chloride in irrigation water. This effect is less in a highly alkaline soil, that is pH (water) is greater than 8.0 or pH (calcium chloride) is greater than 7.3.

High soil chloride may also occur in areas subject to increasing dryland salinisation, due to rising groundwater levels. No research has been carried out to confirm this, but as a precautionary measure it is recommended that potatoes are not grown in these areas.

Irrigation waters with greater than 450 mg/litre chloride, or total dissolved salts greater than 750 mg/litre (equivalent to an electrical conductivity of about 1.2dS/m) have a high risk of producing tubers with high cadmium concentrations.



Tuber cadmium versus chloride concentration in irrigation water at 150 trial sites in southern Australia

Management practices to minimise cadmium levels

Varietal selection

Data collected from CSIRO and state department trials have suggested the following variety ratings for susceptibility to cadmium uptake.

High

Toolangi Delight, Kennebec, Crystal, Nadine

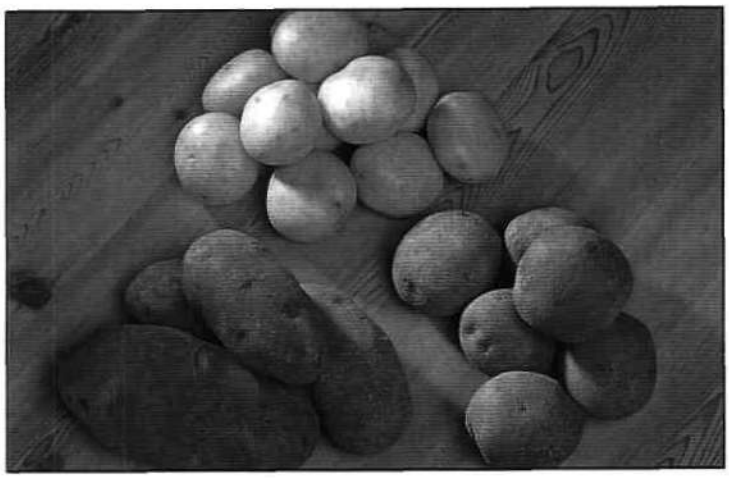
Medium

Wilcrisp, Sebago, Nooksack, Winlock, Tarago, Pontiac, Atlantic, Desiree, Delaware

Low

Wilwash, Russet Burbank, Lemhi Russet

Low or medium rated varieties are recommended where the likelihood of cadmium uptake is high.



Select varieties with low or medium susceptibility to cadmium uptake

Correction of soil pH.

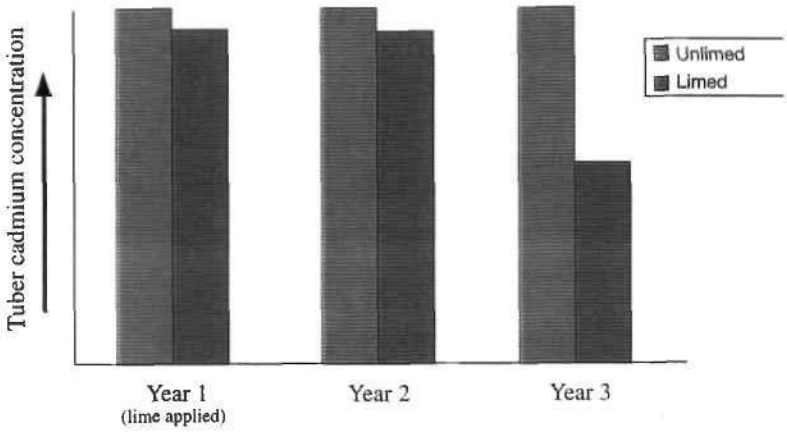
In highly acid soils (pH in water of less than 5.5, or pH in calcium chloride less than 4.8) a liming program should be initiated to increase soil pH. Aim to maintain soil pH (water) between 6.2 and 6.7, or pH (calcium chloride) between 5.5 and 6.0. Avoid overliming which can induce problems of micro-nutrient deficiency and the disease common scab.

Field studies have shown that lime has had little or no effect on tuber cadmium concentrations in the year of application. However, reductions have occurred 2-3 years later.

Potatoes are tolerant of low pH values and so yield increases by liming are unlikely, but responses in crops and pasture during other phases of the rotation are possible.

Field experiments with gypsum were ineffective in reducing tuber cadmium levels and resulted in some small increases. Gypsum has little or no effect on soil pH, ie it is not a liming agent, but is used to reduce the effects of high sodicity in soil, such as hard setting surface crusts or waterlogging. Naturally occurring (mined) gypsum should be considered in place of phosphogypsum for the treatment of sodic soils to be used for potato production, particularly if cadmium uptake is already high. Phosphogypsum is a by-product from the manufacture of phosphatic fertilisers.

A liming program is needed in highly acid soils



An example of tuber cadmium levels in response to liming an acid sandy loam soil

Contacts for further information

General enquiries
Dr Mike McLaughlin
CSIRO Division of Soils/
CRC for Soil and Land Management
Phone: 08 8303 8433
Fax: 08 8303 8565
Email: mike.mclaughlin@adl.soils.csiro.au

Western Australia
Mr Allan McKay
Agriculture WA
Phone: 09 368 3820
Fax: 09 367 2625

South Australia
Mr Norbert Maier
South Australian Research & Development Institute
Phone: 08 8303 9423
Fax: 08 8303 9424

Victoria
Mr Andrew Henderson
Agriculture Victoria
Phone: 03 9210 9222
Fax: 03 9800 3521

Tasmania
Dr Leigh Sparrow
Department of Primary Industry & Fisheries, Tasmania
Phone: 003 6336 5379
Fax: 003 6344 4961

New South Wales
Mr Col Bower
NSW Agriculture
Phone: 063 913 100
Fax: 063 913 605

Queensland
Mr George Rayment
Queensland Department of Primary Industries
Phone: 07 3896 9487
Fax: 07 3896 9623

Acknowledgments
J. Bourne
Land Management Consultant, Cooperative Research Centre for Soil & Land Management

M. Grope, Design, Cooperative Research Centre for Soil & Land Management

APPENDIX 12 Grower brochures 2 – Cadmium in potatoes - managing the risk from saline irrigation water

Cadmium in potatoes

..managing the risk from saline irrigation water

Consumer demand for quality produce is increasing.

Potato tubers exceeding the Maximum Permitted Concentration (MPC) for cadmium set by the Australia New Zealand Food Authority (ANZFA) cannot be used in the domestic market and cause problems in international trading.

Predicting the risk of producing potato crops above the MPC is an important part of managing cadmium in your cropping system.

This leaflet considers the relationship between cadmium concentration of potato tubers and quality of irrigation water.

HRDC

Australian Potato Industry Council

CRC Soil & Land Management

A joint venture

CSIRO

PRIMARY INDUSTRIES AND RESOURCES SA

AGRICULTURE VICTORIA

The problem

In 1997 ANZFA revised limits for cadmium (a toxic heavy metal) in potatoes and other vegetables. The MPC is 0.1 mg cadmium/kg fresh weight, for root, tuber and leafy vegetables. The marketing of these vegetables in Australia with cadmium concentrations above this MPC is not permitted.

Elevated levels of chloride in water increases the solubility of cadmium and other elements present in soil, which increases their uptake by plants. In Australia, salinity in surface and ground-water is due mainly to chloride.

Research has confirmed increases in potato tuber cadmium levels with increasing chloride concentrations in irrigation water. The risk is higher in soils already high in cadmium, usually the result of past heavy applications of phosphate fertiliser containing high levels of cadmium as an impurity.

Cultural practices can help to reduce the risk of high cadmium concentration occuring in potato tubers. See the brochure 'Managing cadmium in potatoes for quality produce.'

Research results

The probability of cadmium exceeding the MPC of 0.1 mg/kg has been estimated from measurements of salinity of irrigation water at 130 irrigated potato sites in five states. See Figure 1.

Figure 1 shows that the probability of cadmium concentrations in tubers reaching the MPC is low when using irrigation water with a conductivity less than 2.0 dS/m. The probability then rapidly increases to above 50% as the salinity of the irrigation water increases above 3.0 dS/m.

Growers are advised to use water with a conductivity of less than 2.0 dS/m.

Research also indicated that the probability of cadmium levels of tubers reaching the MPC was increased if the soil contained more than 15 µg/kg cadmium extracted in 0.01M calcium chloride. Soil cadmium levels are likely to be high in paddocks with a history of heavy applications of phosphate fertiliser containing high levels of cadmium as an impurity.

If possible, avoid growing potatoes on these soils.

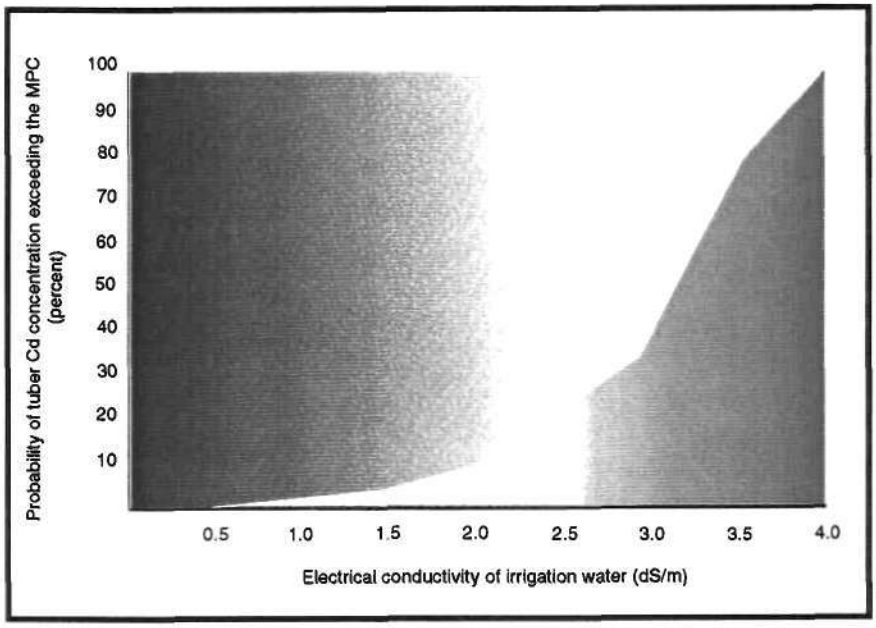


Figure 1. Probabilities of tuber cadmium levels at the MPC with varying levels of salinity of irrigation water

If irrigation water salinity is above 2.0 dS/m

- Chose an alternative irrigation water source with lower salinity.
- Select varieties with low or medium susceptibility to cadmium uptake including; Wilwash, Russet Burbank, Lemhi Russet, Ranger Russet, Winlock, Tarago, Pontiac, Atlantic, Desiree and Delaware.
- Use sulphate of potash rather than muriate of potash to supply potassium.
- Confirm possible problems in high risk situations with in-crop tuber testing. Test tubers early in the season as research has shown that, when water conductivity remains constant through the season, this gives a good indication of a potential problems.

Testing of irrigation water

Preplant

To minimise the risk of producing tubers with high levels of cadmium, measure the salinity of irrigation water. Where the water is high in salinity and there are no alternative sources, potatoes should not be grown.

Post planting

Water quality can change markedly during the irrigation season, with salinity often increasing late in the season. Monitoring the salinity level of irrigation water periodically during the season should be undertaken to determine the risk of higher levels of cadmium being taken up by tubers during part of the growing season.

Testing

Water samples can be sent to a laboratory, but cheap hand-held conductivity meters are now available to test your own samples in the field (see conductivity meters).

Sampling the irrigation water

- If ground water or dam water is used, ensure that the irrigation pump is run for sufficient time to obtain a sample representative of the water in the aquifer or dam.
- Using a clean plastic or glass 500 ml container, rinse it with the water to be tested prior to taking the sample.
- Fill the container with a sample of 500 ml of irrigation water.

Testing the irrigation water with a field meter

- Calibrate the small hand-held conductivity meter according to the manufacturers instructions. Wash the electrodes with rainwater or distilled water before and after each measurement.
- Measure the electrical conductivity (EC) of the water, in deciSiemens per metre (dS/m).
  Note: 1 dS/m=100 mS/m

Conductivity meters

If you cannot access a field meter, consider purchasing one for approximately $100.

Meters are electronic and require calibration. They need to be operated and stored with care (eg not in extremes of temperature).

Seek the advice of a reputable supplier of scientific equipment who will advise which meter best suits your requirements.

Figure 2. Measuring electrical conductivity with a hand-held meter.

Suppliers of conductivity meters include;

Crown Scientific Pty Ltd

NSW : Toll Free: 008 449 115 Tel: 02 9602 7677
Vic : Toll Free: 008 134 175 Tel: 03 9764 4722
Qld : Toll Free: 008 773 442 Tel: 07 3252 1066
SA : Tel: 08 8347 3310
WA: Tel: 08 9352 7000
Tas : Tel: 03 6229 7437

Selby Biolab

Tel: 13 2991
Free Fax: 1800 067 639
Melbourne, Sydney, Brisbane, Perth, Adelaide, Darwin, Hobart, Newcastle, Townsville.

The Cooperative Research Centre for Soil and Land Management does not warrant or recommend any particular manufacturer supplier or model of meter.

Tuber sampling

- For each soil type, potato variety or management unit, take a representative sample of at least 25 small tubers about 50-70 days after planting.
- Sample the crop in at least five locations in the field, digging up about 2 metres of row in each location.
- Take at least 5 tubers (any size) from each of the five locations and bulk the tubers together. Ensure no damaged or diseased tubers are included in the sample.
- Brush off soil and store the tubers in a clean paper bag in a cool place. Send the sample to a laboratory within 3 days for analysis of cadmium concentration. Your state contact can provide details of a reputable laboratory.

Sampling of plant tops to estimate cadmium concentrations in tubers is not recommended, as levels vary with different stages of crop growth.

Figure 3. Sampling tubers for testing.

Acknowledgments

This brochure is based on research supervised by Dr Mike McLaughlin, Cooperative Research Centre for Soil & Land Management (CRCSLM) Adelaide, in collaboration with Norbert Maier from the South Australian Research and Development Institute, and representatives from state agencies in Western Australia, Tasmania, New South Wales and Victoria.

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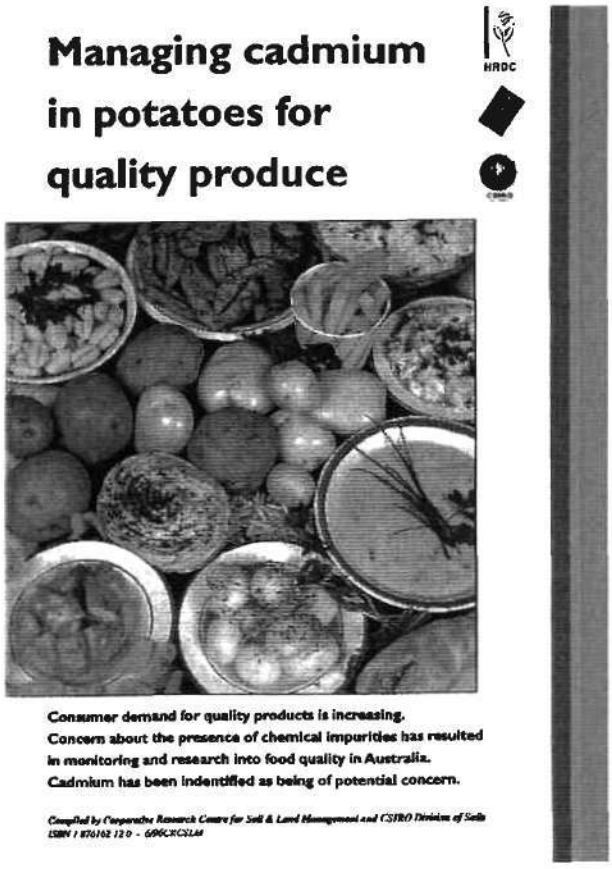
Further information:

Managing cadmium in potatoes for quality produce. CRC for Soil & Land Management, Adelaide. CRCSLM/6/96, available from your state contact.



Contacts:

Dr Mike McLaughlin, CRC Soil and Land Management.
Tel: 08 8303 8433 Fax: 08 8303 8565.

Mr Norbert Maier, South Australian Research and Development Research Institute, Primary Industries and Resources SA.
Tel: 08 8303 9423 Fax: 08 8303 9424.

Mr Allan McKay, Agriculture WA.
Tel: 08 9368 3820 Fax: 08 9367 2625.

Mr Andrew Henderson, Agriculture Victoria.
Tel: 03 9210 9222 Fax: 03 9800 3521.

Dr Leigh Sparrow, Tasmanian Institute of Agricultural Research.
Tel: 03 6336 5379 Fax: 03 6336 5395.

Mr Stephen Wade, NSW Agriculture. Tel: 03 5883 1644.

Mr George Rayment, Queensland Department of Natural Resources. Tel: 07 3896 9487 Fax: 07 3896 9623.

Cooperative Research Centre for Soil & Land Management
Postal address: PMB 2, Glen Osmond, SA 5064
Telephone: 61 8 8303 8670, Facsimile: 61 8 8303 8699
Email: crcslm@adl.soils.csiro.au
WWW: http://www-crcslm.waite.adelaide.edu.au