

VG006

**Effect of soil conditions and fertilizers on
cadmium in vegetables - a national
approach**

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CSIRO Division of Soils**



Know-how for Horticulture™

VG006

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1. EXECUTIVE SUMMARY

A Project funded by the **Horticultural Research and Development Corporation (HRDC)** and the **Fertilizer Industry Federation of Australia (FIFA)** was conducted between July 1991 to June 1994, to study the effect of farm management practices within a national perspective, on cadmium concentrations in vegetables, especially potatoes. The **specific objectives of the study** were to investigate the following:

- fertilizer practice - rates and sources, especially of phosphatic fertilizers and interactions between major nutrients and cadmium;
- the impact of soil cadmium which is residual from past fertilization. Use of cadmium-free fertilizer may in the short to medium term have little impact on cadmium uptake by crops;
- soil acidity as affected by liming and other practices. A balance between the needs of disease control and cadmium availability may be required;
- seasonal factors relating to soil temperature and the need for irrigation. Both water status and temperature could affect cadmium uptake by crops;
- choice of variety and kind of crop.

Both field and glasshouse experiments were conducted, with all State Departments of Agriculture in Australia being involved at various stages of the investigation. Potatoes were chosen as the main test crop as these are the major contributor to dietary cadmium intake in Australia.

- Large variation was found between regions in terms of cadmium concentrations in potato tubers. This was found to be due to differences in soil salinity, soil zinc status and type of cultivar grown. **Soil salinity was found to have a major impact in increasing tuber cadmium concentrations. Irrigation water quality is therefore a critical factor in determining cadmium uptake by irrigated crops.**
- The impact of soil salinity in increasing cadmium uptake by crops was found in glasshouse experiments to be predominantly due to chloride, rather than sulfate, in the irrigation water. **Hence high chloride concentrations in soil, either through irrigation with salty water or due to dryland salinisation, will lead to enhanced cadmium uptake by crops.**

- Where soils had cadmium present from past fertilization, changing the type of P fertilizer applied or its cadmium concentration had no immediate effect on potato tuber cadmium concentrations. **This indicates that cadmium present in the soil, residual from past fertilization, contributes significantly to the total cadmium uptake by the crop.**
- On soils with little Cd accumulated through previous fertilizer applications, addition of single superphosphate containing Cd at ± 35 parts per million at rates up to 100 kg P/ha increased tuber cadmium concentrations at 3 out of 6 field sites and in 1 of 2 glasshouse trials. Use of low-cadmium superphosphate was found to minimise this increase.
- **Addition of zinc to soils at rates up to 100 kg per hectare at planting significantly reduced uptake of cadmium by potato tubers at four out of five sites studied.** These results confirm other data obtained for cereals in zinc-deficient soils.
- Due to the effect of chloride on cadmium availability, potassium chloride (muriate of potash) fertilizer may enhance cadmium uptake by crops. **However, in field experiments we found potassium chloride had little or no effect on tuber cadmium concentrations due to the dominating effect of irrigation water quality.**
- **Choice of crop cultivar was found to have a large influence on tuber cadmium concentrations.** Some of the commonly used commercial cultivars consistently had cadmium concentrations higher than other cultivars. **There appears to be scope for reducing cadmium uptake by crops through breeding of low-accumulating lines.**
- **In the field, the application of lime was ineffective in reducing cadmium uptake.** However, in glasshouse experiments liming was effective in reducing tuber cadmium concentrations. It is important the reasons for this discrepancy be determined as liming is traditionally regarded as the best method of controlling cadmium uptake by crops.
- Glasshouse experiments investigating effect of nitrogen fertilizer type on cadmium uptake indicated that acidifying fertilizers do not necessarily increase cadmium uptake by tubers. **Indeed, we found the highest cadmium concentrations when calcium nitrate was used as the nitrogen source.**
- Zeolite was effective under glasshouse conditions in **reducing** tuber Cd concentrations, but the rate of zeolite required and the cost would prohibit adoption by growers.

2. MAJOR FINDINGS/IMPLICATIONS OF THE STUDY

SALINITY

- Soil salinity was found to be the major factor influencing uptake of cadmium (Cd) by irrigated potato crops in South Australia. Under high salinity conditions potato tubers with high Cd concentrations ($>0.2 \text{ mg kg}^{-1}$ fresh weight) were produced on soils having low Cd concentrations ($<0.25 \text{ mg kg}^{-1}$).
- The impact of salinity was found to be related to concentrations of chloride (Cl) in soil solution. Chloride mobilises Cd in soil and increases concentrations of Cd in soil solution, thus increasing plant uptake. The effects on Cd uptake of sulfate and bicarbonate in irrigation waters were found to be small by comparison.

FERTILIZER CADMIUM CONCENTRATION

- Where soils have cadmium accumulated from past fertilization, changing the type of P fertilizer applied or its cadmium concentration will have little immediate effect on potato tuber cadmium concentrations.
- If the soil is P deficient and does not have a history of Cd applications, then addition of fertilizer Cd to soil will increase tuber Cd concentrations. Low Cd fertilizers minimise this increase. This indicates that cadmium present in the soil, accumulated from past fertilization, contributes significantly to the total cadmium uptake by the crop in soils which have a history of fertilizer application.
- In terms of long-term build-up of Cd in soil it is recommended that low Cd fertilizers be used in all potato production areas.

PHOSPHORUS AND POTASSIUM FERTILIZER TYPE

- Field experiments were conducted in various regions of Australia to determine if Cd uptake by potatoes could be minimised by changes in either phosphorus (P) or potassium (K) fertilizer management.
- Changing the type of P fertilizers (monoammonium phosphate, diammonium phosphate, single superphosphate and reactive rock phosphate) added to crops had little influence on tuber Cd concentrations. This is attributed to the fact that the soils has a history of fertilizer Cd application, little of the Cd added in the fertilizers was taken up by the crop and hence differential effects on soil pH produced by the fertilizers had no effect on plant Cd uptake.
- Changing the chemical form in which K fertilizers (potassium chloride and potassium sulfate) was added to crops had little influence on tuber Cd concentrations. This is attributed to the dominating effect of irrigation water quality in controlling chloride concentrations in soil solution.

POTATO CULTIVARS

- Cadmium accumulation in tubers by current commercial potato cultivars was assessed at 12 sites around Australia having differing soil and environmental conditions. At all but 2 sites there were significant differences in tuber Cd concentrations between cultivars.
- Some major commercial cultivars had tuber Cd concentrations only half that of others.
- Advanced breeding lines showed further potential to reduce Cd accumulation. Mean tuber Cd concentrations of the 14 most common cultivars, averaged across all sites, ranged from 0.03 to 0.05 mg kg⁻¹ fresh weight (FW), below the maximum permitted concentration (MPC) of 0.05 mg kg⁻¹ of Cd (FW). However, at some sites certain cultivars exceeded the MPC.
- A modified joint regression analysis of the data indicated that no cultivars have consistently low or consistently high tuber Cd concentrations across a range of environments. While differences between cultivars were significant, the range in Cd concentrations found between sites was generally greater than the range in Cd concentrations between cultivars at any one site. Thus, soil and other site factors (e.g. irrigation water quality, climate, etc) play a dominant role in controlling Cd accumulation by current commercial cultivars.
- There is a need to breed new cultivars resistant to Cd accumulation under a wide range of environments.

ZINC

- Addition of zinc to soils at rates up to 100 kg per hectare at planting significantly reduced uptake of Cd by potato tubers at four out of five sites studied. These results confirm other data obtained for cereals in zinc-deficient soils. Zinc is known to compete with Cd for uptake by plants and even on soils which are not Zn-deficient (as studied here), may depress Cd uptake.

LIMING

- In the field, liming siliceous sand/sandy loam over clay (Dr/Db/Dy) and siliceous sand (Uc) soils, significantly ($P < 0.05$) increased total tuber yield in only **1 out of 11** experiments.
- In glasshouse studies with potted plants, the application of calcitic lime significantly ($P < 0.05$) **increased** tuber yield in 2 experiments, **decreased** it in another 2 and had **no effect** in 3.
- Application of lime either had **no effect** on or **increased** tuber Cd concentrations under field conditions.
- Under glasshouse conditions application of lime significantly **decreased** tuber Cd concentrations in 5 out of the 6 experiments conducted.

- There was a close correlation ($r^2=0.71$) between Cd concentrations in tubers and Cl concentrations in tubers grown under field conditions. No other elements either in tubers or in leaves correlated closely with Cd in the tuber.

NITROGEN FERTILIZER TYPE

- In glasshouse experiments, comparison of ammonium sulfate, urea, ammonium nitrate and calcium nitrate as the source of N showed that use of calcium nitrate resulted in tubers with higher Cd concentrations compared to other N sources.
- This result may be due to calcium in the fertilizer rendering Cd more plant-available in the soil.

ZEOLITES

- Zeolite was effective under glasshouse conditions in **reducing** tuber Cd concentrations, but the rate of zeolite required and the cost would prohibit adoption by growers.

3. CONCLUSIONS/RECOMMENDATIONS

- 1) Poor irrigation water quality is the greatest factor involved in producing tubers with high Cd concentrations, with Cl being identified as the problem ion. Growers wishing to produce tubers with low Cd concentrations should therefore use good quality irrigation waters with low Cl concentrations.
- 2) Applications of lime cannot be recommended as a means to reduce tuber Cd concentrations in the short term. Indeed, according to our work, under field conditions the application of lime immediately prior to the potato crop has a greater chance of increasing tuber Cd concentrations rather than decreasing them as is commonly believed.
- 3) Despite the above recommendation, it is still prudent to locate potato production on less acidic soils, if possible. These should be naturally less acidic or limed some years prior to potato production. This recommendation may change as further research results are obtained.
- 4) Applications of Zn to soils at planting is likely to reduce accumulation of Cd in tubers. Recommended rates are up to 100 kg ha⁻¹ of Zn as zinc sulfate. **Care should be exercised to use Zn fertilizer with a low Cd concentration, as Zn fertilizers often contain Cd as an impurity.**
- 5) Changing potato cultivar can reduce tuber Cd concentrations. The list of varieties and their relative Cd accumulating potential are shown below.

Tuber Cd Group	Cultivar
High	Toolangi Delight Kennebec Crystal
Medium	Wilcrisp Sebago Nooksack Winlock Tarago Pontiac Atlantic Desiree
Low	Wilwash Russet Burbank Lemhi Russet

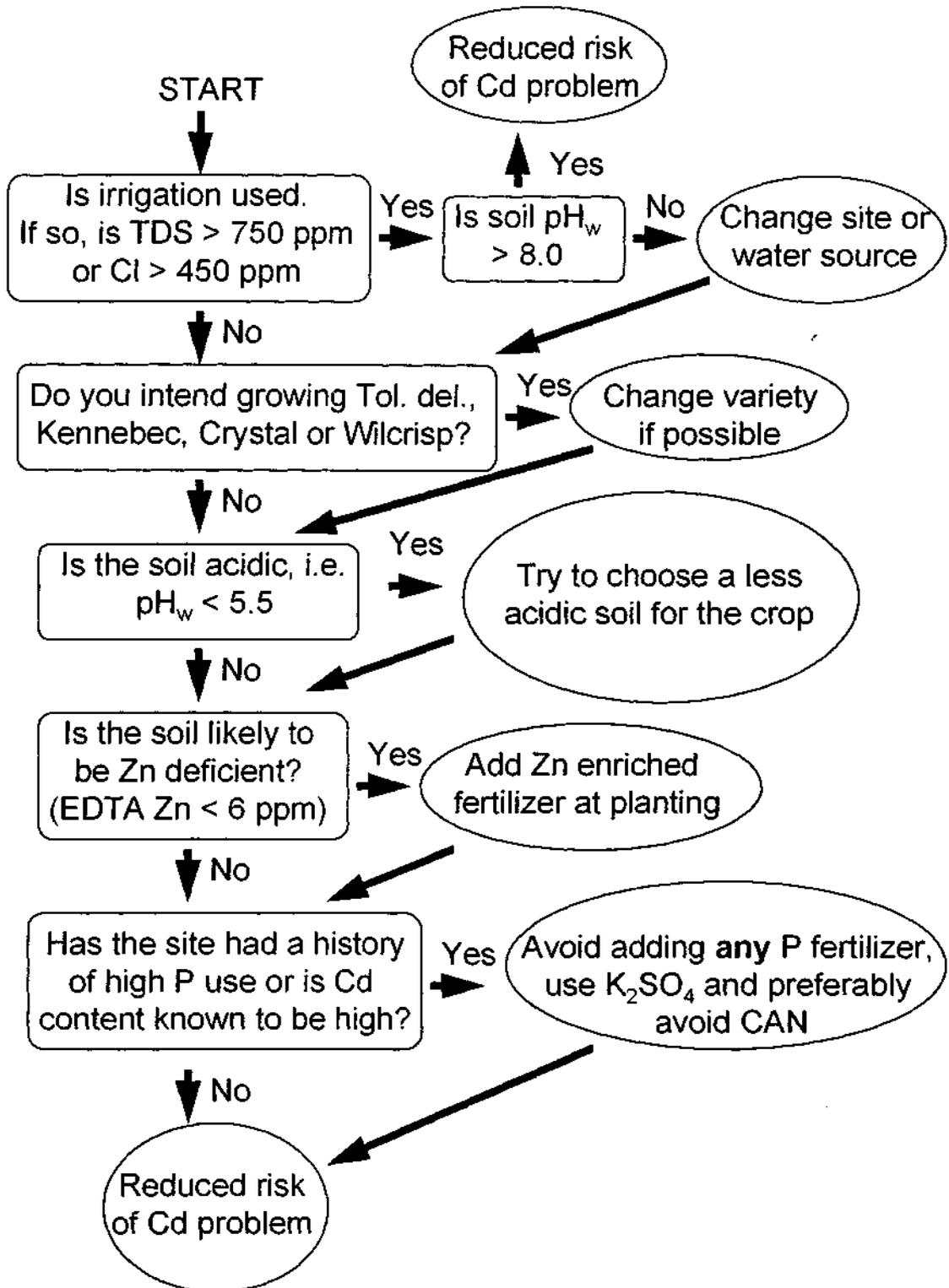
3. CONCLUSIONS/RECOMMENDATIONS CONTINUED

- 6) Low Cd fertilizers should be used in all potato production areas as more Cd is being added to soil than is being removed in produce. It is important that this rate of accumulation be slowed or stopped.
- 7) Where a soil has a history of fertilizer application and is likely to have had Cd added over a number of years, changing to a low Cd fertilizer will have little impact on tuber Cd concentrations in the short term.
- 8) Changing potassium fertilizer from potassium chloride to potassium sulfate may reduce tuber concentrations of Cd if;
 - a) irrigation water chloride concentrations are less than 200 parts per million.
 - b) high rates ($>150 \text{ kg ha}^{-1}$) of potassium fertilizer need to be applied.
 - c) tuber Cd concentrations are not expected to be significantly greater than the MPC.

In other situations the extra cost involved in switching to potassium sulfate may be unjustified.

- 9) On light-textured soils calcium nitrate or calcium ammonium nitrate should not be used as the source of nitrogen in NPK mixes.
- 10) A crude decision support tree (see overleaf) has been developed and will be further refined for distribution to growers.

DECISION SUPPORT TREE FOR Cd MANAGEMENT



NOTES

TDS = TOTAL DISSOLVED SALTS

CAN = CALCIUM AMMONIUM NITRATE

K₂SO₄ = SULFATE OF POTASH

EDTA ZN = ZINC EXTRACTED FROM SOIL BY EDTA SOLUTION

4. DIRECTIONS FOR FUTURE RESEARCH

- A diagnostic test is required to allow growers to identify high risk environments prior to planting of potato crops. This would allow selection of areas for potato production and could trigger extra ameliorative measures if high Cd risk was predicted. It is likely such a test would require both soil and irrigation water quality to be assessed as part of the test.
- The long-term availability of fertilizer Cd to crops needs to be determined. This is necessary if we are to know how long it will take to “run-down” soil Cd concentrations (or availability) after low Cd fertilizers are introduced. It will also allow assessment of the impact of continuing to add more Cd to soil than is removed in harvested produce.
- It is important that the reasons for the discrepancy between data obtained in glasshouse and field liming experiments be determined. Possible factors which could lead to the differences in results obtained under glasshouse and field conditions are:
 - (a) Inadequate time allowed for reaction of lime with soil.
 - (b) Differential soil moisture conditions between glasshouse and field situations. and/or
 - (c) Differences in water quality between glasshouse and field situations.
- The mechanism whereby lime may increase crop Cd concentrations needs to be identified so that soil and environmental factors which lead to this phenomenon can be identified and appropriate remediation techniques developed for these situations.

8. Project Milestones/Schedule of Operations

Task description	ompletion date
Employ staff	30/9/91
Planning with collaborators SA/Vic	30/9/91
Review existing data/research	30/11/91
Establish experimental and analytical procedures	31/12/91
Glasshouse experiments on Cd uptake	31/12/92
Collect soil and potato samples (survey)	30/6/93
Complete analysis of soils to determine soil factors determining Cd uptake	31/7/93
Field experiments with State authorities	30/9/93
Write scientific paper of results from analyses of SA soil survey	31/12/93
Write scientific paper of results of 1992 field trials	31/3/94
Initiate experiments to examine solution chemistry of Cd as affected by salinity	31/3/94
Complete pot experiments examining lime/N source/salinity interactions	30/6/94
Write reports	31/12/94

9. Industry Financial Support:

Levy paying industries

	Total amount contributed
Potato	\$150,000
Total	\$150,000

and

Voluntary contributions

Industry contributor(s): Fertilizer Industry Federation of Australia
(formerly Australian Fertilizer Manufacturers' Committee)

Contact person: Mr B.G.Hunt

Address: GPO Box 2134T,
Phone: 03 602 3688
Melbourne VIC 3001

Fax: 03 602 3977

Amount contributed (each year)

1991/92:	\$50,000
1992/93:	\$50,000
1993/94:	\$50,000

A signed statement from the industry contributor is to be attached to this application. This was provided with initial application.

10. Total Project Costs

1991/92:	\$92,241
1992/93:	\$92,523
1993/94:	\$93,386
Total	\$278,150

6. DETAILS OF PROJECT

Description of the Project

(i) General Objectives

- (a) The major aim was to investigate the effect of farm management practices within a national perspective, on cadmium concentrations in vegetables, especially potatoes. This supported a key recommendation of the National Cadmium Symposium conducted by the D.P.I. and E. in Canberra in March 1988. Factors requiring special attention were:
- fertilizer practice - rates and sources, especially of phosphatic fertilizers and interactions between major nutrients and cadmium;
 - the impact of soil cadmium which is residual from past fertilization. Use of cadmium-free fertilizer may in the short to medium term have little impact on cadmium uptake by crops;
 - soil pH as affected by liming and other practices. A balance between the needs of disease control and cadmium availability may be required;
 - seasonal factors relating to soil temperature and the need for irrigation. Both water status and temperature could affect cadmium uptake by crops;
 - choice of variety and kind of crop.

(ii) The Problem

Nature of problem.

Potatoes and other vegetables, notably the root and leafy vegetables, constitute an important part of the Australian diet (about 100kg/person/year) and all have cadmium concentrations well above the norm of most Australian foods (excepting animal offal products). The NH and MRC have established maximum permissible concentrations (MPC) of cadmium in Australian foods which for vegetables is 0.05mg Cd kg⁻¹ fresh weight. Any decrease in this legal limit under pressures of the current environmental/political climate, or increases in cadmium levels of vegetables in response to farm management practice could bring into jeopardy the marketability of some produce.

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 vegetable 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 low pH, have created conditions ensuring 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.

7. CSIRO AND COLLABORATING PERSONNEL INVOLVED IN THE PROJECT

CSIRO

Dr M.J. McLaughlin
Dr K.G. Tiller
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Mr R.H. Merry
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Mr D. Mowat
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Victorian Dept. Agriculture

Ms Karen Freeman
Mr Roger Kirkham
Mr Rene de Jong

Tasmanian Dept. Primary Industries and Fisheries

Dr Leigh Sparrow

NSW Agriculture

Mr Paul Milham
Mr Ben Dowling

Queensland Dept. Primary Industries

Dr Ken Jackson
Mr Jim Gunton

Northern Territory Dept. Primary Industries

Mr Ray Thompson

8. SCIENTIFIC OUTCOMES

To date 4 papers detailing work carried out under the project have been published in internationally refereed journals. A further 5 journal papers are currently in preparation.

Two conference papers/abstracts have been published and a further 2 are submitted for presentation at a major international meeting in mid 1995. In addition, a paper was delivered to the 2nd International Symposium on the Biogeochemistry of Trace Metals, Taipei, Taiwan in September 1993.

Journal papers published/submitted

- 1) McLaughlin, M.J., Williams, C.M.J., McKay, A., Gunton, J., Jackson, K., Dowling, B., Kirkham, R., Partington, D., Smart, M.S. and Tiller, K.G. 1994. Effect of potato variety on cadmium accumulation in potato tubers. *Aust. J. Agric. Res.* 45: 1483-1495.
- 2) McLaughlin, M.J., Tiller, K.G., Beech, T.A. and Smart, M.K. 1994. Soil salinity causes elevated cadmium concentrations in field-grown potato tubers. *J. Environ. Qual.* 23(5): 1013-1018.
- 3) McLaughlin, M.J., Maier, N.A., Freeman, K., Tiller, K.G., Williams, C.M.J. and Smart, M.K. 1994. Effect of potassic and phosphatic fertilizer type, phosphatic fertilizer Cd content and additions of zinc on cadmium uptake by commercial potato crops. *Fert. Res.* (in press).
- 4) Tiller, K.G., Oliver, D.P., McLaughlin, M.J., Merry, R.H. and Naidu, R. 1994. Managing cadmium contamination of agricultural land. *Adv. Environ. Sci.* (in press).
- 5) McLaughlin, M.J., Tiller, K.G., Naidu, R. and Steven, D.P. 1995. Review: The behaviour and environmental impact of contaminants in fertilizers. *To Aust. J. Soil Res.* (in review).

Conference papers/abstracts

- 6) McLaughlin, M.J., Maier, N., Williams, C.M.J., Tiller, K.G. and Smart, M.K. 1993. Cadmium accumulation in potato tubers - occurrence and management pp.208-213 *In Proc. 7th National Potato Research Workshop, Ulverstone, May 1993.* Ed. J.Fennell. Tasmanian DPI, Launceston.
- 7) 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.*

Journal papers in preparation

- 8) Maier, N.A. and McLaughlin, M.J. 1995. Agricultural limestone is ineffective in controlling cadmium uptake by commercial potato crops. *To Fert. Res.*
- 9) McLaughlin, M.J., Maier, N.A. and Smart, M.K. 1995. Effect of anions in irrigation water on Cd uptake by potatoes. *To Aust. J. Soil Res.*

Journal papers in preparation (cont.)

- 10) Maier, N.A. and McLaughlin, M.J. 1995. Interactions between lime and phosphorus on Cd uptake by potatoes: field and glasshouse experiments. *To Fert. Res.*
- 11) Maier, N.A. and McLaughlin, M.J. 1995. Effect of N-source on Cd uptake by potatoes. *To Aust. J. Exp. Agric.*
- 12) McLaughlin, M.J., Maier, N.A. and Smart, M.K. 1995. Soil solution composition and Cd uptake by potatoes. *To Soil Sci. Soc. Am. J.*

9. TECHNOLOGY TRANSFER/INDUSTRY LIAISON

1) Major meetings

During the course of the project two coordination meetings were held in Adelaide to review the issues, determine research and management priorities and to pass information and research outcomes to industry.

The first meeting was held on 2nd-3rd October 1991 at CSIRO in Adelaide with the aim of reviewing current data then available for Cd in potatoes and determining research priorities for the various groups involved. Standardised sampling and analysis protocols were agreed and it was agreed that a Quality Assurance program be run to ensure consistency between laboratory results. Representatives from both HRDC and the potato industry were present at this meeting.

The second meeting "Cadmium Workshop for the Australian Potato Industry" was held on 5th-6th August 1993 at CSIRO in Adelaide. This meeting had significant industry representation and updated industry on research results, prioritised future research directions and developed a management plan to address the Cd issue. Proceedings of this workshop were published by HRDC in September 1993 (Document/Project PT 342).

2) Grower meetings

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

- 1) Information evening, South East Potato Growers Assoc., Penola, March 5th, 1992.
- 2) Tatiara Potato Growers meeting, Bordertown, May 4th 1992.
- 3) Cd update, SA Potato Industry Liaison Committee Meeting, Adelaide, August 19th, 1992.
- 4) Cd update, SA Potato growers meeting, Adelaide, April 28th, 1993.
- 5) Tatiara Potato Growers meeting, Bordertown, October 10th, 1994.
- 6) Koo-wee-rup/Thorpedale crisping growers meeting, Coralyn, October 19th, 1994.

3) Industry liaison

Throughout the project, close contact has been maintained with the fertilizer industry through the Fertilizer Industry Federation of Australia, Ltd. Assistance was provided to the Phosphate Cooperative Company of Australia Ltd (PIVOT) to produce an information booklet "Cadmium", in January 1992.

Close contact has also been kept with the National Food Authority (NFA). 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 Cd in potatoes.

4) Articles/leaflets/media

Research results from the project have been reported in the following media

- a) Article in Peelings Newsletter October 1993, "Cadmium accumulation in potatoes".
- b) Article in Rural Research, Autumn 1994 edition, "Cadmium: a modern day problem".
- c) Article in Rural Research, Autumn 1995 edition, "Keeping cadmium under control".
- d) Article in Peelings Newsletter, December 1994, "Cadmium update".

5) Decision support software

Many of the findings will be included in information packages and decision support software for growers and technical staff being prepared as part of SARDI PROJECT PT428, which started in July 1994.

10. TECHNICAL PAPERS

APPENDIX 1 Review of the literature with regard to reactions and plant availability of Cd in soil

Introduction

Cadmium (Cd) contamination of agricultural has become increasingly important in recent years due to increased public awareness and concern for food and land quality. Cadmium residues in foods are regularly monitored at both the State and Federal level in Australia and some agricultural produce has been found to exceed maximum permitted concentrations (MPCs).

Given that Cd concentrations have increased in many improved agricultural soils in Australia, research has recently focussed on soil and environmental factors leading to increased soil-plant transfer of this element and on defining farm management factors which minimise Cd uptake by crops and intake by animals.

Cd concentrations in agricultural soils

To assess the impact of fertilization on accumulation of Cd, metal concentrations in virgin (uncultivated) or in cultivated but unfertilized soils must be compared to their fertilized equivalents. For the purposes of this review therefore, background values will be referred to metal concentrations in the natural (or pristine unfertilized) state. Pristine background values are probably represented by Cd concentrations in parent rock material. Cadmium concentrations in crustal rocks varies from $1 \mu\text{g kg}^{-1}$ to $90,000 \mu\text{g kg}^{-1}$ (Page *et al.* 1981; Cook and Freney 1988; Kabata-Pendias and Pendias 1992), with igneous and metamorphic rocks generally having lower Cd concentrations than sedimentary deposits. However, these concentrations can be modified during soil formation by leaching and accumulation processes (important on a geologic time scale), dilution by incorporation of organic matter into soil and bioconcentration due to plant activity.

There are very few data from which to determine background concentrations of metals in Australian soils. Appropriate methods for analysis of metals at low concentrations were only developed over the last 30 years, by which time much of Australia's agricultural land had already been cleared and had received considerable amounts of single superphosphate containing Cd as an impurity. Furthermore, soils in national parks and uncleared land may also receive fertilizer-derived contaminants through deposition of soil from adjacent fertilized areas by wind erosion. Table 1 shows the few data which are available for unfertilized and fertilized rural soils in Australia.

The data of Williams and David (1976) are limited to only 7 sites and the values reported by Hanson (1988) are extremely high when compared to other Australian or international data, and we would question the analytical accuracy of these data. Comparison of the data for unfertilized soils of Merry and Tiller (1991) to values with the international literature is difficult, as most authors report values for fertilized and unfertilized agricultural soils together as "uncontaminated", often for comparison with urban or soils amended with municipal or industrial wastes (Page *et al.* 1981; Dickson and Stevens 1983; Christensen and Tjell 1991; Jensen and Bro-Rasmussen 1992; Holmgren *et al.* 1993). Values for total Cd concentrations reported overseas in "normal" agricultural soils vary from less than 0.01 mg kg^{-1} to over 2.50

mg Cd kg⁻¹, but generally soils fall in the range 0.05 to 1.00 mg Cd kg⁻¹. Jensen and Bro-Rasmussen (1992) recently compiled data on Cd in European agricultural soils classed as "normal". The mean Cd concentrations for various countries ranged from 0.06 mg Cd kg⁻¹ in Finland to 0.50 mg Cd kg⁻¹ in UK, with minima and maxima from 0.03 to 10.00 mg Cd kg⁻¹. Holmgren *et al.* (1993) recently analysed 3045 agricultural topsoils in USA for metal concentration and found Cd concentrations ranged from <0.01 to 2.00 mg Cd kg⁻¹ with a mean value (arithmetic) of 0.265 mg Cd kg⁻¹. Recently, Sillanpaa and Janssen (1992) published data on the concentrations of Cd extracted from over 3,500 soils in 30 countries and found the median Cd concentration was just under 0.06 mg L⁻¹, or 0.05 mg kg⁻¹ assuming an average soil bulk density of 1300 Mg m⁻³. However, as the study was related more to assessment of plant available Cd rather than total Cd, the extractant used was fairly "mild" (0.5M CH₃COOH, 0.5M CH₃COONH₄, 0.02M Na₂EDTA at pH 4.65) and there was no attempt to distinguish between unfertilized and fertilized soils.

Table 1. Cadmium concentrations in Australian unfertilized rural soils.

Reference	Cd concentrations (mg kg ⁻¹)		No. samples	Method of extraction	Notes
	Mean	Range			
<u>Unfertilized</u>					
<u>rural soils</u>					
Williams and David (1976)	0.05	0.02-0.13	5	1.0 N HCl (18 hrs)	NSW paired site study
Hanson (1988)	0.97	0.06-12.02	38	0.05 M EDTA (pH 6.0, 4 hrs)	Vic. soils 0-25 mm layer
Merry and Tiller (1991)	0.51	0.02-7.02	38	0.1 M EDTA (pH 6.0, 7 d)	0-100 mm layer
	0.11	0.01-0.29	69		SA soils 0-50 mm layer
Olsoy <i>et al.</i> (1993)	0.06	0.01-0.20	66		50-100 mm layer
	<0.50	<0.50	120	Conc. HNO ₃ / H ₂ O ₂ /HCl	Soils in Qld. National Parks, 0-150 mm layer.
<u>Fertilized rural</u>					
<u>soils</u>					
Williams and David (1976)	0.45	0.27-0.56	7	1.0 M HCl (18 hrs)	
Hanson (1988)	0.82	0.02-13.90	157	0.05 M EDTA (pH 6.0, 4 hrs)	0-100 mm layer
Hilliard <i>et al.</i> (1988)	0.56	0.01-13.90	120	0.05 M EDTA (pH 6.0, 4 hrs)	0-100 mm layer
Merry and Tiller (1991)	0.18	0.01-0.73	516	0.1 M EDTA (pH 6.0, 7 d)	0-50 mm layer
	0.09	0.01-0.49	503		50-100 mm layer

Cd inputs to agricultural soils in Australia

Inputs of Cd to agricultural soils are predominantly through additions of Cd in phosphatic fertilizers, although atmospheric or other sources (e.g. sewage sludges) may be important in localised areas. Atmospheric deposition of Cd in the vicinity of urban areas in Adelaide,

South Australia were up to $3 \text{ g ha}^{-1} \text{ y}^{-1}$ (Merry and Tiller 1991) or higher, depending on industries present. However, in most rural areas deposition of metals and F will be indistinguishable from background (Merry and Tiller 1991). Measured Cd concentrations in rainfall in this study area were in the range $<0.1\text{-}0.4 \mu\text{g L}^{-1}$ (Merry 1988) with Cd concentrations in streamwaters $0.05 \pm 0.04 \mu\text{g L}^{-1}$ (Fordham 1978). Australian data for the atmospheric input of Cd (about $3 \text{ g ha}^{-1} \text{ y}^{-1}$) downwind from Adelaide metropolitan area accord with values of $1\text{-}5 \text{ g ha}^{-1} \text{ y}^{-1}$ quoted for European rural areas (Hovmand 1981; Tjell *et al.* 1981; Gunnarsson 1983; Hutton and Symon 1986; Jones *et al.* 1987), where urban and industrial atmospheric pollution is more widespread and affects a large proportion of the agricultural land in many countries

Sewage sludge, until recently, has not been applied in appreciable amounts or to significant areas of Australian agricultural land. This situation will soon change because of recent government decisions to ban discharge of sewage, treated or otherwise, into the ocean and to restrict its incineration. Tiller *et al.* (1994) have recently estimated potential sludge-Cd loading to Australian agricultural soils to be about $2\text{-}4 \text{ t y}^{-1}$.

The main source of Cd added to agricultural soils in Australia is through use of phosphatic fertilizers. The high concentrations of Cd in Australian superphosphates were identified by Walkley (1940) but their environmental consequence for soil and food quality in Australia were highlighted later by Williams and David (1973). The main rock phosphate sources for manufacture of phosphatic fertilizers in Australia, until recently, were from the oceanic sedimentary, guano-based deposits with Cd concentrations ranging from $42\text{-}99 \text{ mg kg}^{-1}$. In general, these island sources of phosphate rock had higher Cd concentrations than rocks found in other countries. From information in Williams (1974), David *et al.* (1978), Syers *et al.* (1986), Cook and Freney (1988), Singh (1991), Mordvedt and Beaton (1993), information provided by the Fertilizer Industry Federation of Australia (FIFA) and our own analyses, a list of the Cd concentrations in rock phosphates is shown in Table 2. The highest Cd deposits appear to be in the western USA. From analyses of DAP fertilizers given by Mordvedt *et al.* (1981), the Cd concentration in the western USA rock is calculated to be up to $760 \text{ mg Cd kg}^{-1} \text{ P}$.

In the manufacture of single superphosphate it appears that most of the Cd in the original phosphate rock is found in the final fertilizer (Williams 1977), so that the final Cd concentration in the single superphosphate expressed on a per unit P basis will be similar to the original rock phosphate (both P and Cd concentrations on a per unit weight basis will decrease due to dilution with sulfuric acid). In the manufacture of high analysis fertilizers, some of the Cd in the original phosphate rock appears in the by-product gypsum, but the main proportion of the Cd is transferred to the final product (David *et al.* 1978). Rayment *et al.* (1989) recently compared a small range of low and high analysis fertilizers manufactured in Queensland and found a similar Cd:P ratio ($413 \pm 40 \text{ mg Cd kg}^{-1} \text{ P}$) in both low and high analysis formulations.

The concentrations of impurities in manufactured nitrogenous or potassic fertilizers are generally low (Stenstrom and Vahter 1974, Rayment *et al.* 1989; Zarcinas and Nable 1992; Sauerbeck 1993). Where liming materials or gypsums are by-products of industrial processing (e.g. kiln dust, phosphogypsum, etc) the products may contain significant concentrations of Cd (Zarcinas and Nable 1992), depending on the industrial process involved. Trace element fertilizers, or trace element raw materials used to manufacture trace element enriched phosphatic fertilizers, may be an important source of Cd in some fertilizers. Data for

Australian sourced materials and international data for Cd concentrations in non-phosphatic fertilizers and soil amendments are shown in Table 3.

Table 2. Cadmium and phosphorus concentrations of some phosphate rocks.

Phosphate rock	Cd (mg kg ⁻¹)	P (%)	Cd (mg Cd kg ⁻¹ P)	Reference
USSR (Kola)	0.2	17.2	1	Singh (1991)
South Africa (Phalaborwa)	4	17.2	23	Williams (1974)
Chatham Rise phosphorite	2	8.9	23	Syers <i>et al.</i> (1986)
China (Yunan)	5	14.4	35	Bramley (1990)
Syria (Khneifiss)	5	14.0	36	FIFA (pers. comm.)
Syria (Eastern)	5	13.1	38	FIFA (pers. comm.)
Jordan	6	14.8	27	Bramley (1990)
Australia (Duchess)	7	13.9	50	Williams (1974)
Mexico	8	14.0	57	Syers <i>et al.</i> (1986)
Egypt (Quseir)	8	12.7	61	McLaughlin (unpub. data)
Florida 72%	9	14.4	63	FIFA (pers. comm.)
Egypt (Hamrawein)	9	12.7	67	FIFA (pers. comm.)
Makatea	10	13.0	77	Syers <i>et al.</i> (1986)
Peru (Sechura)	11	13.1	84	Syers <i>et al.</i> (1986)
Israel (Arad)	12	14.1	85	Syers <i>et al.</i> (1986)
Morocco (Khouribga 68 K11)	12	13.6	88	FIFA (pers. comm.)
Florida 73.5%	13	14.7	89	FIFA (pers. comm.)
Tunisia (Gafsa)	38	13.4	108	Syers <i>et al.</i> (1986)
Florida 74/75%	17	15.0	114	FIFA (pers. comm.)
Florida 68%	16	13.6	115	FIFA (pers. comm.)
Mataiva	20	16.0	125	FIFA (pers. comm.)
Morocco (Khouribga 72 K20)	24	14.4	167	FIFA (pers. comm.)
Youssoufia 68 (Y1)	23	13.6	169	FIFA (pers. comm.)
Morocco (Youssoufia 73.5 Y2)	33	14.7	225	FIFA (pers. comm.)
Israel (Zin)	32	14.0	228	Bramley (1990)
Morocco (Boucraa)	38	15.7	240	McLaughlin (unpub. data)
Christmas Island	43	15.3	275	David <i>et al.</i> (1978)
North Carolina (calcined)	43	14.3	300	FIFA (pers. comm.)
North Carolina	47	15.1	311	McLaughlin (unpub. data)
Togo	51	16.0	320	FIFA (pers. comm.)
Banaba (Ocean Island)	99	17.6	563	Williams (1974)
Senegal	90	15.8	570	FIFA (pers. comm.)
Nauru	100	15.6	641	Syers <i>et al.</i> (1986)
Western USA	60-340	NR ^a	NR	Auer (1977)

^a NR = not reported.

A large proportion of the phosphorus applied to Australian soils since the 1920's has been in the form of single superphosphate (Gargett 1983; McLaughlin *et al.* 1992b). About 100 million tonnes of rock phosphate have been imported into Australia over the last 100 years, supplying approximately 15 million tonnes of P (McLaughlin *et al.* 1992b). From data on imports of rock phosphate (Donald 1964; Cook 1982; ABARE 1993) and approximate rock Cd concentrations, it is estimated that over 6000 tonnes of Cd have been added to Australian soils through use of phosphatic fertilizers in the last 90 years.

Table 3. Cadmium concentrations in non-phosphatic fertilizers and soil amendments.

Material (commercial grade)	Cd concentration (mg kg ⁻¹)	Reference
Ammonium sulfate	<0.5	Rayment <i>et al.</i> (1989)
	<1.0	McLaughlin <i>et al.</i> (unpublished data)
Potassium nitrate	<0.5	Rayment <i>et al.</i> (1989)
Ammonium nitrate	<0.5	Rayment <i>et al.</i> (1989)
Urea	<0.5	Rayment <i>et al.</i> (1989)
	<2.0	Zarcinas and Nable (1992)
	<0.1	Stenstrom and Vahter (1974)
	0.1	FIFA (personal communication)
	0.05	Andersson (1976)
Calcium nitrate	0.1	Singh (1991)
	<0.5	Rayment <i>et al.</i> (1989)
Potassium sulfate	<1.0	McLaughlin <i>et al.</i> (unpublished data)
	<0.5	Rayment <i>et al.</i> (1989)
Potassium chloride	<1.0	McLaughlin <i>et al.</i> (unpublished data)
	<2.0	Zarcinas and Nable (1992)
	50.2 ^a	Zarcinas and Nable (1992)
	0.1	FIFA (personal communication)
	24.9	Rayment <i>et al.</i> (1989)
Zinc sulfate	1.5	McLaughlin <i>et al.</i> (unpublished data)
	130.0	FIFA (personal communication)
Copper sulfate	17.2	Rayment <i>et al.</i> (1989)
	5.5	Rayment <i>et al.</i> (1989)
	30.3	FIFA (personal communication)
Manganese sulfate	1.3	FIFA (personal communication)
Magnesium sulfate	<1.0	McLaughlin <i>et al.</i> (unpublished data)
Sodium tetraborate	2.0	Rayment <i>et al.</i> (1989)
Sodium molybdate	6.0	Rayment <i>et al.</i> (1989)
Cobalt sulfate	<1.0	Andersson (1976)
Agricultural lime	<1.0	Rayment <i>et al.</i> (1989)
	<2.0	Zarcinas and Nable (1992)
	14.0 ^a	Zarcinas and Nable (1992)
	1.5	Rayment <i>et al.</i> (1989)
Dolomite	<1.0	McLaughlin <i>et al.</i> (unpublished data)
	<2.0	Zarcinas and Nable (1992)
	2.5	FIFA (personal communication)
	0.12-5.0	Hanson (1988)
Gypsum (natural)	6.4	Rayment <i>et al.</i> (1989)
	3.4-14.0	Hanson (1988)
	0.2	Mays and Mordvedt (1986)
	1.2-3.2	Smith <i>et al.</i> (1994)

^a industrial by-products.

Compared to early analyses by Williams (1970), P fertilizers currently have much lower Cd concentrations due to different sources of raw materials used for manufacture (Zarcinas and Nable 1992; FIFA, pers. comm.). Zarcinas and Nable (1992) noted a significant reduction in

the Cd:P ratio of fertilizers manufactured in South Australia after 1989. The annual import of Cd to Australia from fertilizer or fertilizer raw materials is estimated to be approximately 40 t, one third of which is imported in finished fertilizers and the remainder as phosphate rock. The Australian figures can be compared to fertilizer Cd input values (mean 1985-1987) quoted for European countries by Biberacher and Shah (1990) varying from 1.5 t y^{-1} (Norway) to 84.7 t y^{-1} (France) and a value of 140 t y^{-1} quoted by Fleischer *et al.* (1974) for USA. However, unlike Australia and European nations, USA has significant domestic consumption of indigenous P supplies, which will add to the Cd import figure quoted above.

Assuming this Cd is applied to about 25 million hectares of agricultural land (ABARE 1993), the mean application rate is approximately $1.6 \text{ g Cd ha}^{-1} \text{ y}^{-1}$. This figure compares to previous estimates for fertilizer Cd inputs to Australian soils by Tiller *et al.* (1994) of 1.5 to $3.0 \text{ g ha}^{-1} \text{ y}^{-1}$ and data for UK of $4.3 \text{ g ha}^{-1} \text{ y}^{-1}$ (Hutton and Symon 1986), 3.5 - $4.3 \text{ g ha}^{-1} \text{ y}^{-1}$ in Germany (Sauerbeck 1982; Kloke *et al.* 1984), $3.0 \text{ g ha}^{-1} \text{ y}^{-1}$ in Denmark (Hovmand 1981), 8.9 g Cd ha^{-1} in New Zealand (Bramley 1990), 0.3 - 1.2 g Cd ha^{-1} in USA (Mordvedt 1987) and an average for EEC countries of $2.5 \text{ g ha}^{-1} \text{ y}^{-1}$ (Biberacher and Shah 1990). However, where soils are heavily fertilized, Cd inputs may range up to $35 \text{ g ha}^{-1} \text{ y}^{-1}$. The range in Cd inputs values are consistent with measured increases in Cd concentrations in surface soils due to fertilization, e.g. up to 0.14 and 0.18 mg kg^{-1} soil for cereal and pasture soils, respectively, near Canberra (Williams and David 1973), and about 0.1 mg kg^{-1} for pasture soils near Adelaide (Merry and Tiller 1991). As fertilization is the major source of Cd in Australian soils, there is usually a significant relationship between soil Cd concentrations and soil P concentrations (Merry 1988 - Figure 1).

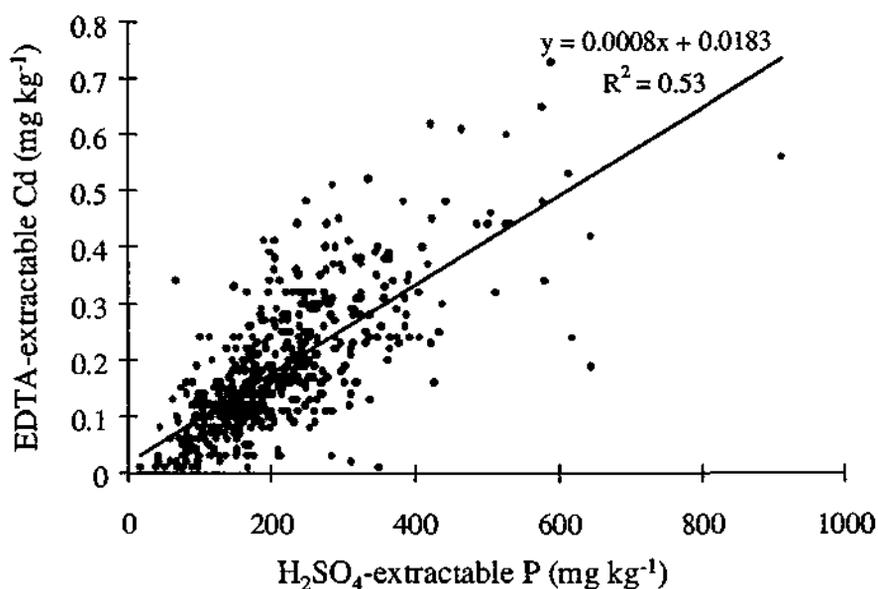


Figure 1. Relationship between extractable P and extractable Cd in a range of soils under pasture in South Australia (from Merry 1988).

The accumulation of Cd in soils from long term application of phosphatic fertilizers is now well documented in studies in many other countries (Mulla *et al.* 1980; Mordvedt *et al.* 1981; Isermann 1982; Smilde and van Luit 1983; Kofoed and Klausen 1983; Hansen and Tjell 1983; Rothbaum *et al.* 1986; Baerug and Singh 1990; Andersson and Siman 1991; Singh 1991). The

major difference between Cd inputs between Australia and European countries is that fertilizers provide the bulk of the Cd inputs to agricultural soils, whereas in Europe atmospheric inputs and sewage sludge or waste material sources may be appreciable. Many reports quote approximately equal inputs of Cd from atmospheric and fertilizer sources, a situation rarely applicable in Australia except near major urban centres.

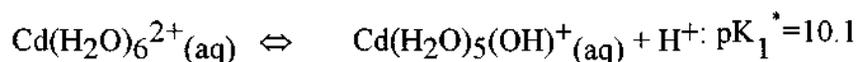
Behaviour of Cd in soil

The natural source of Cd in the soil and aquatic environment is through weathering of Cd-containing parent material and rocks. Under conditions of strong oxidation Cd forms oxidized minerals such as CdO and CdCO₃ (Goldschmidt 1958). Since the third ionization potential for Cd is extremely high, the most important valence state of Cd in the natural environment is +2.

The chemical form of Cd in phosphatic fertilizers has not been clearly identified. According to Williams and David (1973), granules of superphosphate when placed in contact with moist soil for 8 days lost all of their water-soluble P but still retained 60% of their original Cd. These investigators further showed that Cd in the water extracts was approximately proportional to Ca extracted, indicating that Cd was associated with Ca in both the phosphate and sulfate components of the fertilizer. In studies of the phytoavailability of Cd in triple superphosphate (TSP) and diammonium phosphate (DAP), Mordvedt and Osborn (1986) compared Cd uptake from these fertilizers to known Cd compounds. They concluded that Cd in phosphatic fertilizers has a similar phytoavailability to Cd(H₂PO₄)₂ or CdHPO₄, or a mixture of these salts.

Forms of Cd in soil solution

Following release into soil solution Cd²⁺ is rapidly partitioned between the mineral, organic and solution phases. In solution, Cd²⁺, like some of the other metal ions such as Zn²⁺, is associated with a sheath of water molecules (equation 1). The aquo ion is a strong Lewis acid which in the presence of moisture can dissociate a proton:



The high pK₁^{*} means that in most soil solutions which fall in the pH range 4.0-8.0, the concentration of Cd(OH)⁺ is 10² to 10⁶ lower than Cd²⁺.

Cadmium can be also be present in soil solution as a complex ion in association with other ligands, the most important in soil solutions being complexes with Cl⁻, SO₄²⁻, HCO₃⁻ or organic ligands (Table 4).

Cadmium may also associate with ammonium ions to form CdNH₃²⁺ or Cd(NH₃)₂²⁺, but these are only likely to form in the vicinity of dissolving DAP fertilizer granules, where pH and NH₃ concentrations may be high (Lindsay 1979).

Up until recently it was assumed that chloro-complexation was unlikely to be important in terms of Cd phytoavailability in agricultural soils (Chaney 1988), but now it is evident that complexes of Cd with both Cl⁻ and SO₄²⁻ are likely to be important in many saline soils (Hahne and Kroonjite 1973a). Indeed, given the composition of saturation extracts of a wide

range of saline soils in USA given by Jurinak and Suarez (1990), it is likely that Cl^- and SO_4^{2-} complexation of Cd^{2+} is significant in many saline soils (Table 5).

Table 4. Equilibrium association constants of Cd with selected inorganic anions (from Lindsay 1979).

Ligand	Complex	Log K^0
Cl^-	CdCl^+	1.98
	CdCl_2^0	2.60
	CdCl_3^-	2.40
SO_4^{2-}	CdSO_4^0	2.45
NO_3^-	CdNO_3^+	0.31
	$\text{Cd}(\text{NO}_3)_2^0$	0.00
H_2PO_4^-	CdHPO_4^0	-4.00
HCO_3^-	CdHCO_3^+	-5.73
	CdCO_3^0	-14.06
OH	CdOH^+	-10.10
	$\text{Cd}(\text{OH})_2^0$	-20.30

Table 5. Median concentrations of Cl^- and SO_4^{2-} anions in well waters, river waters and saturation extracts of a range of salt-affected soils in USA (from Jurinak and Suarez 1990) and impact on speciation of inorganic Cd in soil solution.

Ligand	Number of samples analysed	Median concentration ($\text{mmol}_c \text{ m}^{-3}$)	Percentage inorganic Cd complexed by ligand at median concentration (%)
Cl^-			
Sat. extract	139	34.8	65
Well water	115	2.5	17
River water	58	1.5	11
SO_4^{2-}			
Sat. extract	134	29.4	50
Well water	23	3.6	23
River water	58	4.1	25

Li *et al.* (1994) also recently found soil salinity to be an important factor in explaining high Cd concentrations in sunflower kernels in certain regions of USA.

In contrast to other trace metals such as copper or zinc, it would appear that organic ligands do not have great significance in the complexation of free Cd^{2+} in soil solutions. A number of studies have indicated that either the free Cd^{2+} ion or Cd complexed by inorganic ligands are the dominant Cd species present in soil solution of most agricultural and sludge-amended soils (Mahler *et al.* 1980; Behel *et al.* 1983; Emmerich *et al.* 1982; Tills and Alloway 1983; Fujii *et al.* 1983; Hirsch and Banin 1990; Holm *et al.* 1993). However, many of the above studies have examined soils in the absence of plant root activity. In the vicinity of plant roots, where organic anion concentrations may be high due to microbial activity or active excretion of organic ligands by plant roots (Merckx *et al.* 1986; Mench and Martin 1991), there is evidence emerging that a significant proportion of the total Cd in solution may exist as organo-

complexes (Hamon *et al.* 1994). This is certainly an area of work which requires further study.

Reactions of Cd with soil surfaces

The mechanisms involved in the retention of Cd^{2+} by iron and manganese oxide minerals, silicate clay minerals and whole soils have been under investigation for many years. These studies reveal that Cd may be retained through both precipitation and sorption processes. As far as precipitation of Cd is concerned, the common anions responsible for the precipitation of Cd are S^{2-} , CO_3^{2-} and PO_4^{3-} . All of these anions can form a range of compounds with Cd which differ in their solubilities and are sensitive to the pH of the system (Lindsay 1979). The precipitation of Cd occurs mainly under conditions of high anion concentrations and at high pH although CdS can form under acidic reducing conditions. The formation of CdCO_3 through precipitation processes has been reported in soils amended with sewage sludge (Soon 1981). There is sufficient evidence now to suggest that CdCO_3 can control Cd^{2+} activity in some very polluted calcareous soils (Street *et al.* 1977; Cavallaro and McBride 1978) and it appears that CdCO_3 provides a limit to Cd^{2+} solubility in soils of high pH. Tiller and co-workers (Brummer *et al.* 1983; Tiller *et al.* 1984a, b) suggested that trace metal concentrations in soil solutions are likely to be controlled by adsorption-desorption equilibria at low metal concentrations whereas precipitation-dissolution reactions become important only at higher metal concentrations when adsorption sites are limited. For most agricultural soils therefore, with relatively low Cd loadings, Cd^{2+} solubility is unlikely to be controlled by the dissolution of known Cd compounds (Lindsay 1979) but rather by sorption/desorption reactions.

Sorption processes can be separated broadly into 2 groups, depending on the affinity of the adsorbent for the adsorbates. When cations are bound by weak electrostatic forces simply to balance the negative charge on surfaces, the process is called 'non-specific sorption' and the Cd ions adsorbed in this way are equivalent to the well defined "exchangeable cations". These non-specifically sorbed Cd ions are easily replaced by ions from neutral salts such as NaCl, CaCl_2 etc. In the second type of sorption, ions are bound much more tightly to the adsorbent surface. This process is termed specific sorption and the sorbed Cd ions are much less easily removed from the surface (Hodgson *et al.* 1964).

Variation in Cd sorption properties has been related to soil characteristics which may vary in different geographical regions. Jenne (1968) reported that the sorption potential for divalent metals is determined primarily by the quantities of soil organic matter and oxides of iron and manganese present in the soil, because these phases have high affinity for metallic cations (Taylor and McKenzie 1966). The primary role of layer silicates may be to provide a substrate on which amorphous Fe and Mn oxide precipitate, although recent results by Zachara *et al.* (1992) suggest that the charge on the layer silicates themselves may be the principal force driving sorption of Cd. There is an extensive literature on the adsorption reactions of Cd with soils and their fine fractions. Many of the conclusions conflict. This may arise from use of local or regionally important soils with particular compositions, for example, dominated by either organic matter (humid temperate areas) or oxides (semi-arid or wet tropics). In addition, many researchers have used unrealistic experimental conditions which prejudice the outcome (see Hendrickson and Corey (1981) for discussion). Some soil properties controlling Cd behaviour are also difficult to measure. It is apparent from the variety of results that the relationship between Cd sorption and commonly measured soil properties may not provide a sound basis for predicting Cd mobility and availability. Much work needs to be done to

investigate whether a unified relationship exists between Cd sorption and soil properties for the range of soils conditions in Australia.

Effect of solution composition on sorption of Cd by soils

In addition to major soil characteristics, there are numerous other factors that influence the dynamic equilibrium between Cd in the soil solution and the sorbed phase. Some of these factors include solution pH, ionic strength, competing effect of other cations, inorganic and organic ligands.

With increasing pH there is a characteristic pH above which sorption of Cd increases rapidly (Garcia-Miragaya and Page 1978; Tiller *et al.* 1979; Christensen 1984a; Gerritse and van Driel 1984; Brummer *et al.* 1988; Basta and Tabatai 1992; Zachara *et al.* 1992; Naidu *et al.* 1994a). However, the effect of pH on sorption of Cd has been shown to be dependent on the Cd loading, the nature of the soil constituents and the Cd retention capacity of soils. It is generally accepted that the specific sorption of heavy metals by soil minerals is mainly related to the hydrolysis of the metal ion (Hodgson *et al.* 1964; Forbes *et al.* 1976).

The presence of certain divalent cations (e.g. Ca^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+}) retards the sorption of Cd by soils due to competition between Cd and the other metal ions (Christensen 1987a, 1987b; Homann and Zasoski, 1987). Many authors have reported greater sorption in the presence of Na^+ than Ca^{2+} ions (Garcia-Miragaya and Page 1976; Christensen 1984a; Boekhold *et al.* 1993; Naidu *et al.* 1994a). The lower sorption in the Ca^{2+} medium was attributed to the competition for sorption sites between Ca^{2+} and Cd^{2+} ions. This has relevance to sodic soils and changes in solution chemistry resulting from additions of gypsum. With reference to the trace metals, there have been many observations of the competition between sorption of Zn and Cd e.g. Tiller *et al.* (1979) and Christensen (1987a).

The influence of anions on Cd sorption has also been studied by a number of groups. Chloride generally reduces Cd sorption by soil (when total solution Cd concentrations are used to measure sorption) and has been identified as increasing the mobility of Cd through soils (Garcia-Miragaya and Page 1976; Doner, 1978; Egozy 1980; O'Connor *et al.* 1984; Boekhold *et al.* 1993). This is ascribed to chloro-complexation of Cd in solution (as discussed above). If solution Cd is corrected for chloro-complex formation, sorption is generally described better by considering Cd^{2+} activity only (Benjamin and Leckie 1982; Boekhold *et al.* 1993) indicating that Cd^{2+} is the preferred species sorbed by the surfaces (at constant pH). The addition of phosphate to solution appears to enhance Cd retention by soil. This effect may be related to precipitation of $\text{Cd}_3(\text{PO}_4)_2$ if P is added to the same solution as the Cd ions, or is due to enhanced sorption as evidenced by increased Cd retention of soils pretreated with P where precipitation of Cd phosphates is not expected (Kuo and McNeal 1984; Naidu *et al.* 1994b). $\text{Cd}_3(\text{PO}_4)_2$ is quite soluble and is not expected to be an important mineral phase in soils (Street *et al.* 1978) except ephemerally in the vicinity of fertilizer granules (Lindsay 1979). Effects of SO_4^{2-} on Cd sorption are less clear as SO_4^{2-} itself is a sorbing species in many soils and sorbed SO_4^{2-} impacts a greater negative charge than Cl^- to the sorbing surface (Benjamin and Leckie 1982; Gessa *et al.* 1984). Garcia-Miragaya and Page (1976) found that increasing SO_4^{2-} concentrations in solution moderately reduced Cd sorption by soil. Benjamin and Leckie (1982) found that increasing SO_4^{2-} concentrations in solution also reduced Cd sorption by model oxides (amorphous iron oxide, silica and gibbsite) and had no effect on Cd sorption by lepidocrocite. Hoins *et al.* (1993) found increasing concentrations of SO_4^{2-} enhanced Cd sorption by goethite. The effects of SO_4^{2-} on Cd sorption will therefore depend on the nature

of the sorbing surfaces present in soil (Naidu *et al.* 1994b). Similar conflicting results have been associated with the effect of soluble organic anions on Cd sorption in soils where organic anions can reduce Cd^{2+} activities in solution and also change the affinity of the sorbing surface for Cd^{2+} (Elliot and Denny 1982; Ram and Verloo 1985; Neal and Sposito 1986). This makes broad generalisations on the effect of ligands in solution on the sorption of soil Cd much more difficult (Harter and Naidu 1995).

“Fixation” of soil Cd

Many investigators have demonstrated that the ease of extraction of applied nutrients and other elements becomes increasingly difficult with increasing periods of reaction with soils. This is often termed “fixation” although the process is not irreversible as the name implies, merely that the rate of desorption is slower than the rate of adsorption (Barrow 1987). This increased retention of added metal ions has been attributed to reactions within the surface layer or inside the structure of minerals. Studies by Brummer and his co-workers (Brummer *et al.* 1988) show that a slow diffusion of heavy metals into the structure of goethite is possible. Such a mechanism may be one of several processes that could explain why ions added to soils become increasingly difficult to desorb and become less available with time. In comparison to other metals, the rate at which Cd becomes firmly bound is not as great as for Zn and Ni (Christensen 1984b, Brummer *et al.* 1988).

Mobility of Cd

The mobility of Cd depends on the quantity added, local environmental conditions such as soil type, soil characteristics, land use, climate etc. and the nature of interactions between the soil solid phase and added Cd. Generally, sorption is the main process that determines the amount of Cd available for leaching since it controls the amount of Cd in soil solution (Boekhold and van Der Zee, 1992). Thus, soil and solution factors that influence sorption reactions (pH, clay type, solution concentrations of Cl^- , SO_4^{2-} , etc.) will also impact mobility of Cd in soils (see above).

Rothbaum *et al.* (1986) reported that leaching losses of Cd may be significant for some New Zealand and British soils. Significant Cd leaching (50%) was inferred from a balance of Cd recovered in the soil versus estimated Cd inputs. As Rothbaum *et al.* did not indicate the extent of analytical/soil variability in relation to the absolute Cd values presented, it is difficult to assess if the differences noted between inputs and Cd recovered can be attributed solely to leaching losses. Furthermore, uncertainties in terms of Cd inputs in fertilizers may constitute a large proportion of the Cd unaccounted for in these experiments.

Leaching losses Cd could be significant in some areas of Australia e.g. soils used for horticulture, although there are no field data to confirm this. Often these areas, which are close to major cities, are on light textured coastal sands with little retention capacity for Cd. Furthermore, these sandy soils are often heavily fertilized as they are preferred for production of vegetables such as carrots, onions and potatoes due to ease of working, harvesting and free draining characteristics. Leaching of Cd, especially from highly contaminated soils poses a threat to groundwater quality. Boekhold and Van der Zee (1992) simulated the long term leaching behaviour of in a sandy Dutch soil. They reported that leaching of Cd from areas receiving high input of Cd ($50 \text{ g ha}^{-1} \text{ y}^{-1}$) can result in the official Dutch reference levels for groundwater being exceeded. However, the concentration of Cd added through fertilizer

applications in Australia are generally below the limit of $50 \text{ g ha}^{-1} \text{ y}^{-1}$ proposed by Boekhold and Van der Zee (1992) for sandy soils. Given that many Australian agricultural soils are either clayey or have dense clayey subsurface soils, the mobility of Cd to groundwaters from fertilizer applications will be limited. However, movement of Cd from surface sandy horizons to layers below the zone of root Cd uptake may be important in some situations, thus reducing the subsequent availability of Cd to plants.

Plant uptake of fertilizer Cd from soil

It is generally thought that the chemical form of Cd taken up by plants is the free uncomplexed Cd^{2+} ion present in soil solution (for reviews see Chaney 1988 and Parker *et al.* 1994). Thus, any treatments or changes in soil conditions which affect the concentration (or activity) of the Cd^{2+} ion will affect plant accumulation of Cd. The soil and plant factors controlling Cd uptake from soils have been extensively studied and reviewed (Page and Bingham 1973; Chaney and Hornick 1978; Davis and Coker 1980; Page *et al.* 1987; Alloway 1990; Jackson and Alloway 1992). Table 6 summarises the factors listed by Chaney and Hornick (1978) as affecting plant uptake of Cd from soil.

Table 6. Factors affecting Cd uptake from soil (from Chaney and Hornick, 1978).

Any factor affecting Cd^{2+} activity
<u>Soil</u>
1. pH.
2. amount of Cd present.
3. metal sorption capacity of soil
a. organic matter
b. cation exchange capacity
c. clay, Fe and Mn oxides.
4. other micronutrients: Zn, Cu, Mn.
5. macronutrients: NH_4 , PO_4 , K.
6. temperature, moisture content, compaction.
7. aeration; flooding = CdS.
8. recurrent vs single application.
<u>Crop</u>
1. species and cultivar.
2. plant tissue: leaf > grain fruit and edible root.
3. leaf age: older > younger.
4. metal interactions.

Most of the above reviews focus on the Cd contamination of soils by addition of sewage sludges to land, with assessment of subsequent plant uptake of added Cd. Many of the soil factors discussed also apply to the behaviour of fertilizer-derived Cd, although the amounts and form of Cd added in sewage sludge may lead to very different reactions in the soil which affect plant uptake of metals.

Soil factors affecting Cd uptake by plants

Soil acidity (pH)

Soil pH is often regarded as the major variable controlling plant uptake of Cd from soils (Chaney and Hornick 1978). Increasing acidity (reducing pH) in solution culture has, however, been found to depress Cd uptake by plants, due possibly to competition between H^+ and Cd^{2+} for uptake (Tyler and McBride 1982; Hatch *et al.* 1988). Accordingly, the pH effects on Cd availability in soils are largely ascribed to the large effect of pH on the retention of Cd^{2+} by soil surfaces. Results from many glasshouse and laboratory liming experiments have confirmed that soil pH has a major effect on Cd uptake by plants (John 1972b; Andersson and Nilsson 1974; CAST 1976; Miller *et al.* 1976; MacLean 1976; Williams and David 1976; Reddy and Patrick 1977; Chaney and Hornick 1978; Street *et al.* 1978; Eriksson 1989; Gorlach and Gambus 1991; Jackson and Alloway 1991). Some of these studies used soils with Cd added as an inorganic salt to enhance treatment effects (John 1972b; Miller *et al.* 1976; MacLean 1976; Williams and David 1976; Street *et al.* 1978; Eriksson 1989) or the Cd was added in sewage sludge (Andersson and Nilsson 1974; Street *et al.* 1978; Giordano *et al.* 1979; Gorlach and Gambus 1991; Jackson and Alloway 1991).

Field data on effects of liming on Cd uptake have also been reported from surveys of sludge-contaminated soils (Chumbley and Unwin 1982; Alloway *et al.* 1990) or normal agricultural soils (Eriksson 1990a; Sillanpaa and Jansson 1992; He and Singh 1993) where plant Cd concentrations were related to field soil properties and soil pH was found to be (negatively) correlated with Cd concentrations in the plant. Data on the effectiveness of reducing crop Cd concentrations with lime under field conditions are less conclusive. Some authors report significant reductions in crop Cd concentrations with lime under field conditions (CAST 1976; CAST 1980; Mordvedt *et al.* 1981) but compared to glasshouse trials the differences noted due to liming under field conditions are inconsistent and of a smaller magnitude (Tiller *et al.* 1994; Oliver *et al.* 1994a). In other studies, lime has little or no effect on crop Cd concentrations in both sludge-amended soils (Pepper *et al.* 1983) and fertilized agricultural soils (Jaakkola 1977) and in some sites may even increase crop Cd concentrations (Andersson and Siman 1991). It is possible that in these situations the soils have a fairly low affinity for Cd and minimal changes in affinity with pH, so that the small increase in Cd^{2+} retention by the soil surfaces due to increasing pH is largely offset by the increased Ca^{2+} concentrations in solution competing with Cd for sorption sites and increasing solution Cd^{2+} . However, this hypothesis requires validation.

Soil Cd concentrations and affinity of soil for Cd

The total Cd concentration in the soil has been found to be of equal importance to soil pH in many studies examining plant Cd uptake (John *et al.* 1972b; Lund *et al.* 1981; Chumbley and Unwin 1982; Jackson and Alloway 1991; Sillanpaa and Jansson 1992; He and Singh 1993). Generally, the higher the Cd concentration the greater the plant Cd concentration.

The interaction between plant Cd uptake and soil affinity for Cd is through the control of Cd^{2+} activity in soil solution. As previously discussed, high affinities for Cd^{2+} will tend to reduce the activity of Cd^{2+} in the soil solution after Cd dissolves from the fertilizer granule and therefore reduces the phytoavailability of inorganic Cd added to soil (John *et al.* 1972b; Haghiri 1974; Miller *et al.* 1976; Chaney and Hornick 1978; Hinesly *et al.* 1982).

Soil micronutrient status

Another important factor controlling Cd accumulation by plants is the micronutrient status of soils, particularly Zn. Chaney and Hornick (1978) review early data on Cd:Zn interactions and recently Tiller *et al.* (1994) reviewed more recent data. Most studies of effects of Zn on Cd uptake have been in glasshouse experiments, often at high concentrations of both Cd and Zn (John *et al.* 1972b; Haghiri 1974; MacLean 1976; Williams and David 1976; White and Chaney 1980) and results have not been conclusive (Tiller *et al.* 1994). In Australia, Oliver *et al.* (1994b) recently demonstrated that treatment of Zn deficiency or near-deficiency in field wheat crops by the application of small amounts of Zn ($<10 \text{ kg Zn ha}^{-1}$) significantly reduced grain Cd concentrations (Figure 2).

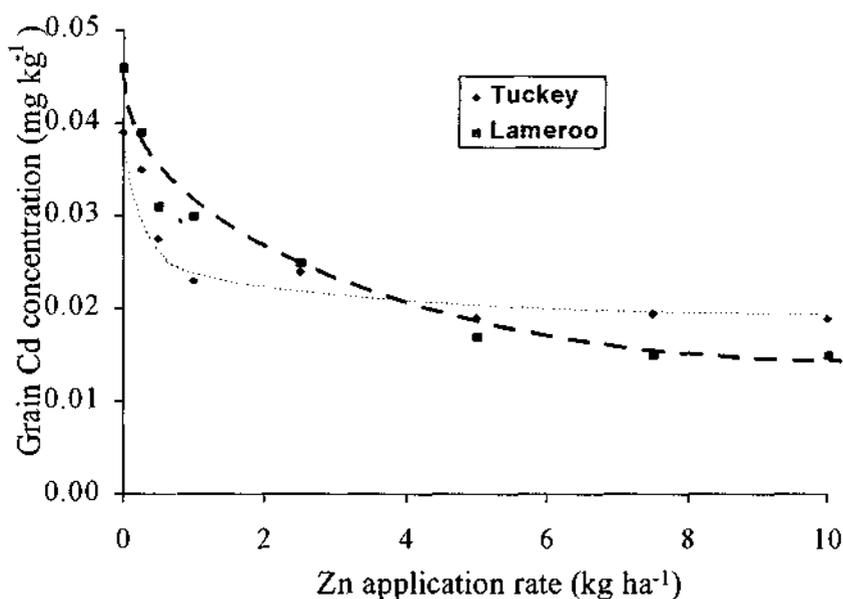


Figure 2. Effect of small applications of Zn on grain Cd concentrations in wheat at 2 sites in South Australia. (from Oliver *et al.*, 1994b).

The mechanism responsible for this has not been determined, but may be related to either the loss of root membrane integrity where plants are Zn deficient, or related to increased Cd availability induced by release of chelating agents from roots when under Zn stress.

Soil salinity

Soil salinisation can be caused by either additions of chloride or sulfate salts in irrigation waters, or by the rise to the surface of these salts in groundwaters (dryland salinisation). Generally the dominant cation in such systems is Na^+ and the dominant anion Cl^- , although some regions may have sulfate- or bicarbonate-rich waters (Jurinak and Suarez 1990). As discussed previously, Cl concentrations in soil may reach concentrations in soil solution sufficiently high to lead to significant complexation with Cd, which reduces Cd sorption and increases total Cd concentrations in soil solution. Previously, it has been demonstrated in glasshouse pot experiments that Cd uptake by Swiss chard was considerably enhanced by Cl salts, where $\text{Cd}(\text{NO}_3)_2$ was added to soil in combination with NaCl and CaCl_2 , (Bingham *et al.* 1983, 1986). However, Bingham *et al.* (1984) found that Cd concentrations in plants were related to Cd^{2+} activities in soil saturation extracts, indicating the salt effect in their work was

due to ion exchange of Ca and Na for Cd, rather than chloro-complexation of Cd. This illustrates the need to work at realistically low Cd concentrations in soil, as the affinity of Cd for soil surfaces will decrease as the surface coverage increases, thus allowing ions such as Ca^{2+} or Na^+ to compete with Cd for sorption sites. Sulfate salinity has been reported to have little impact on plant Cd uptake in both acidic and limed soils (Bingham *et al.* 1984) although the results of this study were unusual in that liming significantly increased Cd concentrations in solution, yet plant Cd concentrations were decreased.

Other factors - macronutrients

Other factors identified as affecting plant uptake of Cd from soils have been soil temperature (Giordano *et al.* 1979; Tiller 1988; Hooda and Alloway 1993), redox potential (Bingham *et al.* 1976; Reddy and Patrick 1977) and addition of macronutrients P and N (John *et al.* 1972; Miller *et al.* 1976; Maclean 1976; Williams and David 1976, 1977; Jaakkola 1977; Eriksson 1990b; Gorchach and Gambus 1991; Willaert and Verloo 1992). Soil temperature and soil redox potential are factors over which there is little control, but additions of N and P to soils, in terms of amounts and chemical form, may be altered by farm management practices. For example, Williams and David (1976) found that wheat crops fertilized with superphosphate and ammonium nitrate accumulated more Cd than crops fertilized with superphosphate only (Figure 3).

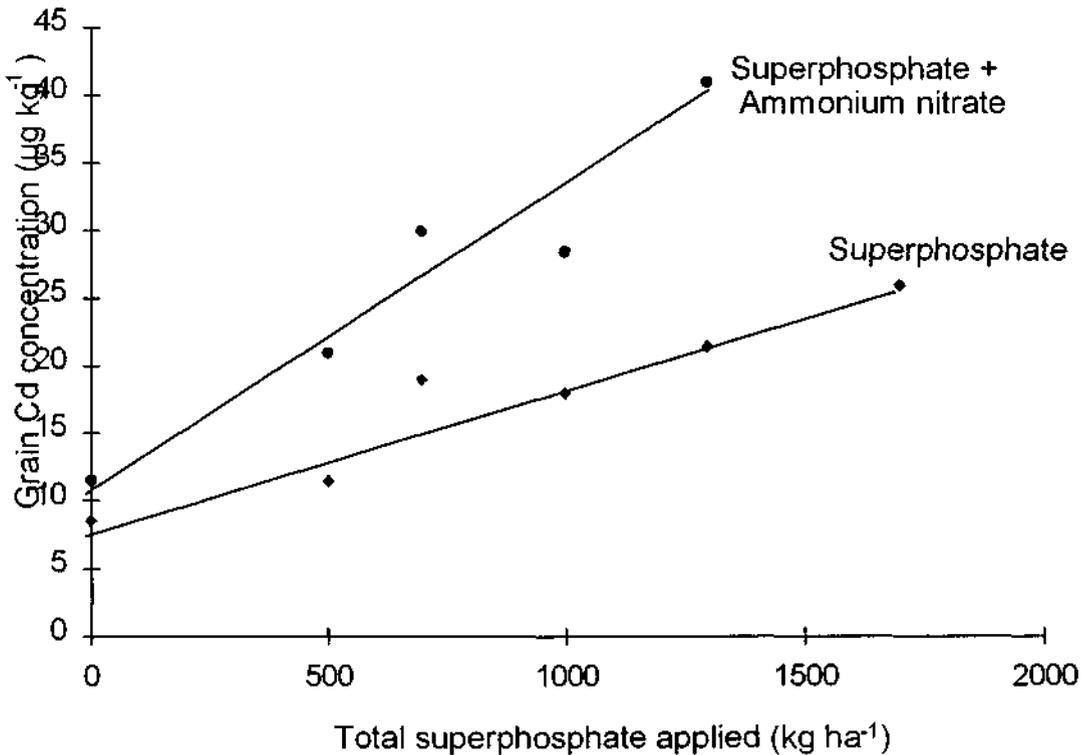


Figure 3. Relationship between total superphosphate applied (over 5 years), nitrogen fertilizer application and grain Cd concentration in field-grown wheat (from Williams and David 1976).

In glasshouse experiments, there are indications that the form of N fertilizer applied is important in terms of controlling Cd uptake by plants. Eriksson (1990b) and Willaert and Verloo (1992) both demonstrated in glasshouse experiments that the more acidifying N fertilizers, such as ammonium sulfate, increased Cd uptake over those having an alkaline effect in soil (Ca nitrate). Similar results have been obtained by Reuss *et al.* (1978) comparing banded superphosphate to banded diammonium phosphate (DAP) in pot trials. They suggested the effect was due to pH changes in the fertilizer band. Waggan *et al.* (1978) and Levi-Minzi and Petruzzelli (1984) were able to show that the alkaline reaction products of DAP dissolution increase Cd retention by soil (compared to mono-ammonium phosphate), thus confirming the results of Reuss *et al.* (1978). High concentrations of all soluble salts in the vicinity of the granules of most fertilizer types may also be expected to increase Cd concentrations in solution through competitive cation exchange (Andersson 1976), provided the solubility product of Cd phosphate ($\log K = 38.1$) is not exceeded. However, there are no data from field experiments which support these findings.

The effect on plant Cd uptake of adding P (without Cd) to soils has also been studied, as well as placement of P in the root zone in glasshouse experiments (Williams and David 1977; Reuss *et al.* 1978). Williams and David (1977) noted that adding P to a soil increases Cd uptake through a stimulation of root proliferation in the zone into which P is added.

Changes in phytoavailability of soil Cd with time

There is conflicting evidence in the literature on the effect of time of contact between soil and Cd on Cd availability. This contrasts with the behaviour of other trace metals such as zinc or nickel which continue to be more strongly bound to soil with time and have reduced phytoavailability with time (Christenssen 1984b; Barrow *et al.* 1989). These so-called "slow" reactions between metals and soil have been discussed previously and relate to the "residual value" for plant growth of an element added to soil. Where the element continues to react with soil the slow reactions are significant and the residual value is low e.g. P, Zn. Where the slow reactions are less significant the residual value is high e.g. Cd. This aspect of Cd behaviour is critical to the discussion of critical levels in soils, for if Cd continues to lose "availability", i.e. has lower plant Cd uptake for a given Cd loading, then higher Cd loadings to soil can be tolerated and critical soil concentrations can be set higher. However, if Cd retention by soil surfaces is fully reversible i.e. no continuing slow reactions reducing availability, then critical levels in crops will be attained sooner given current Cd inputs. Support for the hypothesis that the phytoavailability of Cd does not decrease with time is seen in the data of Eriksson (1989) and Jensen and Mosbæk (1990). The latter authors in particular were able to compare Cd in 200 year-old soils (recently exposed by house demolition) to adjacent soil subject to atmospheric contamination over the last 200 years. Using fertilizer labelled with radioactive Cd, they were able to demonstrate that current fertilizer Cd, Cd added from atmospheric sources (predominantly over the last 50 years) and fertilizer Cd are equally available to plants. Eriksson (1989) studied Cd uptake by ryegrass (*Lolium perenne*) and winter rape (*Brassica napus*) over a 2-year period in a glasshouse experiment and found no significant reduction in the availability of either native Cd in the soil or Cd added as CdCl₂ at the start of the experiment.

By contrast, Brams and Anthony (1988) investigated Cd uptake by wheat under field conditions over a 6 year period after adding CdCl₂ to the soil at rates up to 7.5 kg Cd ha⁻¹. They found that grain Cd concentrations decreased markedly with time but their data also

indicated that 80% of the Cd added initially was not recovered (by 1M HCl) in the soil (sampled to 75 cm) after 6 years. As less than 100g Cd could have been removed in the wheat grain harvested over the 6 year period and Cd was not detected above background concentrations at depth (75 cm), it suggests that Cd was lost from the plots by surface or subsurface movement of soil particles. Hooda and Alloway (1993) recently presented data on changes in phytoavailability of Cd in sludge- and Cd(NO₃)₂-amended soils. Their data indicated that phytoavailability of Cd added as Cd(NO₃)₂ declined only marginally over the course of the experiment (1 year) and the results were not consistent for all treatments.

Measurement of the long term phytoavailability of fertilizer Cd is critical to discussion of metal limits on soils, fertilizers or sewage sludges. Further work should be directed to determining the long-term decline (if any) in Cd phytoavailability with time in a range of soils and definition of the soil properties which enhance these reactions.

Other soil factors affecting Cd uptake by plants are related to agronomic practices such as tillage, crop rotations and other management factors such as residue handling. These may influence a number of physical and chemical factors in soil which could affect Cd uptake from soil. For example, work in this laboratory has identified that wheat crops grown in rotation with lupins generally have higher grain Cd concentrations than wheat grown after other cereals or pasture (Oliver *et al.* 1993). The reasons for this phenomena are currently under investigation.

Plant factors affecting Cd uptake by crops

It has been known for some time that different crop species and cultivars within species accumulate Cd to different degrees if grown on the same soil (Chaney and Hornick 1978; Davis and Coker 1980) and on highly contaminated soils this may be the only management approach which will permit crop growth. In general, leafy vegetables such as silver beet, spinach, lettuce, etc. are Cd accumulators, whereas cereals tend to exclude Cd from their grain. Chaney and Hornick (1978) and Davis and Coker (1980) have both compiled a list of the relative abilities of various species to accumulate Cd.

Cultivar differences in Cd uptake have been reported for a number of food crops (Davies and Lewis 1985), including wheat (Pettersson 1977; Tiller *et al.* 1994), maize (Hinesly *et al.* 1978), barley (Chang *et al.* 1982), rice (Morishita *et al.* 1987), lettuce (Thomas and Harrison 1989), carrots (Harrison 1986), potatoes (Harris *et al.* 1981; Isermann *et al.* 1983) and soybean (Chaney *et al.* 1993).

Conclusions

While many experiments have investigated the behaviour of Cd in soils and Cd uptake by plants, many of these studies have been conducted under unrealistic conditions where significant amounts of Cd have been added to soil to enhance treatment effects. However, reactions of Cd in soil and plant uptake of Cd present in soil may be markedly different where Cd is present in only trace quantities, as is the case normally. There is a need to validate and test under field conditions many of the management options suggested for minimising Cd accumulation by crops.

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APPENDIX 2 Methods of chemical analyses and uptake of Cd by potato plants as affected by stage of growth.

Introduction

Prior to investigation of effects of management on Cd uptake by potatoes, various preliminary methodological studies were undertaken to ensure analyses were valid. The methods outlined below were developed as a result of a coordinating workshop on Cd in potatoes held at CSIRO Division of Soils in October 1991.

Methods

Tubers were rinsed free of soil in tap water, with adhering soil gently removed using a nylon brush. Tubers were then rinsed a second time in clean tap water and finally in Cd-free distilled water. Tuber skin was carefully removed from each tuber slice, ensuring as little flesh as possible was removed with the skin. 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. Concentrations of Cd in a tuber slice were found to be identical to that of the whole tuber.

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 then weighed, dried at 70°C for 48 hours and reweighed. Dried tuber material was ground (<500 µm) using a stainless steel mill. Internal standards were also passed through the mill to check for contamination. Concentrations of Cd in dried, ground tuber material were found to be identical to concentrations determined in undried, homogenised tuber flesh indicating no contamination during sample drying and grinding.

Subsamples (0.5 g) of the dried tuber material were digested with a mixture of concentrated nitric (6 ml) and perchloric acids (1 ml) until the digest mixture was clear. The digest solution was diluted to 20 ml using 0.016M nitric acid. All samples were digested in duplicate with blanks and internal reference materials 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 using graphite furnace atomisation and deuterium background correction. Orthophosphoric acid was used as a modifier.

As part of a quality assurance program to ensure consistent Cd data between laboratories, 2 homogenised materials were circulated to various laboratories for analysis.

Results

Accuracy of the method for Cd determination was confirmed by analysis of the reference materials. Concentrations ($\mu\text{g kg}^{-1}$) of Cd in the rice and cabbage reference materials were 310 ± 20 ($n=21$) and 190 ± 10 ($n=7$), respectively, with certified concentrations of 320 ± 20 and 230 ± 40 , respectively.

In this study all tuber Cd concentrations are reported on a FW basis, either as $\mu\text{g Cd kg}^{-1}$ or as mg Cd kg^{-1} . Typically, the dry matter percentage of tubers ranged from 15 to 25% and differences in dry matter between cultivars did not change their tuber Cd ranking.

There was good agreement between laboratories on the Cd analysis of the homogenised tuber samples (Table 1).

Field and glasshouse sampling

In the field soils were sampled from the same length of crop row from which tubers were removed. Soil in the row down to the furrow depth was thoroughly mixed and a one kilogram sample taken by compositing four subsamples. As potato growers normally bank up the top 150 mm soil into rows during crop growth, this sample is subsequently referred to as topsoil, and included the residues of any fertilizer banded at planting. The topsoil was pushed aside and a minimum of four subsamples of soil taken to a depth between 150 -300mm using a stainless steel auger and composited into a single sample. These samples are subsequently referred to as subsoils.

Table 1. Cadmium concentrations in two homogenised potato materials as determined by a number of laboratories.

Laboratory	No. of analyses	Cadmium concentration ($\mu\text{g kg}^{-1}$)			
		Sample 1		Sample 2	
		Mean	SD	Mean	SD
CSIRO (1)	142	213	19	99	8
CSIRO (2)	2	200	5	105	4
SA SCL	5	198	7	88	2
NSW Agric.	nr	210		100	
QDPI (3)	nr	228		101	
QDPI (4)	nr	200		93	
Tas. DPI	nr	230		120	
Vic. SCL	2	190	28	90	0

1 $\text{HNO}_3 + \text{HClO}_4$, GFAAS.

2 as above plus back extraction using APDC and DIIBK.

3 $\text{HNO}_3 + \text{HClO}_4$, ASV.

4 $\text{HNO}_3 + \text{H}_2\text{O}_2$, GFAAS

Soil sampling and analysis

In glasshouse experiments soils were sampled generally after crop growth by mixing all soil in the pot and taking a 500 g sample for analysis.

Soils were air-dried and crushed to pass a 2 mm sieve prior to analysis.

Chemical analysis

Soil pH and EC were measured in a water suspension of each soil using a soil:water ratio of 1:5. Water-extractable Cl was determined in the 1:5 soil:water extract using an automated ferricyanide method (APHA, 1985). Particle size analysis was by the pipette method after carbonates and organic matter had been removed from the soils using acetic acid and hydrogen

peroxide, respectively (Day, 1965). Exchangeable cation concentrations were determined using the 1M NH_4Cl leaching procedure with an alcohol pre-wash to remove soluble salts (Rayment and Higginson, 1992). Total-C was measured using a LECO furnace (Rayment and Higginson, 1992). Bicarbonate-extractable P was determined according to the method of Colwell (1963) and K was measured in the same extracts by flame atomic emission spectroscopy. EDTA -extractable Cd and Zn concentrations in soil were determined according to the method of Clayton and Tiller (1979).

Concentrations of Cd and Zn in extracts were determined using a Varian Spectra AA-40 flame atomic absorption spectrophotometer using deuterium background correction. Concentrations of P in extracts were determined using the method of Murphy and Riley (1962).

Effect of growth stage of potato plants and size of potato tubers on Cd uptake

Methods

One field trial was established at Balhannah (Adelaide Hills, SA) with SA DPI (collaborator Chris Williams) to investigate the influence of growth stage and plant development on Cd uptake and translocation. A commercial crop was intensively sampled throughout its growth cycle and plant components separated and analysed for Cd concentrations.

To examine the relationship between size and tuber Cd concentration a total of 85 tubers ranging in fresh weight from 40g to 890g were sampled from a 20m by 40m area in a commercial crop of cv. Kennebec. Tuber size was noted and Cd concentration determined as outlined previously.

Results

There appeared to be a linear increase in Cd content of potato stems and leaves, while tuber and stolon Cd concentrations were relatively constant throughout the growth cycle (Figures 1, 2 and 3). Cd concentrations in above ground tissue was significantly higher than below ground tissue.

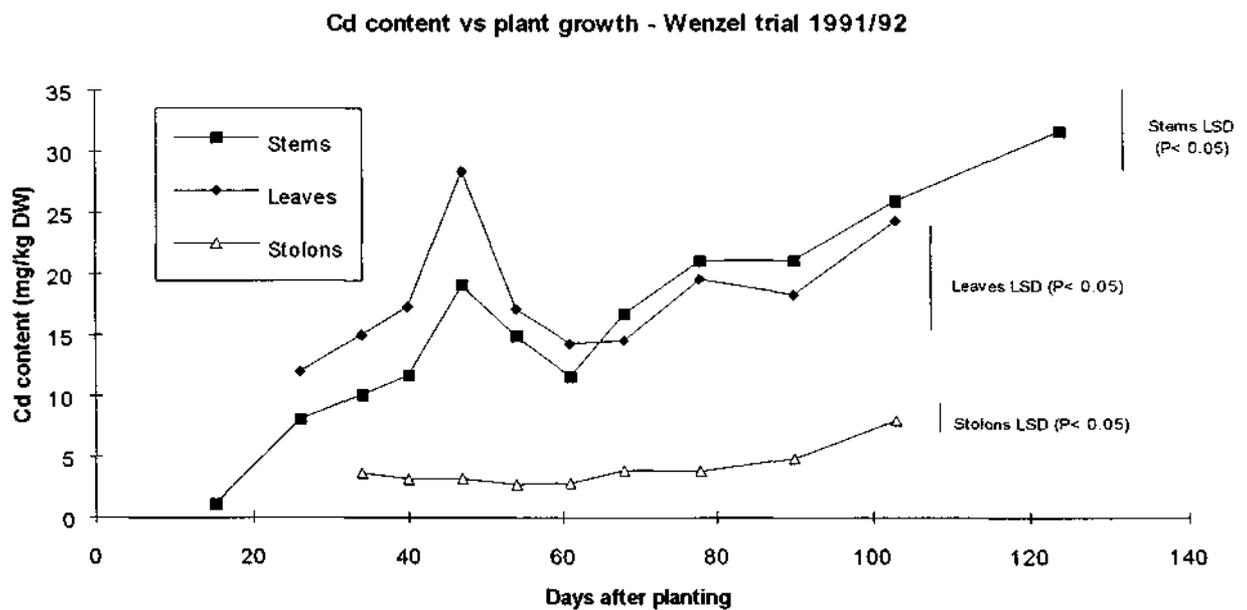


Figure 1. Changes with growth in Cd concentrations in leaves, stems and stolons of potato plants.

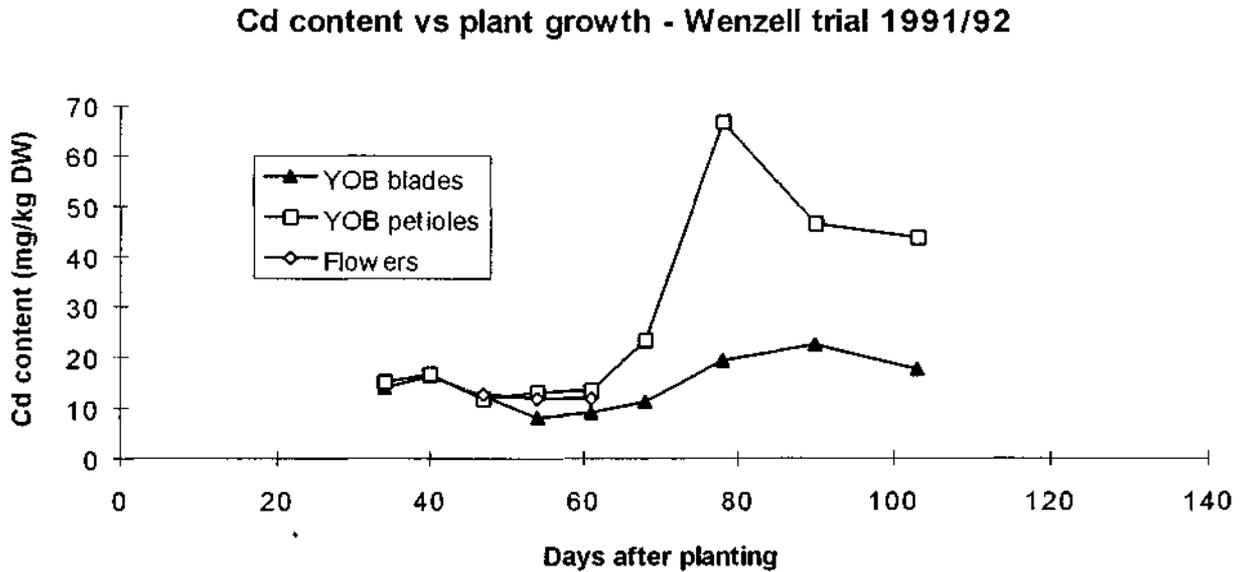


Figure 2. Changes with growth in Cd concentrations in youngest open leaf blades (YOB), petioles and flowers potato plants.

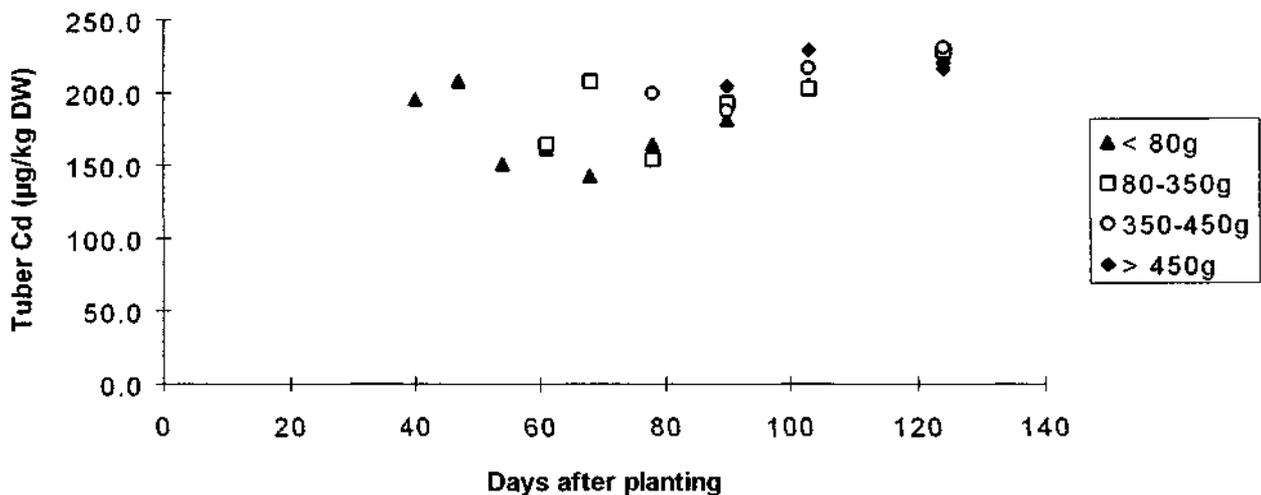


Figure 3. Changes with growth in Cd concentrations in size classes of potato tubers.

The data suggest that Cd is a xylem-translocated element, moved by the transpiration stream. One consequence of this is the difficulty of using plant parts as predictors of tuber Cd concentrations at maturity - the time and growth stage at sampling will alter the critical values markedly. A further implication of the above data is that if the trends found are common to all varieties and growing conditions, an early indication of tuber Cd concentrations at crop maturity made be gained by analysis of the small tubers formed at 40 days after planting.

There was no apparent effect of tuber size on tuber Cd concentrations (Figure 4). More variation in tuber Cd concentrations were found with smaller tubers, thus indicating that use of small tubers early in the growth cycle to predict final tuber Cd concentrations (as discussed above) may be subject to error due to field variability. The Cd data contrast to data for tuber concentrations of Ca (Figure 5), regarded as immobile in plants, but with similar ion size and charge to Cd, and to Zn (Figure 6).

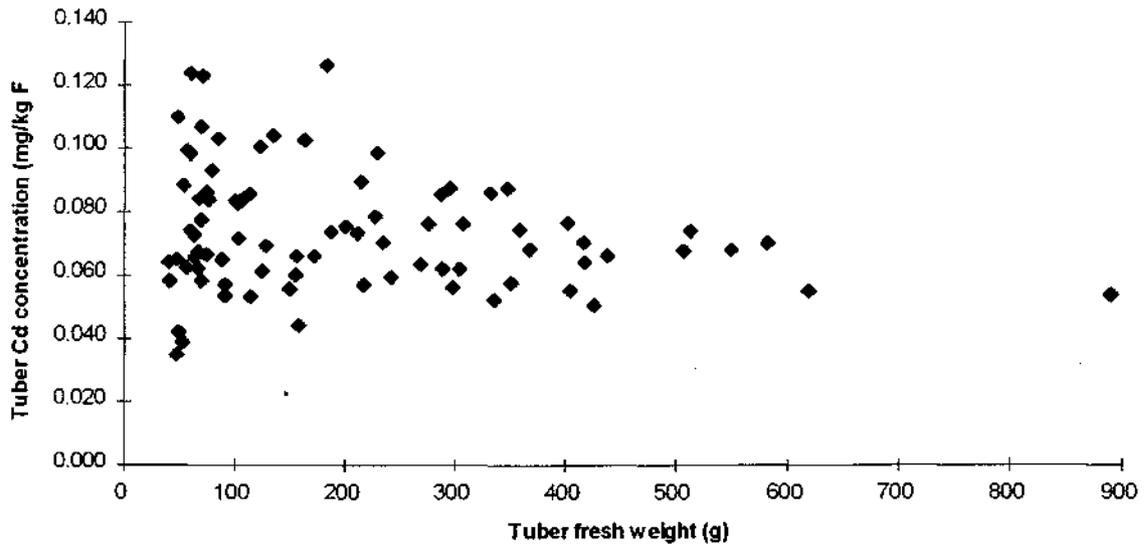


Figure 4. Relationship between tuber size and tuber Cd concentration.

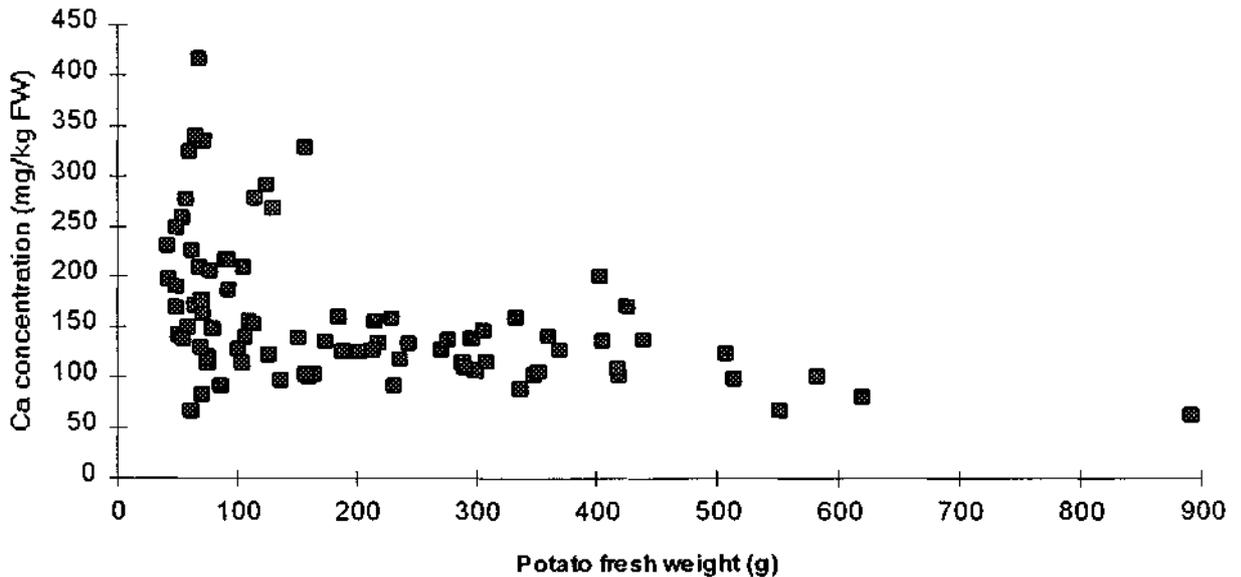


Figure 5. Relationship between tuber size and tuber Ca concentration.

Preliminary glasshouse studies were initiated to attempt to grow potatoes in solution or sand/solution culture but were discontinued as the CSIRO collaborator (Dr Ross Nable) on this part of the project was transferred interstate. Initial experiments were successful in that a system was devised for growing potatoes through to maturity in sand/solution culture.

Removal of tuber skin reduced whole tuber Cd concentrations, but the effect was related to tuber cultivar. Cadmium concentrations in some cultivars was unaffected by removal of skin prior to analysis, while in others the effect was significant e.g. 35% reduction in Kennebec Line 2 (Table 2).

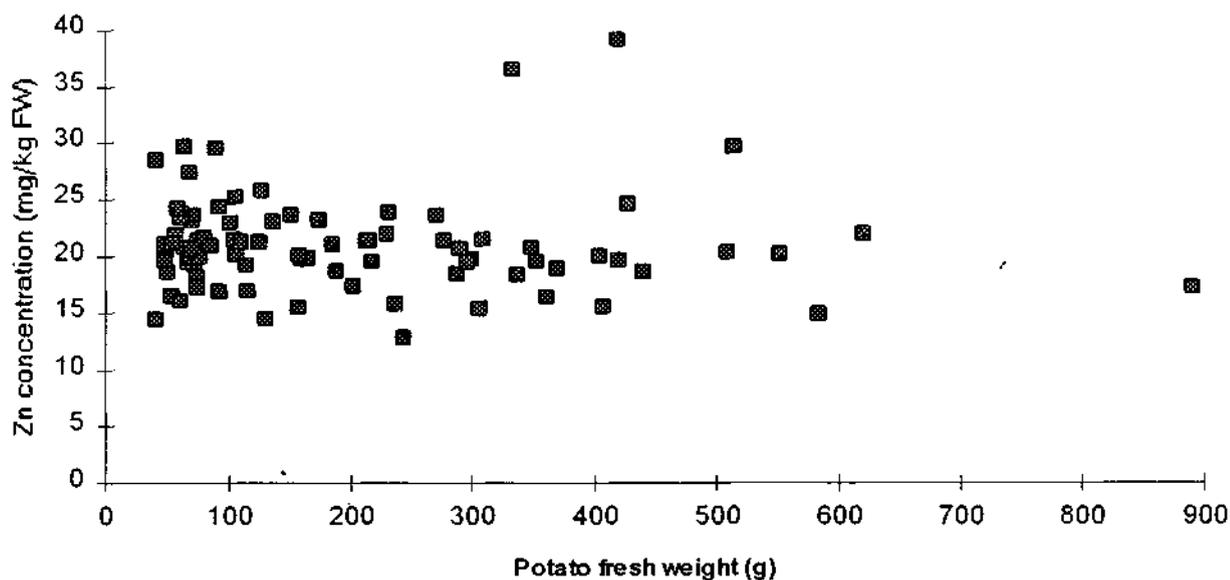


Figure 6. Relationship between tuber size and tuber Zn concentration.

Table 2. Cadmium concentrations in tuber flesh and skin of various cultivars.

Cultivar	flesh	skin
Atlantic	0.038	0.059
Crystal	0.048	0.052
Denali	0.051	0.061
Desiree	0.041	0.059
Kennebec line 2	0.053	0.082
Lemhi russet	0.029	0.039
Nooksack	0.042	0.045
Patrones	0.052	0.066
Pontiac	0.042	0.063
Russet burbank	0.041	0.042
Sebago	0.044	0.055
Shepody	0.043	0.048
Snowchip	0.044	0.062
Tarago	0.036	0.048
Toolangi delight	0.060	0.080
Wilcrisp	0.051	0.068
Winlock	0.036	0.052
Yankee chipper	0.050	0.052
	LSD (P<0.05)=0.019	

Conclusions

Methods of preparation of tuber material for analysis were agreed between the various laboratories investigating Cd uptake by potatoes.

Methods of analysis of tuber material for Cd appear to be straightforward and there was good agreement between participating laboratories for two standard potato materials.

Concentrations of Cd in potato tubers seem to be unaffected by stage of growth, indicating that early indications of tuber Cd concentrations can be gained by analysis of young tubers. However, variability between individual tubers may be large when tubers are small, necessitating that a large numbers of tubers be sampled to gain a close estimate of final tuber Cd concentration. Concentrations of Cd in above ground plant parts increased with plant growth stage and high concentrations of Cd were observed in the leaves and petioles. As the concentrations of Cd in petioles increased with plant growth, whereas tuber Cd concentrations did not, sampling of petioles to indicate tuber Cd concentrations may be inadvisable as stage of plant growth is critical and would introduce significant variation into any relationship obtained.

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APPENDIX 3 Effect of cultivar on Cd uptake by potatoes.

Given the need to control Cd uptake by agricultural crops, various soil and crop management factors require evaluation for their ability to reduce Cd uptake by potatoes. Cultivar differences in Cd uptake may provide a useful management tool to restrict Cd accumulation in tubers. This study presents data from cultivar evaluation trials throughout Australia and indicates the current Cd uptake characteristics of commercial potato cultivars.

Methods

Field experiments

Potato tubers were collected from 3 cultivar evaluation trials in Western Australia, 1 in Northern Territory, 4 in South Australia, 2 in Queensland, 1 in New South Wales and 1 in Victoria. Locations of the trial sites are shown in Figure 1. All crops were irrigated, with planting and harvest times typical for each location. Background site characteristics are shown in Table 1. The sites encompassed a wide range of soil types and growing conditions.

Trials were randomised block designs with 2-4 replicates. Plot sizes varied from 4 rows wide by 2.5m long to 1 row wide by 14 m long. Cultivation, pest and disease control and irrigation were carried out according to local commercial practice. About half of the trials were conducted on-farm within commercial potato crops.

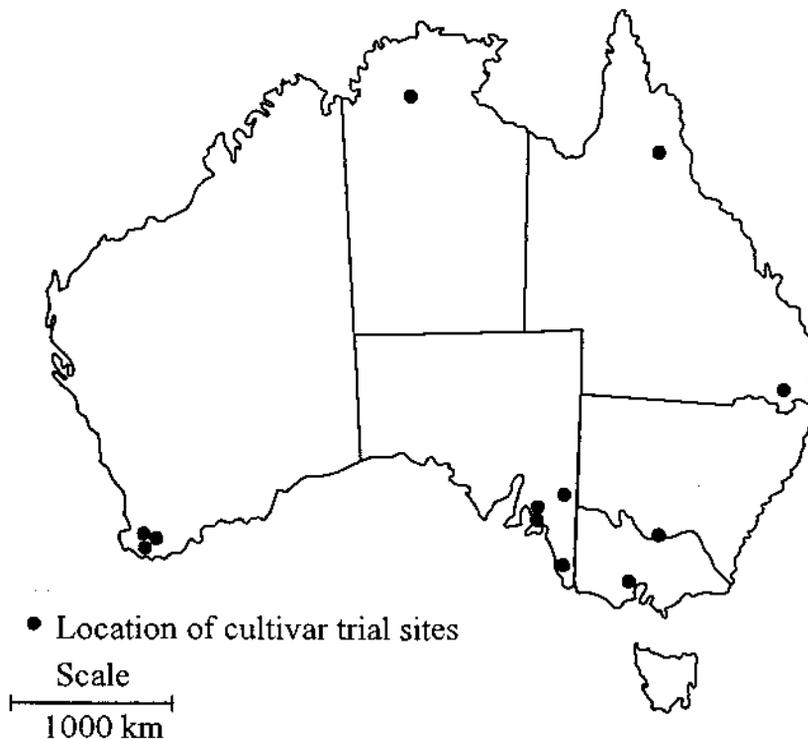


Figure 1. Location of cultivar trial sites.

Tubers were dug after haulms had senesced and a subsample of 12-15 tubers was taken from each plot for Cd analyses.

Table 1. Site details.

Site	Soil Order ^A	No. of cultivars	Row spacing (m)	Recent site history (years)
1	Xeralf	12	0.76	Vegetables (3)
2	Alfisol	31	0.80	Pasture (5)
3	Alfisol	6	0.80	Pasture (5)
4	Alfisol	32	0.80	Pasture (5)
5	Oxisol	13	0.80	Pasture (5)
6	Vertisol	7	0.75	Sorghum (1)
7	Oxisol	6	0.91	Maize (1)
8	Oxisol	8	0.80	Pasture (10)
9	Inceptisol	13	0.76	Pasture (4)
10	Alfisol	8	0.80	Pasture (3)
11	Alfisol	10	0.80	Pasture (3)
12	Alfisol	18	0.80	Pasture (3)

^A USDA Soil Taxonomy (Soil Survey Staff 1992).

Statistical analysis

At each site all data (including data from advanced breeder lines) were subjected to analysis of variance (ANOVA) using a randomised block design to indicate if cultivar effects were significant.

As all cultivars were not common to all sites, interactions between site and named cultivars were also assessed using a modified joint regression analysis based on the method of Finlay and Wilkinson (1963) and Digby (1979). This method was used to assess the effects of environment (soil characteristics, climate, growing conditions etc) on the ability of the cultivar to accumulate or exclude Cd. A modified joint regression analysis of Cd concentrations in tubers for all cultivars was calculated as follows;

$$Y_{ij} = \tau_i + \beta_i \theta_j + \varepsilon_{ij}$$

where Y_{ij} = Cd concentration for i^{th} cultivar in the j^{th} environment,

τ_i = mean Cd concentration for the i^{th} cultivar,

β_i = sensitivity index for the i^{th} cultivar,

θ_j = index of effect of the j^{th} environment constrained so that $\sum \theta_j = 0$, and

ε_{ij} = error term.

If cultivar i has a sensitivity of β_i and two environments (sites) differ in their environmental effect (θ_j) by 1, then the expected Cd concentration in tubers of cultivar i at these sites will differ by β_i . According to Finlay and Wilkinson (1963) a cultivar is sensitive to environmental conditions if β_i is greater than 1.

A generalised relationship between values of β_i and cultivar mean Cd concentration (Y_i) is shown in Figure 2.

Values of b_j of around 1 for any cultivar indicate average "stability" i.e. the cultivar responds to changes in environment in a similar way to the average response of all cultivars. Thus a b_j value of 1 and a high mean Cd level across all sites (Y_j) indicates the cultivar has high tuber Cd concentrations (compared to other cultivars) and responds to site conditions.

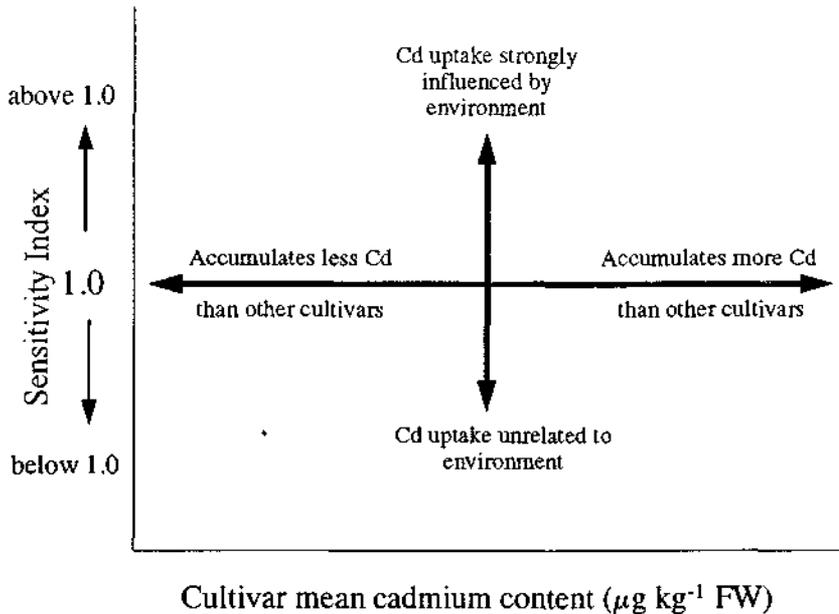


Figure 2. Generalised modified joint regression analysis for Cd uptake by cultivars (adapted from Finlay and Wilkinson, 1963).

A b_j value of 1 and a low mean Cd level across all sites (Y_j) indicates the cultivar has low tuber Cd concentrations (compared to other cultivars) and also responds to site conditions. b_j values greater than 1 indicate a cultivar highly responsive to site conditions i.e. accumulates more Cd (than other cultivars) where site mean Cd concentrations are high and less Cd at sites where site mean Cd concentrations are low. If b_j is less than 1 the cultivar accumulates more Cd than other cultivars at sites where mean Cd concentrations are low and less Cd at sites where mean Cd concentrations are high. A b_j value less than 1 indicates resistance to environmental conditions so that, combined with a low mean Cd concentration, indicates the cultivar resists Cd uptake under all conditions, which is a desirable characteristic.

Results for only 14 of the 23 named cultivars used in the above analyses are presented since only 14 cultivars occurred at a minimum of 4 sites.

Relationships between soil characteristics and tuber Cd concentrations were investigated using simple linear and multiple regression analysis (stepwise forward). The mean or median tuber Cd concentration at each site was used as the response variate. Log transformation of the data was used where variances increased in proportion to mean values.

Results

Tuber Cd concentrations

Site mean tuber Cd concentrations (i.e. averaged across all cultivars at each site), ranged from 11 to 67 $\mu\text{g kg}^{-1}$ FW (Table 2).

Table 2. Mean tuber yield and summary Cd statistics for all sites.

Site	Mean tuber yield (t ha ⁻¹)	ANOVA on cultivar F probability	Tuber Cd concentration (µg kg ⁻¹ FW)			
			Minimum	Maximum	Mean	Median
1	42.9	0.003	43	72	54	51
2	80.5	<0.001	25	60	44	44
3	45.2	<0.007 ^A	37	65	58	58
4	41.0	0.018	31	60	47	47
5	nd ^B	0.002	9	39	24	23
6	45.0	<0.001	13	27	20	20
7	35.9	0.174	6	19	11	11
8	45.8	0.005	7	16	12	12
9	64.4	0.518	19	30	25	24
10	59.2	<0.001	44	109	67	66
11	63.6	<0.001	44	80	61	57
12	81.2	0.003	30	90	55	53

^A Incomplete replication at this site.

^B nd = not determined.

At 5 locations the site mean Cd concentration (averaged across all cultivars) exceeded the MPC of 50 µg kg⁻¹ FW, while at 7 sites at least one cultivar exceeded the MPC (Table 2). From Table 2 it can be seen the range in Cd concentrations found between sites was generally greater than the range in Cd concentrations between cultivars at any one site.

Cultivar effects

At all sites except 7 and 9, there were significant differences in tuber Cd concentrations between cultivars (Table 2).

From the modified joint regression analysis (Figure 3, Table 3) it was evident that the Cd uptake of most of the current commercial potato cultivars is somewhat sensitive to environmental conditions. However, cultivar Russet Burbank had a low mean Cd concentrations and a relatively low value of b_j , indicating some ability to restrict Cd uptake across a range of environments.

None of the 14 cultivar mean Cd concentrations (averaged across all sites) exceeded the MPC of 50 µg Cd kg⁻¹, with values ranging from 29 to 50 µg kg⁻¹ (Table 3). The parents of each cultivar are listed in Table 3 and there is no clear cut or common genetic ancestry associated with high or low Cd accumulating cultivars studied.

Sensitivity indices (b_j values) for most cultivars were around 1.0, indicating that environmental conditions play a dominant role in determining Cd uptake by any cultivar. This is further illustrated by examining the relationship between tuber Cd concentrations (Y_j) and environmental effect index (q_j) for each cultivar separately, examples of which are presented in Figures 4a-4d.

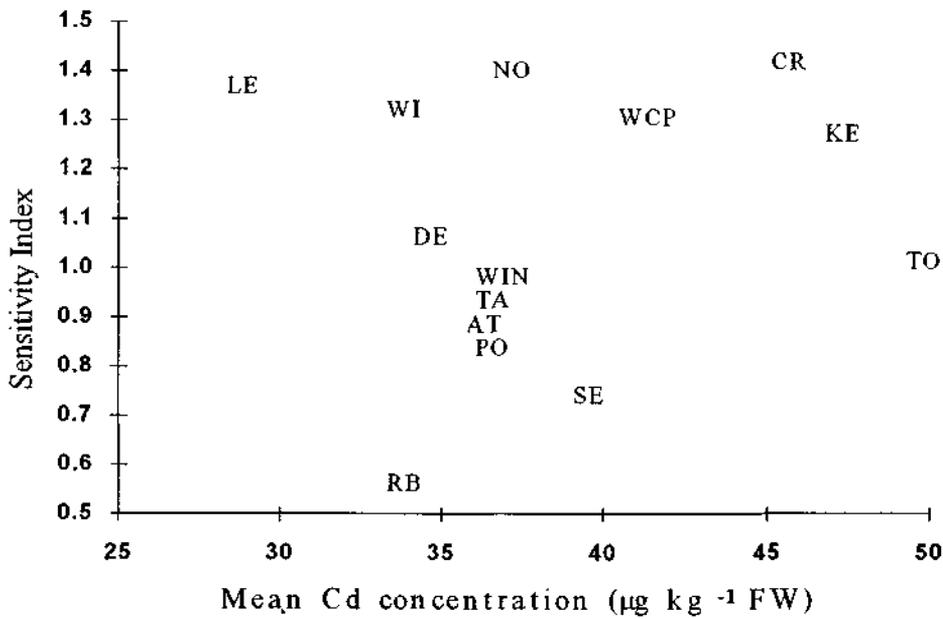


Figure 3. Modified joint regression analysis of major commercial cultivars grown at 12 sites in Australia. LE=Lemhi russet, WI=Wilwash, DE=Denali, RB=Russet Burbank, AT=Atlantic, TA=Tarago, PO=Pontiac, NO=Norking russet, WIN=Winlock, SB=Sebago, WCP=Wilcrisp, CR=Crystal, KE=Kennebec, TO=Toolangi delight.

Table 3. Adjusted tuber cadmium concentrations for different potato cultivars across all sites

Tuber Cd Group	Cultivar	No. sites ^A	Tuber Cd ($\mu\text{g kg}^{-1}$ FW)		S.I. (b) ^B		Parents/Ancestry
			Mean	SD	Mean	SD	
High (>45)	Toolangi Delight	4	50	2	1.02	0.15	Norgleam x Kennebec
	Kennebec	6	48	2	1.27	0.10	B127 x 96-56
	Crystal	4	46	2	1.41	0.16	ND7196-18 x Cascade
Medium (35-45)	Wilcrisp	5	41	2	1.31	0.21	Coliban x 69-32T-4
	Sebago	6	40	2	0.74	0.13	Chippewa x Katahdin
	Nooksack	5	37	3	1.40	0.18	Kennebec x A501-13
	Winlock	7	37	2	0.99	0.11	Bungama x 58-7-215
	Tarago	6	37	2	0.92	0.17	Orion x 60-7-20
	Pontiac	8	36	2	0.89	0.97	Triumph x Katahdin
	Atlantic	8	36	2	0.84	0.97	Wauseon x USDA B5141-6 (Lenape)
	Desiree	5	35	2	1.07	0.15	Urgenta x Depesche
Low (20-35)	Wilwash	4	34	5	1.32	0.31	Norgleam x Coliban
	Russet Burbank	4	34	2	0.57	0.09	Burbank-Early Rose Seedling
	Lemhi Russet	4	29	4	1.37	0.29	Pioneer x A63126-B

^A Number of sites at which each cultivar was present.

^B S.I. = sensitivity index (b) of a given cultivar to environmental effects.

The significantly positive slope of the relationship between Y_j and q_j for each cultivar indicates the dominant effect of site (e.g. soil, climate) in determining Cd concentrations in tubers. Sites such as 6, 7 and 8 produced consistently low tuber Cd concentrations (Table 2, Figure 4).

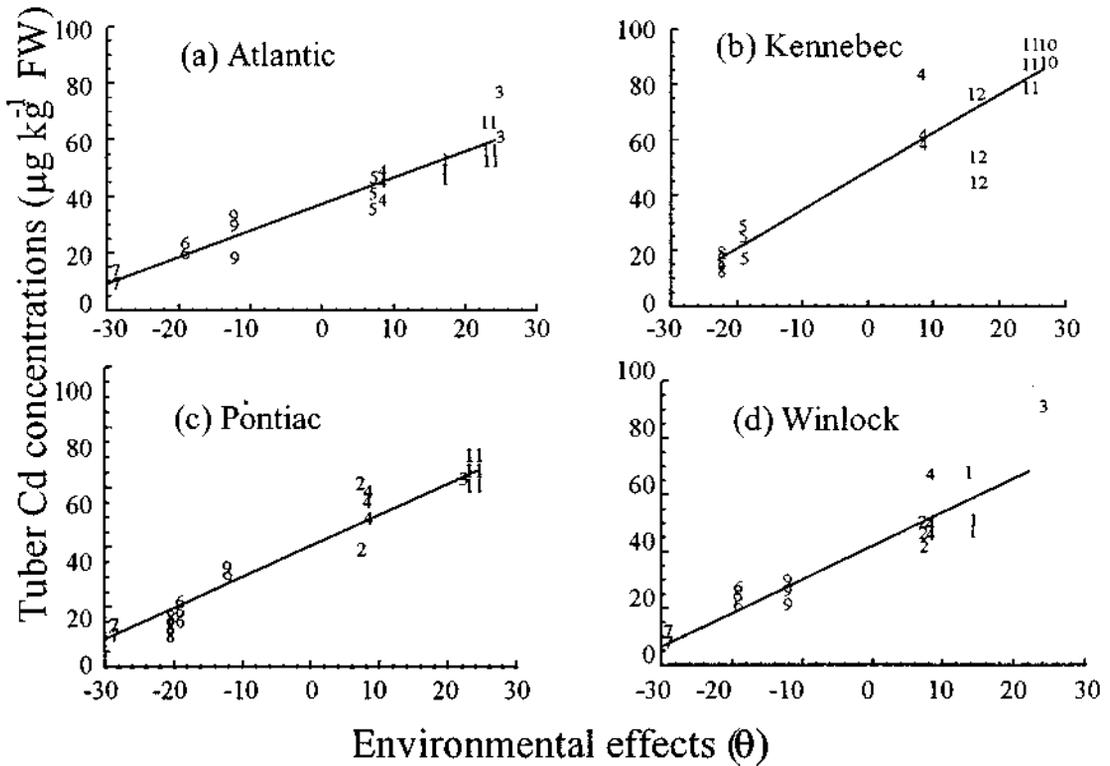


Figure 4. Environmental effects (sites 1-12) on tuber Cd concentrations in four major commercial potato cultivars. Numbers represent individual plot values at each site.

Advanced breeding lines were not included in the modified joint regression analysis as few cultivars were common to more than one site. However, the range in Cd concentrations in advanced breeding lines (unnamed) was four-fold at site 5, with line 86-11-1 showing potential as a low Cd accumulator (Table 4).

Soil characteristics and tuber Cd concentrations

Soils at the trial sites varied in clay content from 1 to 56%, pH varied from 4.6 to 7.8, total C from 0.5% to 4.6%, bicarbonate-extractable P from 26 to 167 mg kg^{-1} and concentrations of EDTA-extractable Cd from 30 to 237 $\mu\text{g kg}^{-1}$ (Table 5).

Simple linear regression relationships between mean tuber Cd concentration at each site and soil characteristics are shown in Table 6. The correlation coefficients were similar whether mean or median tuber Cd concentration were used.

Mean tuber Cd concentrations were negatively correlated with clay content and concentrations of EDTA-extractable Zn in soil. However, EDTA-extractable Zn concentration was positively correlated with clay content, so that a multivariate analysis of the data indicated that only clay

content and pH accounted for significant percentages (Table 7) of the variation in tuber Cd concentration ($\mu\text{g kg}^{-1}$) across sites;

$$\text{Tuber Cd} = 105.7 - 0.96\text{Clay}\% - 8.3\text{pH} : R^2 = 0.75$$

Table 4. Cadmium concentrations in advanced breeding lines (with name for commercial release in parentheses) and named cultivars at 4 sites.

Site Cultivar	1	2	4	5
	Mean Cd concentration ($\mu\text{g kg}^{-1}$ FW)			
Atlantic	45	38	40	
Crystal	72	48	51	
Kennebec		59	63	24
Lemhi russet		29	39	
Russet burbank		41	43	
Sebago		44	49	
Toolangi delight		60	60	
Winlock	47	36	37	
80-93-4		35	43	
80-98-16 (Snowgem)		40	39	
85-11-9 (Wilstore)	57	56	50	
85-34-6 (Evans)	43	35	56	
85-51-1 (Wontscab)	48	44	40	
85-59-10				20
86-11-1				9
86-70-3				28
87-62-14				39
LSD ($P < 0.05$)	14	19	15	12

Discussion

Cultivar differences in Cd uptake have been reported for a number of food crops (Davies and Lewis 1985), including wheat (Pettersson 1977), maize (Hinesley *et al.* 1978), barley (Chang *et al.* 1982), rice (Morishita *et al.* 1987), lettuce (Thomas and Harrison 1989) and carrots (Harrison 1986). However, there is conflicting evidence for differences in Cd uptake between potato cultivars. Harris *et al.* (1981) examined the Cd uptake characteristics of six cultivars of potato grown on a highly contaminated soil (total Cd concentration $19.6 \mu\text{g Cd g}^{-1}$ dry soil). They found no differences between the cultivars and mean Cd concentrations in tubers varied from 150 to $410 \mu\text{g kg}^{-1}$ on a dry weight basis (approximately 30 to $80 \mu\text{g kg}^{-1}$ on a fresh weight basis assuming 20% solids). On the other hand, Isermann *et al.* (1983) examined Cd uptake by 12 cultivars growing on a Cd-contaminated soil in a glasshouse trial and found significant differences in Cd uptake between cultivars. Isermann *et al.* (1983) found that by choosing the appropriate cultivar, Cd concentrations in tubers could be reduced by 50%, a result slightly lower in magnitude than our findings. However, the range of Cd concentrations in tubers analysed by Isermann *et al.* (1983) was 250 - $500 \mu\text{g kg}^{-1}$ FW, one order of magnitude greater than that observed in our experiments.

Table 5. Chemical characteristics of topsoil from the trial sites.

Site	pHA	ECA	Extr.C/A	Total	Clay	Silt	Sand	Exchangeable cations ^B				HCO ₃ ^C	HCO ₃	EDTA ^D	EDTA
								CB	Ca	Mg	Na				
	dS m ⁻¹	mg kg ⁻¹	%	%	%	%	%	cmol ⁺ kg ⁻¹	kg ⁻¹	kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	µg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
1	5.5	0.65	56	0.5	9	6	85	7.8	0.4	0.11	0.38	53	260	67	1.88
2	5.4	0.09	31	2.7	15	25	60	6.0	2.2	0.20	1.11	82	640	155	3.75
3	5.1	0.10	10	0.6	4	6	90	1.7	0.2	0.04	0.33	70	nd	59	1.00
4	5.8	0.19	84	1.1	1	3	96	4.0	0.7	0.14	0.19	52	118	43	2.07
5	4.6	0.14	6	4.6	29	28	43	7.4	1.5	0.1	0.6	45	235	122	3.52
6	7.8	0.18	127	1.7	25	19	56	13.1	12.0	1.27	1.43	167	750	68	10.20
7	5.4	0.06	21	2.3	56	16	28	4.9	1.2	0.06	0.67	90	312	140	7.70
8	7.8	0.13	21	0.9	30	7	63	4.8	2.3	0.03	0.55	26	295	52	6.94
9	7.4	0.35	30	0.6	9	2	89	10.0	0.5	0.09	0.81	28	330	30	1.50
10	5.9	0.10	0.2	2.9	7	4	89	2.9	4.4	0.5	0.6	40	nd	58	2.57
11	5.4	0.09	6.0	4.4	11	5	84	4.4	4.2	0.6	0.6	81	nd	227	4.53
12	5.4	0.10	2.3	4.4	12	6	82	4.4	4.2	0.6	0.4	92	nd	237	5.20

A 1:5 soil water ratio

B Rayment and Higginson (1992)

C Colwell (1963)

D Clayton and Tiller (1979)

Table 6. Simple linear regression correlation matrix (r values) for mean tuber Cd concentration at each site and topsoil characteristics^A.

Site	Tuber Cd	pH	EC	Extr. Cl	Total C	Clay	HCO ₃ P	EDTA Cd
Tuber Cd								
pH	-0.504							
EC	0.066	0.139						
Extr. Cl	-0.285	0.494	0.334					
Total C	0.204	-0.499	-0.511	-0.453				
Clay	<u>-0.772</u>	0.078	-0.289	-0.034	0.166			
HCO ₃ -P	-0.090	0.093	-0.231	0.542	0.189	0.239		
EDTA-Cd	0.245	-0.491	-0.400	-0.411	<u>0.817</u>	0.170	0.338	
EDTA-Zn	<u>-0.598</u>	0.443	-0.346	0.377	0.193	<u>0.706</u>	<u>0.677</u>	0.244

^A 5% and 1% levels of significance = 0.576 and 0.708, respectively.

Table 7. Analysis of variance table for a multiple regression of mean tuber Cd concentration ($\mu\text{g kg}^{-1}$) at each site as related to soil clay content and soil pH..

Change in factor	D.F.	Sum of squares	Mean square	Variance ratio ^A	% variation
+ clay	1	2645.1	2645.1	26.0***	59.5
+ pH	1	880.7	880.7	8.6*	19.8
RESIDUAL	9	916.9	101.9		20.7
TOTAL	11	4442.7	403.9		100

^A*, *** = significant at the 5%, and 0.1% levels.

Presumably these high concentrations resulted from the high level of Cd contamination in the soil (HCl-extractable Cd concentration was 40 mg kg^{-1}). Unfortunately, only cultivar Desiree used by Isermann *et al.* (1983) is commonly grown in Australia, so that further comparison with our results is difficult.

The current major potato cultivars grown in Australia and tested here generally do not exhibit the desirable characteristics of combined inherent low tuber Cd concentrations and resistance to environmental effects on tuber Cd concentration (low b_j values). Only cultivar Russet Burbank showed potential to limit Cd uptake into tubers across all environments.

The ranking of the cultivars tested here (Table 3) should be regarded as preliminary, as all cultivars were not represented at all sites. The modified joint regression analysis may also lead to skewed rankings if a cultivar is present in only one type of environment (e.g. sites with low or high Cd concentrations in soil, low pH etc). However, it is evident that scope exists to modify Cd concentration in tubers by appropriate selection of cultivar. Cadmium concentrations in tubers could be reduced by approximately 50% by choice of current

commercial cultivar. However, such cultivar selection must also take into consideration factors such as yield, disease resistance and market end-use to ensure successful adoption in commercial production systems.

The current work indicates that scope currently exists for selection of current named cultivars for use in commercial production situations where tuber Cd concentrations are likely to be at or just above the maximum permitted concentration of $50 \mu\text{g kg}^{-1}$. It is likely that reductions of the order of 20 to $30 \mu\text{g kg}^{-1}$ of tuber Cd could be achieved by selection of cultivars within the suite of cultivars tested. Also, there is the considerable potential to select certain advanced breeding lines found to be low in tuber Cd for use as parents in breeding programs. Chaney *et al.* (1993) recently examined 200 sunflower genotypes for the ability to reduce the uptake and translocation of Cd to kernels and found a significant range in genotypic variation. Genotype mean Cd concentrations in kernels were found to vary from 310 to $1,340 \mu\text{g Cd kg}^{-1}$ dry weight, a four-fold range in Cd concentrations. Our results at site 5 with some advanced breeding lines gave a similar range in tuber Cd concentrations (Table 4).

There is a need to examine further a far wider range of different *Solanum* species in order to find genetic material which may have acceptable or very low tuber Cd accumulation properties. Also, the potato germplasm collections in Australia and elsewhere should be examined for genotypes with low tuber Cd accumulation. There should be a routine screening of commercial cultivars before release to ensure that high Cd tuber accumulating types are not released. The genetics of Cd accumulation in potatoes has not been studied and work is required in this area.

The link between soil characteristics and tuber Cd concentrations showed that tuber Cd concentrations were negatively related to soil clay content and soil pH. Soil pH and soil texture are often implicated in controlling Cd availability in soils (Alloway 1990; Chaney and Hornick 1977). Increasing clay content improves the soil's ability to sorb Cd, thus reducing phytoavailability, although the strength of the Cd sorption is related to clay mineralogy (Tiller *et al.* 1984). Soil pH is generally regarded as the dominant factor controlling Cd availability in soils, with Cd availability increasing as soil pH decreases (Alloway 1990; Chaney and Hornick 1977). However, the small number of sites and the range of soil conditions represented precludes any firm conclusions as to the soil characteristics which will lead to enhanced Cd concentrations in tubers. A more detailed report of soil survey work is reported in Section 6.4.

Conclusions

There were significant differences between cultivars in tuber Cd concentrations. Tuber Cd concentrations could be reduced at some sites by up to 50% by appropriate choice of cultivar.

The range in tuber Cd concentrations found between sites was generally greater than the range in Cd concentrations between cultivars at any one site i.e. environmental conditions played a dominant role in determining Cd uptake by any cultivar.

High tuber Cd concentrations tended to occur at sites having sandy soils and where soils were acidic, but the data set presented here is too small to draw broad conclusions regarding soil factors controlling Cd accumulation.

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APPENDIX 4 Relationship between soil characteristics and Cd uptake by potato tubers in South Australia.

Introduction

In Australia, the maximum permitted concentration (MPC) for Cd in potato tubers has been set by the Australian National Health and Medical Research Council (NHMRC) at a level of 0.05 mg kg^{-1} on a fresh weight basis (Anon 1993). Assessment of the levels of Cd (and other impurities) in primary produce and foods in Australia is carried out by a number of State and Federal Government agencies. The percentage of potato tubers in these Australian surveys which have Cd concentrations above the MPC varies from about 16-37% of samples tested in surveys conducted to date (Morgan, 1989; Stenhouse 1991; Anon 1992a,b,c). Most of the potatoes analysed in these studies were either purchased at point of sale in commercial markets (Anon 1987, 1992a; Morgan 1989; Stenhouse 1991) or sampled on-farm or from regional stores (Anon 1992b,c). The reasons for elevated concentrations in some potato tubers are unknown. Information on the major soil or management factors responsible for elevated Cd concentrations in food crops is required by both industry and government agencies in many countries to ensure the production of healthy foods. The aim of this study therefore, was to determine the relationship among major plant, management and selected soil factors and elevated Cd concentrations in field-grown potato crops. The experimental program was based in South Australia, but the results have relevance for potato growing areas in other regions and countries.

Methods

Sampling

Eighty-nine commercial potato crops and associated soils in South Australia were sampled over the period February 1992 to July 1992. The sites sampled represented the major potato production areas in South Australia (Figure 1). The possibility that local spatial variability might confuse the relationships between soil characteristics and tuber Cd concentrations was minimised by sampling tubers and soils from the exact same location at each site.

Potato crops were sampled by hand digging tubers from two to three metres of row after haulms had senesced. Twelve to 15 tubers in the size range 80-450 g were collected, with any severely diseased or damaged tubers discarded. Tuber size was found to be unrelated to tuber Cd concentration (Appendix 2). Tuber cultivar was noted and tubers were brushed free of soil and transported to the laboratory for analysis.

Soil Orders (Soil Survey Staff 1992) sampled included Alfisols, Vertisols and Inceptisols with a wide range of physical and chemical characteristics (Table 1). Soils were sampled from the same length of crop row from which tubers were removed. Soil in the row down to the furrow depth was thoroughly mixed and a one kilogram sample taken by compositing four subsamples. As potato growers normally bank up the top 150

mm soil into rows during crop growth, this sample is subsequently referred to as topsoil, and included the residues of any fertilizer banded at planting.

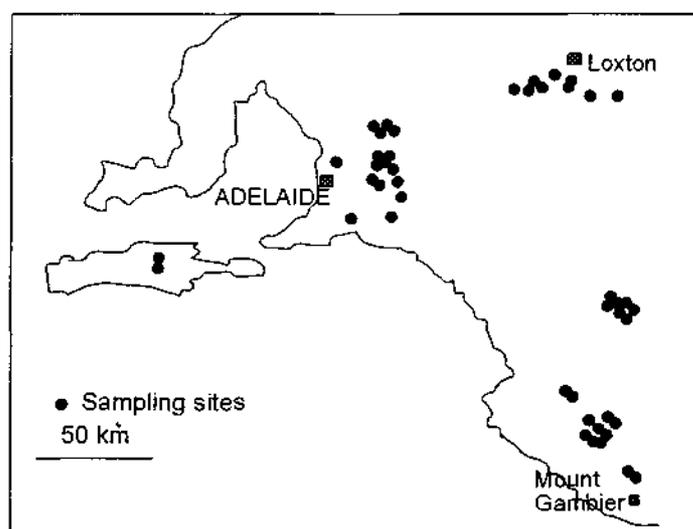


Figure 1. Location of sampling sites in South Australia.

Table 1. Selected chemical characteristics of soils (N=89, depth = 0-150 mm).

Characteristic	Range	Median	Mean
pH (water) ^A	4.4-8.7	5.6	6.1
EC (dS/m) ^A	0.07-1.43	0.29	0.40
Clay (%)	1-40	7	9
Silt (%)	0.5-19	4	5
Sand (%)	43-97	85	82
Total C (%)	0.3-5.0	1.4	1.6
Extractable Cl (mg/kg) ^A	4-1819	142	290
Total P (mg/kg) ^B	26-1071	186	234
EDTA-extractable Cd (mg/kg) ^C	<0.01-0.19	0.07	0.07
EDTA-extractable Zn (mg/kg) ^C	0.7-16.3	2.0	2.8

^A 1:5 soil:water ratio.

^B determined by ignition at 350°C and extraction in 0.5 M H₂SO₄.

^C according to the method of Clayton and Tiller (1975).

The topsoil was pushed aside and a minimum of four subsamples of soil taken to a depth between 150 -300mm using a stainless steel auger and composited into a single sample. These samples are subsequently referred to as subsoils. Soils were air-dried and crushed to pass a 2 mm sieve prior to analysis.

Analysis

Tubers were prepared as outlined in Appendix 2. Instead of dicing and drying tuber material, each tuber slice was homogenised and a subsample of the homogenate weighing approximately one gram (fresh weight) was transferred to a 75 ml digestion tube. The homogenate was digested with re-distilled concentrated HNO_3 , made up to 50 ml volume and Cd concentration in the solution determined by inductively-coupled plasma (ICP) mass spectroscopy using indium as an internal standard. Analysis of NBS rice flour (Ref.No.1568A) by the above method gave a Cd concentration of $0.023 \pm 0.001 \text{ mg kg}^{-1}$, compared to the certified value of $0.022 \pm 0.002 \text{ mg kg}^{-1}$.

Concentrations of Ca, K, Mg, Mn, P, S and Zn in the digest solution were determined by ICP optical spectroscopy. All tuber elemental concentrations are expressed on a fresh weight (FW) basis as Cd food standards in Australia relate to metal concentrations in foods "as consumed".

Soils were analysed as outlined in Appendix 2.

Concentration of Cd in the tubers was related to potato variety, tuber elemental composition and soil characteristics using linear and step-wise (forward) multiple regression analyses. The plant factors included in the model were plant cultivar and tuber concentrations of Ca, K, Mg, Na, P, S, and Zn. The soil factors included were pH_{water} , $\text{pH}_{\text{CaCl}_2}$, EC, extractable-Cl, extractable-P, EDTA-extractable Zn, EDTA-extractable Cd, total-P, H_2SO_4 -Cd, total C and %clay in both the topsoil and subsoil. To normalise the skewed distribution of some of the data sets, data were transformed (square root or logarithm) where appropriate.

Results

A wide range of tuber Cd concentrations was found, with a minimum of 0.005 mg kg^{-1} and a maximum of 0.232 mg kg^{-1} (FW). The mean and median tuber Cd concentrations were 0.066 and 0.059 mg kg^{-1} (FW) respectively. There was marked regional variation in tuber Cd concentrations (Table 2).

Table 2. Regional variation in Cd concentrations in potato tubers in South Australia.

Region	Range	Mean	Median	N
		mg kg^{-1} (fresh weight)		
I	0.015-0.123	0.063	0.062	32
II	0.109-0.232	0.164	0.150	14
III	0.023-0.096	0.063	0.062	12
IV	0.027-0.094	0.042	0.031	5
V	0.031-0.091	0.049	0.036	4
VI	0.005-0.072	0.019	0.008	22

In terms of tuber elemental composition, tuber Cd concentrations were correlated with concentrations of Na, Ca, K and Zn in the tuber (Table 3).

Table 3. Adjusted linear regression coefficients between tuber Cd concentrations (fresh weight basis) and concentrations of other elements in tubers (N=89).

Element	Range of elemental concentrations ^A	Adjusted R ²
Ca (mg/kg)	0.7-136.2	0.41***
K (%)	0.22-0.71	0.40***
Mg (mg/kg)	42.8-263.1	0.15
Na (mg/kg)	5.9-422.3	0.55***
P (%)	0.024-0.065	0.01
S (%)	0.023-0.053	0.06
Zn (mg/kg)	1.56-6.86	0.24*

^A fresh weight basis

*, **, *** = significant at the P<0.05, 0.01 and 0.001 levels, respectively.

Cultivars were predominantly Atlantic, Coliban, Kennebec, Pontiac and Russet Burbank, with small numbers of Crystal, Desiree, Exton and Sebago. Cultivar alone did not fully explain the regionally high Cd concentrations ($R^2=0.23$, $P<0.01$), although this factor was found to significantly improve the multivariate model described below.

H₂SO₄-Cd concentrations in the topsoils varied from 0.03 to 0.54 mg kg⁻¹, and in subsoils from <0.01 to 0.68 mg kg⁻¹. EDTA extractable-Cd in topsoils varied from <0.01 to 0.19 mg kg⁻¹, and in subsoils from <0.01 to 0.17 mg kg⁻¹. Mean and median Cd (H₂SO₄- and EDTA-extractable) concentrations in subsoils were about half those in the topsoil (data not shown). Concentrations of EDTA-extractable Cd in topsoils were positively correlated with total P ($R^2=0.37$, $P<0.001$) and with clay particle size fractions ($R^2=0.31$, $P<0.01$).

There was no consistent relationship ($R^2=0.04$, $P>0.05$) between tuber Cd concentrations and soil pH (Figure 2), with highest Cd concentrations evident at soil pH values of 6.0 to 7.5. Above pH 7.5 Cd concentrations in tubers were less than 0.04 mg kg⁻¹. Similarly, EDTA-extractable Cd concentrations in the soil (Figure 3) could not explain the high tuber Cd concentrations in some regions ($R^2=0.04$, $P>0.05$). There was no direct linear ($R^2=0.02$, $P>0.05$) or curvilinear relationship between concentrations of EDTA-extractable Zn in the soil and tuber Cd concentration (Figure 4). The best relationship between tuber Cd concentrations and soil or plant factors was found with topsoil EC ($R^2=0.57$, $P<0.001$) or extractable-Cl concentrations ($R^2=0.65$, $P<0.001$) in the topsoil (Figure 5). Soil EC was positively related to Cl concentrations ($R^2=0.95$, $P<0.001$), indicating that soluble salts in the soils were dominated by chlorides.

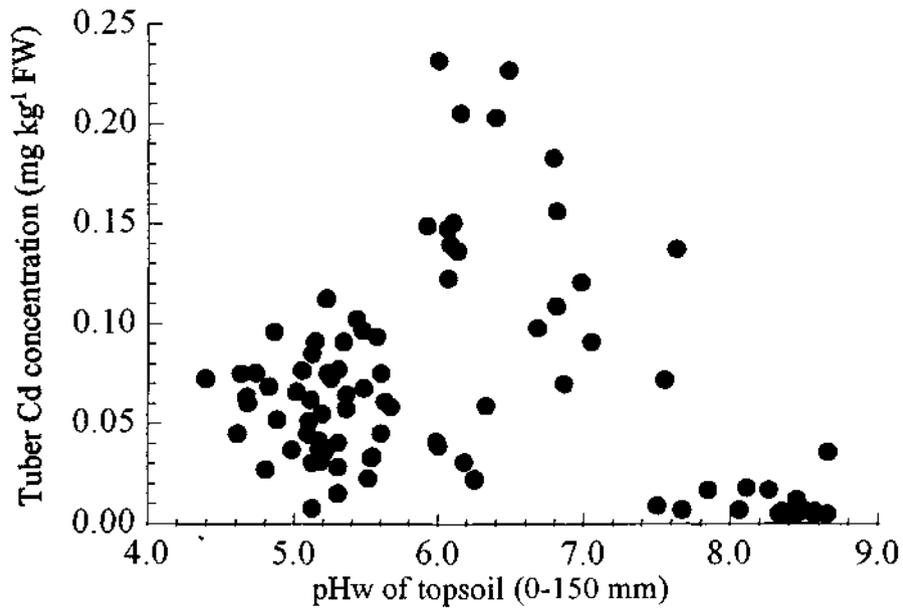


Figure 2. Relationship between tuber Cd concentrations and pH of the topsoil (0-150 mm).

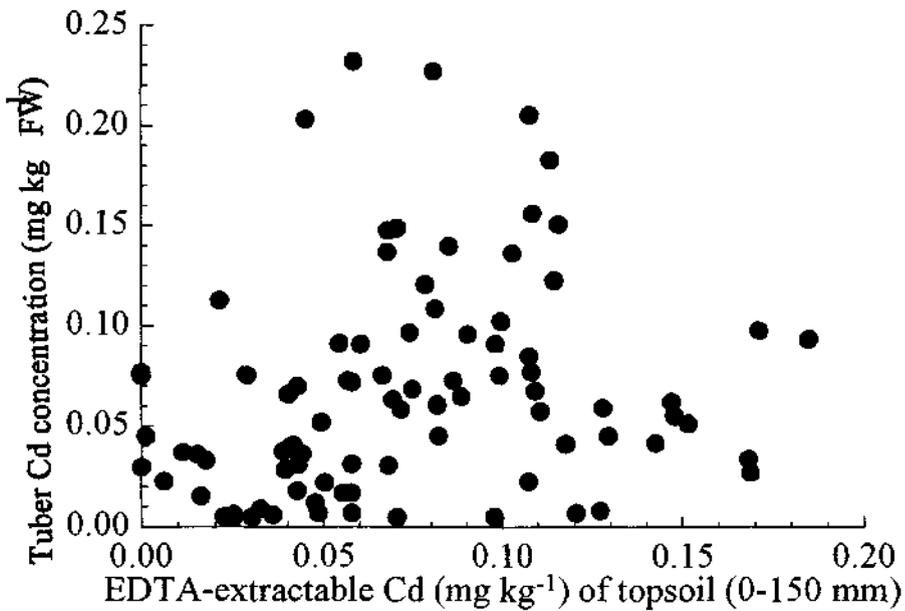


Figure 3. Relationship between tuber Cd concentrations and EDTA-extractable Cd in the topsoil (0-150 mm).

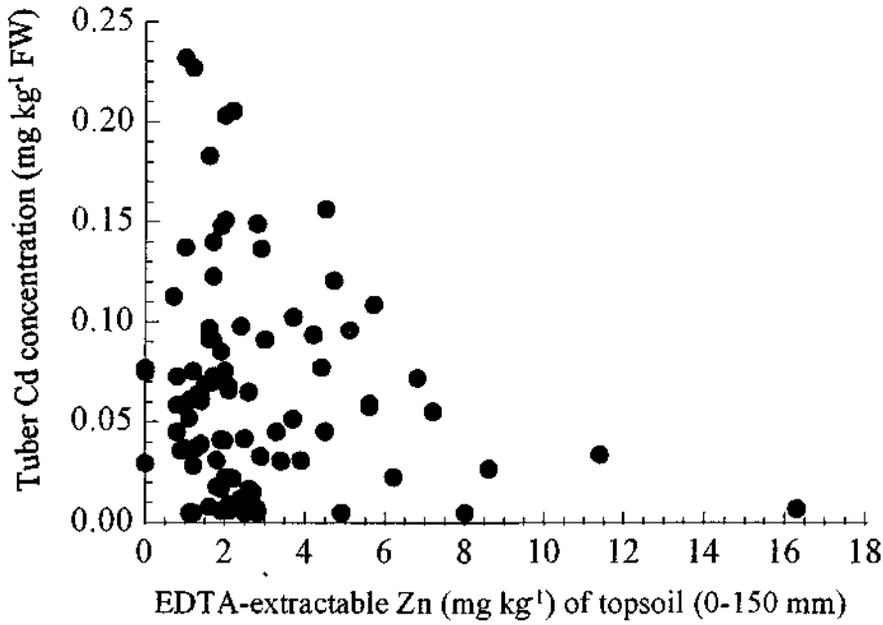


Figure 4. Relationship between tuber Cd concentrations and EDTA-extractable Zn in the topsoil (0-150 mm).

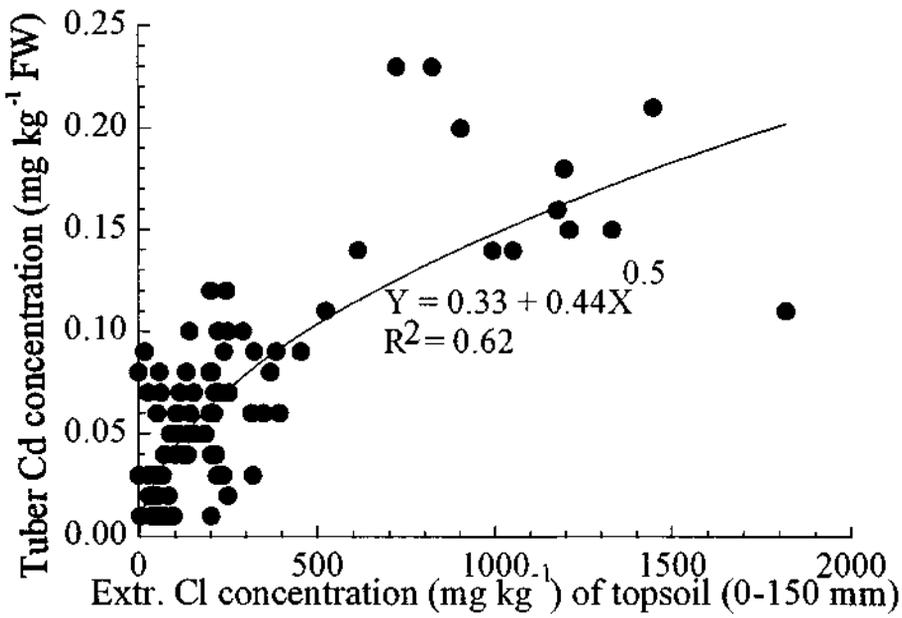


Figure 5. Relationship between tuber Cd concentrations and water-extractable Cl in the topsoil (0-150 mm).

Step-wise (forward) multiple regression analysis of the data indicated that the relationship between topsoil characteristics and tuber Cd concentrations could best be explained by the following equation;

$$\text{Tuber Cd} = 0.006 + 0.005\sqrt{\text{Cl}_t} - 0.004\text{Zn}_t ; R^2 = 0.68 (P < 0.001)$$

where Cl_t and Zn_t are water-extractable Cl and EDTA-extractable Zn in the topsoil, respectively.

The soils were classified into groups having low, medium, high and very high concentrations of water-extractable Cl (0-500, 500-1000, 1000-1500 and 1500-2000 mg kg^{-1}) and EDTA-extractable Zn (0-5, 5-10, 10-15 and 15-20 mg kg^{-1}). The three-dimensional relationship between water-extractable Cl and EDTA-extractable Zn is shown in Figure 6.

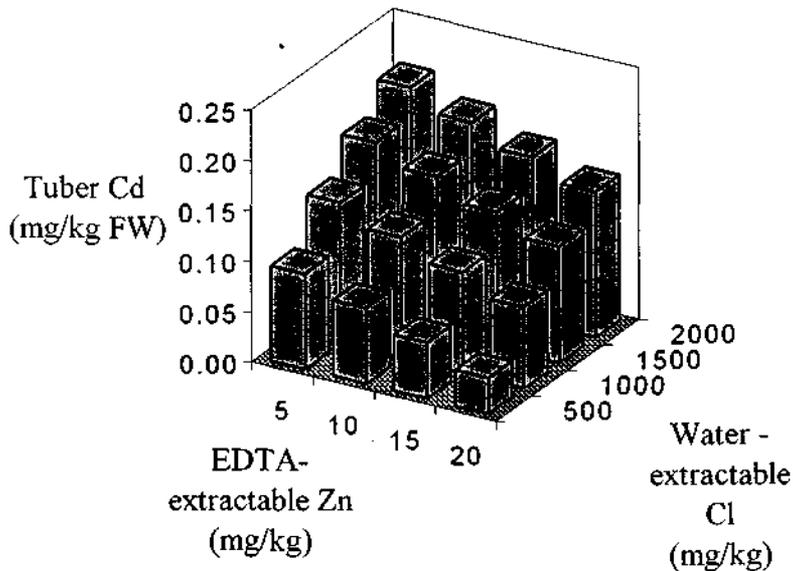


Figure 6. Three-dimensional relationship among tuber Cd concentration, water-extractable Cl and EDTA-extractable Zn in topsoils (0-150 mm).

Inclusion of Cl data from the subsoil and cultivar effects significantly ($P < 0.05$) improved the above relationship (adjusted $R^2 = 0.73$, $P < 0.001$), although the magnitude of the improvements were small and topsoil Cl concentrations still accounted for the largest percentage of the variation (Table 4). Other chemical data for subsoil horizons did not improve the fitted relationship with tuber Cd concentrations.

Table 4. Analysis of variance table for multiple regression of tuber Cd concentration (mg kg^{-1} fresh weight basis) on water-extractable Cl, EDTA-extractable Zn in soils and potato cultivar.

Change in factor	Degrees of freedom	Sum of squares	Mean Square	Variance ratio	% Variation
+ Cl _t ^A	1	0.1591	0.1591	195.4***	65.2
+ Cl _s ^B	1	0.0056	0.00056	6.9*	2.3
+ Zn _t ^C	1	0.0070	0.0070	8.6**	2.9
+cultivar	8	0.0145	0.0018	2.22*	5.9
Residual	79	0.0723	0.0010		23.7
Total	82	0.2441	0.0030		100

^A Cl_t = square root transformed data for water-extractable Cl (mg kg^{-1}) in topsoil (0-150 mm)

^B Cl_s = square root transformed data for water-extractable Cl (mg kg^{-1}) in subsoil (150-300 mm)

^C Zn_t = EDTA-extractable Zn (mg kg^{-1}) in topsoil (0-150 mm)

*, **, *** = significant at the $P < 0.05$, 0.01 and 0.001 levels, respectively.

Discussion

Soil pH is usually regarded as the major variable controlling Cd availability in soils, with addition of limestone being the soil management factor most often used to minimise Cd uptake by crops (Miller et al. 1976; Chaney and Hornick 1977; Page et al. 1981; Eriksson 1989; Alloway 1988; Alloway et al. 1990; Smilde et al. 1992). We found the highest concentrations of Cd in tubers in a region where soils were neutral or alkaline (pH 6.0-7.5), but these soils were predominantly saline. Irrigation waters in this area had electrical conductivities in the range 2.5-3.5 dS/m, with Cl concentrations in waters in the range 11-34 mM. Chloride forms relatively strong complexes with Cd, with stability constants for the mono- and di-chloro complexes being 10^{-2} and $10^{-2.6}$, respectively (Smith and Martell 1981). As a result, Cl has been found to significantly reduce sorption of Cd by soils (Garcia-Miragaya and Page 1976; O'Connor et al., 1984; Boekhold et al. 1993). Other workers have shown that in glasshouse experiments, where $\text{Cd}(\text{NO}_3)_2$ was added to soil in combination with NaCl and CaCl_2 , Cd uptake by Swiss chard was considerably enhanced by the Cl salts (Bingham et al. 1983, 1984). We therefore propose that the cause of the elevated Cd concentrations in potato tubers in this study is due to the effect of Cl mobilising Cd within the soil and increasing its availability to plants. Unfortunately, tuber Cl concentrations were not determined, but concentrations of Na in the tubers were correlated with tuber Cd concentrations. Moreover, Na is the major cation balancing Cl in irrigation waters in the areas under study and there was a positive relationship between Na and Cd concentrations in tubers (Table 3). Sodium may also be implicated in enhancing Cd uptake by tubers due to Na in irrigation waters displacing Cd from soil exchange sites into solution, although

Bingham (1986) found that Cd uptake by Swiss chard was not enhanced by adding Na_2SO_4 to soil. This aspect is currently under investigation.

The data presented here indicate that soil salinity effects may dominate soil pH effects on Cd phytoavailability, and that high Cd concentrations may be measured in crops growing on neutral or alkaline soils which have relatively low Cd concentrations. These data raise the issues of using limestone additions to soil to control Cd uptake by crops and the utility of soil guidelines, based on extractable or total metal concentrations, for disposal of Cd-containing organic or industrial wastes (e.g. composted municipal soil waste or sewage sludges). Compared to non-saline soils, in saline soils the effectiveness of limestone in decreasing crop Cd concentrations may be markedly reduced, while phytoavailability of Cd in sewage sludges or other wastes may be markedly increased. These aspects need to be addressed as recycling of waste materials to land is increasing dramatically in many countries and effective means need to be devised for controlling Cd uptake by crops grown on saline soils, or irrigated with saline waters or effluents.

A number of studies have investigated the relationship between soil characteristics and plant Cd uptake, although many of the studies have been carried out in glasshouse experiments with sewage sludge or contaminated soils, or with Cd added as inorganic salts (Miller et al. 1976; Bingham et al. 1983, 1984, 1986; Alloway et al. 1990; Smilde et al. 1992). In agricultural soils such as those studied here, amounts of Cd added through atmospheric deposition or fertilizers are often much less and total Cd concentrations are lower than where sewage sludge has been used. The soils sampled in this study were remote from industrial or urban regions, so that Cd inputs from the atmosphere were negligible (Merry et al. 1991). While a complete profile of changes in Cd concentration with depth was not established at each site, median concentrations of EDTA- and H_2SO_4 -extractable Cd in subsoils were about half those in the topsoil, suggesting that little of the Cd in these soils originated from the parent material. None of the sites sampled had ever had sewage sludge or composted sewage wastes applied to the soil. The major Cd inputs to these soils therefore derived from phosphatic fertilizers. Depending on the source of phosphate rock used in fertilizer manufacturing, Cd concentrations in phosphatic fertilizers in Australia currently range from 50 to 400 mg Cd per kg of P (Corry et al. 1993), although concentrations are declining due to changes in the source of phosphate rocks used for fertilizer production and pressure from the agricultural industries for low Cd fertilizers. Given typical rates of fertilizer addition to soils in southern Australia, 10 kg P ha^{-1} yr^{-1} to pastures and 100 kg P ha^{-1} yr^{-1} to potatoes, annual Cd inputs to soils under pasture are of the order 0.5-4.0 g ha^{-1} yr^{-1} , and in potato production 5-40 g ha^{-1} yr^{-1} . In the topsoils studied here, which were under horticultural cropping in rotation with pastures, values for H_2SO_4 - and EDTA-extractable Cd were low, with values for EDTA-extractable Cd varying from 0.01-0.19 mg kg^{-1} , with a median value of 0.07 mg kg^{-1} . These values can be compared to values for EDTA-extractable Cd in over 500 pasture soils (0-50 mm) in South Australia of 0.01-0.73 mg kg^{-1} with a median value of 0.16 mg kg^{-1} (Merry et al. 1991). Assuming that the ignition-sulfuric acid extraction procedure used in this study solubilised all Cd present in the soils, the range of "total" Cd concentrations found (median and maximum 0.11 and 0.54 mg kg^{-1} , respectively) is in the lower part of the range of those found in non-polluted agricultural soils in other countries. For example, in a survey of 3045

agricultural soils in the United States (Holmgren et al., 1993), where the median and maximum concentrations were 0.20 and 2.0 mg kg⁻¹, respectively.

In terms of textural class, the soils were predominantly sands, loamy sands, sandy loams, sandy clay loams and sandy clays. The high percentage of sand in most of the soils is a reflection that commercial potato production in South Australia favours the use of light textured soils. These soils are naturally low in P and Cd with most of the Cd present likely to have been derived from Cd impurities in phosphatic fertilizers, hence the significant positive relationship between total P and EDTA-extractable Cd.

Despite having relatively low Cd concentrations in soil, potato tubers accumulated significant concentrations of Cd. The tuber Cd concentrations found in this study were slightly higher than those reported in other countries where potatoes were grown on uncontaminated land (Anon 1983; Wolnik et al. 1983; Jorhem et al. 1984; Weigert et al. 1984; Wiersma et al. 1986; Andrey et al. 1988). It is interesting to note that Wolnik et al. (1983) reported Cd concentrations in potato tubers on a state by state basis for the U.S.A. finding a range of 0.002-0.182 mg kg⁻¹ (n=297), a median value of 0.028 mg kg⁻¹ and considerable variation between states in both median and maximum tuber Cd concentrations. However, no site or soil details were given to explain the regional differences.

The small but significant negative correlation between tuber Cd concentrations and EDTA-extractable Zn concentrations in soil agree with results of Abdel-Sabour et al., (1988) who noted that increasing Zn concentrations in soil inhibited Cd uptake by Swiss chard and maize. Similar results have been found in field-grown wheat in South Australia when soils were Zn-deficient (Oliver et al. 1993).

A significant percentage (55%) of the samples analysed in this study exceeded the Australian MPC of 0.05 mg kg⁻¹. However, Australian standards for metal impurities in foods are significantly lower than standards set in other countries which regulate food quality. If current Australian standards are to remain at their present low levels, it will be necessary to examine management practices to minimise tuber Cd concentrations, particularly in those areas with saline irrigation waters, or production should be encouraged in other areas with better quality irrigation water.

Conclusions

Potato is an important contributor to the dietary intake of Cd in Australia. Within South Australia, Cd concentration in potato tubers was positively correlated to concentrations of water-extractable Cl in soil, weakly correlated to potato cultivar, negatively correlated to concentrations of EDTA-extractable Zn in soil and unrelated to soil pH. The largest percentage of the variation was accounted for by water-extractable Cl. The regionally high Cd concentrations in tubers were therefore caused by use of saline (chloride) irrigation waters. Chloride added in irrigation water mobilises Cd in the soil and increases its plant availability. If the currently strict Australian food Cd standards are to remain in force, it is important that management practices be developed to minimise Cd uptake by potatoes grown in these areas, or production should be encouraged in other areas with better quality irrigation water.

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APPENDIX 5 Effect of fertilizer management on Cd uptake by potatoes

Introduction

Various agronomic practices have been suggested for minimising Cd uptake by agricultural crops, including addition of lime or zinc and reducing fertilizer Cd content (Andersson, 1976; Chaney and Hornick, 1978; Mordvedt *et al.*, 1981). Soil pH is often regarded as the major variable affecting plant uptake of Cd from soil (Chaney and Hornick, 1978). From results of glasshouse experiments, Reuss *et al.* (1978) suggested that modification of the type of P fertilizer applied to soil (in NPK mixes) could also influence Cd uptake by plants, with di-ammonium phosphate (DAP) inhibiting Cd uptake compared to triple superphosphate (TSP). Levi-Minzi and Petruzzelli (1984) and Waggan *et al.* (1978) showed that Cd in DAP was much more strongly sorbed to soil in the vicinity of the fertilizer granule compared to Cd in mono-ammonium phosphate (MAP), due mainly to changes in pH of soil in the fertilizer diffusion zone. Potassic fertilizers, through the influence of the counter anions chloride (Cl^-) or sulphate (SO_4^{2-}), may also influence Cd availability. This is due to the effect of Cl^- complexing free Cd^{2+} in the soil solution therefore reducing Cd sorption (Andersson, 1976; Bingham *et al.*, 1984; Garcia-Miragaya and Page 1978), while SO_4^{2-} was reported to have no effect on Cd availability (Bingham *et al.*, 1986).

The aim of this study was to investigate under field conditions if Cd uptake by potato could be minimised by changes in fertilizer management.

Methods

Phosphate fertilizer type, Cd concentration of P fertilizer and potassium fertilizer type were investigated at 3 sites (sites 1-3) in southern Australia. Sites were chosen on the basis that they had been in intensive potato production for some time and were likely to have significant historical inputs of Cd in phosphatic fertilizers. At all three sites a randomised block design was used with four-fold replication. The treatment combinations were;

- (a) four phosphatic fertilizer types in factorial combination with either high Cd concentrations ($>300 \text{ mg Cd kg}^{-1} \text{ P}$) or low Cd concentrations ($<100 \text{ mg Cd kg}^{-1} \text{ P}$) in the fertilizer, and
- (b) the four phosphatic fertilizer types with high Cd concentrations in factorial combination with potassium chloride (KCl) or potassium sulfate (K_2SO_4) as the potassium source.

General site and soil details are shown in Table 1.

Table 1. General experimental details.

Site	Soil Order ^a	Plot size	Cultivar	Seed spacing	Planting date	Harvest date
1	Oxisol	6m X 2 rows	Russet Burbank	35cm	2/12/91	19/5/92
2	Alfisol	7m X 1 row	Atlantic	25cm	10/12/91	4/5/92
3	Alfisol	7m X 1 row	Onka	25cm	25/11/91	30/3/92
4	Entisol	5m X 1 row	Russet Burbank	35cm	16/10/91	20/3/92
5	Inceptisol	2m X 1 row	Sebago	20cm	21/8/91	22/1/92

^a USDA Soil Taxonomy [30]

Phosphatic fertilizers tested were single superphosphate (SSP), reactive phosphate rock (RPR) and MAP and DAP. These fertilizers were chosen for their ability to induce different conditions of pH in the fertilizer band. Rather than adding pure Cd salts to the fertilizer mixtures, commercial sources of low Cd and high Cd fertilizers were obtained (Table 2). Commercial KCl, K₂SO₄ and ammonium sulfate ((NH₄)₂SO₄) fertilizers used had low Cd concentrations.

Table 2. Fertilizers used.

Fertilizer	%P	%N	%K	Cd mg kg ⁻¹	Cd mg kg ⁻¹ P
SSP ^a - Low Cd	8.8	-	-	3.6	41
SSP - High Cd	8.8	-	-	35.7	406
MAP ^b - Low Cd	21.8	10.0	-	6.0	28
MAP - High Cd	22.0	12.6	-	94.5	433
DAP ^c - Low Cd	20.0	18.0	-	6.5	32.5
DAP - High Cd	20.0	19.0	-	75.0	375
RPR ^d - Low Cd	12.7	-	-	7.7	61
RPR - High Cd	15.5	-	-	47.0	303
KCl	-	-	50.0	<1.0	-
K ₂ SO ₄	-	-	41.5	<1.0	-
(NH ₄) ₂ SO ₄	20.5	-	-	<1.0	-

^a Single superphosphate

^b Monoammonium phosphate

^c Diammonium phosphate

^d Reactive phosphate rock

Fertilizers were blended to produce an N:P:K mix supplying 100 kg N ha⁻¹, 100 kg P ha⁻¹, 150 kg K ha⁻¹ and 10 kg Mg ha⁻¹ (as MgSO₄). These application rates were chosen on the basis of commercial practice in the areas under study. Sulfur added in the fertilizer N:P:K mixes was adjusted (using gypsum, Cd content < 1.0 mg kg⁻¹) so that a minimum of 100 kg S ha⁻¹ was applied.

Zinc (Zn) addition was investigated at 5 sites in southern Australia, with applications rates of 0, 5, 10, 25, 50 and 100 kg Zn ha⁻¹ at sites 1-3 and at rates of 1, 15 and 30 kg Zn ha⁻¹ at sites 4 and 5. Zn was applied as zinc sulfate (ZnSO₄), banded with the N:P:K fertilizer (P supplied as SSP (High Cd source), K as KCl, N as (NH₄)₂SO₄). Technical grade ZnSO₄ (Cd content 1.6 mg kg⁻¹) was used as a source of Zn as some commercial Zn additives may contain unacceptable amounts of Cd as an impurity.

Potato seed pieces were planted by means of a tractor-towed single- or double-row planter. Cultivars used are shown in Table 1. Fertilizers were placed as a double band 5 cm to either side below the seed piece. Plots within rows were separated by 1 m planting of the potato cultivar Pontiac (an easily identified red-skinned cultivar). Cultivation (banking), pest and disease management and irrigation were carried out by the grower. Crops were sprinkler irrigated, generally every 5-10 days depending on weather conditions, receiving approximately 20-30mm water with each irrigation. Nitrogen status of the crops was assessed during growth by analysis of petiole sap (Williams and Maier, 1990) and N applied as a side dressing if required.

Tubers were either hand or machine-dug after haulms had senesced and whole plot yields recorded. Tubers were graded into the following size grades, <80g, 80-350g and >350g. As fertilizer management may influence tuber quality, in terms of crisp colour and after-cooking darkening, a 4-5 kg subsample of tubers was assessed for crisp colour and after-cooking darkening (Dahlenberg et, 1990). A further 5 to 10 kg subsample of the whole plot yield was used for tuber Cd analysis.

Cadmium analyses

Tubers were prepared and analysed as outlined in Appendix 2.

Soil sampling and analyses

At each trial site, a representative sample of soil from the 0-150 mm depth was taken, dried at 40°C and crushed to pass a 2 mm stainless steel sieve. Soil analyses were as outlined in Appendix 2.

Statistical analysis

Effects of fertilizers on yield, cooking quality and Cd concentrations were assessed using an incomplete factorial ANOVA.

Results

Soil characteristics

Soils at the trial sites varied in clay content from 1 to 26%, pH varied from 4.7 to 7.4, total C content varied from 0.6% to 4.5%, bicarbonate-extractable P varied from 28 to 123 mg kg⁻¹ and concentrations of EDTA-extractable Cd varied from 0.030 to 0.188 mg kg⁻¹ (Table 3).

Table 3. Soil characteristics

Site	pH _w ^a	EC ^a	Extractable C ^a	Total C ^b	Clay <2µm	Silt 2-50µm	Sand 0.05-2mm	HCO ₃ p ^c	EDTA Zn ^d	EDTA Cd ^d	Exchangeable cations (cmol ⁺ kg ⁻¹) ^e				Mineralogy ^f
		dS m ⁻¹	(mg kg ⁻¹)	(%)	(%)	(%)	(%)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	Ca	Mg	Na	K	
1	5.0	0.15	22	4.5	26	37	37	98	2.48	0.125	8.8	1.4	0.07	0.69	Ka,Hm/Gt,Il,Qtz
2	5.6	0.47	224	0.9	6	3	90	63	10.92	0.103	3.6	0.9	0.07	0.8	Il,Ka,Qtz,Hm/Gt
3	4.7	0.28	177	1.4	10	11	79	51	3.14	0.188	2.4	0.7	0.10	0.51	Ka,Il,Hm/Gt/Qtz
4	5.8	0.19	84	1.1	1	3	96	52	2.07	0.043	4.0	0.7	0.14	0.19	Ka,Il,Qtz,Hm/Gt
5	7.4	0.35	30	0.6	9	2	89	28	1.50	0.030	10.0	0.5	0.09	0.81	RIM,Il,Ka,Hm/Gt,Qtz

^a 1:5 soil water ratio

^b LECO combustion method (Rayment and Higginson, 1992)

^c Colwell (1963) method

^d Clayton and Tiller (1975) method

^e 1M NH₄Cl, pH 7.0, pretreatment for soluble salts (Rayment and Higginson, 1992)

^f dominant mineral phases in order of abundance: Il=illite, Ka=kaolinite, Qtz=quartz, Hm/Gt=hematite and/or goethite, RIM=randomly interstratified smectitic material (Norrish and Pickering, 1983).

Tuber yield and cooking quality

There were no significant ($P>0.05$) effects of fertilizer treatments on either tuber yield, tuber dry matter percentage or tuber cooking quality (data not shown). Average yields varied from 45 to 52 t ha⁻¹.

Tuber Cd concentrations

The effects of P fertilizer type and P fertilizer Cd content on tuber Cd concentrations are shown in Table 4.

Table 4. Effect of P fertilizer type and Cd content on cadmium concentrations in potato tubers at sites 1-3.

Site	SSP ^a	SSP	DAP	DAP	MAP	MAP	RPR	RPR	LSD ($P<0.05$)
	Low ^b	High	Low	High	Low	High	Low	High	
Tuber Cd concentrations (mg kg ⁻¹ FW)									
1	0.016	0.018	0.015	0.018	0.027	0.018	0.018	0.015	0.009
2	0.166	0.186	0.164	0.188	0.155	0.185	0.182	0.192	ns
3	0.071	0.083	0.074	0.064	0.072	0.072	0.058	0.082	0.019

^a SSP = single superphosphate, DAP = diammonium phosphate, MAP = monoammonium phosphate, RPR = reactive phosphate rock.

^b Low = <100mg Cd kg⁻¹ P, High >300mg Cd kg⁻¹ P.

There was no consistent effect of either P fertilizer type or Cd content on Cd concentrations in tubers. At site 2 there were no significant differences between any P fertilizer treatment. At site 1 tuber Cd concentrations were low and the only fertilizer giving significantly higher Cd concentrations in tubers than other treatments was MAP Low. At site 3, tubers had lower Cd concentrations in treatment RPR Low compared to tubers grown with high Cd sources of SSP and RPR. On plots receiving no P fertilizer, tuber Cd concentrations were not significantly different to P-fertilized plots (data not shown). The largest difference observed was inter-site variation, with site 2 having a site mean Cd concentration (0.177 mg kg⁻¹) almost ten times higher than site 1 (0.018 mg kg⁻¹). If all data were pooled and site was used as a blocking factor in the ANOVA, site differences were significant at the 0.1% level while treatment effects (if any) were significant only at the 5% level.

Effects of changing the source of K in the N:P:K fertilizer were also not significant compared to variation between sites (Figure 2).

Application of Zn at planting significantly ($P<0.05$) reduced Cd concentrations in tubers at four of the five sites (Table 5). However, inter-site differences in Cd concentrations were again dominant.

Site mean tuber Cd concentrations were best related to levels of water-extractable Cl in the soil prior to planting (Figure 3), which was found to be related to irrigation water quality (linear $R^2=0.94$, $P<0.001$) at each of the sites (data not shown).

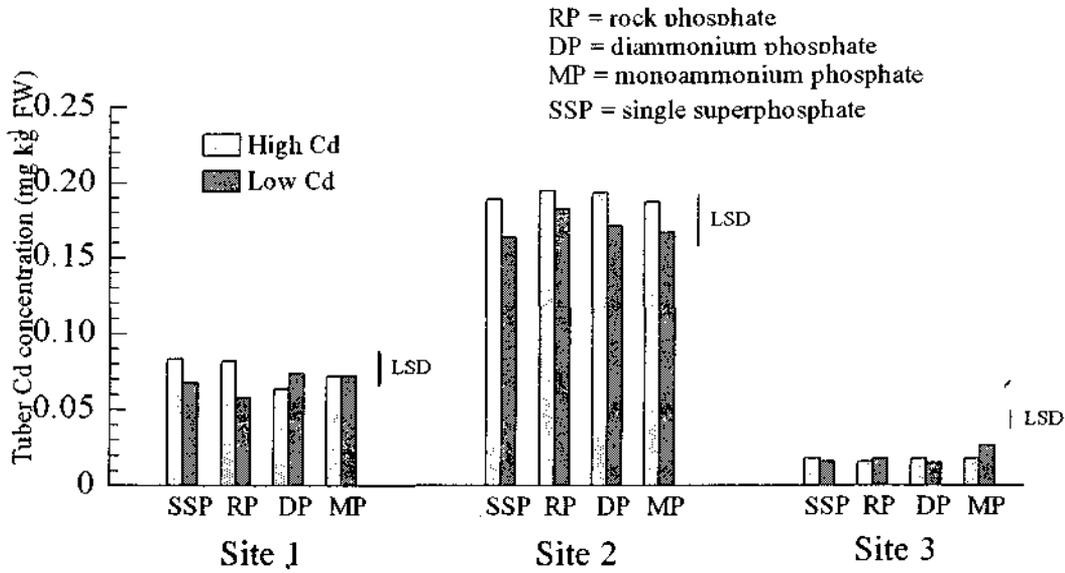


Figure 2. Effect of fertilizer type and quality on concentrations of Cd in potato tubers at 3 sites in southern Australia.

Table 5. Effect of addition of Zn fertilizer on cadmium concentrations in potato tubers at sites 1-5.

Site	Rate of Zn addition (kg ha ⁻¹)						LSD (P<0.05)
	0	5	10	25	50	100	
Tuber Cd concentrations (mg kg ⁻¹ FW)							
1	0.024	0.017	0.016	0.014	0.013	0.012	0.007
2	0.185	0.163	0.166	0.162	0.152	0.139	0.039
3	0.086	0.070	0.073	0.080	0.068	0.064	0.020
4	0	15	30				
4	0.042	0.032	0.032	0.009			
5	0.019	0.020	0.022	ns			

Concentrations of Cl in tubers (data not shown) were also closely related to tuber Cd concentrations (linear $R^2=0.79$, $P<0.001$), and to concentrations of Cl in soil prior to planting (linear $R^2=0.98$, $P<0.001$).

Discussion

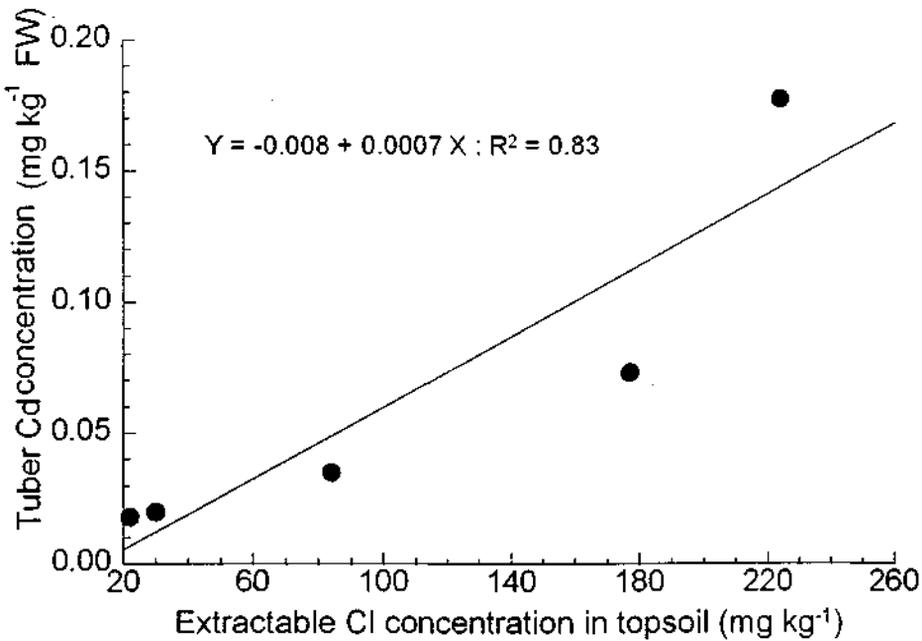


Figure 3. Relationship between site mean Cd concentration in potato tubers (fresh weight basis) averaged across all treatments and concentrations of water-extractable Cd (1:5 soil:solution ratio) in soil.

The sites used in this study were relatively uncontaminated by industrial Cd emissions and therefore had low total soil Cd concentrations. The five sites studied had EDTA-extractable Cd concentrations ranging from 0.030-0.188 mg kg⁻¹. These values can be compared to values for EDTA-extractable Cd in over 500 pasture soils (0-50 mm) in South Australia of 0.01-0.73 mg kg⁻¹ with a median value of 0.16 mg kg⁻¹ (Merry and Tiller, 1991). The Cd concentrations in potatoes found at site 2 were at the upper end of the range of Cd concentrations in potato tubers reported internationally [Andrey *et al.*, 1988; Anon, 1983; Jorhem *et al.*, 1984; Weigert *et al.*, 1984; Wiersma *et al.*, 1986; Wolnik *et al.*, 1983). Soils with relatively low Cd concentrations can therefore produce tubers with relatively high Cd concentrations, due to differences in soil conditions or crop management which increase Cd phytoavailability (discussed below).

Potatoes are normally grown in rotation with pastures and/or other vegetable crops, usually once every four to six years. In many cases the bulk or all of the fertilizer P applied to these rotations is applied during the potato cropping phase, where P inputs are often large (100-200 kg P ha⁻¹), particularly on oxisols or ultisols with high P requirements. Assuming that P fertilizer has a Cd content of 300 mg Cd kg⁻¹ P, then approximately 30-60 g Cd ha⁻¹ may be applied prior to planting of the potato crop. Despite these large Cd inputs (in comparison to pastures or cereal crops), this study demonstrates that changing the Cd content of the P fertilizer applied to the potatoes had insignificant effects on Cd accumulation in tubers. Sparrow *et al.* (1992) also recently found at one site that Cd content of P fertilizer had little effect on Cd uptake by potato tubers. The results presented here confirm that residual Cd in the soil, both "natural" Cd and Cd accumulated through previous fertilizer additions, is the dominant source of Cd

taken up by potato crops. The impact of the accumulated Cd on Cd concentrations in potatoes is determined by soil and environmental factors which vary between sites.

Where soils are in intensive potato production, introduction of low Cd fertilizers will not be immediately reflected in lower Cd concentrations in produce. However, the introduction of P fertilizers with lower Cd concentrations is important if the rate of Cd accumulation in soils is to be reduced. In this series of experiments Cd inputs varied from 2.8 g (MAP Low) to over 40 g Cd ha⁻¹ (SSP High), while Cd removal in tubers varied from 0.8 (site 1) to 9.6 g ha⁻¹ (site 2). Even where Cd removal in produce was high (e.g. site 2) P fertilizers with low Cd concentrations (<100 mg Cd kg⁻¹ P) would be required to appreciably reduce continued Cd accumulation in the soil, assuming no losses through leaching. To ensure Cd inputs equal Cd removed in produce for most commercial potato crops, where yields of around 50 t FW ha⁻¹ are common and tubers have Cd concentrations in the range 0.01 to 0.07 mg kg⁻¹ FW, growers will need to use ultra low Cd products (<50 mg Cd kg⁻¹ P) or reduce rates of fertilizer P application.

In this study the lack of any consistent effect of banded P fertilizer type contrasts with the results of Reuss *et al.* [29] who found that Cd in DAP was less available to plants than Cd in TSP. Their studies were carried out in the glasshouse, while it is known that rooting densities and soil moisture conditions are very different to those under field crops. Furthermore, under field conditions if the primary source of Cd taken up by the crop is outside the fertilizer band, then current P fertilizer type and its influence on soil pH in the fertilizer band will have little effect on Cd phytoavailability.

Changing K fertilizer from KCl to K₂SO₄ had no effect on tuber Cd concentrations in this study. Addition of Cl salts to soil have previously been found to increase the phytoavailability of Cd in soils in glasshouse experiments (Bingham *et al.*, 1984). In Appendix 4 it was demonstrated that soil salinity is the dominant factor controlling Cd concentrations in irrigated commercial potato crops in South Australia. We suggested that the effect of Cl in enhancing plant uptake of Cd is related to enhanced diffusion of Cd through the soil to the root surface when Cd is chloro-complexed (Appendix 4). Data in this work lend support for this hypothesis as there was a significant relationship between soil salinity (at planting) and tuber Cd concentrations (Figure 2). Unfortunately, soil salinity was not determined in the soils at the time of crop harvest. The soil analysis data in Table 2 therefore do not reflect soil conditions during crop growth, as the soil samples were taken at the time of crop planting. Soil salinities and pH change dramatically during the crop growth period, due to addition of elements in irrigation water and microbial and plant growth factors (e.g. nitrification of N fertilizers and plant uptake of N). It is therefore difficult to compare the Cl concentrations in soil in this study to those of Appendix 4, as the latter were determined on soils after crop growth. However, the soil Cl concentrations in Table 3 were a reflection of additions of Cl to the soil in irrigation waters in previous seasons, and the soil Cl concentrations prior to planting were significantly (P<0.001) correlated with irrigation water Cl concentrations at each site and with concentrations of Cl in potato tubers. Reducing inputs of Cl to soil by changing from KCl to K₂SO₄ as a source of K in the N:P:K mix therefore, were totally swamped in this study by irrigation water quality factors. Given a typical K application to potatoes of 150 kg ha⁻¹ and a minimum irrigation water

requirement of 300 mm per growing season, the effect of changing from KCl to K₂SO₄ in reducing Cl addition to soil was equivalent to a change in irrigation water Cl concentration of less than 50 mg L⁻³.

The negative interaction between added Zn and plant Cd uptake noted at four of the five sites has been observed by a number of authors [Abdel-Sabour *et al.*, 1988; Honma and Hirata, 1978). Abdel-Sabour *et al.* (1988) noted that increasing Zn concentrations in soil inhibited Cd uptake by Swiss chard and maize. Similar results have been found in field-grown wheat in areas of South Australia where Zn deficiency is common (Oliver *et al.*, 1994). The reductions in tuber Cd concentrations due to zinc addition were of the order 25-50%, similar to the results of Oliver *et al.* (1994) for wheat. However, at the two sites where Cd concentrations in tubers exceeded the Australian MPC of 0.05 mg kg⁻¹, application of Zn failed to reduce tuber Cd concentrations to values below the MPC. Inter-site differences in tuber Cd concentrations at the same rate of added Zn were large and the reduction in tuber Cd concentrations through adding Zn were unrelated to the initial Zn status of the soil, as indicated by EDTA-extractable Zn values (Table 3).

While the primary aim of this study was not to evaluate inter-site variation, site effects were dominant over fertilizer management treatments and it is interesting to note the relationship between tuber Cd concentrations and soil and crop characteristics. With only five sites studied, it is difficult to precisely determine the soil or site factors responsible for inter-site variation. Many of the major variables thought to be responsible for controlling phytoavailability of soil Cd e.g. soil pH, texture, soil Cd concentration, clay mineralogy, plant cultivar etc [11] were not independently related at these five sites. For example, site 3 had the highest Cd concentration in soil, but it was also the most acidic while site 5 had the lowest Cd concentration in soil, but was the most alkaline. Nevertheless, we can infer that potato cultivar was unlikely to be the cause of the high tuber Cd concentrations at sites 2 and 3. The highest Cd concentrations were found at site 2, which was planted with cultivar Atlantic. Cultivar Atlantic is not noted for accumulating high concentrations of Cd, and has a similar ranking in terms of Cd uptake as Russet Burbank and Sebago (Appendix 3), cultivars grown at sites 1, 4 and 5. Site 1 was on a heavy-textured soil rich in iron oxides which bind Cd strongly (Tiller *et al.*, 1984) and the soil was less saline, both factors which favour low Cd uptake by plants. Site 3 had tuber Cd concentrations three times those of site 1. The soil at this site was acidic, had the highest concentration of EDTA-extractable Cd and Cl concentrations in soil (and in irrigation water) were higher, factors which favour high Cd uptake. In the case of site 2, a combination of light-textured soil coupled with very poor quality irrigation water (1000 mg Cl L⁻¹) is likely to have led to the high tuber Cd concentrations.

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APPENDIX 6**Effect of current seasons lime applications on the yield and cadmium concentration of potato tubers (*Solanum tuberosum* L.)****INTRODUCTION**

Cadmium (Cd) has accumulated in many agricultural soils in Australia due to fertilisation with phosphatic fertilisers containing high concentrations of Cd (Tiller et al 1994). In southern Australia, Cd concentrations in potatoes often approach or exceed the Australian Maximum Permitted Concentration (MPC) of 0.05 mg kg⁻¹ fresh weight (FW) (Anon 1992a,b,c; Morgan 1989; Stenhouse 1991; NFA, 1993). It is therefore necessary to investigate farm management practices which could be used to reduce Cd accumulation in potato crops. Soil pH is regarded as the major factor controlling the plant availability of Cd in soil, with use of agricultural lime being the main management option suggested for minimizing Cd uptake by agricultural crops (Page and Bingham 1973; Chaney and Hornick 1978; Alloway 1990). In southern Australia, potatoes are often grown on acidic soils, so that the use of lime to raise soil pH may control Cd accumulation in potato tubers in these areas.

Murphy *et al.* (1967) reported that the incorporation of up to 7.6 t/ha of lime into the surface layer significantly reduced the tuber yield of Katahdin and Russet Burbank potatoes. They could not provide an explanation for the inverse lime - yield relationship. Jackson *et al.* (1982) working in Oregon with soils derived from pumice-volcanic ash parent material, found that tubers yields decreased significantly as pH increased from 4.5 to 6.4. Bolton (1977), working in Britain, reported that for the cv. Pentland Crown grown in a sandy-clay loam, total tuber yield was not affected by liming at 2 sites if a complete NPKMg fertiliser was applied. MacLean *et al.* (1967) found that liming acid peat soils (Histosols) to pH_w above 4.1-4.3 did not increase yield. Hossner and Doll (1970) studied the effects of applied lime and Mg, and soil K concentrations on the yield of potatoes (cv. Sebago) grown in a loamy sand. In 2 experiments over 2 years the application of 6.7 t/ha of hydrated lime did not significantly increase tuber yield. Lee and MacDonald (1977) used pot experiments to study the growth and yield of the cvv. Netted Gem, Sebago, Katahdin and Green Mountain grown in loam soil (Ultisol) at pH_w 4.6, 5.3 and 5.7. In both experiments raising the pH of the soils from 4.6 to 5.3 or 4.6 to 4.9 significantly increased tuber yield. Raising the pH to 5.7 or 5.2 did not result in a further increase in yield. van Lierop *et al.* (1982) reported on a pot experiment which studied the effects of liming on tuber (cv. Kennebec) yields. Eight sandy soils (Spodosols) typically used for potato production Quebec were used. The pH_w of the unlimed soils ranged from 4.6 to 5.0. The application of lime significantly increased (mean of 40%) tuber yield on 3 of the 8 soils. Increases in yield did not generally occur above pH 4.9. These studies show that liming can significantly affect tuber yield, therefore any study to assess the practical usefulness of liming to reduce Cd accumulation in tubers needs to determine tuber yield response as well.

This study reports a series of field and glasshouse experiments investigating the effect of applications of agricultural lime on **i)** soil pH and electrical conductivity (conductance); **ii)** Cd accumulation in tubers; and **iii)** tuber yield. We also present the coefficients of determination (r²) for relationships between Cd concentrations in tubers and the concentrations of other nutrients in leaves and tubers.

MATERIALS AND METHODS

Glasshouse experiments

Six glasshouse experiments were carried out over a period of 2 years. Details of planting dates, cultivars used and harvest and leaf sampling dates are presented in Table 1.

The experimental design was a randomized block, with 2 replicates in experiments G1 and G2, 4 in G3 and G6, 5 in G5 and 6 in experiment G4.

The experimental procedure was as follows:

- 1) Soil, from the A horizon, was collected from sites in the Mt Lofty Ranges and South East of South Australia. Each soil was air dried and sieved to <5 mm before use. For each experiment 300 mm diameter, free draining pots and 15 kg of air dry soil were used.
- 2) The soil from each pot was spread on a plastic sheet to <10-20 mm in depth. Finely ground agricultural lime (100%, <0.25 mm) was broadcast over the soil and thoroughly mixed with the soil. The rates of applied lime were in the range 0-20 t/ha, calculated on the basis of the surface area of the pots.

Table 1. Experimental details

Experiment ^A	Soil	Plot size	Date lime	Date crop	Date	Date	Cultivar ^C
<i>Glasshouse experiments</i>							
G1	MLR		9.viii.91	10.ix.91	19.xi.91	10.ii.92	RB, Kenn
G2	LSE		23.viii.91	2.x.91	25.xi.91	3.ii.92	RB, Kenn
G3	MLR		5.xii.91	27.ii.92	6.iv.92	10.vi.92	RB, Atl,
G4	LSE		23.xii.91	24.ii.92	7.iv.94	14.vii.92	RB
G5	LSE		18.viii.92	15.ix.92	3.xi.92	8.ii.93	RB
G6	LSE		21.i.93	15.ii.92	23.iii.93	8.vi.93	RB, Atl
G7	MLR		21.i.93	15.ii.92	23.iii.93	8.vi.93	Atl
<i>Field experiments</i>							
F1	LSE	3 x 3.5 m	26.ix.91	19.x.91	3.xii.91	17.iii.92	RB
F2	LSE	3 x 3.5 m	9.x.91	28.x.91	13.xii.91	2.iii.92	Kenn
F3	MLR	3 x 3.5 m	10.x.91	30.x.91	17.xii.91	10.iii.92	Atl
F4	LSE	5 x 3.5 m	6.x.92	12.xi.92	17.xii.92	4.ii.93	Shepody
F5	LSE	5 x 3.5 m	7.x.92	n.a.	17.xii.92	8.vi.93	RB
F6	LSE	5 x 3 m	n.a.	n.a.	7.i.93	31.iii.93	Pont
F7	LSE	3.5 x 2 m	13.xi.92	n.a.	26.i.92	25.iii.93	Crystal
F8	MLR	3.5 x 2 m	26.x.92	n.a.	8.i.93	22.vi.93	Kenn
F9	MLR	6 x 1 m	n.a.	n.a.	8.i.93	16.vi.93	Rb, Atl

^A G, Glasshouse experiments; F, Field experiments.

^B MLR, Mount Lofty Ranges; LSE, Lower South East.

^C RB, Russett Burbank; Kenn, Kennebec; Atl, Atlantic; Pont, Pontiac.

n.a., Not available.

- 3) The soil was replaced into the pot and wetted up. Soil moisture was maintained at field capacity (approximately -10 kPa) during the incubation period. Depending on the experiment, the incubation period was from 4-12 weeks and the pots were kept in a shed at room temperature.
- 4) Immediately prior to planting, the soil was again spread on a plastic sheet and a subsample was collected for chemical and physical analysis.
- 5) Nitrogen (N, as ammonium nitrate), phosphorus (P, as superphosphate) and potassium (K, as potassium sulfate) were broadcast at rates equivalent to 100-175 kg N/ha, 20-75 kg P/ha and 100-240 kg K/ha, depending on soil type and soil test values. The basal fertilisers were thoroughly mixed into the soil, after which approximately two thirds of the soil was replaced into the pot.
- 6) Tuber seed pieces (one per pot) were planted to a depth of 2-3 cm, after which the pots were placed in a glasshouse.
- 7) For each pot, the remaining soil was added when the plants were 20-25 cm tall to minimize the risk of tubers developing above the soil surface.
- 8) Depending on stage of growth, the plants were watered 1-6 times a week using either rain or tap water. For some soils, N and K were applied as side-dressings 2-3 times during the growth period to ensure these nutrients did not limit growth or yield response. During growth, each plant was supported by a trellis.
- 9) After haulm senescence, the contents of each pot were tipped onto a table and the tubers harvested. A soil sample was also collected for chemical analysis. After washing, the fresh weight of tubers was determined for each pot.

Field experiments

General site characteristics, including planting and harvest dates, cultivars used, plot dimensions and leaf sampling dates are presented in Table 1. Experiments F1-F8 were located in commercial plantings and experiment F9 at the Lenswood Centre, PI(SA). The experimental design was a randomized block with 3-4 replicates.

The field procedure was as follows:

- 1) After initial cultivations, plots were marked out and at some sites, soil samples to 0-15 and 16-30 cm depths, were collected from each plot. The number of rows per plot was 4 at sites F1-F6, 2 at sites F7-F8 and 1 at site F9.
- 2) Finely ground agricultural lime (100%, <0.25 mm) was spread by hand onto the plots at rates in the range 0-15 t/ha.
- 3) The lime was incorporated to a depth of 150-200 mm using a rotary hoe. The plots were then left undisturbed for 2-4 weeks, prior to planting.
- 4) After the incubation period, soil samples to 0-15 and 16-30 cm depths, were collected from each plot.

- 5) The tubers were mechanically planted.
- 6) N, at 50-150 kg N/ha, P at 50-100 kg P/ha and K, at 100-200 kg K/ha were applied either at planting or as side-dressings, depending on soil test data, soil type and cropping history.
- 7) Cultivation, pest and disease management and irrigation were carried out by the grower or by farm staff at the Lenswood Centre site. Crops were sprinkler irrigated, generally every 5-10 days depending on weather conditions, receiving approximately 20-30 mm water with each irrigation.
- 8) After haulm senescence, soil samples to 0-15 and 16-30 cm through the mound, were collected from each plot.
- 9) Tubers from 2 rows, 2 metres long, with the exception of site F9 (one row by three metres) were dug by hand and the total of fresh weight of tubers for each plot was recorded.
- 10) The tubers were placed into sacks and transported to the laboratory, where they were stored in open crates at 12 °C for post harvest assessment and laboratory analysis.

Soil sampling

To characterise the soil at each site, 20 cores, 5 cm diameter, were collected to 0-15 and 16-30 cm depths from each experimental area. For the field work, the experimental plots were also sampled by collecting 6 cores, to 0-15 and 16-30 cm depths, from each plot at the times specified in Table 1. For each depth, the samples were bulked, thoroughly mixed and sub-sampled for analysis.

Leaf sampling

The index tissue sampled was the 5th leaf from the growing terminal. For the field experiments, 20-30 leaves were collected from each plot on the date specified in Table 1. On the basis of plant development, sampling occurred in the field when the length of the longest tubers was in the range 20-40 mm. For the glasshouse experiments, the number of leaves sampled ranged from 2-10, depending on the number of stems produced.

Chemical analysis of soils

All soil samples were air dried before being sieved (< 2 mm stainless steel mesh) prior to chemical analysis.

Soils were analysed as outlined in Appendix 2.

Chemical analysis of plant materials

Cadmium.

Preparation of tubers and Cd analysis of tuber material was performed as outlined in Appendix. Cadmium concentrations in the tubers are reported on a fresh weight (f wt) basis and in the 5th leaf on a dry weight (d wt) basis.

Other elements

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

Statistical analysis

The effect of lime on soil pH and conductance, tuber yield and Cd concentrations in tubers was determined by analysis of variance. Coefficients of determination (r^2) were also determined for the relationships between N, P, K, Ca, Mg, Na, Cl, S, B, Cu, Zn, Mn and Fe concentrations in tubers and leaves and Cd concentrations in tubers.

RESULTS

Soil chemical and physical properties

Some chemical and physical properties of the soils from each experiment are given in Table 2.

All sites chosen had acid surface (0-15 cm) soils, with the pH values in the range 4.1-5.8 (Table 2). For the glasshouse experiments, the soil types ranged from sand (G3, G4 and G6) or loamy sand (G1 and G5) to sandy loam (G2 and G7). For the field experiments, the surface (0-15 cm) soils also ranged from sand (F1 and F5-F7) or loamy sand (F4, F8 and F9) to sandy loam (F2 and F3). The soils were siliceous sand/sandy loam over clay (Dy/Dr/Db) or siliceous sand (Uc) soils.

All except 2 of the soils chosen (G3 and G6) had organic-C values $>1.5\%$ in the surface (0-15 cm) layer indicating moderate to high fertility levels. Extractable P concentrations ranged from 7 to 65 mg/kg in the soils used for the glasshouse experiments and from 16 to 98 mg/kg in the surface (0-15 cm) soils of the field sites (Table 2). This range of values suggests widely different histories of application of P fertiliser between the sites.

Soil pH

Main effects

The applications of lime significantly ($P < 0.05$) increased soil pH in all experiments (Table 3). However, the rate of lime required to raise the pH by 1 to 2 units varied considerably between experiments. For example, increasing the rate of applied lime from nil to 5 t/ha, increased pH from 5.6 to 7.2 in experiment F1, in contrast, in experiment F6, pH increased from 5.2 to only 5.6.

Table 2. Selected chemical and physical properties of soils used in glasshouse and field experiments

Soil		pH _w	Org-C (%)	Ext-P (mg/kg)	Exch-Ca cmol(+)/kg	C.E.C.	Sand (%)	Silt (%)	Clay (%)
Depth (cm)									
<i>Glasshouse experiments</i>									
G1		4.9	2.1	18.2	1.34	5.3	84	9	7
G2		4.7	2.3	65.1	3.98	7.3	86	1	13
G3		4.7	1.1	9.5	1.09	2.5	95	1	4
G4		4.9	2.2	19.4	1.34	5.9	90	2	8
G5		4.1	2.4	11.7	2.17	4.6	87	5	8
G6		4.7	1.4	7.1	0.51	3.4	93	1	6
G7		4.9	2.3	28.6	2.35	5.8	84	6	10
<i>Field experiments</i>									
F1	0-15	5.3	2.0	18.0	3.36	5.0	96	3	1
	16-30	5.4	0.3	6.9	0.65	1.5	96	3	1
F2	0-15	5.8	2.4	18.2	5.28	10.4	79	10	11
	16-30	-	1.0	19.4	6.81	13.4	61	10	29
F3	0-15	4.7	2.0	43.7	3.53	8.9	74	12	14
	16-30	-	0.4	6.8	6.59	12.3	56	10	34
F4	0-15	5.0	1.9	66.0	2.50	5.8	87	8	5
	16-30	4.9	1.0	20.6	1.36	3.7	87	7	6
F5	0-15	4.8	1.8	16.1	1.32	4.5	91	5	4
	16-30	5.0	1.8	13.1	1.21	4.0	91	5	4
F6	0-15	5.3	2.2	33.8	2.17	6.1	91	5	4
	16-30	5.2	1.2	28.7	1.17	4.0	88	7	5
F7	0-15	5.5	2.2	11.1	1.97	5.3	90	5	5
	16-30	5.1	0.6	7.4	0.77	2.4	91	5	4
F8	0-15	5.3	2.1	68.4	2.04	4.8	88	8	4
	16-30	5.1	1.0	30.8	1.08	3.9	89	7	4
F9	0-15	5.4	2.0	97.7	9.01	8.6	81	7	12
	16-30	5.3	1.7	75.7	10.37	7.0	81	8	11

^A G, Glasshouse experiments; F, Field experiments.

The pH values also varied between sampling times. For example, in experiments F1, F3, F4, F8 and G2-G5 pH determined at harvest was significantly ($P < 0.05$) higher, by 0.1-0.5 of a unit, compared with pH values measured at planting (Table 3). In experiments F5, G1 and G6, pH values significantly decreased by 0.2-0.4 units, during this period.

Soil depth also affected pH. In all except 1 field experiment (F2), pH was significantly ($P < 0.05$) lower at the 16-30 cm depth compared with the surface (0-15 cm) soil. (Table 3). This shows the limitation of the method of incorporation (i.e. rotary hoeing) used in the field experiments.

Table 3. Main effects of lime, sampling time and depth on soil pH for field and glasshouse experiments

Rate	Field experiments									Glasshouse experiments					
	F1	F2	F3	F4	F5	F6	F7	F8	F9	G1	G2	G3	G4	G5	G6
	<i>Lime (t/ha)</i>														
0	5.6	5.6	4.8	5.0	4.7	5.2	5.5	5.2	5.4	4.8	5.1	4.8	4.8	4.4	4.3
0.5										5.0	4.8				
1	6.2	5.9	4.9							4.9	4.9				
1.5	6.2	5.9	5.0												
2	6.4	6.1	5.3								5.1				
2.5					5.2	5.5	5.8	5.9							5.5
3	6.2	6.1	5.6								5.3				
4		6.1	5.7								5.5				
5	7.2	6.5	5.8		5.5	5.6	6.2	6.3	6.6	6.1				6.2	6.2
6											5.8				
7.5				5.9			6.7	6.6				6.5			
10	7.3	6.6	6.2		5.9	5.9			6.8	6.6	6.4			7.1	6.8
15	7.7	7.0	6.8	6.2		5.9	6.9	7.2			7.1				
20													7.7	7.4	
<i>L.s.d.</i>	0.4	0.4	0.2	0.2	0.2	0.1	0.3	0.2	0.1	0.2	0.3	0.1	0.1	0.1	0.1
	<i>Sampling time</i>														
Plant.	6.4	6.2	5.3	5.5	5.5	5.6	6.1	6.2	6.3	5.6	5.4	5.6	6.2	6.2	5.9
Harv.	6.8	6.2	5.8	5.9	5.2	5.6	6.3	6.3	6.3	5.4	5.7	5.7	6.3	6.3	5.5
<i>L.s.d.</i>	0.2	<i>n.s.</i>	0.1	0.1	0.2	<i>n.s.</i>	<i>n.s.</i>	0.1	<i>n.s.</i>	0.1	0.1	0.07	0.1	0.08	0.1
	<i>Soil depth (cm)</i>														
0-15	6.8	6.2	5.8	6.1	5.7	6.1	6.6	6.4	6.4						
16-30	5.7	6.0	5.3	5.3	4.9	5.2	5.8	6.1	6.2						
<i>L.s.d.</i>	0.2	<i>n.s.</i>	0.1	0.1	0.2	0.1	0.2	0.1	0.1						

For glasshouse experiments G1, G2 and G6 there were significant ($P < 0.05$) differences in soil pH, depending on which cultivar grew in the pots. However, the differences were small and of little practical significance. For example, in experiments G1 and G2 the soils from pots in which the cv. Russet Burbank grew had a higher pH (5.6 and 5.8, respectively) compared with soils from pots in which the cv. Kennebec grew (5.4 and 5.4, respectively). In experiment G6, the soil from pots in which the cv. Atlantic grew had significantly ($P < 0.05$) higher pH (5.8) compared with the soil from pots in which the cv. Russet Burbank had grown (5.6).

Interactions

There were significant lime x sampling time interactions in experiments G1, G3, F1 and F3 ($P < 0.05$), and G5 and G6 ($P < 0.001$). The interactions were grouped into 3 categories, 1) those experiments (e.g. G5, G6 and F1) in which there was a significant difference in pH between sampling times at nil or low rates of lime (eg. 1-3 t/ha) and not at the higher rates (eg. 5-15 t/ha). For example, in experiments G5 and F1, when nil lime was applied the pH of the soil at harvest (4.7 and 6.1, respectively) was significantly higher compared with planting (4.1 and 5.1, respectively). In contrast, at 15 or 20 t/ha lime the mean pH values were in the range 7.4-

7.8. ii) those experiments (eg. G1 and F3) in which there was a significant difference in pH between sampling times at the higher rates of lime (eg. 10 or 15 t/ha) but not at the nil or low rates (eg. 1-3 t/ha). For example in experiment F3, for the nil lime treatment the pH at planting (4.7) and harvest (4.9) were similar. In contrast, when 15 t/ha of lime was applied the pH at planting (6.4) was significantly lower than the pH at harvest (7.2).

For the field experiments, there were significant lime x depth interactions in experiment F3 ($P < 0.01$) and experiments F4-F6 ($P < 0.001$). The interactions occurred because the differences in pH between the 0-15 and 16-30 cm depths depended on the rate of applied lime. For example, in experiment F6 at nil, 5 and 15 t/ha of applied lime the pH in the surface (0-15 cm) was 5.3, 6.0 and 6.8, respectively. In contrast at 16-30 cm the values were 5.1, 5.2 and 5.1, respectively. These data highlight the problem of effectively incorporating lime to depth in the field.

In experiments F9 ($P < 0.05$), F4 ($P < 0.01$), and F5 and F6 ($P < 0.001$) there were significant sampling time x depth interactions. The interactions could be categorized as follows, i) the change in pH with depth was greater at harvest compared with planting (experiments F6 and F9). For example, in experiment F9 at planting the mean pH decreased from 6.3 at 0-15 cm to 6.2 at 16-30 cm, however, at harvest the decrease was from 6.5 to 6.1. ii) the change pH with depth varied with sampling time (eg. F4 and F5). For example, in experiment F5 the pH of the surface (0-15 cm) soil did not change between planting (5.7) and harvest (5.65), in contrast, at 16-30 cm the pH decreased from 5.2 to 4.7, respectively.

Conductance

Main effects

The application of lime significantly ($P < 0.05$) increased conductance in experiments G1-G3 and F1-F7 (Table 4). However, the magnitude of the changes varied between experiments. In experiment F9 conductance decreased with increasing rates of lime.

The effect of sampling time on soil conductance was not consistent between experiments. For example, in experiments G2, G3 and F4 conductance significantly ($P < 0.05$) decreased between planting and harvest (Table 4). In contrast, in experiments G5 and F9 the changes were not significant, while in all other experiments, conductance increased significantly ($P < 0.05$) during this period. The increase may have been due to the accumulation of salts from the application of fertilisers and irrigation water.

Soil conductance was significantly higher in glasshouse soils at planting compared to field soils. This is presumably due to greater mineralisation of organic matter and minimal leaching of nutrient ions under glasshouse conditions.

Soil conductance also varied with soil depth. For example, in field experiments F1 and F9 conductance was significantly higher at 16-30 cm compared with 0-15 cm (Table 4). In all other experiments it was significantly ($P < 0.05$) lower.

Interactions

Only in experiment F7 was there a significant ($P < 0.001$) lime x sampling time interaction. At this site, changes in conductance due to the application of lime were greater at harvest than at

planting. For example, increasing the rate of applied lime from nil to 2.5 t/ha increased conductance from 0.21 to 0.22 at planting, but from 0.52 to 0.86 at planting.

Table 4. Main effects of lime, sampling time and depth on soil conductance for field and glasshouse experiments

Rate	Field experiments									Glasshouse experiments					
	F1	F2	F3	F4	F5	F6	F7	F8	F9	G1	G2	G3	G4	G5	G6
	<i>Lime (t/ha)</i>														
0	0.14	0.44	0.39	0.12	0.19	0.13	0.37	0.43	0.8	0.14	0.38	0.43	0.51	0.41	0.40
0.5										0.15	0.48				
1	0.13	0.34	0.41							0.17	0.42				
1.5	0.15	0.54	0.46												
2	0.16	0.42	0.44								0.43				
2.5					0.20	0.13	0.54	0.38							0.40
3	0.20	0.48	0.40								0.45				
4		0.49	0.36								0.47				
5	0.15	0.40	0.46		0.21	0.14	0.41	0.39	0.4	0.23				0.39	0.40
6											0.54				
7.5				0.18			0.42	0.42				0.54			
10	0.27	0.62	0.60		0.23	0.16			0.5	0.27	0.54			0.44	0.4
15	0.23	0.54	0.52	0.20		0.19	0.49	0.45			0.57				
20													0.54	0.43	
<i>l.s.d.</i>	0.08	0.17	0.14	0.05	0.04	0.03	0.07	<i>n.s.</i>	0.1	0.06	0.08	0.05	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
	<i>Sampling time</i>														
Plant.	0.11	0.27	0.23	0.21	0.08	0.08	0.23	0.16	0.6		0.68	0.52	0.48	0.41	0.40
Harv	0.25	0.68	0.67	0.13	0.33	0.22	0.66	0.67	0.5		0.28	0.46	0.57	0.42	0.50
<i>l.s.d.</i>	0.04	0.08	0.07	0.04	0.03	0.02	0.05	0.06	<i>n.s.</i>		0.04	0.05	0.09	<i>n.s.</i>	
	<i>Soil depth (cm)</i>														
0-15	0.25	0.68	0.67	0.25	0.25	0.22	0.56	0.50	0.5						
15-30	0.37	0.47	0.48	0.08	0.17	0.09	0.33	0.33	0.6						
<i>l.s.d.</i>	0.05	0.10	0.07	0.04	0.03	0.02	0.05	0.06	0.1						

There were significant sampling time x depth interactions in experiments F9 ($P<0.05$), F4 and F8 ($P<0.01$), and F5 and F6 ($P<0.05$). The interactions occurred because at 0-15 cm there were larger and significant changes in conductance between planting and harvest, compared with the 16-30 cm depth. For example, in experiment F4, at 0-15 cm conductance decreased from 0.32 at planting to 0.18 at harvest. At 16-30 cm, the change was negligible, 0.09 to 0.08.

Tuber yield

The effect of current seasons lime applications on tuber yield was inconsistent. For example, the application of lime significantly ($P<0.05$) decreased (experiments F1, G3 and G5), increased (experiment G1) or increased and then decreased yield at the highest rate of lime (experiment F9) (Table 5). In all other experiments the effect of lime was not significant ($P>0.05$).

Table 5: Effect of rate of applied lime (t/ha) on the total fresh weight of tubers from field (t/ha) and glasshouse (g/plant) experiments

Rate	Field experiments									Glasshouse experiments					
	F1	F2	F3	F4	F5	F6	F7	F9	G1	G2	G3	G4	G5	G6	
0	65.0	53.4	73.7	40.5	60.6	65.2	58.4	50.3	348.0	607.6	301.1	341.3	942.7	414.0	
0.5									353.2	758.7					
1	62.1	58.7	68.4						437.0	607.8					
1.5	65.5	55.0	70.2												
2	57.8	58.6	70.7							751.1				499.3	
2.5					68.2	59.9	57.6								
3	59.9	61.1	66.5							683.2					
4	59.4	60.7	67.1							673.3					
5	58.4	62.6	68.9		62.7	58.8	64.3	63.9	576.7				963.6	485.0	
6										755.6					
7.5				40.3			61.8				220.3				
10	48.6	61.4	71.0		69.0	56.8		54.4	628.1	715.8			842.9	407.0	
15	54.3	56.0	71.4	42.0		55.8	51.3			719.2					
20										502.1		306.2	813.2		
<i>l.s.d.</i>	<i>8.8</i>	<i>n.s.</i>	<i>7.5</i>	<i>174.1</i>	<i>n.s.</i>	<i>54.7</i>	<i>n.s.</i>	<i>90.0</i>	<i>n.s.</i>						

In experiments F9, G1, G3 and G4 the lime x cultivar interactions were not significant, indicating that in each experiment the response to lime was similar for the cultivars tested. In experiment G2 the interaction was significant ($P < 0.001$). Increasing the rate of applied lime from nil to 20 t/ha decreased the yield of Kennebec from 1019 to 64 g/plant. In contrast, the yield of Russet Burbank increased from 196 to 939 g/plant.

Cadmium concentrations in tubers

In the field experiments, the application of lime, up to 15 t/ha, did not significantly reduce Cd in tubers (Table 6a). Further, in experiments F5 and F6 it significantly ($P < 0.05$) increased Cd concentrations. In contrast with the field experiments, the application of lime significantly reduced Cd concentrations in tubers in all except 1 glasshouse experiment (Table 6b). In experiment G1, Cd concentrations decreased however, the effect was not significant due possibly to limited replication of treatments (Table 1).

There were significant lime x cv. interactions in experiments G3 ($P < 0.001$) and G6 ($P < 0.05$).

In experiment G3, Cd concentrations in tubers of the cv. Pontiac (0.138 mg/kg) were significantly higher compared with the cvv. Russet Burbank (0.078 mg/kg), Atlantic (0.080 mg/kg) and Desiree (0.076 mg/kg). Significant differences between cvv. also occurred in experiment G6, in which Cd concentrations in tubers of the cv. Atlantic (0.03 mg/kg) were higher than the cv. Russet Burbank. In field experiment F9, the differences in Cd concentration between the cvv. Russet Burbank (0.015 mg/kg) and Atlantic (0.016 mg/kg) were not significant.

Table 6a. Effect of rate of applied lime (t/ha) on cadmium concentrations (mg/kg f wt) in tubers harvested from field experiments

Rate	F1	F3	F4	F5	F6	F7	F8	F9
0	0.033	0.042	0.073	0.027	0.075	0.135	0.182	0.015
0.5								
1	0.037	0.041						
1.5	0.035	0.047						
2	0.038	0.051						
2.5				0.032	0.097	0.155	0.185	
3	0.037	0.054						
4	0.039	0.050						
5				0.035	0.083	0.129	0.197	0.015
6	0.033	0.060						
7.5			0.084			0.152	0.209	
10	0.037	0.052		0.036	0.074			0.017
15	0.032	0.053	0.095		0.071	0.160	0.229	
20								
<i>l.s.d.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.005	<i>n.s.</i>	<i>n.s.</i>	0.026	<i>n.s.</i>

Table 6b. Effect of rate of applied lime (t/ha) on cadmium concentrations (mg/kg f wt) in tubers harvested from glasshouse experiments

Rate	G1	G2	G3	G4	G5	G6
0	0.106	0.048	0.102	0.215	0.044	0.032
0.5	0.080	0.061				
1	0.077	0.035				
1.5						
2		0.053				
2.5						0.031
3		0.044				
4		0.041				
5	0.071				0.029	0.027
6		0.029				
7.5			0.084			
10	0.069	0.031			0.021	0.024
15		0.025				
20				0.060	0.020	
<i>l.s.d.</i>	<i>n.s.</i>	0.021	0.015	0.075	0.009	0.005

Based on data for all experiments, the relationships between Cd concentrations in tubers and rate of applied lime (Figure 1a) and soil pH_w at harvest (Figure 1b) were poor. High Cd concentrations were associated with high soil conductance at harvest (Figure 1c).

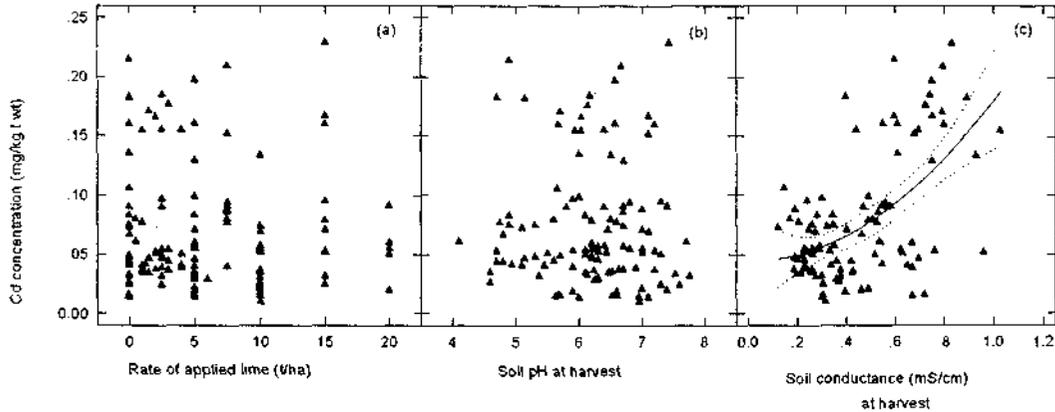


Figure 1. Relationships between (a) rate of applied lime, (b) soil pH_w and (c) conductance at harvest and Cd concentrations in tubers. Dotted lines indicate the 95% confidence limits.

Cadmium concentrations in 5th leaf

Data on the effect of applied lime on Cd concentrations in the 5th leaf were only collected in 2 experiments. In experiment G5, increasing the rate of applied lime from nil to 10 t/ha significantly decreased Cd concentrations from 2.52 to 0.78 mg/kg, d wt. Similarly, in experiment G6, Cd concentrations decreased from 1.23 to 0.75 mg/kg, d wt. In this experiment Cd concentrations in leaves of the cv. Atlantic (0.98 mg/kg, d wt) were significantly higher compared with the cv. Russet Burbank (0.88 mg/kg, d wt). The lime x cv. interaction was not significant.

Correlations between Cd concentrations in tubers and the concentrations of other elements in the tuber and fifth leaf

Regression analysis and visual inspection of the graphs showed that there were significant positive relationships between Ca (Figure 2), Mg, Na, Cl and Fe concentrations in 5th leaf, and K, Mg, Na, Cl and Zn concentrations in tubers and the concentration of Cd in tubers (Table 7). The relationship between Cu concentrations in the 5th leaf and Cd concentrations in tubers was negative. Except for Cl concentrations in tubers, the amount of variation in tuber Cd concentration accounted for by these relationships was low.

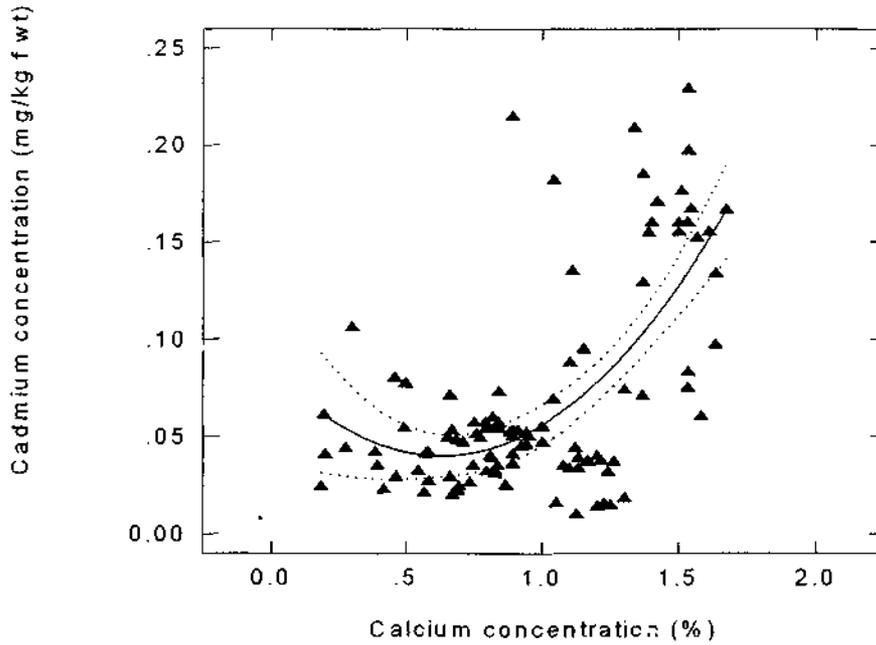


Figure 2. Relationship between Ca concentrations in 5th leaf and Cd concentrations in tubers.

Table 7. Coefficients of determination (r^2) for relationships between cadmium concentrations in tubers and other elements in 5th leaf and tubers.

Nutrient	5th leaf				Tuber			
	r^2	F value	Probability	n	r^2	F value	Probability	n
N	0.02	1.7	n.s.	71	n.a.			
P	0.03	2	n.s.	75	0.02	1.2	n.s.	73
K	0.04	3.3	n.s.	75	0.13	10.9	<0.01	73
Ca	0.27	27.4	<0.001	75	0.003	0.2	n.s.	73
Mg	0.31	32.2	<0.001	75	0.18	16.1	<0.001	73
Na	0.24	23.6	<0.001	75	0.31	32.6	<0.001	73
Cl	0.33	33.6	<0.001	71	0.74	173.7	<0.001	63
S	0.05	3.6	n.s.	75	0.02	1.5	n.s.	73
B	0.002	0.1	n.s.	73	0.001	0.01	n.s.	73
Cu	0.21	19.6	<0.001	75	0.02	1.1	n.s.	73
Zn	0.003	0.2	n.s.	75	0.07	5	<0.05	73
Mn	0.01	0.09	n.s.	75	0.05	3.4	n.s.	73
Fe	0.06	4.4	<0.05	71	n.a.			

DISCUSSION

Most of the soils used in this study were light-textured and had pH values less than 6 prior to application of lime. These soils are typical of many potato-growing regions in southern Australia. Application of lime raised soil pH by one to three units depending on soil type and rate of lime application, with six of the 16 experiments having pH values above 7 at the highest application rates used.

Liming generally increased the EC of soils, and while under field conditions soil EC values generally increased between planting and harvest, the EC values for soils in glasshouse trials generally decreased over the plant growth period. Presumably, the latter is due to the fact that plant uptake of nutrient elements and salts during growth reduces salt concentrations in soil, where good quality water is used to grow plants. In the field, use of poorer quality irrigation water led to salt build-up in most soils. Tuber yields were generally unaffected by liming.

Potatoes are generally regarded as being highly tolerant of acidic soil conditions, and our data supports this observation. In light-textured soils, application of lime may induce deficiencies of some trace elements in crops. From analysis of leaf samples collected during the early tuber growth period, there was no indication of deficiency for any macro- or micronutrient, given current criteria for South Australian potato crops. A further concern with use of lime on soils used for potato production is the increased risk of infection of the crop with common scab [Huber 1990]. We observed no increased incidence of scab with liming at any site.

Concentrations of Cd in tubers grown under field conditions were either unaffected by liming or were increased compared to unlimed controls. By contrast, large reductions in concentrations of Cd in tubers were observed with experiments under glasshouse conditions. The reasons for these differential responses to lime are unknown. It has been known for some time that metal accumulation by crops under glasshouse conditions is markedly different to that in the field, even where the same soil and treatments are used. This has been attributed to differences in rooting habit and soil temperature and moisture conditions between the two environments. Under field conditions, where crops are irrigated rather than rain fed, differences in water quality between glasshouse and field environments may also lead to different metal concentrations in plants.

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APPENDIX 7	Effect of lime and phosphorus on the growth, yield and N, P, and Cd concentrations in potatoes (<i>Solanum tuberosum</i> L.).
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INTRODUCTION

Potatoes are considered to be tolerant of acid soil conditions (Anonymous 1973; Sutherland 1979) and liming of soils used for potato growing is not commonly practiced because of the effect of decreasing acidity on the incidence of scab (Odland and Allbritten 1950; Doyle and MacLean 1960). However, in some potato growing regions of southern Australia, cadmium (Cd) residues often exceed the maximum permitted concentration (MPC) and management options which reduce Cd uptake need to be identified. Liming may be one such option (Page and Bingham 1973).

Phosphorus (P) is a major nutrient applied to potato crops. Depending on the soil type and residual P status, rates up to 150-250 kg P/ha may be applied. However, the application of P fertilisers has been identified as a major source of Cd taken up by plants (Tiller et al., 1994). Few studies have been published on the effect of increasing rates of superphosphate on Cd uptake by potatoes growing in siliceous sand/sandy loam over clay (Dy/Dr/Db) or siliceous sand (Uc) soils. Published studies on the effect of lime application on P availability and uptake by plants are contradictory (Haynes 1984; Sumner and Farina 1986). For potatoes, Bolton (1977) found that increasing rates of lime increased P concentrations in leaves especially if P fertiliser was omitted. At nil P, concentrations increased from 0.15-0.16 to 0.20-0.25% P. Lee and MacDonald (1977) reported that the application of dolomite significantly increased Ca (1.10 to 1.35%) and Mg (0.20 to 0.51%) concentrations but did not affect P (0.24-0.26%) concentrations.

In this paper we report on 3 field and 2 glasshouse experiments in which the effects of applying lime and P on the growth, yield, N and P concentrations in 5th leaf and Cd concentrations in tubers of the cvv. Russet Burbank, Pontiac and Crystal.

MATERIALS AND METHODS

Glasshouse experiments

Two glasshouse experiments were conducted during 1991/92 (G4) and 1992/93 (G5) at the Northfield Research Laboratories. Details of lime applications, planting, leaf sampling and harvest dates are presented in Table 1.

The experimental design was a randomized block, with 2 lime x 2 P treatments replicated 6 times in experiment G4, and 3 lime x 2 P treatments replicated 5 times in experiment G5. The cvv. grown were Russet Burbank, Pontiac and Crystal in experiments F5, F6 and F7, respectively in the field experiments, and Russet Burbank in the glasshouse experiments.

Table 1. Experimental details

Experiment	Plot size	Date of lime	Date crop	Date	Date of
<i>Glasshouse experiments</i>					
G4	-	23.xii.91	24.ii.92	7.iv.92	14.vii.92
G5	-	18.viii.92	15.ix.92	3.xi.92	8.ii.93
<i>Field experiments</i>					
F5	5 x 3.5 m	7.x.92	n.a.	17.xii.92	8.iv.93
F6	5 x 3 m	n.a.	n.a.	7.i.93	31.iii.92
F7	3.5 x 2 m	13.xi.92	n.a.	26.i.92	25.iii.93

The experimental procedure was as follows:

- 1) Soil, from the A horizon, was collected from sites in the Mt Lofty Ranges (G4) and South East (G5) of South Australia. Each 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.
- 2) The soil from each pot was spread on a plastic sheet to <10-15 mm in depth. Depending on the treatment, finely ground agricultural lime (100%, <0.25 mm) was broadcast over the soil and then thoroughly mixed with the soil. The rates of lime were equivalent to 0 and 20 t/ha in experiment G4 and 0, 5 and 10 t/ha in experiment G5. The rates were calculated on the basis of the surface area of the soil in the pots.
- 3) The soil was placed back into the pot and 'wetted up'. Soil moisture was maintained at field capacity (approximately -10 kPa) during the incubation period. The moist incubation period was approximately 8 weeks in experiment G4 and 4 weeks in experiment G5 (Table 1). During this period the pots were kept in a shed at room temperature.
- 4) In both experiments the P treatment, equivalent to 75 kg P/ha as superphosphate, was incorporated into the soil 1 week before planting. At the same time, in experiment G4 N, equivalent to 50 kg N/ha as ammonium sulfate, and K, equivalent to 120 kg K/ha as potassium sulfate, were also applied to all pots. In experiment G5, N, equivalent to 50 kg N/ha as calcium nitrate, and K, equivalent to 100 kg K/ha as potassium sulfate were applied to all pots. The rates of N and K applied depended on soil type and soil test values. The basal fertilisers were thoroughly mixed into the soil, after which approximately two thirds of the soil was replaced into the pot.
- 5) Immediately prior to planting, a subsample of soil was collected from each pot for chemical analysis.
- 6) Tuber seed pieces (one per pot) were planted and covered with 2-3 cm of soil, after which the pots were placed in a glasshouse.
- 7) 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.

- 8) Depending on stage of growth, the plants were watered 1-6 times a week using either rain or tap water. In experiment G4, 2 side-dressings of N, each equivalent to 50 kg N/ha, were applied on the 13th and 26th of March 1992. In experiment G5, side-dressings of K, equivalent to 37.5 kg K/ha, were applied on the 8th and 20th of October. Three side-dressings of N, equivalent to 37.5, 50 and 37.5 kg N/ha were also applied on the 8th and 20th October and the 20th November, respectively. The side-dressings were applied to ensure these nutrients did not limit growth or yield response. During growth, each plant was supported by a trellis.
- 9) After haulm senescence, the contents of each pot were tipped onto a table and the tubers harvested. A soil sample was also collected for chemical analysis. After washing, the fresh weight of tubers was determined for each pot.

Field experiments

Three field experiments, located in commercial plantings, were conducted during 1992/93 in the lower (sites F5 and F6) and upper (site F7) South East of South Australia. Lime application, leaf sampling and harvest dates are presented in Table 1.

The experimental design was a randomized block. There were 2 lime x 3 P rates in experiment F5, and 5 lime x 2 P rates in experiments F6 and F7. The treatments were replicated 3 times in experiments F5 and F7, and 4 times in experiment F6.

The field procedure was as follows:

- 1) After initial cultivations, soil samples were collected across the experimental area for chemical and physical analysis to characterise the soil at each site. Plots were then marked out.
- 2) Finely ground agricultural lime (100%, <0.25 mm) was spread by hand over the plots at rates in the range 0-15 t/ha.
- 3) The lime was incorporated to a depth of 150-200 mm using a rotary hoe. The plots were then left undisturbed for 2-4 weeks, prior to planting.
- 4) After the incubation period, soil samples to 0-15 and 16-30 cm depths, were collected by sampling through the mounds of each plot.
- 5) The tubers were mechanically planted.
- 6) Before banking, the P treatments were applied, either broadcast (experiments F5 and F6) or banded along the rows (experiment F7) and incorporated into the soil. In experiments F5 and F6, N at 150 kg N/ha as ammonium nitrate and K, at 200 kg K/ha as potassium sulfate, were also applied. In experiment F7, The N and K rates applied were 50 kg N/ha and 100 Kg K/ha, respectively. The growers applied further rates of N, K and trace element sprays to the plantings, including the experimental plots, during the growing season. The rates applied depended on soil type, cropping history and soil test data.

- 7) Cultivation, pest and disease management and irrigation were carried out by the grower. Crops were sprinkler irrigated, generally every 5-10 days depending on weather conditions, receiving approximately 20-30 mm water with each irrigation.
- 8) After haulm senescence, soil samples to 0-15 and 16-30 cm through the mound, were collected from each plot.
- 9) Tubers from 2 rows, 2 metres long and located in the centre of the plot, were dug by hand and the total of fresh weight of tubers for each plot was recorded.
- 10) The tubers were placed into sacks and transported to the laboratory, where they were stored in open crates at 12 °C for post harvest assessment and laboratory analysis.

Soil sampling

To characterise the soil at each site, 20 cores, 5 cm diameter, were collected to 0-15 and 16-30 cm depths from each experimental area, after the initial soil preparation. For the field work, the experimental plots were also sampled immediately before planting and harvest by collecting 6 cores, to 0-15 and 16-30 cm depths, from each plot at the times specified in Table 1. For each depth, the samples were bulked, thoroughly mixed and sub-sampled for analysis.

Leaf sampling

The index tissue sampled was the 5th leaf from the growing terminal. For the field experiments, 20-30 leaves were collected from each plot on the date specified in Table 1. On the basis of plant development, sampling occurred in the field when the length of the longest tubers was in the range 20-40 mm. For the glasshouse experiments, the number of leaves sampled ranged from 2-10, depending on the number of stems per plant.

Chemical analysis of soils

All soil samples were air dried before being sieved (< 2 mm stainless steel mesh) prior to chemical analysis.

Soils were analysed as outlined in Appendix 2.

Chemical analysis of plant materials

Cadmium

Preparation of tubers and Cd analysis of tuber material was performed as outlined in Appendix 2.

Other elements

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

Statistical analysis

The effects of rate of applied lime and P on soil pH and conductance, tuber yield, plant height, number of tubers and stems per plant, dry matter leaf, stem and leaf+stem yields, and elemental concentrations in 5th leaf and tubers were determined by analysis of variance.

RESULTS AND DISCUSSION

Soil chemical and physical properties

Selected chemical and physical properties of the soil used in each experiment are presented in Table 2.

Table 2. Selected chemical and physical properties of the field and glasshouse soils

	Soil depth (cm)	pH _w	Total carbon (%)	Ext-P (mg/kg)	C.E.C.	Sand (%)	Silt (%)	Clay (%)
<i>Glasshouse experiments</i>								
G4		4.9	2.2	19	5.9	90	2	8
G5		4.1	2.4	12	4.6	87	5	8
<i>Field experiments</i>								
F5	0-15	4.8	1.8	16	4.5	91	5	4
	16-30	5.0	1.8	13	4.0	91	5	4
F6	0-15	5.3	2.2	34	6.1	91	5	4
	16-30	5.2	1.2	29	4.0	88	7	5
F7	0-15	5.5	2.2	11	5.3	90	5	5
	16-30	5.1	0.6	7	2.4	91	5	4

All sites chosen had acid surface (0-15 cm) soils, with the pH values in the range 4.1-5.5 (Table 2). For the glasshouse experiments, the soil types ranged from sand (G4) to a loamy sand (G5). For the field experiments, the surface (0-15 cm) soils were a sand. All the soils chosen had organic-C values >1.5% in the surface (0-15 cm) layer indicating moderate to high fertility levels. Extractable P concentrations ranged from 12 to 19 mg/kg in the soils used for the glasshouse experiments and from 11 to 34 mg/kg in the surface (0-15 cm) soils of the field sites (Table 2). This range of values suggests different histories of application of P fertiliser between the sites.

Soil pH

Main effects

The applications of lime significantly ($P < 0.05$) increased soil pH in all experiments (Table 3). The application of P as superphosphate was only significant ($P < 0.05$) in experiment G5, however, the effect was small and of little practical importance.

Interactions. The lime x P interaction was not significant at any site (data not presented).

Conductance

Main effects

The effects of increasing rates of applied lime and P on soil conductance measured at harvest were inconsistent. For example, in experiments G5, F6 and F7 increasing the rate of applied lime from nil to 10 or 15 t/ha significantly ($P < 0.05$) increased soil conductance (Table 4). Further, in experiment G5 the application of P significantly decreased conductance, and in experiment F5 conductance increased up to the highest rate of P. Although the effects were statistically significant the changes were small and of little practical significance. At all other sites the effects were not significant.

Table 3. Main effects of lime (t/ha) and P (kg/ha) as superphosphate, on pH determined at harvest for glasshouse and field (0-15 cm) soils.

Rate	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
	<i>Lime</i>				
0	4.5	4.7		5.4	5.9
2.5				5.8	6.3
5		6.0	5.9	6.1	6.8
7.5					7.1
10		7.0	6.5	6.6	
15				6.9	7.3
20	7.6				
<i>l.s.d. (P=0.05)</i>	0.4	0.3	0.3	0.2	0.5
	<i>Phosphorus</i>				
0	6.0	5.8	6.3	6.2	6.7
50			6.0		
75	6.1	6.1			
100			6.3	6.1	6.6
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	0.2	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>

Interactions

There were significant lime x P interactions in experiments G4 and F7. In experiment G4, at nil P, increasing the rate of applied lime from nil to 20 t/ha increased conductance from 0.67 to 0.94 mS/cm. In contrast, when P was applied at rate equivalent to 75 kg P/ha, conductance decreased from 0.74 to 0.69 mS/cm. In experiment F7, at nil P the maximum conductance occurred at 3 t/ha of lime, compared with 15 t/ha when 100 kg P/ha was applied.

Table 4. Main effects of rate of applied lime (t/ha) and P kg/ha) as superphosphate, on soil conductance determined at harvest for glasshouse and field (0-15 cm) soils

Rate	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
	<i>Lime</i>				
0	0.71	0.39		0.29	0.62
2.5				0.32	0.91
5		0.40	0.39	0.30	0.69
7.5					0.71
10		0.51	0.39	0.34	
15				0.40	0.95
20	0.81				
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	0.1	<i>n.s.</i>	0.07	0.15
	<i>Phosphorus</i>				
0	0.80	0.48	0.35	0.32	0.77
50			0.38		
75	0.72	0.39			
100			0.43	0.34	0.77
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	0.09	0.07	<i>n.s.</i>	<i>n.s.</i>

Tuber yield

The application of 10-20 t/ha lime significantly ($P < 0.05$) decreased tuber yield in experiments G4, F6 and F7 (Table 5). In contrast the application of P significantly increased yield in all except 1 (experiment F6) experiment. For loamy sand to sandy clay loams, Maier *et al.* (1989) grouped sites with extractable P concentrations in the surface (0-15 cm) soil: < 30 mg/kg deficient; 30-40 mg/kg marginal; and >40 mg/kg adequate. The main effects for these experiments (Table 5) are consistent with this classification.

The lime x P interactions were not significant at any site.

Number of tubers and stems per plant

The application of lime significantly decreased the number of set tubers per plant in experiments G5, F6 and F7 (Table 6).

There was a significant ($P < 0.001$) interaction between lime x P in experiment G5. In this experiment when no P was applied the application of lime did not affect the number of tubers set per plant. However, at 75 kg P/ha, increasing the rate of lime from nil to 10 t/ha significantly decreased the number of tubers/plant from 31 to 10.

Table 5. Main effects of rate of applied lime (t/ha) and P (kg P/ha) on the total fresh weight of tubers from field (t/ha) and glasshouse (g/plant) experiments.

Rate	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
	<i>Lime</i>				
0	293.8	536.7		65.2	56.0
2.5				58.8	54.0
5		591.5	60.0	59.9	56.4
7.5					58.5
10		506.4	61.4	56.8	
15				55.8	46.3
20	230.1				
<i>l.s.d. (P=0.05)</i>	46.0	<i>n.s.</i>	<i>n.s.</i>	7.7	7.0
	<i>Phosphorus</i>				
0	200.7	182.0	54.5	57.7	49.8
50			61.8		
75	323.3	907.7			
100			65.8	60.9	58.7
<i>l.s.d. (P=0.05)</i>	46.0	83.5	10.7	<i>n.s.</i>	4.4

Table 6. Main effects of rate of applied lime (t/ha) and P (kg P/ha) on the total number of tubers per plant in field and glasshouse experiments.

Rate	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
	<i>Lime</i>				
0	18	18		10	13
2.5				9	11
5		13	14	8	11
7.5					12
10		9	14	8	
15				8	11
20	19				
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	4	<i>n.s.</i>	1	1.5
	<i>Phosphorus</i>				
0	13	8	15	8	11
50			14		
75	24	19			
100			14	9	12
<i>l.s.d. (P=0.05)</i>	4	3	<i>n.s.</i>	<i>n.s.</i>	0.9

The application of lime or P did not significantly affect the number of stems per plant in experiments G4, F5 and F6. The mean number of stems at the optimum P rate was 11, 4 and 5 in experiments G4, F6 and F7, respectively. In experiment G5, the effect of applied lime was not significant, however, increasing the rate of applied P from nil to 75 kg P/ha increased the number of stems from 2 to 3 ($P < 0.05$). There was no significant lime x P interaction in any experiment.

Plant height and dry matter production

Main effects

The application of lime did not significantly affect plant height, or dry matter leaf, stem and leaf+stem yields (data not presented). In experiment G5, increasing the rate of lime from nil to 5 t/ha decreased the total stem dry weight from 12.3 to 8.8 g/plant ($P<0.05$). The effect was not significant in experiment G4.

In contrast with the effect of lime, the application of P significantly increased leaf, stem and total tops dry matter yields and plant height in both glasshouse experiments (Table 7). These growth responses are consistent with the tuber yield responses which occurred when fertiliser P was applied to these P deficient soils.

Table 7. Main effects of P on leaf, stem and total top dry matter yields (g/plant) and plant height (cm) for glasshouse experiments G4 and G5

Rate (kg/ha)	Leaf		Stem		Tops		Height	
	G4	G5	G4	G5	G4	G5	G4	G5
0	9.7	12.0	4.2	3.6	13.9	15.6	605	733
75	12.5	37.8	5.8	16.7	18.4	54.5	813	1279
<i>l.s.d.</i> ($P=0.05$)	1.8	6.1	1.0	2.4	2.3	7.5	85	128

Total-N and phosphorus concentrations in the 5th leaf

Nitrogen

The effect of applied lime on total-N concentrations in the 5th leaf was not significant in any experiment (data not presented). In contrast, the application of P significantly increased total-N concentrations in experiments G4, F5 and F7 (Table 8). The importance of the synergistic interaction between P and N for the interpretation of plant test data have been discussed by Maier *et al.* (1994).

The lime x P interactions were not significant at any site.

Phosphorus

Increasing rates of lime significantly ($P<0.05$) decreased P concentrations in the 5th leaf in experiments G4 and F7. In experiment G4, increasing the rate of applied lime from nil to 20 t/ha decreased P concentrations from 0.41 to 0.34%, respectively. In field experiment F7, P concentrations decreased from 0.35 to 0.28% when the rate of applied lime increased from nil to 20 t/ha. In the experiments where the effects were not significant, mean P concentrations were in the range 0.49-0.58%, G4; 0.44-0.46%, F5; and 0.46-0.52%, F6.

The application of P significantly increased P concentrations in the 5th leaf in all except 1 (experiment F6) experiment (Table 8).

Cadmium concentrations in tubers

In the field experiments, the application of lime, up to 15 t/ha, did not significantly reduce Cd in tubers (Table 9). In contrast with the field experiments, the application of lime significantly reduced Cd concentrations in tubers in both glasshouse experiments.

Table 8. Main effects of phosphorus on the concentrations of total-N and P in the 5th leaf.

Rate (kg/ha)	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
<i>Total-N (%)</i>					
0	5.5	n.a.	5.6	6.4	5.2
50			6.9		
75	6.1	n.a.			
100			6.2	6.2	5.5
<i>L.s.d. (P=0.05)</i>	0.3		0.3	<i>n.s.</i>	0.2
<i>Phosphorus (%)</i>					
0	0.23	0.33	0.34	0.52	0.23
50			0.49		
75	0.53	0.74			
100			0.51	0.47	0.38
<i>L.s.d. (P=0.05)</i>	0.07	0.08	0.05	<i>n.s.</i>	0.03

Table 9. Main effects of rate of lime (t/ha) and phosphorus (kg/ha) on cadmium concentrations (mg/kg fwt) in tubers.

Rate	Glasshouse experiments		Field experiments		
	G4	G5	F5	F6	F7
<i>Lime</i>					
0	0.159	0.053		0.073	0.108
2.5				0.082	0.132
5		0.023	0.033	0.078	0.129
7.5					0.140
10		0.018	0.034	0.074	
15				0.067	0.142
20	0.045				
<i>L.s.d. (P=0.05)</i>	0.033	0.018	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
<i>Phosphorus</i>					
0	0.068	0.028	0.032	0.072	0.115
50			0.033		
75	0.136	0.035			
100			0.035	0.078	0.146
<i>L.s.d. (P=0.05)</i>	0.033	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.016

The application of P, as superphosphate, significantly increased Cd concentrations in tubers in experiments G4 and F7 (Table 9). In the other experiments, even though the effects were not statistically significant, the trend was positive in all experiments.

The lime x P interaction was significant ($P < 0.05$) in experiment G4.

In an earlier study we also found that increasing rates of P, as superphosphate, significantly increased Cd concentrations in tubers at 2 out of 3 sites (Table 10; N. A. Maier unpublished data).

Table 10. Further data on the effect of increasing rates of applied P, as superphosphate, on cadmium concentrations (mg/kg fwt) in tubers.

Rate (kg/ha)	Site		
	1	2	3
0	0.072	0.117	0.176
80	0.073	0.132	0.218
160	0.070	0.137	0.249
320		0.145	
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	0.012	0.026

Effect of Cd concentration in superphosphate

In 1 glasshouse experiment (experiment G6) we compared the effect on Cd concentrations in tubers of using superphosphate low in Cd. The rate of P applied was equivalent to 75 kg P/ha. The application of low Cd superphosphate significantly decreased the Cd concentration in tubers (Table 11).

Table 11. Effect of applying superphosphate containing different amounts of Cd on the concentration of Cd in tubers.

Cd concentration (mg Cd/kg)	Lime (t/ha)	
	5	10
4	0.019	0.014
28	0.030	0.021
<i>l.s.d. (P=0.05)</i>	0.003	

GENERAL DISCUSSION

The lack of any effect of lime on tuber Cd concentrations under field conditions confirms results from earlier experiments (Appendix 6). Cadmium concentrations in tubers were significantly reduced by application of lime under glasshouse conditions.

The effect of P fertilizer was inconsistent, with 3 out of 6 field trials and 1 out of 2 glasshouse experiments indicating a significant effect. It is interesting to note that the soils where application of P had a significant effect on Cd uptake by tubers were the soils having high Cd concentrations initially (i.e. without P). In glasshouse experiments, Williams and David (1977) noted that adding P to a soil increases Cd uptake through a stimulation of root proliferation in the zone into which P is added. Sparrow et al. (1993) compared Cd uptake by potatoes fertilised with both low- and high-Cd DAP in field trials and found little differences

in Cd uptake between the two sources, with Cd concentration in tubers being related to the rate of P applied, rather than the rate of Cd applied. These data support the early results of Williams and David and are in agreement with the data presented here

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compared with liming in 1 experiment (F4), and liming significantly reduced medulla CCI in the same experiment.

Table 3a. Effect of gypsum and lime on total tuber yield and after-cooking darkening index, of tubers.

Data are from field experiments F4, F7, F8, F10 and F11

Variable	Yield (t/ha)				After-cooking darkening			
	F4	F7	F10	F11	F4	F7	F10	F11
Control	40.5	56.0	39.2	36.4	112	19	86	n.a.
Lime	40.3	56.4	33.9	38.3	89	21	85	n.a.
Gypsum	38.8	54.2	34.9	36.9	162	18	103	n.a.
<i>l.s.d. (P=0.05)</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	72	<i>n.s.</i>	<i>n.s.</i>	

Table 3b. Effect of gypsum and lime on medulla crisp colour index (CCI) and dry matter content (%) of tubers.

Data are from field experiments F4, F7, F8, F10 and F11

Variable	Medulla CCI				% Dry matter		
	F4	F7	F10	F11	F4	F7	F8
Control	93	215	60	4	19.5	14.9	18.0
Lime	28	167	168	31	19.7	14.8	18.2
Gypsum	83	168	85	0	20.5	14.4	19.5
<i>l.s.d. (P=0.05)</i>	62	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>

Leaf and tuber chemical composition

The effects of applied lime and gypsum on leaf and tuber chemical composition were variable. Nutrients for which significant effects occurred are presented in Table 4.

5th leaf

Liming significantly increased Ca, and to a lesser extent Mg concentrations, and decreased B and Mn concentrations in leaves sampled at early tuber set (Table 4). In contrast, gypsum did not affect nutrient levels, although there was a tendency for higher Mn concentrations in leaves sampled from plants in the gypsum plots. Carter and Cutcliffe (1990) also found that the application of up to 4.3 t/ha gypsum only increased the Ca content of Brussels sprout leaves in 1 out of 6 experiments. Applying gypsum also increased K and S concentrations, and did not affect N, P and Mg concentrations.

Tuber

The effects of incorporating 5 t/ha lime or gypsum on tuber nutrient content were small and not consistent between sites. The application of gypsum increased Ca concentrations in tubers in 2 experiments. Liming or the application of gypsum were ineffective in reducing Cd

accumulation in tubers. In fact in 1 experiment, gypsum significantly increased Cd concentrations (Table 4).

Table 4. Effect of gypsum and lime on the concentration of selected elements in 5th leaf and tubers.

Data are from field experiments F4, F7, F8, F10 and F11

Variable	Leaf				Tuber				
	F4	F7	F8	F11	F4	F7	F8	F10	F11
<i>Calcium</i>									
	(% d wt)				(mg/kg d wt)				
Control	0.84	1.11	1.04	0.92	127	252	202	162	151
Lime	1.10	1.37	1.53	0.94	199	240	283	209	167
Gypsum	0.87	0.94	1.08	0.93	172	274	211	176	218
<i>l.s.d. (P=0.05)</i>	0.16	0.42	0.35	<i>n.s.</i>	29	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	51
<i>Magnesium</i>									
	(% d wt)				(mg/kg d wt)				
Control	0.42	0.62	0.55	0.64	767	1112	1189	1149	895
Lime	0.40	0.73	0.57	0.61	881	1106	1086	1158	899
Gypsum	0.38	0.67	0.57	0.59	764	1123	1149	1126	995
<i>l.s.d. (P=0.05)</i>	0.02	0.10	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	93
<i>Cadmium (mg/kg f wt)</i>									
Control	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.07	0.13	0.18	0.091	0.045
Lime					0.09	0.13	0.20	0.099	0.046
Gypsum					0.09	0.13	0.20	0.103	0.059
<i>l.s.d. (P=0.05)</i>					<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.012
<i>Boron (mg/kg d wt)</i>									
Control	25	35	20	28	6	4	5	7	7
Lime	20	34	13	25	5	5	5	8	6
Gypsum	26	38	22	27	6	5	2	7	7
<i>l.s.d. (P=0.05)</i>	2	<i>n.s.</i>	6	3	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
<i>Manganese (mg/kg d wt)</i>									
Control	193	130	243	108	6	8	9	5	5
Lime	123	89	45	72	6	7	6	6	5
Gypsum	218	160	323	153	6	8	8	6	6
<i>l.s.d. (P=0.05)</i>	37	50	179	49	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.7

REFERENCES

- Carter, M. R., and Cutcliffe, J. A. (1990). Effects of gypsum on growth and mineral content of Brussels sprouts, and soil properties of Orthic Podzols. *Fertilizer Research* 24, 77-84.

APPENDIX 12**Comparison of the effects of zeolite and lime on the yield , growth, leaf chemical composition and cadmium concentrations in potatoes (*Solanum tuberosum* L.)****INTRODUCTION**

Zeolites may be used to minimize Cd uptake by potato crops. Constraints to the use of zeolite may be the high cost of the material, but if only small additions are required to significantly reduce Cd uptake, the material could be commercially useful.

The aim of this experiment therefore was to determine if zeolite could be used to reduce Cd uptake by potato tubers.

MATERIALS AND METHODS**Experimental details**

Zeolite treatments were included in glasshouse experiments G5 and G6. Soil preparation, planting, assessment of yield and quality, chemical analyses and statistical analysis of the data, were similar to those reported in earlier papers in the report (eg. Appendix 6).

Soils

The soils were sand (G4) and loamy sand (G5).

RESULTS AND DISCUSSION**Soil pH and conductance**

Lime significantly increased soil pH as found previously (Appendices 6-8). Zeolite had no effect on soil pH at low rates of application, but increased soil pH when used at high application rates (Table 1).

Zeolite had no consistent effect on soil EC values (Table 1).

Yield and growth responses

There was little impact of either lime or zeolite on plant dry matter production or tuber yields. The number of tubers per plant was significantly reduced by both lime and zeolite (Table 2).

Chemical composition of 5th leaf

The application of calcitic lime significantly decreased P, S and Mn concentrations, and increased Ca and Mg concentrations (Table 3). The effect of zeolite was inconsistent.

Leaf Cd concentrations were significantly reduced by both lime and zeolite.

Table 1. Effect of zeolite and lime on soil pH and conductance.

Factor	Rate		pH		Conductance (mS/cm)	
	(t/ha)	(g/pot)	Planting	Harvest	Planting	Harvest
<i>Experiment G6</i>						
Lime	0	0	4.5	4.2	0.41	0.43
	2.5	15.4	5.8	4.9	0.37	0.55
	5.0	30.8	6.3	5.6	0.35	0.62
Zeolite	2.5	15.4	4.6	4.1	0.37	0.53
	5	30.8	4.7	4.0	0.30	0.66
	<i>l.s.d. (P=0.05)</i>		0.3	0.3	<i>n.s.</i>	0.12
<i>Experiment G5</i>						
Lime	0	0	4.1	4.7	0.46	0.37
	10	61.6	7.2	7.0	0.39	0.53
	20	123.2	7.5	7.4	0.43	0.44
Zeolite	-	500	5.3	5.6	0.50	0.38
	<i>l.s.d. (P=0.05)</i>		0.2	0.2	<i>n.s.</i>	<i>n.s.</i>

Table 2. Effect of zeolite and lime on tuber yield, number of tubers and stems per plant, plant height and leaf and stem dry matter yields.

Variable	Rate (t/ha)	Rate (g/pot)	Tubers (g/plant)	Number tubers/plant	Number stems/plant	Height (cm)	Leaves (g/plant d.wt)	Stems (g/plant d.wt)
<i>Experiment G6</i>								
Lime	0	0	363.0	14	8	99.5	21.1	7.6
	2.5	15.4	441.0	18	7	113.3	19.4	10.8
	5	30.8	464.9	16	10	111.5	20.9	10.9
Zeolite	2.5	15.4	419.7	15	8	108.3	19.4	8.5
	5	30.8	473.3	14	7	107.5	19.5	8.2
	<i>l.s.d. (P=0.05)</i>		<i>n.s.</i>	<i>n.s.</i>	1.5	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
<i>Experiment G5</i>								
Lime	0	0	950.8	30	3	1290	41.2	21.9
	10	61.6	856.9	10	2	1278	39.5	14.1
	20	123.2	813.8	11	3	1320	38.3	12.6
Zeolite	-	500	910.5	16	2	1303	41.0	16.8
	<i>l.s.d. (P=0.05)</i>		90.3	7	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	5.1

Chemical composition of tubers

Cadmium concentrations in tubers were decreased by application of both lime and zeolite. The magnitude of the reduction was similar for both materials.

Table 3. Effect of zeolite and lime on the concentration of elements in the 5th leaf

Factor	Rate		P (%)	K (%)	Ca (%)	Mg (%)	S (%)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Cd (mg/kg d)
	(t/ha)	(g/pot)									
<i>Experiment G6</i>											
Lime	0	0	0.82	4.75	0.18	0.23	0.48	9	65	53	1.15
	2.5	15.4	0.85	4.83	0.47	0.31	0.44	7	47	58	0.87
	5	30.8	0.74	4.51	0.69	0.35	0.43	6	44	52	0.77
Zeolite	2.5	15.4	0.90	4.93	0.20	0.24	0.47	9	59	62	0.88
	5	30.8	0.89	5.08	0.20	0.26	0.45	9	56	61	0.85
<i>l.s.d. (P=0.05)</i>			0.01	<i>n.s.</i>	0.11	0.04	0.03	<i>n.s.</i>	10	<i>n.s.</i>	0.20
<i>Experiment G5</i>											
Lime	0	0	0.84	4.88	0.27	0.28	0.47	8.4	93	95	2.52
	10	61.6	0.66	5.55	0.56	0.34	0.52	7.5	78	50	0.78
	20	123.2	0.59	5.21	0.67	0.35	0.46	5.2	63	49	0.78
Zeolite	-	500	0.76	4.74	0.44	0.38	0.44	23.5	60	79	0.59
<i>l.s.d. (P=0.05)</i>			0.14	0.64	0.05	0.03	0.06	2.6	20	8	0.25

Table 4. Effect of zeolite and lime on the concentration of elements in tubers.

Factor	Rate		K (%)	Ca (mg/kg)	Mg (mg/kg)	S (%)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Cd (mg/kg f)
	(t/ha)	(g/pot)								
<i>Experiment G6</i>										
Lime	0	0	1.97	273	931	0.23	2.3	37	9	0.024
	2.5	15.4	2.07	476	1123	0.19	1.8	32	10	0.024
	5	30.8	2.21	595	1235	0.20	1.8	26	10	0.022
Zeolite	2.5	15.4	1.96	303	958	0.22	1.6	37	9	0.020
	5	30.8	1.98	316	974	0.23	1.7	38	10	0.020
<i>l.s.d. (P=0.05)</i>			0.14	133	76	0.03	0.7	10	<i>n.s.</i>	0.003
<i>Experiment G5</i>										
Lime	0	0	<i>n.a.</i>	0.043						
	10	61.6								0.021
	20	123.2								0.021
Zeolite	-	500								0.026
<i>l.s.d. (P=0.05)</i>										0.003

DISCUSSION

In these experiments the use of zeolites showed no advantages over lime in terms of reducing tuber Cd concentrations. Given the extra cost involved in use of zeolite there appear to offer

few advantages over lime. Only one type of zeolite was tested in these experiments and it may be worthwhile screening other zeolites for their potential to reduce Cd availability to plants.

APPENDIX 13	Effect of depth of incorporation of lime on soil pH and conductance, and cadmium concentrations in potato (<i>Solanum tuberosum</i> L.)
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INTRODUCTION

We have found that in glasshouse pot experiments, liming was highly effective in reducing Cd concentrations in tubers (Appendices 6-12). In field experiments, the application of lime did not have a significant effect, or in a few experiments Cd concentrations significantly increased.

Factors which may account for the ineffectiveness of liming reported in our and published studies include:

- 1) Inadequate incorporation/mixing - In field experiments, lime was broadcast by hand and 'rotary hoed in'. If the soil is moist this may lead to 'caking' of the lime, and therefore the lime is not thoroughly/evenly mixed into the soil. In the glasshouse work, the soil was dried before mixing and incorporation.
- 2) Inadequate depth of incorporation - Conventional rotary hoes are only effective to 15-20 cm. Therefore much of the potato plants root zone is not affected by liming. In the pot experiments the whole root volume was limed.
- 3) Inadequate incubation/time - In both field and glasshouse experiments incubation time was 'short' (3-8 weeks). In the pot experiments, the soils were kept moist (field capacity) during the incubation period. In the field experiments, there was no control over soil moisture levels during incubation. Some soils may have been too dry. The period of incubation may not be a major factor because in the pot work some short incubation periods (3-4 weeks) were used, however liming was still effective.

We therefore conducted a field and pot experiment to determine the effect of placement of lime/depth of incorporation on Cd concentrations in tubers. In the field experiment, the effect of applying P (at 15-30 cm) on Cd uptake was also investigated.

MATERIALS AND METHODS

Field experiment

During 1993/94 an experiment located in a commercial crop, was conducted in the lower South East, using the cv. Russet Burbank. Rates of lime up to 10 t/ha were incorporated by rotary hoeing, into the following depths: 0-15, 0-15+15-30 and 15-30 cm. To place the lime at 15-30 cm, a grader was used to remove the surface 0-15 cm soil. After the subsurface treatments had been applied and incorporated, the surface soil replaced and the treatments for the 0-15 cm soil were applied. Half of each plot also received an application of 100 kg P/ha at the same time the lime was applied to the 15-30 cm layer. The experimental design was a randomized block and treatments were replicated 3 times.

Field operations, assessment of yield and quality, chemical analyses and statistical analysis of the data, were similar to those reported in previous papers in the report (eg. Appendix 6).

Glasshouse experiment

In experiment G7, a rate of lime equivalent to 10 t/ha was incorporated either i) throughout the soil; ii) into the soil placed in the bottom half of the pot; and iii) into the soil placed into the top half of the pot. Other experimental details are presented in previous papers (eg. Appendix 6). The cv. grown was Atlantic.

RESULTS AND DISCUSSION

Soil pH and conductance

Depending on the depth the calcitic lime was applied to, pH significantly increased by 1-2 units, in both field (Table 1) and glasshouse (Table 2) experiments.

Table 1. Effect of depth of incorporation and rate of lime on pH and conductance.

Soil samples were collected on 6/4/94 and data are for site F12

Depth of incorporation (cm)		pH		FC (mS/cm)	
0-15	15-30	0-15	15-30	0-15	15-30
Rate applied (t/ha)		0-15	15-30	0-15	15-30
0	0	5.7	5.3	0.22	0.15
2.5	0	6.1	5.4	0.29	0.21
5	0	6.4	5.4	0.35	0.28
10	0	7.0	5.6	0.26	0.11
2.5	2.5	6.3	5.6	0.29	0.14
5	5	6.7	5.6	0.35	0.16
10	10	7.3	6.5	0.26	0.19
0	2.5	6.2	5.6	0.22	0.11
0	5	6.3	5.5	0.23	0.17
0	10	6.3	5.8	0.26	0.14
l.s.d. (P=0.05)		0.5		0.10	

Cadmium concentrations in tubers

There was no significant effect of liming the subsoil in the **field experiment**, with lime either having no effect or increasing tuber Cd concentrations (Table 3)

Table 2. Effect of depth of incorporation of lime on pH and conductance of soil sampled from the top and bottom halves of pots at harvest.

Data are for experiment G7

Rate (t/ha)	Incorporation	pH		Conductance (mS/cm)	
		Top half	Bottom half	Top half	Bottom half
0	-	4.6	4.3	0.11	0.15
10	Throughout	7.0	7.2	0.11	0.26
10	Bottom half	4.7	6.8	0.07	0.25
10	Top half	6.7	4.4	0.10	0.26
<i>L.s.d. (P=0.05)</i>		0.2	0.3	<i>n.s.</i>	<i>n.s.</i>

Table 3. Effect of depth of incorporation and rate of lime and phosphorus application on cadmium concentration in tubers.

Depth of incorporation		P applied (kg/ha)	
0-15	15-30	0	100
Rate applied (t/ha)		0	100
0	0	0.042	0.049
2.5	0	0.046	0.054
5	0	0.062	0.057
10	0	0.051	0.055
2.5	2.5	0.047	0.057
5	5	0.056	0.057
10	10	0.055	0.050
0	2.5	0.043	0.049
0	5	0.056	0.055
0	10	0.049	0.053
<i>L.s.d. (P=0.05)</i>		0.012	<i>n.s.</i>

Data from the pot experiment were similar where lime also resulted in increases in tuber Cd concentrations, when only the top or bottom half of the soil volume or rot zone was limed. The only likely explanation for this effect is the displacement of Cd from soil surfaces by Ca, thus leading to enhanced Cd uptake by the crop.

Table 4. Effect of depth of incorporation of lime on cadmium concentration in tubers.

Data are for experiment G7

Rate (t/ha)	Incorporation	Cadmium (mg/kg f wt)
0	-	0.045
10	Throughout	0.045
10	Bottom half	0.069
10	Top half	0.083
<i>L.s.d. (P=0.05)</i>		0.024

accumulation in tubers. In fact in 1 experiment, gypsum significantly increased Cd concentrations (Table 4).

Table 4. Effect of gypsum and lime on the concentration of selected elements in 5th leaf and tubers.

Data are from field experiments F4, F7, F8, F10 and F11

Variable	Leaf				Tuber				
	F4	F7	F8	F11	F4	F7	F8	F10	F11
<i>Calcium</i>									
	(% d wt)				(mg/kg d wt)				
Control	0.84	1.11	1.04	0.92	127	252	202	162	151
Lime	1.10	1.37	1.53	0.94	199	240	283	209	167
Gypsum	0.87	0.94	1.08	0.93	172	274	211	176	218
<i>l.s.d. (P=0.05)</i>	0.16	0.42	0.35	<i>n.s.</i>	29	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	51
<i>Magnesium</i>									
	(% d wt)				(mg/kg d wt)				
Control	0.42	0.62	0.55	0.64	767	1112	1189	1149	895
Lime	0.40	0.73	0.57	0.61	881	1106	1086	1158	899
Gypsum	0.38	0.67	0.57	0.59	764	1123	1149	1126	995
<i>l.s.d. (P=0.05)</i>	0.02	0.10	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	93
<i>Cadmium (mg/kg f wt)</i>									
Control	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.07	0.13	0.18	0.091	0.045
Lime					0.09	0.13	0.20	0.099	0.046
Gypsum					0.09	0.13	0.20	0.103	0.059
<i>l.s.d. (P=0.05)</i>					<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.012
<i>Boron (mg/kg d wt)</i>									
Control	25	35	20	28	6	4	5	7	7
Lime	20	34	13	25	5	5	5	8	6
Gypsum	26	38	22	27	6	5	2	7	7
<i>l.s.d. (P=0.05)</i>	2	<i>n.s.</i>	6	3	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
<i>Manganese (mg/kg d wt)</i>									
Control	193	130	243	108	6	8	9	5	5
Lime	123	89	45	72	6	7	6	6	5
Gypsum	218	160	323	153	6	8	8	6	6
<i>l.s.d. (P=0.05)</i>	37	50	179	49	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.7

REFERENCES

- Carter, M. R., and Cutcliffe, J. A. (1990). Effects of gypsum on growth and mineral content of Brussels sprouts, and soil properties of Orthic Podzols. *Fertilizer Research* 24, 77-84.

APPENDIX 12**Comparison of the effects of zeolite and lime on the yield, growth, leaf chemical composition and cadmium concentrations in potatoes (*Solanum tuberosum* L.)****INTRODUCTION**

Zeolites may be used to minimize Cd uptake by potato crops. Constraints to the use of zeolite may be the high cost of the material, but if only small additions are required to significantly reduce Cd uptake, the material could be commercially useful.

The aim of this experiment therefore was to determine if zeolite could be used to reduce Cd uptake by potato tubers.

MATERIALS AND METHODS**Experimental details**

Zeolite treatments were included in glasshouse experiments G5 and G6. Soil preparation, planting, assessment of yield and quality, chemical analyses and statistical analysis of the data, were similar to those reported in earlier papers in the report (eg. Appendix 6).

Soils

The soils were sand (G4) and loamy sand (G5).

RESULTS AND DISCUSSION**Soil pH and conductance**

Lime significantly increased soil pH as found previously (Appendices 6-8). Zeolite had no effect on soil pH at low rates of application, but increased soil pH when used at high application rates (Table 1).

Zeolite had no consistent effect on soil EC values (Table 1).

Yield and growth responses

There was little impact of either lime or zeolite on plant dry matter production or tuber yields. The number of tubers per plant was significantly reduced by both lime and zeolite (Table 2).

Chemical composition of 5th leaf

The application of calcitic lime significantly decreased P, S and Mn concentrations, and increased Ca and Mg concentrations (Table 3). The effect of zeolite was inconsistent.

Leaf Cd concentrations were significantly reduced by both lime and zeolite.

Table 1. Effect of zeolite and lime on soil pH and conductance.

Factor	Rate		pH		Conductance (mS/cm)	
	(t/ha)	(g/pot)	Planting	Harvest	Planting	Harvest
<i>Experiment G6</i>						
	0	0	4.5	4.2	0.41	0.43
Lime	2.5	15.4	5.8	4.9	0.37	0.55
	5.0	30.8	6.3	5.6	0.35	0.62
Zeolite	2.5	15.4	4.6	4.1	0.37	0.53
	5	30.8	4.7	4.0	0.30	0.66
	<i>l.s.d. (P=0.05)</i>		0.3	0.3	<i>n.s.</i>	0.12
<i>Experiment G5</i>						
	0	0	4.1	4.7	0.46	0.37
Lime	10	61.6	7.2	7.0	0.39	0.53
	20	123.2	7.5	7.4	0.43	0.44
Zeolite	-	500	5.3	5.6	0.50	0.38
	<i>l.s.d. (P=0.05)</i>		0.2	0.2	<i>n.s.</i>	<i>n.s.</i>

Table 2. Effect of zeolite and lime on tuber yield, number of tubers and stems per plant, plant height and leaf and stem dry matter yields.

Variable	Rate (t/ha)	Rate (g/pot)	Tubers (g/plant)	Number tubers/plant	Number stems/plant	Height (cm)	Leaves (g/plant d wt)	Stems (g/plant d wt)
<i>Experiment G6</i>								
	0	0	363.0	14	8	99.5	21.1	7.6
Lime	2.5	15.4	441.0	18	7	113.3	19.4	10.8
	5	30.8	464.9	16	10	111.5	20.9	10.9
Zeolite	2.5	15.4	419.7	15	8	108.3	19.4	8.5
	5	30.8	473.3	14	7	107.5	19.5	8.2
	<i>l.s.d. (P=0.05)</i>		<i>n.s.</i>	<i>n.s.</i>	1.5	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
<i>Experiment G5</i>								
	0	0	950.8	30	3	1290	41.2	21.9
Lime	10	61.6	856.9	10	2	1278	39.5	14.1
	20	123.2	813.8	11	3	1320	38.3	12.6
Zeolite	-	500	910.5	16	2	1303	41.0	16.8
	<i>l.s.d. (P=0.05)</i>		90.3	7	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	5.1

Chemical composition of tubers

Cadmium concentrations in tubers were decreased by application of both lime and zeolite. The magnitude of the reduction was similar for both materials.

Table 3. Effect of zeolite and lime on the concentration of elements in the 5th leaf

Factor	Rate		P (%)	K (%)	Ca (%)	Mg (%)	S (%)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Cd (mg/kg d)
	(t/ha)	(g/pot)									
<i>Experiment G6</i>											
Lime	0	0	0.82	4.75	0.18	0.23	0.48	9	65	53	1.15
	2.5	15.4	0.85	4.83	0.47	0.31	0.44	7	47	58	0.87
	5	30.8	0.74	4.51	0.69	0.35	0.43	6	44	52	0.77
Zeolite	2.5	15.4	0.90	4.93	0.20	0.24	0.47	9	59	62	0.88
	5	30.8	0.89	5.08	0.20	0.26	0.45	9	56	61	0.85
<i>l.s.d. (P=0.05)</i>			0.01	<i>n.s.</i>	0.11	0.04	0.03	<i>n.s.</i>	10	<i>n.s.</i>	0.20
<i>Experiment G5</i>											
Lime	0	0	0.84	4.88	0.27	0.28	0.47	8.4	93	95	2.52
	10	61.6	0.66	5.55	0.56	0.34	0.52	7.5	78	50	0.78
	20	123.2	0.59	5.21	0.67	0.35	0.46	5.2	63	49	0.78
Zeolite	-	500	0.76	4.74	0.44	0.38	0.44	23.5	60	79	0.59
<i>l.s.d. (P=0.05)</i>			0.14	0.64	0.05	0.03	0.06	2.6	20	8	0.25

Table 4. Effect of zeolite and lime on the concentration of elements in tubers.

Factor	Rate		K (%)	Ca (mg/kg)	Mg (mg/kg)	S (%)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)	Cd (mg/kg f)
	(t/ha)	(g/pot)								
<i>Experiment G6</i>										
Lime	0	0	1.97	273	931	0.23	2.3	37	9	0.024
	2.5	15.4	2.07	476	1123	0.19	1.8	32	10	0.024
	5	30.8	2.21	595	1235	0.20	1.8	26	10	0.022
Zeolite	2.5	15.4	1.96	303	958	0.22	1.6	37	9	0.020
	5	30.8	1.98	316	974	0.23	1.7	38	10	0.020
<i>l.s.d. (P=0.05)</i>			0.14	133	76	0.03	0.7	10	<i>n.s.</i>	0.003
<i>Experiment G5</i>										
Lime	0	0	<i>n.a.</i>	0.043						
	10	61.6								0.021
	20	123.2								0.021
Zeolite	-	500								0.026
<i>l.s.d. (P=0.05)</i>										0.003

DISCUSSION

In these experiments the use of zeolites showed no advantages over lime in terms of reducing tuber Cd concentrations. Given the extra cost involved in use of zeolite there appear to offer

few advantages over lime. Only one type of zeolite was tested in these experiments and it may be worthwhile screening other zeolites for their potential to reduce Cd availability to plants.

APPENDIX 13**Effect of depth of incorporation of lime on soil pH and conductance, and cadmium concentrations in potato (*Solanum tuberosum* L.)****INTRODUCTION**

We have found that in glasshouse pot experiments, liming was highly effective in reducing Cd concentrations in tubers (Appendices 6-12). In field experiments, the application of lime did not have a significant effect, or in a few experiments Cd concentrations significantly increased.

Factors which may account for the ineffectiveness of liming reported in our and published studies include:

- 1) Inadequate incorporation/mixing - In field experiments, lime was broadcast by hand and 'rotary hoed in'. If the soil is moist this may lead to 'caking' of the lime, and therefore the lime is not thoroughly/evenly mixed into the soil. In the glasshouse work, the soil was dried before mixing and incorporation.
- 2) Inadequate depth of incorporation - Conventional rotary hoes are only effective to 15-20 cm. Therefore much of the potato plants root zone is not affected by liming. In the pot experiments the whole root volume was limed.
- 3) Inadequate incubation/time - In both field and glasshouse experiments incubation time was 'short' (3-8 weeks). In the pot experiments, the soils were kept moist (field capacity) during the incubation period. In the field experiments, there was no control over soil moisture levels during incubation. Some soils may have been too dry. The period of incubation may not be a major factor because in the pot work some short incubation periods (3-4 weeks) were used, however liming was still effective.

We therefore conducted a field and pot experiment to determine the effect of placement of lime/depth of incorporation on Cd concentrations in tubers. In the field experiment, the effect of applying P (at 15-30 cm) on Cd uptake was also investigated.

MATERIALS AND METHODS**Field experiment**

During 1993/94 an experiment located in a commercial crop, was conducted in the lower South East, using the cv. Russet Burbank. Rates of lime up to 10 t/ha were incorporated by rotary hoeing, into the following depths: 0-15, 0-15+15-30 and 15-30 cm. To place the lime at 15-30 cm, a grader was used to remove the surface 0-15 cm soil. After the subsurface treatments had been applied and incorporated, the surface soil replaced and the treatments for the 0-15 cm soil were applied. Half of each plot also received an application of 100 kg P/ha at the same time the lime was applied to the 15-30 cm layer. The experimental design was a randomized block and treatments were replicated 3 times.

Field operations, assessment of yield and quality, chemical analyses and statistical analysis of the data, were similar to those reported in previous papers in the report (eg. Appendix 6).

Glasshouse experiment

In experiment G7, a rate of lime equivalent to 10 t/ha was incorporated either i) throughout the soil; ii) into the soil placed in the bottom half of the pot; and iii) into the soil placed into the top half of the pot. Other experimental details are presented in previous papers (eg. Appendix 6). The cv. grown was Atlantic.

RESULTS AND DISCUSSION

Soil pH and conductance

Depending on the depth the calcitic lime was applied to, pH significantly increased by 1-2 units, in both field (Table 1) and glasshouse (Table 2) experiments.

Table 1. Effect of depth of incorporation and rate of lime on pH and conductance.

Soil samples were collected on 6/4/94 and data are for site F12

Depth of incorporation (cm)		pH		EC (mS/cm)	
0-15	15-30	0-15	15-30	0-15	15-30
Rate applied (t/ha)					
0	0	5.7	5.3	0.22	0.15
2.5	0	6.1	5.4	0.29	0.21
5	0	6.4	5.4	0.35	0.28
10	0	7.0	5.6	0.26	0.11
2.5	2.5	6.3	5.6	0.29	0.14
5	5	6.7	5.6	0.35	0.16
10	10	7.3	6.5	0.26	0.19
0	2.5	6.2	5.6	0.22	0.11
0	5	6.3	5.5	0.23	0.17
0	10	6.3	5.8	0.26	0.14
l.s.d. (P=0.05)		0.5		0.10	

Cadmium concentrations in tubers

There was no significant effect of liming the subsoil in the **field experiment**, with lime either having no effect or increasing tuber Cd concentrations (Table 3)

Table 2. Effect of depth of incorporation of lime on pH and conductance of soil sampled from the top and bottom halves of pots at harvest.

Data are for experiment G7

Rate (t/ha)	Incorporation	pH		Conductance (mS/cm)	
		Top half	Bottom half	Top half	Bottom half
0	-	4.6	4.3	0.11	0.15
10	Throughout	7.0	7.2	0.11	0.26
10	Bottom half	4.7	6.8	0.07	0.25
10	Top half	6.7	4.4	0.10	0.26
<i>l.s.d. (P=0.05)</i>		0.2	0.3	<i>n.s.</i>	<i>n.s.</i>

Table 3. Effect of depth of incorporation and rate of lime and phosphorus application on cadmium concentration in tubers.

Depth of incorporation		P applied (kg/ha)	
0-15	15-30	0	100
Rate applied (t/ha)			
0	0	0.042	0.049
2.5	0	0.046	0.054
5	0	0.062	0.057
10	0	0.051	0.055
2.5	2.5	0.047	0.057
5	5	0.056	0.057
10	10	0.055	0.050
0	2.5	0.043	0.049
0	5	0.056	0.055
0	10	0.049	0.053
<i>l.s.d. (P=0.05)</i>		0.012	<i>n.s.</i>

Data from the **pot experiment** were similar where lime also resulted in increases in tuber Cd concentrations, when only the top or bottom half of the soil volume or rot zone was limed. The only likely explanation for this effect is the displacement of Cd from soil surfaces by Ca, thus leading to enhanced Cd uptake by the crop.

Table 4. Effect of depth of incorporation of lime on cadmium concentration in tubers.

Data are for experiment G7

Rate (t/ha)	Incorporation	Cadmium (mg/kg f wt)
0	-	0.045
10	Throughout	0.045
10	Bottom half	0.069
10	Top half	0.083
<i>l.s.d. (P=0.05)</i>		0.024