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# The Distribution of Heavy Metals in Soil and Metal Uptake into Vegetation, at Beaumont Leys Sewage Farm, Leicester.

# Part II. An Assessment of the Efficiency of Remedial Soil Treatment. The Heatherbrook Respreading Exercise

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Beaumont Leys is the site of a former sewage farm which is the subject of comprehensive redevelopment by the City of Leicester Council. Remedial measures agreed between the City Council and the Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL) were designed to minimise any risks to human health from metallic contamination in the soil.

This study has assessed the effectiveness of the soil stripping and respreading operations carried out on site.

Detailed soil analyses before and after redevelopment have demonstrated the success of this strategy; significant lowering of average contamination levels and reduction of maximum metal levels has been achieved.

Beaumont Leys is an area to the north of Leicester which was occupied from the 1890s to 1966 by the City of Leicester sewage works. Extensive site redevelopment is now underway. The design of the development took credence of the results of soil analyses carried out in  $1971-2^{1,2}$  with measures agreed between the City of Leicester Council and the ICRCL designed to minimise any risk to human health during the projected lifetime of the development from metallic contamination present on the site.

Briefly, topsoil from the sludge spreading area was removed and the land used for industrial development. This highly contaminated topsoil, e.g. with levels in excess of 20 mg/kg of cadmium in the dry soil (D.S.), was used as a base material for landscaping projects where it was covered with other less contaminated topsoil, (cadmium 10–15 mg/kg of D.S.) before being seeded to form open grassy areas of amenity "parkland". Local authority and private housing schemes were provided with limited garden areas and considerable care was

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taken to ensure that the topsoil used for the gardens contained no more than 5 mg of cadmium/kg of D.S.

The cadmium content of the soil was of most concern on the Beaumont Leys development on the grounds of toxicity or absorption by crops; therefore the concentration of cadmium was used as the indicator of acceptability of the soil for a particular end use. Before a new area was developed for housing the results of the 1972 survey were examined and any sample point (on an intersection of a 200 ft grid) which had a cadmium content in excess of 5 mg/kg of D.S. was identified. This point was then judged to be the centre of a square with 50 ft sides and the topsoil contained within it was removed to be used elsewhere on the development in a less critical area. This approach did not result in a shortage of topsoil because only 60 per cent. of the original topsoil was required for the final development because of the construction of roads, paths and buildings.

Where an area of land was identified with an acceptable soil cadmium concentration of less than 5 mg/kg the remaining topsoil was stripped off by a mechanical scraper and deposited in horizontal layers to form a composite heap of stripped soil.

When the housing development was completed this topsoil was recovered by digging vertically into the heaps and respreading this "mixed" soil back into gardens and other areas of human contact. It was assumed that this mixing produced a more homogeneous concentration of metals in the soil over the whole site and reduced any hot spots, i.e. small areas with high metal levels not discovered in the original soil survey.

In 1979 the Department of the Environment's Central Unit of Environment Protection (now the Central Directorate of Environmental Protection) awarded the Leicestershire County Analyst's Laboratory a contract to investigate the efficiency of the stripping/respreading operations, and to determine in practice, using normal building site activities, whether the presumed reduction of maximum metal contents and lowering of average contamination levels were achieved.

### **Present Investigation**

This present investigation covered an area of approximately 4 hectares (10 acres) on a local authority housing development in an area known as Heatherbrook. The design essentially followed that of the 1972 survey<sup>1,2</sup>; 20 grid points were taken at the intersections of the 200 ft grid used in the original survey.

In order to assess whether more intensive sampling would provide more precise information on the distribution of metallic contaminants a further 75 samples were taken on a 50 ft grid within the central area (Fig. 1).

All 95 topsoil samples were collected from the greenfield site in 1979, and after the topsoil was stripped, 18 subsoil samples on the 200 ft grid were obtained.

Subsoil samples were analysed because results in the 1972 survey suggested that the metallic contamination was not confined to the surface layers but had penetrated into the subsoil<sup>1,2</sup>. However, recent work<sup>3</sup> has shown that the metal contamination was confined to the topsoil at Beaumont Leys.





HEAVY METALS

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#### TABLE I

	200 ft	200 ft grid		10 samples at perimeter of 50 ft grid		50 ft grid	
No. of	20	17	10	10	05	05	
samples Respreading	Before	After	Before	After	Before	After	
Cadmium Range:							
Minimum	0.6	1.6	1.3	1.6	0.7	0.8	
Maximum	7.2	3.1	4.3	2.9	5.1	4.1	
Mean	3.0	2.5	2.7	2.6	2.7	2.7	
Std. dev.	1.6	0.4	$1 \cdot 0$	0.4	1.0	0.6	
99 per cent. upper							
tolerance*	7.6	3.7	6.0	3.9	5.3	4.3	
Lead Range:							
Minimum	35	78	95	78	77	65	
Maximum	424	166	154	150	410	265	
Mean	158	121	125	123	128	137	
Std. dev.	92	23	17	21	41	38	
99 per cent.							
tolerance	421	188	180	191	236	237	
Zinc							
Range:			10.5				
Minimum	89	166	185	166	143	82	
Maximum	569	280	360	279	400	408	
Mean	285	239	265	246	261	275	
Std. dev. 99 per cent. upper	111	33	56	34	56	53	
tolerance	602	335	448	357	409	415	

#### OCCURRENCE OF HEAVY METALS IN SOIL (MG PER KG OF DRY SOIL). EFFECTS OF RESPREADING TOPSOIL

\* See text.

By 1981 the housing development was complete and further soil samples were taken. Where it was not possible to resample at the precise location of the original samples, the closest suitable place was chosen. In total, 17 of the original 20 major 200 ft grid points were resampled for both top and subsoil and all 75 topsoil plus 73 subsoil samples from the 50 ft grid were collected. The results of the analytical studies are presented in Tables I–IV.

As there was a delay of three years betweeen receiving the initial greenfield site samples and those taken after respreading (due to contractual difficulties with the developers), the original samples were analysed concurrently with the respread soils in 1981.

Cadmium, lead and zinc were estimated on all samples: chromium, copper and nickel were additionally determined on the 20 topsoil samples from the 200 ft grid.

#### TABLE II

	200 ft grid 20	200 ft grid 17	
No. of samples	Original	Respread	
Chromium			
Range:			
Minimum	26	145	
Maximum	994	416	
Mean	306	248	
Std. dev.	236	72	
99 per cent.			
upper			
tolerance*	981	458	
Copper			
Range:			
Minimum	36	52	
Maximum	207	94	
Mean	91	80	
Std. dev.	42	11	
99 per cent.			
upper			
tolerance	211	112	
Nickel			
Range.			
Minimum	24	33	
Maximum	86	57	
Mean	55	49	
Std dev	17	6	
99 per cent	±1	0	
upper			
tolerance	104	67	

#### OCCURRENCE OF HEAVY METALS IN SOIL (MG PER KG OF DRY SOIL). EFFECTS OF RESPREADING TOPSOIL

\* See text.

#### EQUIPMENT AND REAGENTS

- 1. Glen Creston Cross Beater Mill.
- 2. Instrumentation Laboratory Atomic Absorption spectrophotometer 157 model with deuterium background correction.
- 3. All chemicals were A. R. grade or equivalent from B. D. H. or Fisons.
- 4. All glassware was borosilicate glass from Corning, and was acid washed before use.
- 5. Element standards of 1000 mg/l were diluted appropriately before use.

#### SAMPLING

Approximately 1 kg of soil was submitted in a sealed, labelled, polythene bag and each sample was visually assessed on receipt at the laboratory. The difference in physical appearance between topsoil and subsoil was used as an initial sorting test to ensure that samples of topsoil were not contaminated with subsoil and vice versa. The soils of mixed origin were rejected and resampling of that location was carried out. Stones larger than 0.5 cm were removed and the

#### TABLE III

No. of samples	200 ft 10 Original	grid 10 Respread	200 ft 18 Original	grid 17 Respread	50 ft grid 85 Respread
Cadmium					
Range:					
Minimum	0.2	< 0.1	< 0.1	< 0.1	< 0.1
Maximum	0.9	0.4	0.9	0.5	1.7
Mean	0.5	0.2	0.5	0.2	0.3
Std dev.	0.2	0.1	0.2	0.1	0.3
99 per cent. upper					
tolerance*	1.3	0.5	1.1	0.5	1.1
Lead					
Range:					
Minimum	20	6	16	6	6
Maximum	50	33	50	48	101
Mean	30	17	32	17	22
Std dev.	10	7	10	10	17
99 per cent. upper					
tolerance	63	39	61	46	77
Zinc					
Range:					
Minimum	58	35	40	35	48
Maximum	185	86	185	92	206
Mean	106	65	105	64	76
Std dev.	42	14	37	15	30
99 per cent. upper					
tolerance	243	111	212	108	155

#### OCCURRENCE OF HEAVY METALS IN SOIL (MG PER KG OF DRY SOIL). EFFECTS OF RESPREADING SUBSOIL

\* See text.

remaining material was air dried at room temperature for approximately 3 days, when no obvious sign of moisture remained, milled through a 2 mm screen, and stored in labelled polythene bags to await analysis.

As the metallic concentration of the soil was to be expressed on a dry weight basis the residual moisture was determined by drying 2 g of air dried soil at 105°C to constant weight.

## DETERMINATION OF THE CONCENTRATION OF TOTAL METALS IN THE SOIL

The method of analysis has been described in detail previously<sup>3</sup>. Briefly the air-dried soil was treated with boiling 2M hydrochloric acid to extract the "total" metals into solution. This solution was then directly used for quantification of the metals using flame AAS.

#### **Observations**

Only 17 of the original 20 samples on the 200 ft grid could be taken after respreading. However, because the three missing soils were situated on the extremities of the sampling grid, it was considered that their absence was unlikely to affect the overall conclusions of the experiment.

The ten soil samples taken on the 200 ft grid form the perimeter of the 50 ft

## TABLE IV

		Presen	t survey
Element	1972	Original	Respread
Cadmium			
Range:			
Minimum	1.6	0.6	1.6
Maximum	9.0	7.2	3.1
Mean	4.2	3.0	2.5
Std dev	1.7	1.6	0.4
00 per cent upper	1.7	1.0	04
tolerance*	9.1	7.6	3.7
Chromium			
Range:			
Minimum	31	26	145
Maximum	1410	994	416
Mean	290	306	248
Std dev	322	236	72
90 per cent upper	344	250	12
tolerance	1211	081	159
tolerance	1211	981	438
Copper			
Range:			
Minimum	20	36	52
Maximum	198	207	94
Mean	81	91	80
Std. dev.	42	42	11
99 per cent, upper			
tolerance	201	211	112
Lead			
Range:			
Minimum	40	35	78
Maximum	412	424	166
Mean	156	158	121
Std. dev	88	92	23
99 per cent, upper			
tolerance	408	421	188
Nickel			
Range:			
Minimum	55	24	33
Maximum	120	86	57
Mean	92	55	49
Std. dev.	19	17	6
99 per cent, upper		••	
tolerance	146	104	67
Zinc			
Range:			
Minimum	25	89	166
Maximum	600	569	280
Mean	264	285	239
Std dev	133	111	33
90 per cent upper	155	111	55
tolerance	644	602	325
tolerance	044	002	555

## OCCURRENCE OF HEAVY METALS IN SOIL (*MG PER KG OF TOPSOIL*. HEATHERBROOK TOPSOIL, 20 SAMPLES FROM 200 FT GRID: PREVIOUS AND *PRESENT SURVEY*

\* See text.

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grid. The reason for analysing all 85 samples from the closer grid was to assess, more accurately, the distribution of the metallic contaminants and hence the development potential of the land. Obviously the benefit of sampling from a closer grid must be balanced against the time and cost of obtaining the extra information. However, errors of judgement, based on insufficient or inadequate data may invoke cost penalties in terms of additional site restoration costs.

In the case of cadmium, the metal of most concern in the Heatherbrook soil, the increased effort of sampling on the 50 ft grid would not have influenced the way in which the site was developed because the original topsoil from the Heatherbrook area had a reasonably uniform soil metal concentration within the area of the 50 ft grid (also see below). An area with a more heterogeneous soil metal concentration would have yielded much more benefit.

One of the overall objectives of the stripping/respreading exercise, to reduce maximum concentrations of metals in the soil was successful. The 99 per cent. upper tolerance limit (the concentration of metal which is only exceeded in 1 per cent. of the soil) for cadmium was reduced from 6.0 to 3.9 mg of Cd/kg in 10 samples from the 200 ft grid, 7.6 to 3.7 mg of Cd/kg for 20 samples on the same grid, and 5.3 to 4.3 mg of Cd/kg in samples from the 50 ft grid.

These figures are most significant in that previous guidelines, produced by the D.O.E.<sup>4</sup> suggested an "acceptable" concentration of 5.0 mg of Cd/kg of D.S. (later reduced to 3.0 mg Cd/kg of D.S. for small gardens<sup>5</sup>; thus the respreading exercise had reduced the 99 per cent. upper tolerance limit of the soil cadmium concentration to such a degree that the use of the soil for small domestic gardens was acceptable.

The reasons for the difference in tolerance limits between the metal concentration of the larger area (the 20 samples on the 200 ft grid) and that of the smaller inner area represented by 10 or 85 samples was twofold. First was the uneven geographical distribution of metals; although on Heatherbrook the soil metal concentrations are generally fairly uniform there is a gradient which causes metal levels to increase with increasing proximity to the old sludge spreading area, and hence there was bias in the distribution of the metals in the original soil. When this soil was homogenised during the scraping, stockpiling and respreading this bias was much reduced. Four of the 20 samples on the 200 ft grid were closer to the highly contaminated area than any of the other 85 samples, and it was these four samples which contributed most to this bias. The second reason for the variation was that these areas with the highest cadmium content (7 mg/kg) were scraped free of the topsoil, which was then isolated and not incorporated back into the Heatherbrook topsoil stockpiles.

Although only cadmium has been detailed, the other metals analysed show the same general beneficial trend of the stripping/respreading exercise with consequent lowering of the 99 per cent. upper tolerance limits over the whole site.

Metal concentrations in the subsoil were very low, and were further reduced after respreading. This reduction was probably due to artifacts, e.g. analytical samples being more closely examined for the presence of topsoil in the resampled subsoils, rather than any real physical mixing effect during respreading of the topsoil.

## Conclusions

The analysis of Heatherbrook topsoils before the scraping commenced indicated that the metal contamination was widespread over the site and although there was variation in the degree of contamination, this variation rarely exceeded one order of magnitude. However the process of mixing and respreading did nevertheless result in increased homogeneity and modest reductions in concentrations. It could, therefore, be envisaged that on other sites where the metallic concentration in the soil was more heterogeneous, the effect of scraping/stockpiling/respreading could be more dramatic and could significantly assist successful redevelopment of the land. It may also be possible to obtain a significant reduction in development costs in certain sites and with thorough analytical backup, considerable confidence in the success of such an exercise could be achieved.

## QUALITY ASSURANCE OF ANALYTICAL DATA

Soil analyses carried out on Beaumont Leys almost twenty years ago included little analytical quality assurance, as it was then essential that the overall pattern of metallic contamination should be determined in a very limited time, occasional results which did not fit into that pattern, were rarely investigated further. Analytical instrumentation was limited, and techniques now considered to be standard, e.g. background correction for AAS, were not available on commercial equipment. This project involved fewer analyses and therefore much more credence had to be taken of each individual result.

The Heatherbrook project involved samples being examined before and after respreading, therefore the overriding importance was to achieve analytical comparability between the two sets of data. Samples collected in 1978 from the greenfield site were therefore analysed alongside the soils submitted after respreading.

Approximately 25 soils were analysed together, and the quality assurance procedure below was carried out in order to achieve batch to batch consistency.

At the start of the project it was not possible to locate a "standard" soil with certified values for cadmium and lead, it was therefore decided that ADAS Soil Science laboratory at Derby should collect and prepare six soils containing a range of metal concentrations. The soils originated from various locations but included a number from Beaumont Leys.

#### QUALITY ASSURANCE PROCEDURE

- 1. With every batch of Heatherbrook samples, a "standard"ADAS soil (containing a similar concentration of metals) was analysed for cadmium, lead and zinc. Chromium, copper and nickel were only determined when the Heatherbrook soils themselves required a more comprehensive analysis.
- 2. One single extraction of the ADAS "standard" soil was re-estimated with each batch of analyses to test the instrumental reproducibility.
- 3. A number of Heatherbrook soil samples were analysed together in a single batch having been previously analysed at different times.
- 4. At the time of sampling of the greenfield Heatherbrook site in 1978, ten specimen soils were divided, (with only a cursory attempt made to

homogenise them) between the Leicestershire County Analyst's Laboratory and ADAS Shardlow. Each laboratory analysed the samples using their standard techniques in order to assess interlaboratory comparability.

## Discussion

Batch to batch reproducibility was shown to be acceptable. Standard deviations were generally less than 10 per cent. of the mean for cadmium, lead

Element	Min.	Max.	Mean	Std dev.	
Cadmium	1.4	1.8	1.5	0.1	
Lead	85	102	91	4	
Zinc	150	190	168	10	
(B) EIGHT SEPARATE	EXTRACTIC	NS FOR CH	ROMIUM, C	OPPER AND	NICKEL
Element	Min.	Max.	Mean	Std dev.	
Chromium	120	160	139	16	
Copper	50	82	60	9	
Nickel	32	40	37	3	
C) SINGLE EXTRACTIO	N. FIFTEEN E	STIMATION	S FOR CAD	MIUM, LEA	D AND ZIN
Element	Min.	Max.	Mean	Std dev.	
Cadmium	1.5	2.0	1.6	0.2	
Lead	89	97	92	2	
	100	200	101	10	

# TABLE V REPEATABILITY OF ANALYTICAL DETERMINATIONS (MG/KG OF DRY SOIL).

#### TABLE VI

#### REPEATABILITY OF ANALYTICAL DETERMINATIONS (*MG/KG OF DRY SOIL*). (A) HEATHERBROOK TOPSOIL—21 SAMPLES REANALYSED

	Cadmium		Lead		Zinc	
	1	2	1	2	1	2
Range: Minimum	0.5	0.8	74	56	128	82
Maximum	4.6	4.1	221	212	434	408
Mean	3.0	2.9	147	139	303	281
Std. dev.	0.9	0.8	41	39	76	79

## (B) HEATHERBROOK SUBSOIL-9 SAMPLES REANALYSED

	Cadmium		Lead		Zi	Zinc	
i	1	2	1	2	1	2	
Range: Minimum	<0.1	<0.1	6	6	38	32	
Maximum	0.3	0.4	33	32	92	91	
Mean	0.2	0.2	17	17	67	66	
Std. dev.	< 0.1	<0.1	7	7	15	16	

Column 1-soils analysed together.

Column 2-soils analysed in several batches.

#### TABLE VII

Element	ADAS Predevelopment	L.C.C. Predevelopment	L.C.C. Respread	
Cadmium				
Range: Minimum	1.3	1.3	1.6	
Maximum	4.0	4.3	2.9	
Mean	2.4	2.7	2.6	
Std. dev.	0.8	1.0	0.4	
99 per cent. upper toleranc	e 5.0	6.0	3.9	
Chromium				
Range: Minimum	ADAS did	102	145	
Maximum	not analyse	390	341	
Mean	the soils	222	241	
Std. dev.	for	86	65	
99 per cent. upper toleranc	e chromium	502	453	
Copper				
Range: Minimum	63	59	52	
Maximum	110	114	94	
Mean	86	80	81	
Std. dev.	16	17	12	
99 per cent. upper toleranc	e 138	136	119	
Lead				
Range: Minimum	84	95	78	
Maximum	164	154	150	
Mean	115	125	123	
Std. dev.	20	17	21	
99 per cent. upper toleranc	e 181	180	191	
Nickel				
Range: Minimum	41	41	33	
Maximum	74	80	57	
Mean	58	55	49	
Std. dev.	12	13	7	
99 per cent. upper toleranc	e 98	98	70	
Zinc				
Range: Minimum	218	185	166	
Maximum	375	360	279	
Mean	278	265	245	
Std. dev.	52	56	34	
99 per cent. upper tolerand	e 446	448	357	

#### DETERMINATION OF HEAVY METALS IN SOIL. INTERLABORATORY TRIAL USING 10 SAMPLES OF HEATHERBROOK TOPSOIL\*

\* Results are expressed as milligrams of the element per kg of dry soil with the exception of the ADAS results which are expressed as milligrams of the element per litre of air dried and ground soil.

and zinc but slightly greater variations were noted for the other metals, probably because of the few replicates. The single extraction which was re-estimated with each batch provided a similar order of variation to the batch to batch reproducibility.

Analytical variation of the inter-laboratory trial was minimal. Small differences may have been attributable to the samples not being homogenised before being split and also the fact that the metallic content of the soil was calculated by ADAS as a weight/volume relationship with units of milligrams of the element/litre of the air dried and ground soil whereas the L.C.C. analytical results are all calculated as milligrams of the element/kilogram of air dried soil,

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i.e. weight in weight. However, it is understood that normally the relationship is close to 1:1.

## Conclusions

The analytical quality assurance scheme was devised as an attempt to quantify analytical variations during the project. This was particularly essential during our research project with the D.O.E. which ran from 1978–84 because of the prolonged timescale together with staff and instrumental changes in the intervening period. About 10 per cent. of the analytical work was devoted to AQA.

Generally, precision of soil analyses was shown to be excellent using the methods described and although a degree of accuracy was inferred the lack of standard materials prevented the actual confirmation.

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# The Distribution of Heavy Metals in Soil and Metal Uptake into Vegetation, at Beaumont Leys Sewage Farm, Leicester.

## Part III: Analysis for Cadmium, Lead and Zinc in Vegetables Grown in a Soil Contaminated with Sewage Sludge

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The concentrations of cadmium, lead and zinc were determined in vegetables grown over three growing seasons in topsoil previously contaminated with sewage sludge at Beaumont Leys, Leicester.

The soil was analysed before any vegetables were planted and again after the final harvest, to confirm that there had been no significant change in metal concentrations in the intervening period.

Potatoes were grown every year, lettuces for two years and beetroots, cabbages and parsnips for one year. During one year two varieties of lettuce were grown.

Compared to the concentrations of metals in retail samples of the different vegetables, the concentrations in crops grown in the Beaumont Leys "garden plot" showed evidence of increased uptake in some instances. Thus cadmium and zinc concentrations were higher in parsnips; concentrations of metals were not increased in potatoes, however. In no instance did the concentration of lead in any of the garden plot vegetables exceed the statutory limit for lead in food<sup>1</sup>.

The results show that the concentrations of cadmium, lead and zinc in beetroots, lettuces and parsnips grown in soil containing cadmium at approximately 6 mg/kg were higher than the concentrations of the metals in retail samples of these vegetables. It is likely, however, that lower concentrations of the metals can be expected in vegetables grown in similar garden soil on the Beaumont Leys Development where cadmium concentrations are generally less than 3 mg/kg and the concentrations of lead and zinc can also reliably be expected to be lower than in the garden plot soil.

The development of the Beaumont Leys area of Leicester from a sewage farm to a residential area has been documented earlier<sup>2,3,4,5</sup>. The County Analyst's Laboratory had been associated with the analysis of environmental samples from the site from an early stage, but it was not until 1982 that a detailed study of the uptake by vegetables of metals from Beaumont Leys soil commenced under the sponsorship of the Department of the Environment (D.O.E.) Central Directorate of Environmental Protection.

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This "garden plot" experiment was designed to investigate whether the local residents would be likely to derive any increased intake of metals from vegetables grown in their own gardens, compared to that obtained by consuming a similar range of vegetables grown elsewhere.

## CONSTRUCTION OF THE GARDEN PLOT

An area  $7 \text{ m} \times 10 \text{ m}$  in size was excavated, to a depth of 0.75 m, with particular attention being given to remove all topsoil. A 0.3 m layer of crushed brick was spread over the exposed subsoil followed by 0.5 m of selected topsoil containing between 6 and 9 mg of cadmium per kg of dry soil (D.S.), a concentration which was between two to three times the projected 3 mg of cadmium per kg of D.S. (maximum) used in the residential gardens at Beaumont Leys.

Once the topsoil was in place (May 1982) it was rotavated and prepared for growing vegetables during the summer of 1982.

#### SOIL SAMPLING

A comprehensive investigation of the concentration of metals in the soil of the garden plot was carried out immediately before any vegetables were grown.

A 1 m grid was set up and, after allowing 0.5 m around the perimeter of the plot which was to be left unplanted to prevent any edge effect, the  $6 \text{ m} \times 9 \text{ m}$  grid provided 54 interactions. A soil sample of approximately 500 g was taken from the top six inches of soil at each intersection.

Further samples were taken at the end of the project in August 1984, to assess if there had been any significant change in the soil metal concentrations during the three growing seasons.

## CROP LAYOUT

The plot was divided into three sections, and rows of each vegetable were planted in every section. When the crops were harvested three further subdivisions were made at right angles to the original three segments to produce nine sub-plots (Figure 1). Each group of vegetables from each sub-plot was treated as a discrete sample for the purposes of harvesting, sampling and analysis.

A	Sub-plot I X X X	Sub-plot 4 X X X	Sub-plot 7 X X X
в	ххх	ххх	x x x
с	Sub-plot 2 X X X	Sub-plot 5 X X X	Sub-plot 8 X X X (0.5 m) to minimize
D	x x x	ххх	X X X
E	Sub-plot 3 X X X	Sub-plot 6 X X X	Sub-plot 9 X X X
F	× × ×	ххх	X X X
_	ii i_2_3	¦ 4_5_6	Sampling 78_9 Sampling points

Fig. 1. The arrangement of sub-plots within a 1 m grid garden plot.

#### VEGETABLES

The vegetables were selected to represent foodstuffs from a range of botanical structures, and were also typical of those grown by a householder in his back garden.

Potatoes-edible portion is a stem tuber.

Lettuce-the edible leaves have a short growing season.

Beetroot & Parsnips—the root is consumed in both, but beetroot is fast growing and surface rooted whereas parsnip is slow growing and deep rooted.

Winter Cabbage-the edible leaves have a long growing season.

The varieties selected were popular with local amateur gardeners and consequently were freely available as seed.

#### HORTICULTURAL PRACTICE

In May 1982 seedlings of beetroot, variety "Detroit" and lettuce "Webb's Wonderful" plants (in peat blocks) were transplanted into the plot and "seed" of the potato "Arran Pilot" were set.

For the 1983 growing season, the lettuce "Webb's Wonderful" and a cos variety "Lobjoits Green" were planted alongside the "Arran Pilot" potatoes. Parsnips "Asmer Improved Marrow" were sown directly into the ground and a winter brassica "January King", variety "Asmer Special" was established in peat blocks before being transplanted into the plot at the seedling stage.

Because of problems with site maintenance it was only possible to plant the "Arran Pilot" potatoes in 1984.

Throughout each growing season the plot was kept weed free and during 1983 the soil was watered as required. Fertilizer was used to help establish the plants; slug pellets and insecticide were used to help prevent the loss of the crop to pests.

The plot was rough dug each autumn after harvesting and rotavated in the following spring before planting the next series of crops.

#### HARVESTING THE CROPS

The vegetables from each sub-plot were collected in polythene bags when they were mature and immediately returned to the laboratory where any damaged or unsuitable specimens were rejected and those remaining were prepared for analysis.

It should be noted that all of the vegetables appeared normal during the project and they all provided adequate material for the chosen analytical regime.

#### LOCALLY PURCHASED VEGETABLES

Throughout the duration of the "garden plot" experiment, local vegetables, either available from Leicestershire markets or from local market gardens (away from the Beaumont Leys area) were examined for comparison with those grown on the contaminated land.

These vegetables were prepared and analysed in a manner similar to those

from the "garden plot"; duplicate determinations on each sample were carried out using flame AAS, except for cadmium and lead in the potato samples which were determined by furnace atomisation atomic absorption spectrophotometry.

## **Equipment and Apparatus**

Drying Oven—Baird & Tatlock, Unitemp Analytical Balance—Sartorius, 1602 Hammer Mill—Glen Creston, Cross Beater Blender—Waring, Commercial 91-358 Sieve, 500 micron—Endecotts stainless steel Water Bath (with heating control)—Techne TE-8J Water Bath Racks—made by Richardson's of Leicester Polystyrene Jars (250 ml)—Sterilin, 190 C Polystyrene Jars (30 ml)—Sterilin, 128A Atomic Absorption Spectrophotometers: —Instrumentation Laboratory IL357 —Instrumentation Laboratory IL254 Fastac

*Furnace*—Instrumentation Laboratory IL655 *Pyrolytically Coated Furnace Tubes*—Instrumentation Laboratory IL29657

#### REAGENTS

1. Nitric acid. (SG 1.42) Aristar or A.R. Grade.

2. Glass Distilled Water.

3. *Standard Elemental Solutions*. 1000 mg of the relevant element/litre diluted down as necessary for AAS standards.

#### Methods

PREPARATION OF VEGETABLES FOR ANALYSIS

The analysis was carried out on that part of the vegetable which was normally consumed: therefore to provide an analytical sample the preparation of the vegetable essentially followed normal domestic procedures used in the preparation of vegetables for culinary use.

For potatoes, parsnips, and beetroots, a selection of medium-sized vegetables was taken from each sub-plot, washed and scrubbed under running water, then scraped or peeled and diced before being placed in large brown paper bags. These bags were weighed and dried at 100°C overnight in a fan oven. The following morning the bags were removed from the oven, cooled and reweighed. Each dry sample was homogenized to pass a 0.5 mm sieve and stored in a 250 ml screw-capped jar to await analysis.

Typically, five lettuces and two cabbages were collected from each sub-plot; the outer leaves of each plant were rejected. The remaining leaves were removed, weighed, washed under running water and then dried with a clean cloth to absorb the surplus water before being transferred to paper bags to be dried and homogenized as above.

#### PREPARATION OF SOILS FOR ANALYSIS

When the soils arrived at the laboratory they were air dried at room temperature and then milled to pass a 2 mm screen. After further mixing a 250 g portion was stored to await analysis. A 2 g sub-sample of this soil was dried at 100°C to constant weight, to establish the percentage of water still associated with the air-dried soil. The moisture content was subsequently used to convert all the analytical results obtained from the soil to a dry weight basis.

## **Analytical Procedure**

Aliquots of  $1 \pm 0.1$  g of either vegetable or soil were accurately weighed into 30 ml polystyrene tubes, and the metals solubilized by the method of Williams<sup>6</sup>. To each tube, 10 ml of nitric acid was added, and then the caps screwed tightly, and the contents mixed. After 24 hr at room temperature, the tubes were heated at 70°C for 4 hr in a water bath. The caps were then carefully loosened to release the pressure in the tubes, and heating continued for a further 2 hr. The digestion tubes were then allowed to cool. The contents of each were made up to 25 ml with distilled water, and filtered through No. 1 filter paper into fresh tubes. The solutions were analysed directly for cadmium, lead and zinc content, using atomic absorption spectroscopy.

Five analytical replicates of each vegetable material from each sub-plot were analysed in this way, and typically one batch of 80 digests could be analysed per day. The determination of the metal content of the digests was carried out using flame AAS. However, for cadmium in potatoes, cabbage, and parsnips, and for lead in potatoes, beetroot, lettuce, and cabbage, levels were below the level of detection possible using the flame technique and furnace atomisation was necessary for quantification.

The soils were analysed in duplicate and all the determinations were made using flame atomic absorption spectroscopy.

#### ATOMIC ABSORPTION SPECTROSCOPY

The instrument was calibrated using aqueous standard solutions containing appropriate concentrations of the analyte in 5 per cent. nitric acid. The detailed instrumental conditions were set according to the manufacturer's handbook<sup>7</sup>.

The filtered digests were aspirated directly into an air/acetylene flame for all determinations of cadmium, lead and zinc in soils, and for the vegetable extracts containing higher concentrations of cadmium and lead.

### FURNACE AAS

When the concentration of cadmium and lead was below the practical detection limit of flame AAS, the metals were quantified using furnace AAS. In 1982 and 1983, using the IL357 AAS, separate atomisations were necessary for each metal, but in 1984 with the purchase of a Video 22 twin channel instrument cadmium and lead could be estimated simultaneously during a single atomisation.

The furnace system was set up using the following conditions:

1. Using a pyrolytically coated graphite tube.

- 2. Deposit at 150°C.
- 3. Ramp to 400°C in 15 sec.
- 4. Ash at 400°C for 5 sec.
- 5. Atomise at 1400°C.

Distilled water was atomized until a stable absorbance close to zero was obtained, followed by a mixed standard solution containing 3  $\mu$ g of cadmium/ litre and 50  $\mu$ g of lead/litre in 5 per cent. nitric acid. When the replicate atomizations had produced an absorbance of acceptable precision, the system was calibrated with five standards in the range 1–10  $\mu$ g of Cd/litre and 5–200  $\mu$ g of Pb/litre.

The autosampler was loaded in such a way that for every ten solutions that were atomized, two blanks and two standard solutions were included.

Each solution was atomized in duplicate, and the mean figure (normally the relative standard deviation is less than 10 per cent.) was used to calculate the amount of metal in the vegetable.

## Results

Summaries of the results of the soil and vegetable analyses are presented in Tables I and II. Detailed analytical results are to be found in the Appendix—Tables XII–XXIII.

## Discussion

The results of the 1982 and 1984 soil analyses (Table I) confirm that the garden plot could be regarded as a single uniform plot. There was some evidence that the cultivation practices from 1982–1984 had further homogenized the soil, as some of the extreme values found in 1982 were reduced, producing a modest fall in the standard deviation in the 1984 survey for each metal. There was no evidence from this experiment that the metal content of topsoil had diminished with time.

Metal accumulation in plants can occur in soils treated with sewage sludge, There is a wide range of factors which affect, or are suspected of affecting, uptake including the type and condition of the soil and its pH, the form of the metal, the presence of other metals in the soil matrix, the plant species and particular cultivar, the type of plant tissue tested and the season of the experiment<sup>8,9,10</sup>.

	Cadmium		Lead		Zinc	
	1982	1984	1982	1984	1982	1984
	mg/kg of dry soil					
Mean	6.5	6.4	480	460	680	640
Std dev.	0.6	0.5	45	40	60	50
Range: Min.	5.2	5.4	380	370	550	550
Max.	8.8	7.4	570	540	830	750

TABLE I GARDEN PLOT SOIL SURVEY 1982 AND 1984:

CHROMIUM, LEAD AND ZINC CONTENTS OF SOILS (SUMMARY)

#### TABLE II

Vegetable	Cadmium	Lead	Zinc	
	mg/kg of fresh vegetables			
Beetroot				
Garden plot	0.20	0.04	20.7	
Retail	<0.05	<0.1	4.7	
Cabbage				
Garden plot	0.05	0.02	8.4	
Lettuce				
Webb's garden plot 1982	0.58	0.05	18.1	
Webb's garden plot 1983	0.49	0.17	10.4	
Cos garden plot	0.37	0.05	9.6	
Retail summer varieties	<0.05	<0.10	3.0	
Retail autumn varieties	<0.05	<0.10	4.0	
Parsnips				
Garden plot	0.09	0.36	14.9	
Retail	<0.05	<0.1	2.8	
Potatoes				
Garden plot 1982	0.05	0.02	4.0	
Garden plot 1983	0.06	0.02	3.9	
Garden plot 1984	0.05	0.02	3.8	
Retail	0.04	0.07	2.6	

#### MEAN CONCENTRATION OF METALS FOUND IN VEGETABLES

In this project the concentrations of cadmium, lead and zinc varied between the different vegetables (Table II) and this may, in some varieties, have been affected by particular environmental conditions. The three growing seasons happened to coincide with three very different seasonal weather patterns; for example a dry cool spring followed by a wet summer (1982) and a wet spring followed by long hot summer (1983). However only potatoes were cultivated every year, and they had essentially similar concentrations of cadmium, lead and zinc to both local retail samples and potatoes grown on untreated soils<sup>8,9,10</sup> (Table III). Although potatoes have been shown to take in cadmium and zinc when grown in soils treated with sewage sludge<sup>8,9</sup>, other crops are more sensitive indicators of metal uptake. Unfortunately, however, the restricted timescale of the experiment only allowed the cultivation of the other vegetables during one or two growing seasons.

Of the root vegetables, beetroot accumulated zinc and cadmium compared to retail samples, but the data were similar to the results of comparable growth trials on soils treated with sewage sludge (Table III). Parsnips, appear not to accumulate cadmium but they did contain a higher lead and zinc level than their respective vegetables from retail sale. The higher concentrations of lead found in the parsnips are in contrast to earlier results published by MAFF<sup>10</sup>. (See Table III.) It is possible that the accumulation of the different metals is related to the different growth and physiological characteristics of the two vegetables.

The lettuces were grown in two years, and accumulated both cadmium and zinc relative to the retail samples. However, the concentrations of zinc, and to a lesser extent, lead in the lettuce leaves did vary significantly in consecutive

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	So So Cadmium	Soils treated with sewage sludge Cadmium Lead Zinc		U Cadmium	Untreated soil Lead	ls Zinc		
		mg/kg fresh weight						
Beetroot	0.14	0.02-	19-	<0.01-	_	3.7-		
		0.07	34	0.06		3.9		
Cabbage	0.03-	<0.01-	12-	<0.01-	<0.01-	2.1-		
	0.06	0.25	17	0.03	0.51	3.0		
Lettuce	0.03-	<0.01-	7–	<0.01-	—	4.0-		
	0.35	0.44	38	0.39		4.2		
Parsnips	0.10-	0.05-	20-	<0.01-		4-1-		
5	0.13	0.08	29	0.37		4.5		
Potatoes	0.12-	0.02-	5.2-	<0.01-	<0.01-	3.4-		
	0.21	0.08	11	0.06	0.14	3.9		

## TABLE III CONCENTRATION OF METALS FOUND IN VEGETABLES: MAFF SURVEYS\*

\* See references 8, 9, 10.

growing seasons. This indicates that environmental factors could have affected the efficiency of metal uptake, although it was not possible to detect any obvious pattern to the results. The cadmium concentrations found in this experiment were generally higher than those found previously where soil cadmium levels were comparable8.

Although it is not yet possible to predict accurately the metal concentrations likely to be found in plants grown in a particular soil of known composition, within certain limits, there is a more or less direct relationship between the level of cadmium in the soil and the concentration of cadmium in plants grown in that soil<sup>11</sup>. The soil in the gardens at Beaumont Leys generally contains less than 3 mg of cadmium per kg, which is approximately half that found in the experimental garden plot soil, and therefore the intake of metals into the average diet is likely to be reduced compared to that from vegetables grown in the garden plot.

## Conclusion

It is possible that a proportion of the population who intensively grow vegetables in their gardens at Beaumont Leys may be exposed to increased metal intakes of cadmium, lead and zinc compared to residents purchasing all their fresh vegetables from retail outlets. However because of the physical constraints of garden size and the lower concentrations of cadmium, lead and zinc in the soil of these gardens, the evidence from this garden plot experiment suggests that any increase in intake of these metals in the total diet is likely to be modest.

## Analytical Quality Assurance (AQA)

### INTRODUCTION

It became clear initially that a great many metal determinations would be necessary if the project were to be successfully completed. However by the time

that the analytical protocol had been established the original projections of sample numbers had multiplied many-fold. Therefore, it became essential to select a digestion technique which fulfilled the criteria, and to assess its performance characteristics.

The technique of Williams<sup>6</sup> was reported to be both precise and accurate; involve little manipulation; be capable of rapid throughput of samples; and produce an ideal matrix for the estimation of metal concentrations in organic material by atomic absorption analysis: on this basis it was selected for use.

As this method was new to the laboratory initially an attempt was made to assess both the repeatability and accuracy using Bowen's Kale.

Replicate digests of Bowen's Kale and also blank determinations using AR grade soluble starch in place of the kale were prepared using the Williams' technique. The concentration of cadmium, lead and zinc in the kale, and the zinc on the blanks was determined by flame AAS, but the concentration of cadmium and lead in the starch blanks was below the practical limit of detection for flame analysis and was therefore determined using furnace AAS.

	Cadmium	Lead	Zinc
Replicate	mg/kg	mg/kg	mg/kg
1	1.50	2.00	32.25
2	1.50	2.25	32.00
3	1.25	2.00	32.50
4	1.50	2.00	32.50
5	1.25	2.00	32.50
6	1.00	3.25	32.50
7	1.00	2.25	31.50
8	1.00	2.75	32.25
Mean	1.25	2.33	32.50
Std dev.	0.20	0.43	0.50
Quoted figures	$0.89 \pm 0.25$	$2.49 \pm 0.57$	$32.29 \pm 2.75$

TABLE IV ANALYTICAL QUALITY ASSURANCE: METALIC CONTAMINANTS IN BOWEN'S KALE

TABLE V

ANALY IICAL QUALITY ASSURANCE: DIGESTION BLAN	ALYTICAL QUALITY AS	SURANCE: DIO	GESTION BL	ANKS
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	Cadmium	Lead	Zinc		
Replicate	mg/kg of starch				
 1	0.03	0.09	<0.01		
2	<0.01	0.11	<0.01		
3	0.04	0.06	<0.01		
4	0.02	0.07	<0.01		
5	0.01	0.04	<0.01		
6	<0.01	0.07	<0.01		
7	<0.01	0.04	<0.01		
8	<0.01	0.04	<0.01		
Mean	0.01	0.07	<0.01		
Std dev.	0.02	0.03	0.0		

#### S. D. MUSGROVE

## Discussion

The determination of lead and zinc in the kale was shown to be agreeably close to the quoted values, however, the cadmium results were somewhat lower than anticipated. This was probably caused by using the flame AAS technique at the limits of its sensitivity, hence a reading of 0.03-0.04 mg of cadmium per litre was within the specification, but 0.02 and 0.05 mg of cadmium per litre were outside. This lack of sensitivity initiated the wider use of furnace atomization to determine the concentrations of metals in the vegetables.

The "blank" determinations were specifically carried out to assess if the digestion process extracted any metals from the apparatus; substituting water for the kale would not have produced a comparable digestion system, therefore AR soluble starch was chosen as a material of plant origin which was readily available in a relatively pure form. There are no published purity criteria for lead nor cadmium in the starch, and the concentrations of these elements in the digest blanks undoubtedly includes a contribution from the starch itself.

#### Conclusions

The digestion method worked very well, but as the flame AAS was only able to determine to the nearest 0.25 mg of metal per kilogram of kale, the more sensitive furnace AAS was necessary to determine the lower metal concentrations expected to be found in some vegetables. The method of Williams was therefore adopted as the standard digestion method for the analysis of the vegetables for the duration of the project, but as this preparative work was somewhat limited a rolling programme of quality assurance was subsequently incorporated into each season's analyses.

## YEAR 1, 1982-(1) ANALYTICAL PRECISION

An estimate of the precision of the batch analysis was made by re-analysing crop samples from three separate sub-plots after the main body of the work had been completed.

## Discussion

The batch to batch reproducibility was shown to be excellent, and the minimal variations were deemed not to be significant in the context of the project.

## YEAR 1, 1982-(2) STANDARD ADDITION WITH FURNACE ATOMISATION

The lead concentrations in all the vegetables grown on the garden plot in 1982 and the cadmium concentration in potatoes were below the limit of detection by flame AAS, and consequently those parameters were determined using furnace AAS.

Although the results obtained from the furnace appeared to be satisfactory, it is acknowledged that the furnace technique can suffer from greater interferences. It was therefore considered necessary to confirm the furnace analysis results by the standard addition technique.

It was assumed that the metals present, in the replicate acid digests from each vegetable, were in a similar elemental form and matrix: all the results from one

TAB	LE	VI	

		Cadi	nium	Le	ead	Zi	inc
	Ru	in 1	2	. 1	2	1	2
Vegetable	Sub-plot		п	mg/kg of each vegetable*			
Beetroot	1	0.20	0.18	0.03	0.04	16.9	17.7
	2	0.21	0.22	0.03	0.03	22.2	21.7
	4	0.18	0.19	0.02	0.04	19.6	20.4
Mean		0.20	0.20	0.03	0.04	19.6	19.9
Webbs	1	0.55	0.56	0.04	0.04	16.0	17.4
lettuce	5	0.40	0.41	0.04	0.04	13.0	13.1
	8	0.59	0.60	0.04	0.05	18.0	18.8
Mean		0.51	0.52	0.04	0.04	15.7	16.4
Potato	1	0.04	0.03	0.03	0.04	3.8	3.9
	3	0.06	0.05	0.01	0.02	4.0	4.1
	6	0.06	0.06	0.02	0.02	3.7	3.9
Mean		0.05	0.05	0.02	0.03	3.8	4.0

# ANALYTICAL QUALITY ASSURANCE: PRECISION OF ANALYTICAL DETERMINATIONS OF METALLIC CONTAMINANTS

\* All of the results are the mean values of five replicate analyses in each case.

#### TABLE VII

	Direct estimation	By standard addition			
	µg of meta	µg of metal/litre of digest			
Lead					
Beetroot	4.6	4.9			
Lettuce	20.4	20.8			
Potato	3.4	5.2			
Cadmium Potato	7.2	6.8			

ANALYTICAL QUALITY ASSURANCE: METALS IN VEGETABLES—DETERMINATION USING THE METHOD OF STANDARD ADDITION

type of vegetable could therefore be confirmed by reference to the standard addition technique carried out on a single vegetable digest.

In 1982, the results from the direct determination of cadmium and lead in potatoes, and lead in beetroot and lettuce were therefore confirmed by the standard addition technique.

## Discussion

The results showed minimal differences between the direct readings and those obtained by standard addition. Even the variations between the two sets of results for lead in potato were not significant when related to the fresh weight.

This was reassuring, as had the standard addition technique been deemed

essential to produce accurate results the workload would have needed to be significantly increased.

## YEAR 2, 1983—(1) SPIKING EXPERIMENTS

It was decided to continue to develop the AQA programme by digesting five replicates of each vegetable sample, together with a similar number of acid blanks and a set of starch digests. In addition two further replicates, would be spiked with two concentrations of each of the three metals of interest.

The spike solution was added at a concentration high enough for analysis by flame AAS.

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ANALYTICAL QUALITY ASSURANCE: "SPIKING" EXPERIMENTS—RECOVERY OF METALS ADDED TO VEGETABLE DIGESTS

	Cadmium mg/l of digest		Lead		Zinc mg/l of digest				
Addition			mg/l of digest						
in mg Sample	0.0	0.10	0.20	0.00	0.10	0.20	0.00	2.0	4.0
Acid blank	0.00	0.10	0.18	0.00	0.10	0.20	0.00	1.8	3.8
Starch	0.00	0.09	0.18	0.00	0.09	0.15	0.00	1.8	3.3
Lettuce Cos	0.28	0.38	0.48	0.03	0.14	0.22	7.6	9.6	11.1
Webbs	0.32	0.41	0.51	0.10	0.16	0.27	6.9	8.7	10.5
Parsnips	0.02	0.11	0.21	0.05	0.18	0.28	2.3	4.3	6.1
Potatoes	0.01	0.09	0.17	0.00	0.12	0.20	0.7	2.5	4.2
Cabbage	0.02	0.12	0.23	0.00	0.11	0.20	3.0	5.0	7.2
Overall recovery		0.09	0.19		0.09	0.18		1.9	3.7

## Discussion

The results were most encouraging: almost quantitative recoveries were achieved, by replicate analytical runs at different times, by different staff.

#### YEAR 2, 1983—(2) COMPARABILITY TRIAL.

As this project was only a small part of the investigation being carried out on Beaumont Leys at the time, it was decided that samples should be analysed by ourselves and another major contractor in order that all the data could be seen to be comparable. A series of dried and ground vegetables supplied by the contractor, two samples of parsnip, two samples of potato and one of dried beetroot were analysed by both laboratories, using their own methods and equipment.

#### Discussion

Although there was some evidence that the samples as received were not as homogeneous as the ones prepared in our own laboratory, it was concluded that there was little significant difference in the results from the laboratories had the results been calculated to a fresh vegetable weight basis.

#### YEAR 3, 1984—(1) ANALYSIS OF NBS STANDARD MATERIALS

Because of site maintenance problems, only potatoes were cultivated in 1984,

		Leics. Co	unty Analyst	Other laboratory		
		Cadmium	Lead	Cadmium	Lead	
		100000	mg/kg of dried v	vegetable powder	r.	
Beetroot	Mean Range No. of	2·2 1·8–2·4	0·28 0·19–0·28	1·9 1·8–2·0	0·09 0·06–0·21	
n .	analyses	5	5	10	10	
Parsnip A	Mean Range No. of	0.28	0·36 0·32–0·43	0.23 0.21-0.32	0.15 0.10-0.19	
	analyses	5	5	10	10	
Parsnip B	Mean Range No. of	0·47 0·43–0·50	0·29 0·25–0·32	0·46 0·39–0·49	0·22 0·14-0·27	
	analyses	5	5	10	10	
Potato A	Mean Range No. of	0·25 0·24-0·25	<0.01 < 0.01	0.15 0.12-0.19	<0.05	
	analyses	5	5	10	10	
Potato B	Mean Range No. of	0·35 0·32–0·36	<0·05 <0·05–0·10	0·27 0·26–0·29	<0.05	
	analyses	5	5	10	10	

## TABLE IX ANALYTICAL QUALITY ASSURANCE: INTER-LABORATORY TRIAL. ANALYSIS OF DRIED VEGETABLE POWDER FOR METALLIC CONTAMINANTS

TABLE X

ANALI IICAL QUALITI ASSURANCE: ANALI SIS OF NBS RICE.	FLOUR
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	Cadmium	Lead	Zinc	
_		mg/kg of flour		
NBS certification	$0.029 \pm 0.004$	No figures quoted	$\begin{array}{c} 19{\cdot}4\\ \pm 1{\cdot}0 \end{array}$	
1	0.035	0.11	18.6	
2	0.032	0.11	18.7	
3	0.034	0.08	18.3	
4	0.033	0.11	18.2	
Mean	0.0335	0.10	18.5	

and the prepared samples were analysed alongside NBS Rice Flour which was selected for having a metallic composition in a similar range to that expected in the potatoes.

The same analytical protocol was retained as in 1982, but as low levels of metals had been found in potatoes in previous years, it was considered judicious to spike the samples at levels for furnace AAS, to produce an addition of 1.0 and 2.0 mg and 25 and 50 mg of lead per litre of digest to the dry vegetable powders before digestion.

#### TABLE XI

	Cadmium			Lead						
		µg/litre of digest								
Addition	0.0	1.0	2.0	0	25	50				
Potatoes	7.8	9.0	10.2	8	24	39				
Rice flour	1.3	2.5	3.6	4	29	31				

## SPIKING EXPERIMENTS: RECOVERIES OF ADDED CADMIUM AND LEAD

## Discussion

The rice flour was analysed in order to assess the accuracy of the method and although the actual readings from the furnace atomization of the digest solution had to be determined down to  $0.1 \,\mu g/l$  for cadmium, the results for the analysis of both lead and cadmium were in broad agreement with the certification values.

Considering the extremely low spike additions for cadmium the recovery of the element was acceptable, however the similar experiment using lead produced disappointing results, especially at the higher addition of 50 µg/l of digest.

The lead spike, with hindsight, was excessive with respect to the amount of lead naturally present but this should not have affected the accuracy of the determination.

As with all spiking experiments it was not possible to confirm that the added lead was incorporated into the digest matrix in the same way as the native element. Perhaps the added lead may have been lost from the furnace tube before the atomization temperature of the native lead.

#### AOA CONCLUSION

The continuing programme of quality assurance added considerably to the overall workload but this was totally justified as, by minimizing analytical variation a much greater confidence was achieved in the results, and in consequence there was a significant increase in the sensitivity of the overall experiment.

## Acknowledgement

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## Appendix

#### TABLE XII

#### METALLIC CONTAMINANTS IN GARDEN PLOT SOILS

	Cadr	nium	Lead		Zi	nc	
Plot			mg/kg o	f dry soil			
Reference	1982	1984	1982	1984	1982	1984	
A1	8.8	6.7	560	490	830	710	
2	5.9	7.2	490	540	700	750	
3	6.8	7.4	530	500	740	700	
4	7.1	6.8	510	500	760	710	
5	6.4	6.4	500	500	700	650	
6	6.9	6.9	520	480	740	720	
7	6.5	6.7	530	440	730	700	
8	6.8	6.4	460	420	700	680	
9	5.6	6.7	380	510	600	680	
B1	7.5	7.0	530	530	750	700	
2	6.9	6.9	570	530	710	680	
3	6.2	7.0	410	490	690	700	
4	6.7	6.4	530	480	680	630	
5	6.2	6.9	440	470	700	680	
6	6.9	7.2	450	490	700	680	
7	7.6	6.8	530	570	770	650	
8	6.6	6.3	470	480	660	620	
9	6.0	6.5	470	470	660	670	
C1	7.0	6.5	440	500	710	590	
2	6.0	6.5	500	490	720	570	
3	6.2	6.2	440	480	660	570	
4	6.3	6.7	480	510	640	610	
5	5.9	6.5	450	450	630	590	
6	6.3	6.6	460	520	690	560	
7	6.4	6.7	470	480	650	690	
8	7.1	6.4	510	400	750	620	
9	6-4	6.0	440	410	670	610	
D1	6.6	6.0	510	420	740	620	
2	6.7	6.0	470	440	700	570	
3	5.5	6.0	530	460	580	610	
- 4	5.9	6.2	420	460	640	600	
5	6.2	5.4	440	400	630	570	
6	6.7	5.7	490	490	700	600	
7	6.6	5.9	450	490	640	610	
8	7.1	6.5	480	500	710	640	
9	6.1	6.7	470	490	700	680	
E1	7.8	5.9	570	400	770	600	
2	5.5	6.0	400	450	610	610	
3	6.5	6.1	480	520	590	620	
4	6.0	6.4	420	460	630	640	
5	5.2	5.7	410	430	550	550	
6	6.1	5.9	470	410	630	610	
7	5.9	6.4	440	460	600	650	
8	6.1	6.7	440	470	640	660	
9	6.2	7.2	530	520	710	710	

### TABLE XII—continued

	Plot	Cadı	nium	Le mg/kg o	ead of dry soil	Z	inc	
F	Reference	1982	1984	1982	1984	1982	1984	
F	51	6.0	6.4	510	490	650	620	
	2	6.5	6.4	460	440	710	610	
	3	7.3	6.0	540	420	710	630	
	4	6.4	5.7	490	400	700	600	
	5	6.0	5.8	450	420	610	620	
	6	5.5	5.8	430	440	580	600	
	7	5.7	5.4	400	380	570	550	
	8	6.4	5.7	460	370	610	590	
	9	6.2	6.1	440	380	630	620	
Ν	/lean	6.5	6.4	480	460	680	640	
S	tandard							
	deviation	0-6	0.5	45	40	60	50	
R	Range	5-2 to	5-4 to	380 to	370 to	550 to	550 to	
	C	8-8	7-4	570	540	830	750	
9	5 per cent.							
	confidence	5-3 to	5-4 to	390 to	380 to	560 to	540 to	
	limits	7.7	7-4	570	540	800	600	

## TABLE XIII

METALLIC CONTAMINANTS IN VEGETABLES. 1982 GARDEN PLOT: POTATOES

0.1.1.4	Mana	Deres	ikg of fre	sn eaible lissi	Maan	D
Sub-plot	Mean	Range	Mean	Range	Mean	Range
1	0.03	0.03-0.04	0.04	0.03-0.06	3.9	3.8-3.9
2	0.04	0.04 - 0.05	0.02	0.01 - 0.02	3.7	3.6-3.8
3	0.05	0.05 - 0.06	0.02	0.02 - 0.03	4.1	4.1-4.2
4	0.05	0.05	0.02	0.01 - 0.02	$4 \cdot 1$	4.1-4.2
5	0.04	0.04-0.05	0.02	0.01 - 0.02	3.9	3.8-4.0
6	0.06	0.05-0.06	0.02	0.02-0.03	3.9	3.9-4.1
7	0.04	0.06	0.03	0.02 - 0.03	3.6	3.5-3.7
8	0.06	0.05 - 0.05	0.02	0.02 - 0.03	4.4	4.3-4.4
9	0.05	0.05	0.02	0.01 - 0.02	4.0	3.9-4.0
Mean		0.05		0.02	4	··0
Std dev.	<	0.01	<	0.01	0	.2
Range	0.03	3-0.06	0.0	1-0.06	3.5	-4.4

#### TABLE XIV

METALLIC CONTAMINANTS IN VEGETABLES. 1983 GARDEN PLOT: POTATOES

Ca		lmium mg	L kg of fre	.ead sh edible tissi	d Zinc edible tissue		
Sub-plot	Mean	Range	Mean	Range	Mean	Range	
1	0.05	0.04-0.05	0.03	0.02-0.05	4.2	4.1-4.3	
2	0.07	0.06-0.08	0.02	0.02-0.03	4.3	4.0-4.3	
3	0.06	0.06-0.07	0.02	0.02	4.0	3.9-4.1	
4	0.06	0.06	0.01	0.01 - 0.02	3.6	3.5-3.6	
5	0.07	0.06-0.08	0.02	0.01 - 0.03	3.9	3.8-4.0	
6	0.06	0.06-0.07	0.02	0.02 - 0.03	3.3	3.2-3.5	
7	0.06	0.05-0.06	0.01	0.01 - 0.02	4.3	4.0-5.3	
8	0.06	0.05-0.07	0.01	0.01	3.7	3.5-4.1	
9	0.06	0.06-0.07	0.01	0.01	4.0	3.9-4.2	
Mean		0.06		0.02	3	.9	
Std dev.	<	0.01	<	0.01	0	.3	
Range	0.04	4-0.08	0.01	-0.05	3.2	-5.3	

TABLE XV

#### METALLIC CONTAMINANTS IN VEGETABLES. 1984 GARDEN PLOT: POTATOES

	C	Cadmium mg		Lead kg of fresh edible tissu		inc	
Sub-p	olot Mear	Range	Mean	Range	Mean	Range	
1	0.04	0.04-0.05	0.07	0.07-0.08	4.2	4.1-4.3	
2	0.05	0.04-0.05	0.03	0.03-0.04	3.7	3.6-3.8	
3	0.04	0.04-0.05	0.02	0.02-0.03	3.9	3.9-4.0	
4	0.04	0.03-0.04	0.02	0.02-0.03	3.5	3.4-3.6	
5	0.05	0.04-0.05	0.01	0.01 - 0.02	3.7	3.7-3.8	
6	0.06	0.05-0.06	0.01	0.01 - 0.02	3.9	3.8-3.9	
7	0.05	0.05	0.02	0.01 - 0.02	3.8	3.8-3.9	
8	0.05	0.04-0.05	0.02	0.01 - 0.02	3.6	3.5-3.7	
9	0.05	0.04-0.05	0.01	0.01 - 0.02	4.1	4.0-4.2	
Mean		0.05		0.02	3	3.8	
Std de	ev.	<0.01		0.02	0	0.2	
Rang	e 0.	03-0.06	0.0	1-0.08	3.4	-4.3	

TABLE XVI

#### METALLIC CONTAMINANTS IN VEGETABLES. 1982 GARDEN PLOT: BEETROOT

	Cad		nium Lead		Zinc		
Sub-plot	Mean	Range	Mean	Range	Mean	Range	
1	0.18	0.16-0.19	0.04	0.03-0.05	17.7	17.4-18.1	
2	0.22	0.18 - 0.24	0.03	0.03	21.7	16.3-25.8	
3	0.20	0.19 - 0.22	0.04	0.04	18.7	18.1-19.7	
4	0.19	0.17 - 0.20	0.04	0.03-0.04	20.4	20.1-21.6	
5	0.24	0.22 - 0.25	0.05	0.04-0.06	23.8	22.3-24.8	
6	0.20	0.19 - 0.22	0.05	0.04-0.06	18.6	15.8-25.2	
7	0.18	0.18	0.05	0.04-0.06	20.4	19.9-20.7	
8	0.18	0.17 - 0.20	0.04	0.04-0.05	22.9	20.3-24.7	
9	0.22	0.20-0.23	0.06	0.05 - 0.07	21.9	20.4-22.9	
Mean	0	.20		0.04	2	0.7	
Std dev.	0	.02	<	0.01	_	2.0	
Range	0.16	6-0.25	0.03	-0.07	15.8	-25.8	

	Cadmium		L mg/kg fi	Lead me/ke fresh weight		Zinc	
Sub-plot	Mean	Range	Mean	Range	Mean	Range	
1	0.56	0.54-0.58	0-04	0-03-0-05	17-4	17.1-17.9	
2	0.77	0.75-0.77	0.05	0-05	23.7	22.6-24.6	
3	0.48	0.46-0.50	0.04	0-03-0-05	15-6	14.9-16.1	
4	0.45	0.44-0.46	0.03	0.03-0.04	13.7	13-6-13-9	
5	0.41	0.38-0.43	0.04	0.03-0.04	13-1	12.2-14.5	
6	0.68	0.67-0.68	0.07	0.06-0.08	22.1	21-2-23-0	
7	0.56	0.56-0.57	0.04	0.04	17.8	17-4-18-2	
8	0.60	0.57-0.62	0.05	0.04-0.08	18.8	18-2-19-1	
9	0.67	0.65-0.69	0.05	0.04-0.05	21.0	20.3-22.2	
Overall mean	(	).58	0	0.05	1	8.1	
Std dev.	0	)•11	0	0.01		3.5	
Range	0.38	8-0.77	0.03	3-0.08	12.2	2-24.6	

## TABLE XVII

METALLIC CONTAMINANTS IN VEGETABLES. 1982. GARDEN PLOT: WEBBS LETTUCE

## TABLE XVIII

## METALLIC CONTAMINANTS IN VEGETABLES. 1983. GARDEN PLOT: CABBAGE

	Cac	Cadmium		Lead		inc	
Sub-plot	Mean	Range	Mean	Range	Mean	Range	
1	0.05	0.04-0.06	0.04	0.03-0.04	7.7	7.4-8.0	
2	0.04	0.04	0.01	0.01-0.02	8.6	8.0-9.1	
3	0.04	0.04-0.05	<0.01	<0.01	9.0	8.5-9.2	
4	0.06	0.05-0.06	0.04	0.04-0.05	8.5	8.1-9.0	
5	0.04	0.04-0.05	0.03	0.03	8.7	8.4-9.1	
6	0.06	0.06	0.02	0.02	8.7	8.5-9.0	
7	0.11	0.09 - 0.12	<0.01	< 0.01	8.4	8.1-8.9	
8	0.04	0.04-0.05	<0.01	<0.01	7.9	7.5-8.3	
9	0.05	0.04-0.05	<0.01	<0.01	7.8	7.7-7.9	
Mean	(	).05	0	.02	8	3-4	
Std dev.	(	0.02	0	.02	C	)•4	
Range	0.04	4-0.12	<0.0	010.05	7.4	-9.2	

#### TABLE XIX

Sample Lead Zinc Cadmium mg/kg fresh weight Mean of duplicate digestions 1 3.1 0.04 0.10 23 0.11 2.2 0.05 0.05 0.102.50.03 0.102.5 4 5 6 2.8 0.080.090.05 0.132.6 7 0.03 2.8 0.068 0.04 0.03 2.5 9 0.09 < 0.013.1 10 0.020.012.5 11 0.040.111.9 0.070.06 $2 \cdot 1$ 12 0.04 13 0.073.3 14 0.02 0.09  $2 \cdot 1$ 15 0.03 0.022.6 16 0.020.11 $2 \cdot 1$ 0.02 0.09 17 2.5 18 0.03 0.013.0 19 0.02<0.012.3 Mean 0.04 0.07 2.6

# METALLIC CONTAMINANTS IN RETAIL VEGETABLES: POTATOES FROM GROWERS IN LEICESTERSHIRE

TABLE XX

#### METALLIC CONTAMINANTS IN RETAIL VEGETABLES: LETTUCE SUBMITTED TO L.C.C. FROM GROWERS IN LEICESTERSHIRE

Sample	Cadmium	Lead	Zinc	
	mg	g/kg fresh weig	ıt	_
1	<0.05	<0.1	6.1	
2	<0.05	< 0.1	4.2	
3	<0.05	< 0.1	3.5	
4	<0.05	< 0.1	6.0	
5	<0.05	<0.0	2.1	
6	<0.05	0.1	3.3	
7	<0.05	<0.1	3.9	
8	<0.05	< 0.1	2.6	
9	<0.05	0.1	4.1	
Mean	<0.05	<0.1	4.0	

## TABLE XXI

## METALLIC CONTAMINANTS IN RETAIL VEGETABLES: LETTUCES—SUMMER 1985 (a) Soft leaf varieties

San	nple	Cadmium	Lead g/kg fresh weig	Zinc	
	1	0.1	<0-1	2.9	
	2	<0.05	<0-1	2-4	
	3	<0.05	0-3	8-1	
	4	<0.05	<0.1	6-3	
	5	<0.05	<0.1	2.5	
	6	<0.05	<0.1	2.7	
	7	<0.05	< 0.1	3.5	
1	8	<0.05	< 0.1	2.3	
Mean		<0.05	<0.1	3.8	

## (b) Webb's type

Sample	Cadmium	Lead	Zinc						
mg/kg fresh weight									
1	<0.05	<0.1	1.9						
2	<0.05	0.2	4.5						
3	<0.05	< 0.1	2.4						
4	<0.05	< 0.1	0.8						
5	< 0.05	< 0.1	2.3						
6	< 0.05	< 0.1	1.5						
7	<0.05	< 0.1	5.0						
8	<0.05	< 0.1	0.8						
9	<0.05	< 0.1	1.5						
Mean	<0.05	< 0.1	2.3						

## TABLE XXII

## METALLIC CONTAMINANTS IN LEICESTERSHIRE RETAIL VEGETABLES: BEETROOT

Sample	Cadmium mg/kg fresh ea	Lead dible weight	Zinc	
1	<0.05	<0.1	3.3	
2	<0.05	< 0.1	6.7	
3	<0.05	< 0.1	3.2	
4	<0.05	< 0.1	4.1	
5	<0.05	< 0.1	4.8	
6	<0.05	< 0.1	2.5	
7	<0.05	< 0.1	16.0	
8	<0.05	< 0.1	4.3	
9	<0.05	< 0.1	2.5	
Mean	<0.05	< 0.1	4.7	

TABLE 2	XXIII
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METALLIC CONTAMINANTS IN LEICESTERSHIRE RETAIL VEGETABLES: PARSNIPS

Sample	Cadmium	Lead	Zinc	
	mgrkgjresne	uible ussue		
1	<0.05	<0.1	3.6	
2	<0.05	< 0.1	1.9	
3	<0.05	< 0.1	3.9	
4	<0.05	<0.1	2.4	
5	<0.05	<0.1	2.2	
6	<0.05	<0.1	3.5	
7	<0.05	<0.1	2.4	
8	<0.05	< 0.1	3.0	
9	< 0.05	< 0.1	2.6	
Mean	<0.05	< 0.1	2.8	

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## **Book Reviews**

POISON DETECTION IN HUMAN ORGANS: FOURTH EDITION. By A. S. CURRY. Springfield: Charles C. Thomas. 1988. Price \$54.50. 335 pp. ISBN 0398 05425 8

It is necessary at the outset for the reviewer to declare an interest. When the first edition of this book appeared in 1963 I was engaged in practical analytical toxicology at the bench and welcomed a manual which was so clearly based on the practical experience of an innovative scientist. In the succeeding years we became close colleagues and friends and the book moved progressively through further editions in 1969 and 1976. In that period both the author and reviewer moved further away from the bench but were fortunate to retain close contact with practising toxicologists both within our employing organisation and outside, particularly through the International Association of Forensic Toxicologists (TIAFT) of which Alan Curry was a founder member and President. This latest edition has built solidly on the earlier editions and provides an up to date text on the investigation of poisoning.

The theme of the work is that only by systematic analysis will the unexpected toxic agent be detected when investigating an undiagnosed illness (Part 1) or a sudden or unexplained death (Part 2). Thus, anyone asked to look for a specific poison can refer to Part 3 for the appropriate method but if the results are negative or if the investigation is for legal purposes a broader spectrum approach is required. The value of this book is that it can be read and studied to develop a sound knowledge of analytical toxicology, and students and practitioners alike will appreciate the gems of practical experience scattered through it. At the risk of being declared old-fashioned the author has retained some of the older and traditional techniques since he recognises that resources are limited and geographical distances large in many countries of the world. In any case disruption of electrical and gas supplies are not unknown in the developed countries. The author shares with the late Professor George Clarke and many others the view that much effective toxicological screening can be carried out without modern instruments and for that reason alone I would commend the book to our third-world colleagues. The book is well referenced including recent journals, proceedings and review articles. This means, to borrow a current advertising slogan, that if Curry cannot help you he knows a man (or woman) who can!

The appearance of a fourth edition is thoroughly justified and deserves a place at the laboratory bench and in personal and corporate libraries.

P. G. W. COBB

HAIR ANALYSIS: APPLICATIONS IN THE BIOMEDICAL AND ENVIRONMENTAL SCIENCES. By A. CHATT and S. A. KATZ. VCH: Weinheim. 1988. Price DM 74 (£25). 134 pp. with 5 figures and 33 tables.

This book provides a comprehensive review of the use of hair trace element levels as indicators of nutritional status, disease, heavy-metal poisoning and environmental exposure. After discussing theories explaining the biological incorporation of trace elements into the hair and the external factors possibly affecting this, the extent to which they have been used as indicators is reviewed in depth. Protocols for the collection and preparation of hair samples are presented followed by details of the methods of analysis which have been used. As is usual with analytical works today, there is a chapter on quality assurance. With over 500 references to original and review sources anyone entering into this field would appear to be well served.

After reading the book one cannot be other than impressed by the efforts of workers in this area in tackling a difficult analytical and interpretive problem. Certainly much misplaced effort in the forensic science field would have been avoided if the protagonists of the use of neutron activation analysis for the individualisation of human hair had been as systematic. However, this reviewer is not persuaded by the authors that the efforts required in hair analysis for most of the purposes discussed are likely to be cost effective however elegant the techniques. In an area of demonstrated value, the investigation of chronic arsenical poisoning, the forensic science literature seems to have been ignored totally. Since the problems discussed in the book have been very thoroughly investigated and reported, anyone called upon to assist in a case of this type is strongly advised to refer to that source.

I commend the book as a useful addition to the analytical literature but would not expect the number of users of this diagnostic method to increase significantly.

P. G. W. COBB