# FINAL REPORT

# An investigation by laser ablation and inductively coupled mass spectrometry of the gradation and levels of metal contaminants in UK grown fruits, vegetables and cereals – 2012/13
# FS 102002

## 22nd January 2014


## David J. Bellis, Andrew A. Meharg, Eva M. Krupp and Jörg Feldman

## University of Aberdeen


*This report has been produced by **[University of Aberdeen]** under a contract placed by the Food Standards Agency (the Agency). The views expressed herein are not necessarily those of the Agency. **[University of Aberdeen]** warrants that all reasonable skill and care has been used in preparing this report. Notwithstanding this warranty, [**University of Aberdeen**] shall not be under any liability for loss of profit, business, revenues or any special indirect or consequential damage of any nature whatsoever or loss of anticipated saving or for any increased costs sustained by the client or his or her servants or agents arising in any way whether directly or indirectly as a result of reliance on this report or of any error or defect in this report.*

**Contents**

**Summary**

A field study of UK grown fruits, vegetables, and cereals was conducted in October-November 2012 and August-September 2012. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis indicated elevated amounts of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb and U in the skin of vegetables and fruit compared with the flesh. The data indicated that these elements were accumulated in less than 0.5 mm thickness from the skin surface. The relative concentration of elements at different points on skin of vegetables and fruits varied, by up to one order of magnitude, indicating a heterogeneous distribution. In cereals Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb and U were elevated in bran and germ compared to the endosperm.

Element concentrations in vegetable and fruit determined by ICP-MS after acid digestion were higher in peel fraction (skin approx. 1 mm thickness) compared to the remaining flesh. The range in peel (and mean in parenthesis) was 3.2 to 290 (100) μg $kg^{-1}$ V, 4.4 to 390 (90) μg $kg^{-1}$ Cr, 22 to 1200 (230) μg $kg^{-1}$ Ni, 330 to 6000 (2800) μg $kg^{-1}$ Cu, 800 to 22,000 (8000) μg $kg^{-1}$ Zn, 1.7 to 170 (30) μg $kg^{-1}$ As, 3.0 to 400 (50) μg $kg^{-1}$ Cd, 1.2 to 50 (7.8) μg $kg^{-1}$ Hg, 6.1 to 890 (86) μg $kg^{-1}$ Pb and 1.1 to 30 (7.3) μg $kg^{-1}$ U. The range in flesh (and mean in parenthesis) was 1.2 to 43 (6.7) μg $kg^{-1}$ V, 1.1 to 87 (14) μg $kg^{-1}$ Cr, 4.2 to 750 (124) μg $kg^{-1}$ Ni, 340 to 3700 (15,000) μg $kg^{-1}$ Cu, 130 to 15,000 (5400) μg $kg^{-1}$ Zn, 1.0 to 60 (6.6) μg $kg^{-1}$ As, 1.0 to 240 (26) μg $kg^{-1}$ Cd, 1.6 to 22 (6.5) μg $kg^{-1}$ Hg, 1.0 to 260 (25) μg $kg^{-1}$ Pb and 1.1 to 21 (5.6) μg $kg^{-1}$ U. Elevated concentration of Cadmium and Lead approaching or exceeding Maximum (permissible) Levels established by the European Community were observed in potatoes collected in Derbyshire and Wales. The range in whole cereal grains (and mean in parenthesis) was 15 to 33 (6.7) μg $kg^{-1}$ V, 18 to 65 (14) μg $kg^{-1}$ Cr, 38 to 820 (124) μg $kg^{-1}$ Ni, 3100 to 7400 (15,000) μg $kg^{-1}$ Cu, 17,000 to 42,000 (5400) μg $kg^{-1}$ Zn, 6.2 to 17 (6.6) μg $kg^{-1}$ As, 25 to 130 (26) μg $kg^{-1}$ Cd, 1.6 to 21 (6.5) μg $kg^{-1}$ Hg, 2.3 to 47 (25) μg $kg^{-1}$ Pb and 9.5 to 27 (5.6) μg $kg^{-1}$ U.

## 1. Background

During growth, fruit, vegetables and cereals take up metal contaminants from the surrounding soil area. Arsenic, cadmium, lead and mercury have no known beneficial health effects, while trace amounts of other metals such as chromium, copper, iron, aluminium, manganese and zinc can act as nutrients and are essential for health. However, all of these may be harmful if excessive amounts are consumed.

The European Food Safety Authority (EFSA) has previously concluded that dietary exposure to inorganic arsenic, cadmium, lead and mercury should be reduced. In addition, the Joint Food and Agriculture Organization (FAO) and the World Health Organization (WHO) Expert Committee on Food Additives (JECFA) agree that it is not possible to set a tolerable lead intake. Therefore, it is of benefit to minimise the exposure to lead from all sources.

European Commission Regulation (EC) No. 1881/2006 (as amended) has established maximum levels (MLs) for contaminants in various foodstuffs (Table 1.1).

.

Table 1.1. Maximum Levels for metals (mg/kg wet weight) as defined in European Commission Regulation (EC) No 1881/2006 (amended).

| Foodstuffs | | Maximum levels (mg/kg wet weight) |
|---|---|---|
| 3.1 | **Lead** | |
| 3.1.9 | Cereals, legumes and pulses | 0.20 |
| 3.1.10 | Vegetables, excluding brassica vegetables, leaf vegetables, fresh herbs and funghi, for potatoes the maximum level applies to peeled potatoes | 0.10 |
| 3.1.11 | Brassica vegetables, leaf vegetables and the following funghi: *Agaricus bisporus* (common mushroom) *Pleuortus ostreatus* (oyster mushroom), *Lentinula edodes* (Shiitake mushroom) | 0.30 |
| 3.1.12 | Fruit excluding berries and small fruit | 0.10 |
| 3.1.13 | Berries and small fruit | 0.20 |
| | | |
| 3.2 | **Cadmium** | |
| 3.2.12 | Cereals excluding bran, germ, wheat and rice | 0.10 |
| 3.2.14 | Bran, germ, wheat and rice | 0.20 |
| 3.2.15 | Vegetables and fruit, excluding leaf vegetables, fresh herbs, fungi, stem vegetables, root vegetables and potatoes | 0.050 |
| 3.2.16 | Stem vegetables, root vegetables and potatoes, excluding celeriac. For potatoes the maximum level applies to peeled potatoes. | 0.10 |
| 3.2.17 | Leaf vegetables, fresh herbs, celeriac and the following funghi: *Agaricus bisporus* (common mushroom) *Pleuortus ostreatus* (oyster mushroom), *Lentinula edodes* (Shiitake mushroom) | 0.20 |

Norton et al. (2012, 2013)[1-3], published studies on arsenic cadmium, copper, lead and zinc in fruit and vegetables grown in the UK. Sampling areas selected during these previous studies contained elevated levels of these metals either naturally from rocks and sediments or as a result of anthropogenic activities such as mining. A comparison was conducted between unpeeled and peeled fruits and vegetables to establish the levels of metals present. For apples, beetroots, courgettes, cucumbers, parsnips, and squashes there was no significant difference between unpeeled and peeled produce. For carrots, potatoes, and swedes there was more arsenic in the unpeeled produce compared to peeled produce. Potatoes and swedes had lower cadmium concentrations in the peeled produce compared to the unpeeled produce, whilst both potatoes and swedes had a higher concentration of lead in unpeeled produce compared to peeled produce. Carrots and swedes had lower copper in the peeled produce compared to the unpeeled produce. This data was supported by a limited studying using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The aim of this project was to conduct more extensive LA-ICP-MS measurements of selected fruits, vegetables and to include cereals such as wheat and barley to establish the distribution of metal contaminants such as arsenic, cadmium, lead, copper and zinc within these crops and carry out quantitative analyses to determine the levels of metals present.

## 2. Field study of fruits, vegetables, and cereals

Selection of sampling locations

The field study was designed to collect produce including fruits, vegetable and cereal grains from different counties located in England, Wales and Scotland, and 2 counties in Northern Ireland. Figure 2.1 highlights the counties in orange where previous sampling already took place in a pilot study (Cornwall, Devon and Aberdeenshire). Counties for the proposed sampling included Kent, Gloucestershire, and Swansea in the south of England and Wales respectively; Suffolk, Norfolk, Lincolnshire, Nottinghamshire, Derbyshire in east and central England; Lancashire and Yorkshire in north west and north east England and finally Perth/Kinross in east Scotland. In Northern Ireland, County Down and Armagh were targeted The choice of sampling areas followed trace elemental hot spots within the British Isles including arsenic, cadmium and lead; different climate regions but also soil type and agricultural (horticulture + cereal crops) producing areas.
The choice of sampling locations for this study also accounted for differences in regional climates and soil types. Due to the position of the UK in the mid-latitude westerly wind belt on the edge of the Atlantic Ocean with its warm waters, but also closeness to the continental influences of mainland Europe, different regional climate sections can be distinguished (Figure 2.1b; 1 -8). Generally it can be found that places in the east and south of the UK tend to be drier, warmer, sunnier and less windy in comparison to those further west and north (Met Office: http://www.metoffice.gov.uk/climate/uk/regional/). As a consequence of differing climates, differences in soils are also given (Soil Atlas of Europe, 2005). Soil and climate conditions determine the type of agriculture.

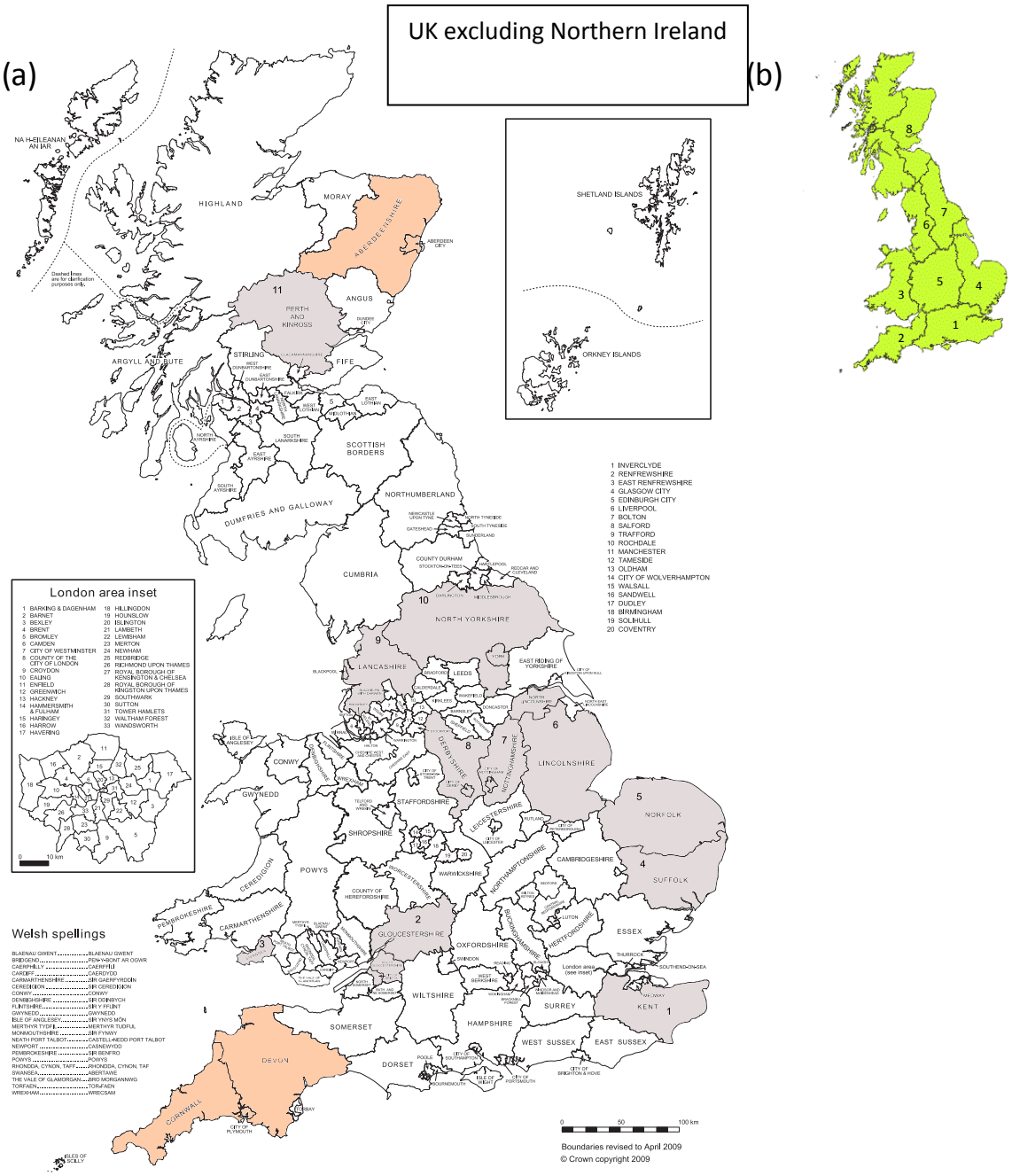


Figure 2.1 Coastline of Great Britain and administrative boundaries reproduced from Ordnance Survey map data by permission of Ordnance Survey © Crown copyright 2013. Areas which have been previously sampled within a pilot study for the Food Standard Agency are highlighted in orange. Proposed sampling areas are highlighted in grey and labelled 1 -11. b) 8 regional climate regions of GB where sampling is proposed to be undertaken: 1. Southern England; 2. South West England; 3. Wales; 4. Eastern England; 5. Midlands; 6. North Western England + Isle of Man; 7. North East England; 8. Eastern Scotland. © Crown copyright 2010.

Figure 2.2 illustrates major vegetable and cereal crop producing areas within the UK. The main produce can be found in east England including cereal crops (wheat, barley, sugar beet), potatoes, turnips and carrots (UK Agriculture; http://www.ukagriculture.com/crops/). In Scotland, the main cereal crops are wheat and barley, which are mostly located to the east of the country in places such Grampian, Scottish Borders, Lothian but also East Central and

Fife. Horticulture (fruit and vegetables) are only small holdings in comparison to cereal crop production. However, these holdings are dispersed around the lowland areas, whereas mixed farming areas tend to be concentrated in the north east of Scotland (The Scottish Government; http://www.scotland.gov.uk/Publications/2011/06/15143401/56). Figure 2.2 shows the major vegetable and cereal producing regions of the UK.

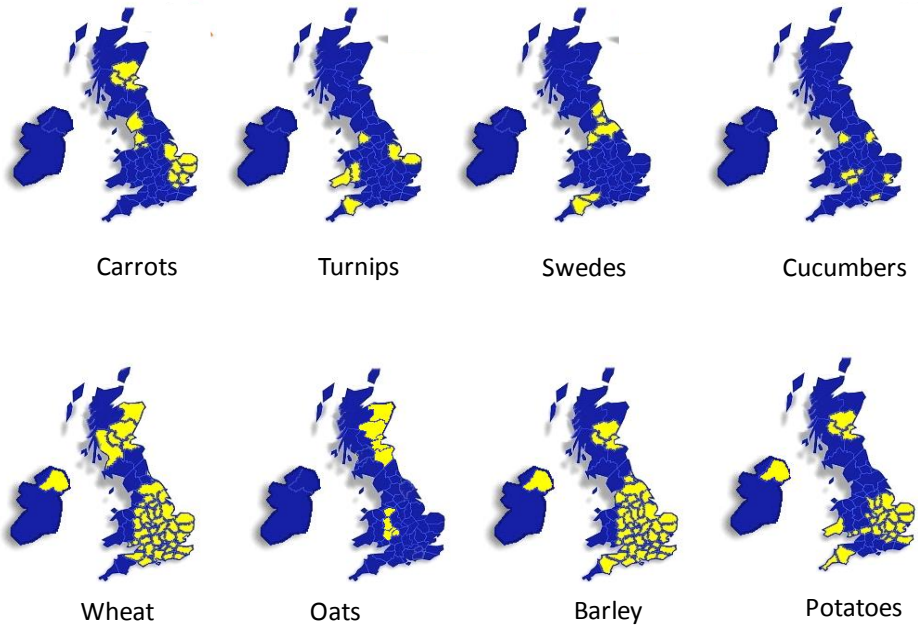


Figure 2.2 Major vegetable and cereal crop producing regions in the UK (source UK Agriculture;http://www.ukagriculture.com/crops/crops_regions_vegetable.cfm%20and%20http://www.ukagriculture.com/crops/crops_regions_arable.cfm)

Field studies were conducted in October to November 2012 (the start date of project being 1st October 2012) and August to September 2013. The late start date in 2012 restricted the proposed sampling plan as little produce remained in the fields. Only Suffolk potato, parsnip and carrot, Lincolnshire Beet, and Welsh carrot and parsnip were located *in situ*. As an alternative produce was obtained from farm shops, and a sample of soil was taken from the field(s) where the produce was sourced from. Also due to the late start mostly root vegetables were collected during this phase. In August to September 2013 mostly fruits and cereals were collected from the field/orchard of growth. Root vegetables were also obtained in Northern Ireland from both farm shops and directly from fields.

In October 2012 root vegetables including various varieties of potatoes (*Solanum tuberosum*), carrots (*Daucus carota subsp. Sativus*), beetroot (*B. vulgaris L. subsp. Conditiva*), turnips (*Brassica rapa subsp. Rapa*), swedes (Brassica napus subsp. Rapifera) and parsnips (Pastinaca sativa) were collected from locations in Kent, Suffolk, Lincolnshire, Leicestershire, Yorkshire, South Wales, Gloucestershire, Lancashire and Perth and Kinross. In September 2013 various varieties of apples (*Malus domestica*) and pears (*Pyrus Rosaceae*) were collected from Kent, Suffolk and Northern Ireland. Cereal crops included wheat (*Triticum spp*.), barley (*Hordeum vulgare L.*) and oats (*Avena sativa*). Root vegetables were also collected in 2013 from Northern Ireland.

Exact sample locations were recorded but are not presented here to ensure anonymity of the suppliers. Samples were selected on the basis of availability and were either taken directly from the growing field or from a shop/supplier where the field of growth could be reliably determined. Five individual specimens of each were obtained from each location (where available). A soil sample thought to be representative of the field of growth was also obtained.

After collection, crop and soil samples were temporarily stored in a cold room at 5°C until they were prepared for longer-term storage. The more perishable samples were prepared first. Vegetable and fruit samples were washed to remove soil or adhered particles using tap water as may normally be performed prior to preparation. A commercially available ceramic knife and peeler were used for the preparation of vegetables and fruits into three sub-samples. Firstly a slice through the flesh and skin of the vegetable or fruit was made and immediately flash frozen using liquid nitrogen. The remainder of the vegetable was peeled to separate 'peel' and 'flesh' sub-samples, each of which was homogenised and subsequently (flash) frozen. Samples were stored in a -20°C freezer prior to analysis.

## 3. Laser ablation ICP-MS analysis of spatial distribution

### 3.1 Introduction

Laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS) is an established analytical method employed for measuring amounts (or isotope ratios) of elements in solid sample with a spatial distribution in the micrometer range.[4] Briefly, a sample with a flat surface is presented to a focussed laser beam which, upon firing, ablates or removes a small amount of material from the surface of the sample in the form of a small cloud of particles. An argon gas flow (typically 1.5 L $min^{-1}$) is used to transport to the ICP-MS. Here, the particles are atomised and ionised by the high temperatures within the argon based ICP. The resulting ions are focussed by the mass spectrometer allowing electronic detection of the isotopes of individual elements. The intensity of the measured signal is usually assumed to be proportional to the concentration of the element in the sample.

LA systems mount the sample on a controllable XYZ stage allowing the position of the sample to be changed with respect to the fixed laser beam. As a result LA-ICP-MS is commonly used to observed relative changes in the concentration of elements across a sample. Typically this is achieved by moving a sample at a constant rate, for example 50 µm $s^{-1}$, in a straight line along a sample. The resulting element signal measured by ICP-MS is against time, taking measurements about every second for example. This data is usually displayed as a XY plot where the X axis is time or calculated distance and the Y axis element intensity showing spatial variation of the element in one-dimension (1-D). A development of this procedure is to scan multiple lines in sequence over a rectangular area. The multiple lines can be plotted on an XYZ contour plot where X and Y are distance (coordinates) and Z the intensity shown as contour lines, colour or colour intensity. This approach has been widely applied to soft biological samples, as first demonstrated by Feldmann et al. (2002)[5], and is now typically referred to as "Bioimaging" or Mass Spectrometry imaging (MSI).[6,7]

LA-ICP-MS has been applied to various plant materials including the annual rings of trees,[8] bark and bark pockets,[9,10] and leaves.[11,12] Apart from the publications of Norton et al. (2012, 2013)[4-6] described above, there are relatively few examples of LA-ICP-MS being applied to food crops and those are limited to rice[13,14] and wheat[15-16] grains. Rice and wheat grains were prepared by simple slicing sectioning. Vegetable and fruit samples including potato, carrot, beetroot, parsnip and apple were prepared as described below.[1-3] "All the produce was thoroughly washed with tap water, as per typical food preparation. Samples were then diced (~1 $cm^3$) and 3 skin containing dice samples were randomly chosen per item. The cubes were then flash frozen using liquid nitrogen (-192°C) and stored frozen at -20°C until sectioning. Sections were prepared from each batch at -15°C using a cryostat (Model OTF including microtome 5030, Bright). A cube from each batch was chosen for sectioning; the cube was mounted on a sample holder and fixed on it using Tissue-Tek O.C.T. paste (Sakura Finetek Europe). The microtome used prepared thin-sections of up to 35µm depth. The slices were thaw-mounted onto microscope slides and allowed to air-dry at room temperature, and subsequently, stored frozen at -20°C until the day of analysis."

3.2 Sample preparation and instrumentation for LA-ICP-MS

We were unable to reliably replicate the cryostat-air drying method as described above. Thin sections of 30 µm, being the maximum thickness setting of the cryostat, had no structural integrity and could not be prepared. This was presumably a result of the higher water content of the vegetables and fruit when compared to a biological (animal) soft tissue. The minimum 'wet' sample thickness that could be achieved was about 300 µm, achieved by moving the knife position of the cryostat (A. Mestrot, personal communication). After thaw mounting and drying these 'thicker' sections, visible distortion of the section was observed upon drying. In particular, the skin part of the sample was significantly pronounced compared to the flesh, as the skin section has lower water content than the flesh. Given that the LA-ICP-MS system requires a flat surface to ensure comparable focus across the section this represents a problem. Trial measurements indicated that that skin element intensities were substantially underestimated using this method as will be discussed later.

It was therefore decided to develop a new sample preparation procedure. As described in Section 2, slices of the vegetable or fruit samples through flesh and skin were prepared by hand-cutting with a ceramic knife, flash frozen with liquid nitrogen, and stored at -20°C. On the day of the LA-ICP-MS measurement, the slices were removed from the freezer and placed in a polystyrene box containing ice packs (refrigerant liquid packs) stored in the same freezer. Immediately prior to LA-ICP-MS measurement the slice was removed from this box and sectioned using a hand-held mandoline (sleekslice, Chefn Corporation, Seattle, WA). This procedure was found to reliably produce slices of about 1000 µm thickness (Fig. 3.1). The section was placed onto a cleaned glass microscope slide and allowed to thaw for a few minutes at room temperature (16°C in the LA-ICP-MS laboratory), before placing in the sample chamber of the LA system. Cereal samples (wheat and barley) were stored at room temperature and prepared by hand-cutting with a scalpel. Measurements were started about 4 minutes after placing in the sample cell.

Figure 3.1 Preparation of vegetables and fruit for LA-ICP-MS via mandolin slicing (left) and mounted thin section of Kent Potato (Shetland Black) (right).

The LA system was a New Wave UP213 (ESI, Freemont, CA) equipped with a SuperCell$^{TM}$ low-volume sample cell. An Ar carrier gas flow through the sample cell of 0.3 L min$^{-1}$ and a make-up gas (to ICP) flow of 1.2 L min$^{-1}$ Ar. The ICP-MS system used was an Agilent 7500ce (Agilent Technologies, Wokingham, UK). The instrument was initially optimized under wet plasma (nebulisation) conditions according to the manufacturer's instructions. Further optimisation for dry plasma (LA) conditions was performed using the QC standards described below. LA parameters were optimised on test samples the applied consistently for all subsequent samples. An LA beam diameter (round aperture) of 100 µm diameter was selected, using a scan rate of 50 µm s$^{-1}$, and LA energy fluence of about 0.1 J cm$^{-2}$.

## 3.3 Quality control of LA-ICP-MS measurements

Quality control (QC) of LA-ICP-MS measurements is a problematic area for which there are few well defined procedures. It is critical, however, to ensure comparability of data acquired from multiple samples over multiple analysis days, a required in this project. No commercially available QC samples are available and few methods have been published. One method adapted his 'ink jet printed images' method described previously.[18]

Blue ink used in ink jet printers, which employ the RBY (red-yellow-blue) colour scheme, contains appreciable amounts of Cu. Patterns of blue ink printed on paper can thus be used for control or test samples for LA-ICP-MS.[16] Importantly, the size and intensity of the printed feature can be varied, the latter through adjusting the "transparency" setting. Figure 3.2 shows the pattern developed for this study designed in Microsoft PowerPoint. Four parallel lines of 500 µm thickness spaced at 3.75 mm and printed with 25%, 50%, 75% and 100% colour density (i.e. 75%, 50%, 25%, and 0% transparency setting respectively). Multiple patterns were printed using a HP Deskjet 1000 with a HP 301 CH563E Tricolor ink cartridge.

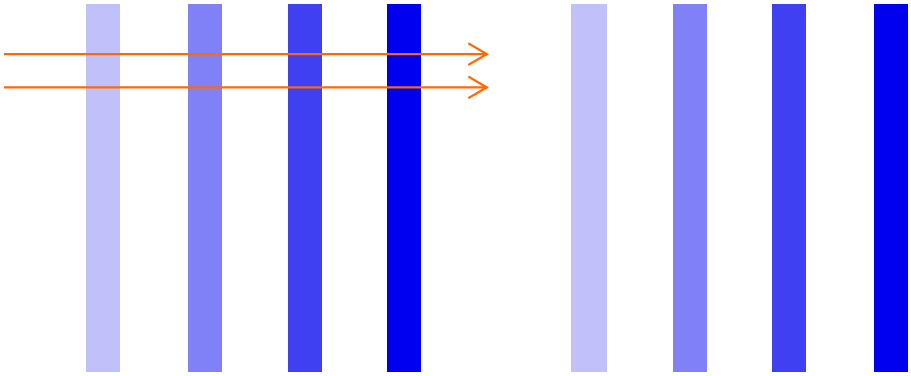

Figure 3.2. Ink jet printed images used for quality control of LA-ICP-MS measurements. Arrows show direction and extent of LA-ICP-MS measurements.

Example results of the use of the ink jet patterns as QC standards are given in Figure 3.3, showing the measured signal for $^{13}C$ and $^{63}Cu$ over time. The initial 30 s and final 60 s of the analysis shows the signal prior to and following firing of the laser. $^{13}C$ shows the amount of paper ablated and is relatively constant whilst $^{63}Cu$ shows the ink line. Given that the scan rate was 50 µm $s^{-1}$, 100 s of analysis time corresponds to 5 mm. Figure 3.3a shows duplicate analysis of the patterns prior to sample analysis and Figure 3.3b duplicate analysis of the patterns following several hours of vegetable sample analysis.

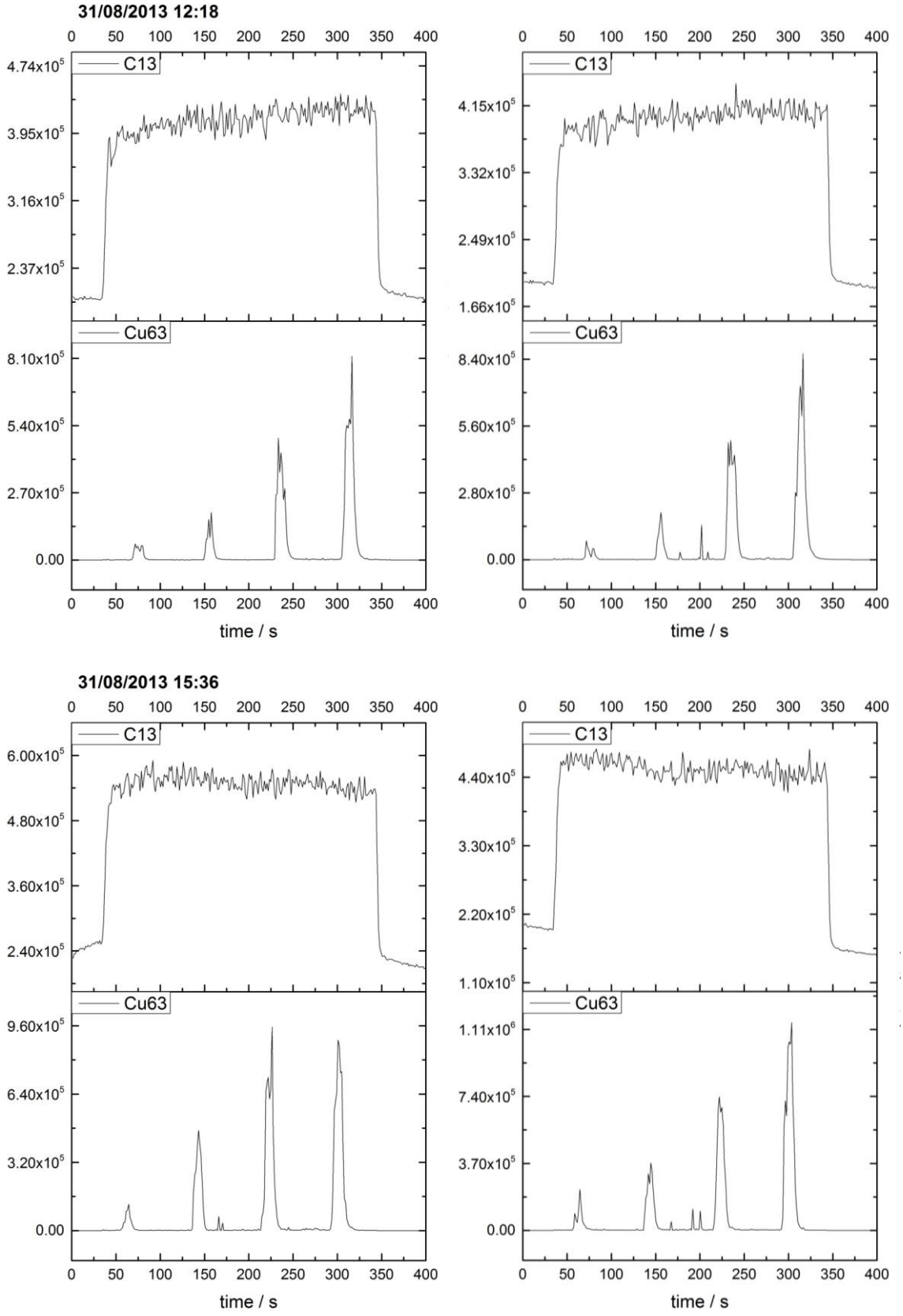


Figure 3.3. LA-ICP-MS analysis of ink jet printed patterns (a) in duplicate from 12.18 on and (b) in duplicate from 15.36 on 31/08/2013. Y axis is intensity in counts.

The plot in Figure 3.4 shows the long term trend in the signals obtained from the QC ink patterns during the course of the sample analysis. There was day-to-day drift in the signal intensities that were observed. Signal intensities were therefore normalized to the average carbon signal prior to calculation of peak parameters. This data indicates that the LA-ICP-MS system was operating in a reproducible fashion over time. Table 3.1 provides summary statistics of the full data set.

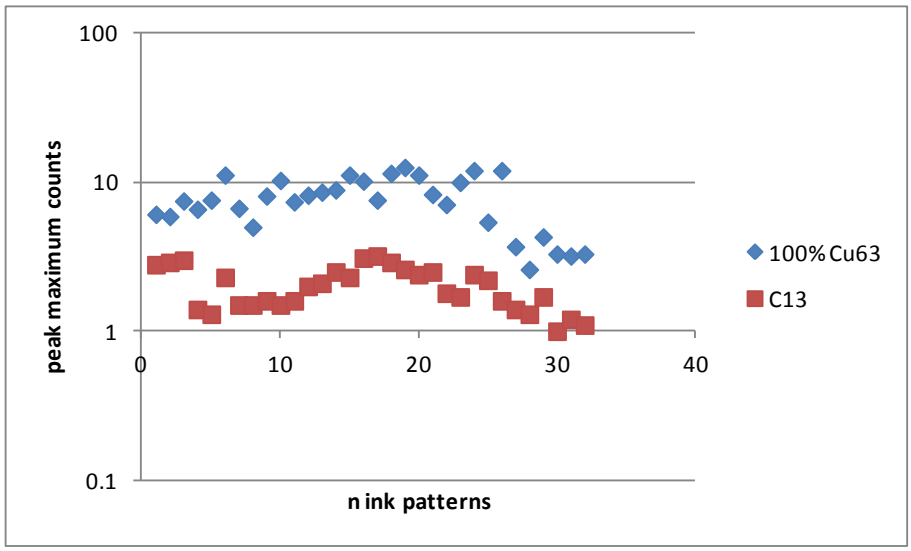


Figure 3.4. Variation in $^{13}C$ (average signal) and $^{63}Cu$ (100% colour peak maximum) in ink jet patterns over time.

The X axis of the line scans, plotted here in seconds, is easily converted into distance by multiplying by the speed (in this case 50 µm $s^{-1}$). The size of the recorded peak, however, is affected by other factors of the LA-ICP-MS system. One factor is the volume of the LA sample cell. In this case we employed a low volume cell with lamina flow to minimise spreading of the peak. The LA produced particles must also be transported to the ICP-MS along a Teflon tube of about 1 m length, where further spreading of the peak can take place, as individual particles may be transported at different speed due their size or due to collisions with the tubing wall or each other. As the approximate width of the ink jet patterns is known (500 µm), we can examine this effect. Table 3.1 gives the FWHM (Full Width Half Maximum) of the Cu peaks. The lines with lower colour density show lower FWHM, most likely because less ink is printed (dots and gaps). It can be seen that the FWHM is a good approximation of the actual feature width, but about 90% narrower. If the width at the base of the peak was used it would be substantially wider than the feature width, and FWHM was more easily obtained from the OriginLab software used for the data analysis. As a result, measured FWHM was multiplied by a factor of 1.1 to provide an approximation of the true feature width.

Table 3.1. Summary statistics of Variation in $^{13}C$ (average signal) and $^{63}Cu$ (all peak maximums) in ink jet patterns over time.

| | 25% Cu | 50% Cu | 75% Cu | 100% Cu | C |
|---|---|---|---|---|---|
| mean counts x$10^5$ | 1.5 | 3.5 | 6.4 | 7.7 | 2.0 |
| SD counts x$10^5$ | 0.7 | 1.4 | 2.8 | 2.9 | 0.6 |
| | | | | | |
| mean FWHM mm | 0.28 | 0.40 | 0.45 | 0.46 | - |
| SD FWHM mm | 0.13 | 0.06 | 0.07 | 0.07 | - |

3.4 LA-ICP-MS analysis of vegetables

Figures 3.5 to 3.11 provide examples of LA-ICP-MS line scans of each vegetable and fruit type that were analysed. The full data set of all samples analysed is provided in Appendix i a. The initial 30 s and last 60 s of the plots shows the signal recorded prior to firing the laser and after the laser was shut off, respectively. The laser was directed to start in the flesh of the section and move towards and through the outer skin. This progression is well observed by the carbon signal. The increase in the carbon signal from the background shows the vegetable or fruit flesh is being ablated. The skin of the vegetable or fruit shows an increase in carbon signal. This would be expected as skin has lower water content and thus higher carbon content than flesh.

We observed distinct peaks of the other elements, including the heavy metals, coinciding with the carbon peak indicating the skin. This was observed in all of the measured sections. In contrast, there were low levels of elements recorded in the flesh. These data were analysed using OriginLab software to calculate peak height, FWHM, and average flesh signal, as summarized in Table 3.2 and provided in full in Appendix i b. Whilst duplicate analyses were normally comparable, there was a high level of variability in the magnitude of the peak heights, which did not show systematic change with location. Much of this variability can be attributed to the very small amount of skin sampled by the 100 µm diameter laser beam, meaning that the peak height may not be representative of the sample as a whole. This variability is also observed in the calculated skin/flesh ratio. The accuracy of the ratio measurement will also be affected by the typically low intensities recorded in the flesh. It is clear, however, that the height of the carbon peak was relatively much lower than the heights of the other element peaks. This shows that the elevation of elements in the skin cannot be an artefact of increased ablation of the skin compared to the flesh.

In contrast to the peak heights the calculated FWHM and thus calculated thickness of the skin was much more consistent. The average skin width indicated by the carbon peak was 0.47 mm (and thus very similar to the ink patterns). The average thickness of the other element peaks was lower than this value apart from Hg which was equivalent. This could indicate that elements are contained within the skin and do not pass through, though as carbon and Hg are more volatile elements following laser ablation they can suffer more peak spreading. Figures 3.12 and 3.13 provides a comparison of the respective skin/flesh ratio and skin width (FWHM x 1.1 referred to hereafter as FWHM*) for C and Pb.

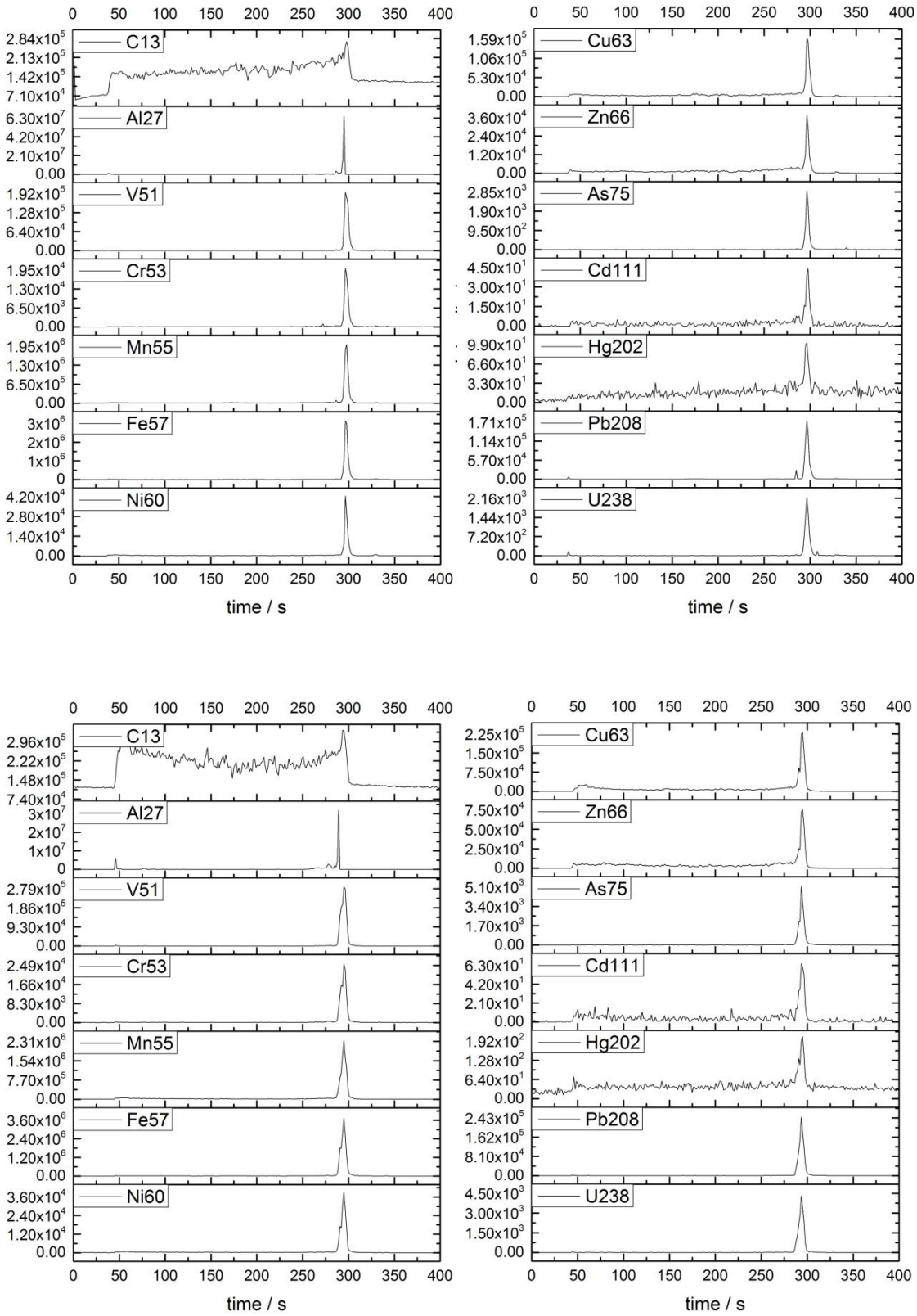


Figure 3.5 LA-ICP-MS analysis of Lancashire Carrot in duplicate (#4)

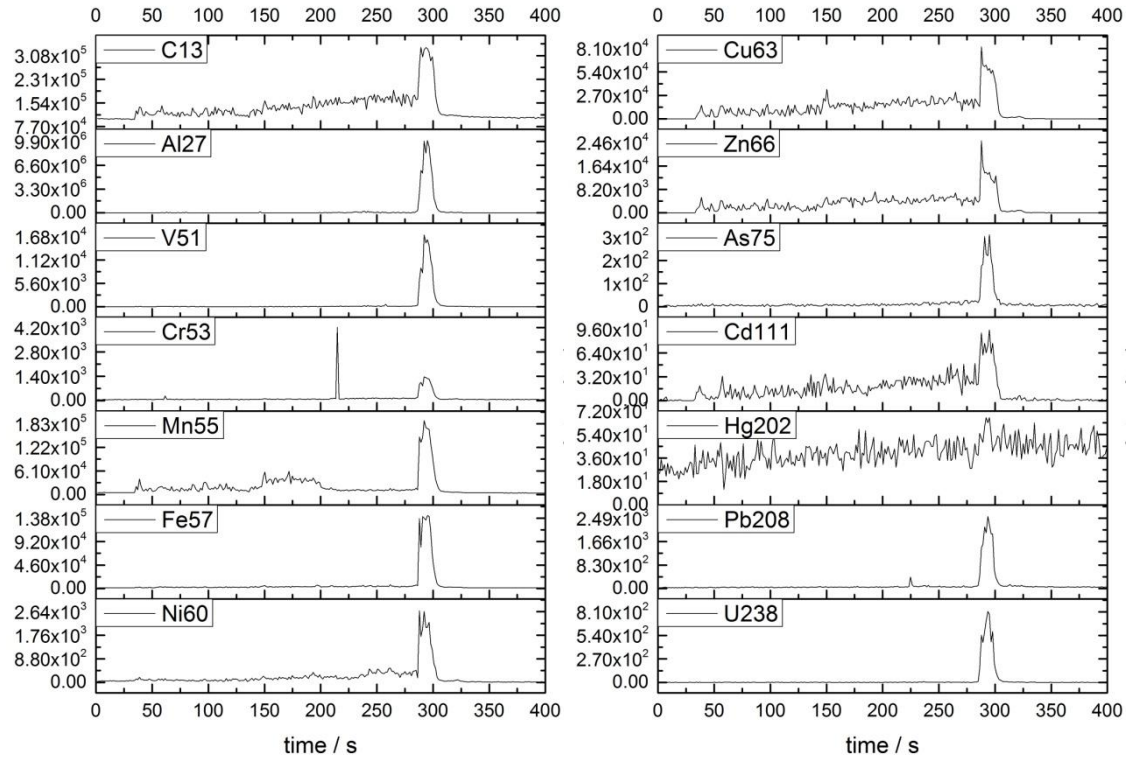


Figure 3.6. LA-ICP-MS analysis of Kent Potato (Estima #5 (2))

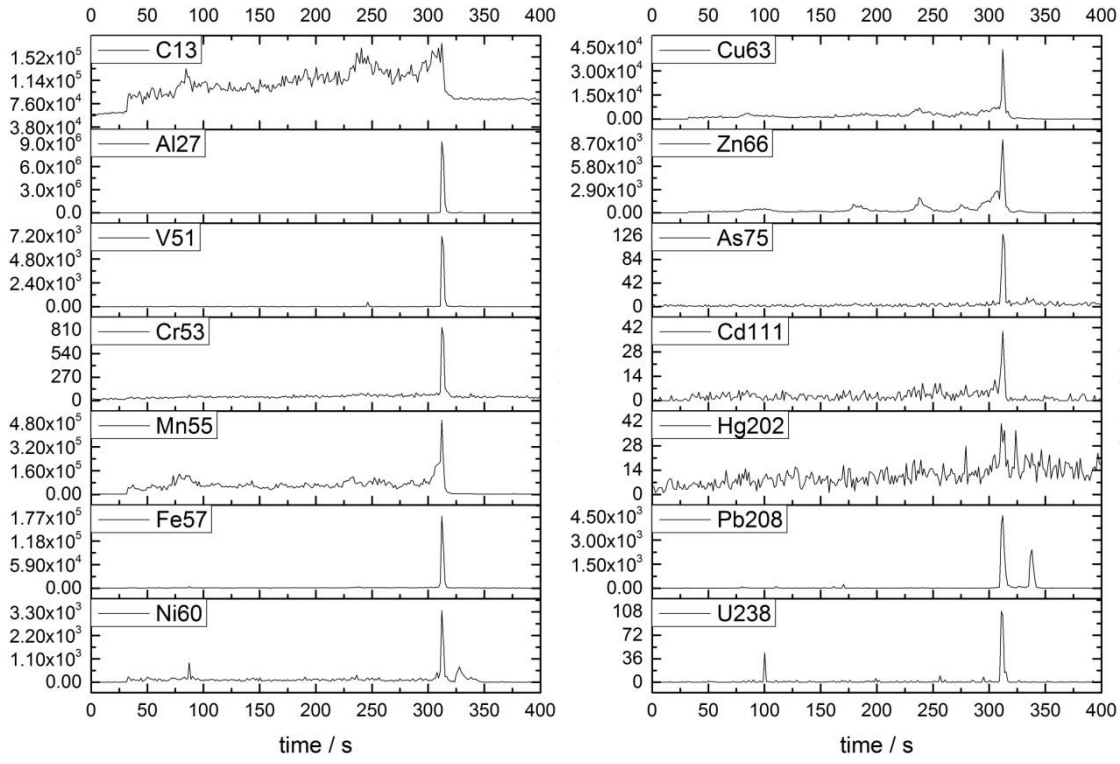


Figure 3.7 LA-ICP-MS analysis of Lincolnshire Beet (#4)

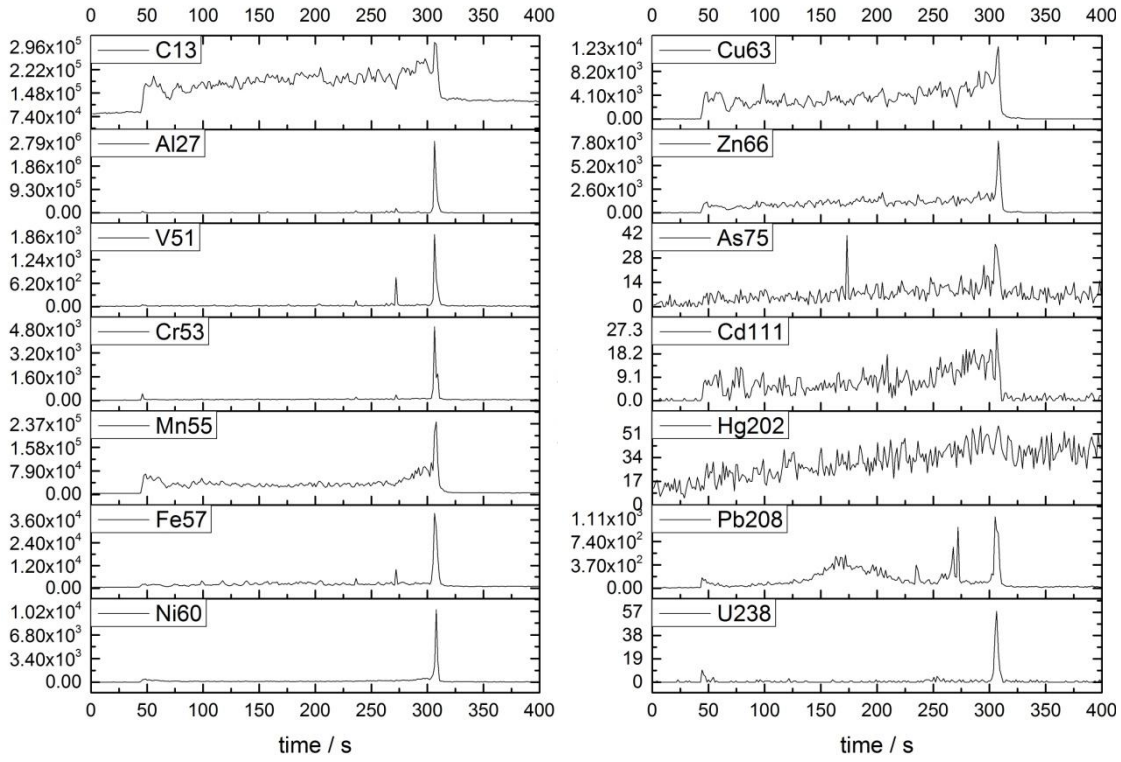


Figure 3.8 LA-ICP-MS analysis of Leicestershire Parsnip (#3)

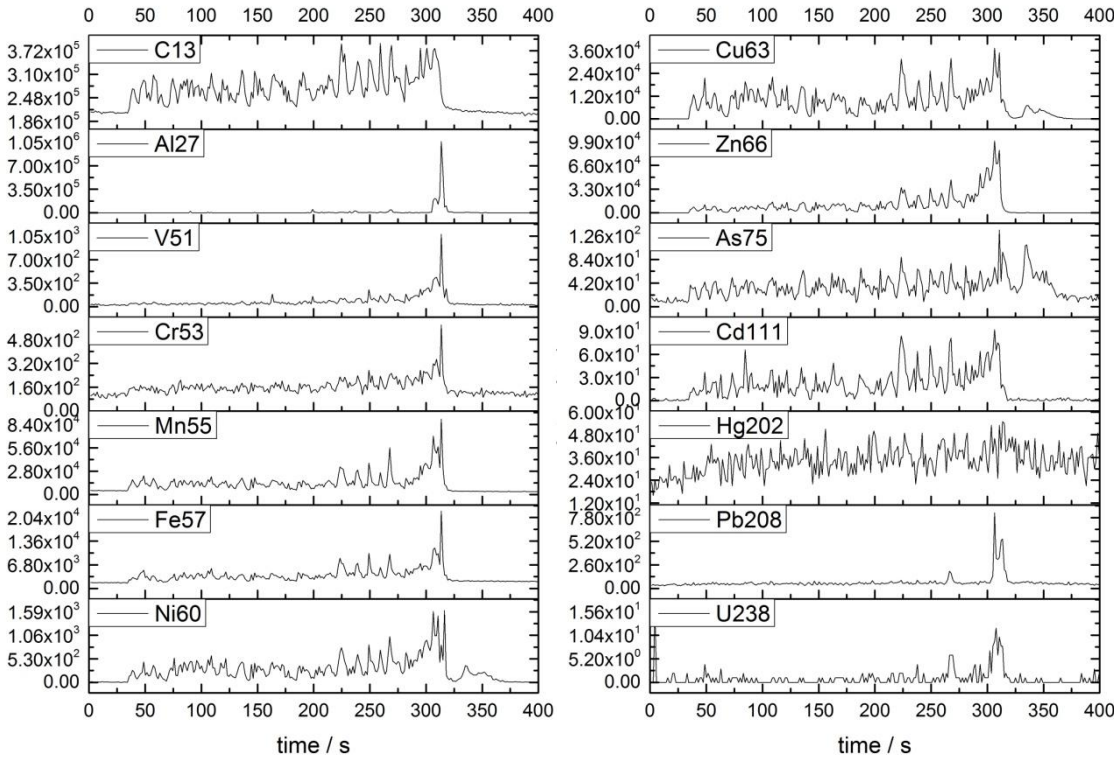


Figure 3.9 LA-ICP-MS analysis of Lancashire Turnip (#1 (2))

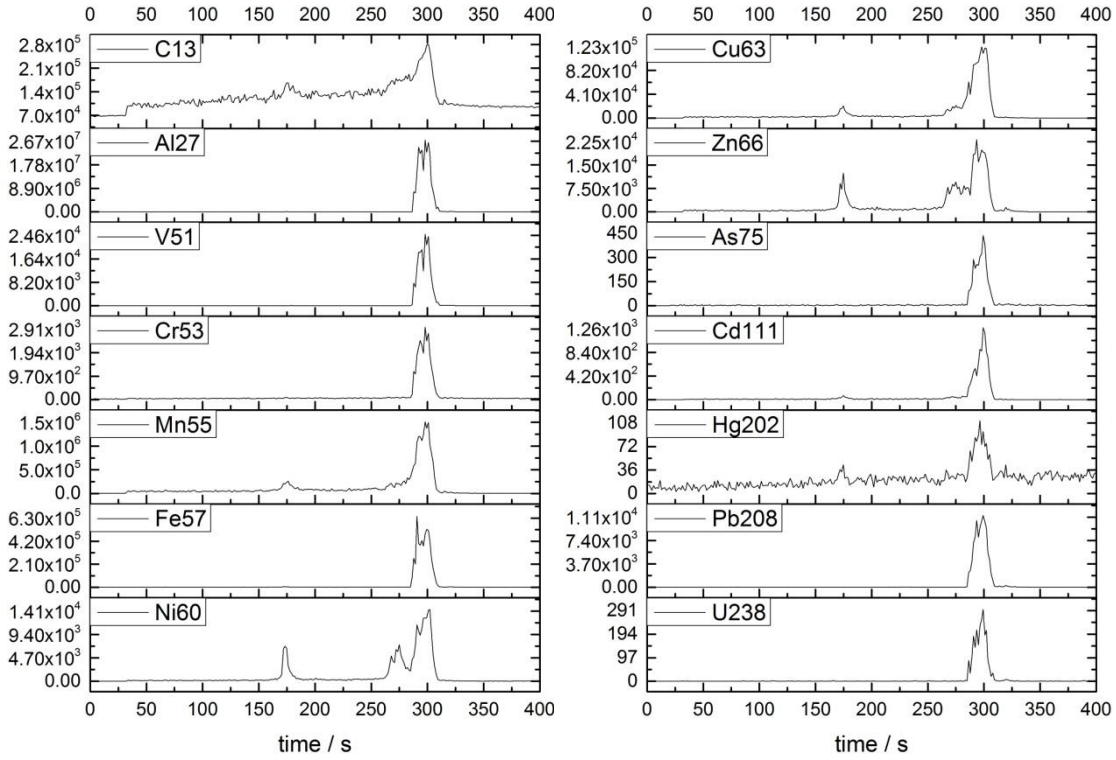


Figure 3.10 LA-ICP-MS analysis of Leicestershire Beetroot (#5)

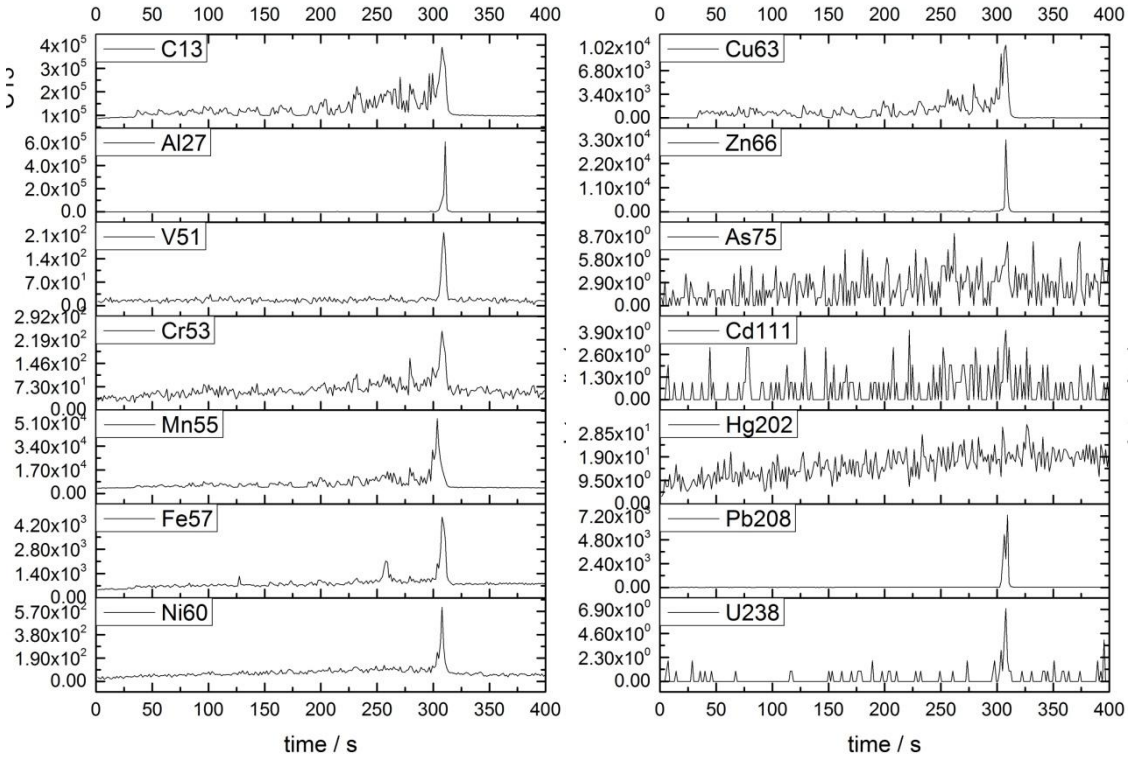


Figure 3.11 LA-ICP-MS analysis of Kent Apple (Discovery #1)

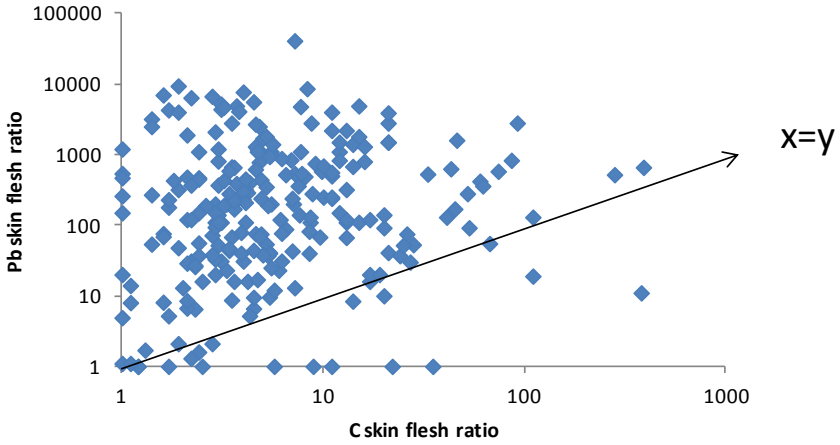


Figure 3.12 Comparison of skin/flesh ratio (peak height/flash average) for $^{13}C$ and $^{208}Pb$ in all vegetables listed by location.

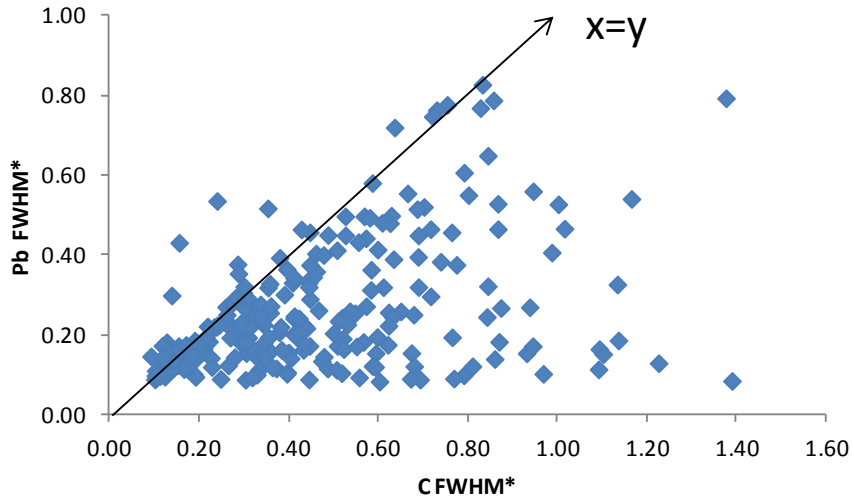


Figure 3.13 Comparison of FWHM* (mm) for $^{13}C$ and $^{208}Pb$ in all vegetables listed by location.

| N=244 | C13 | Al27 | V51 | Cr53 | Mn55 | Fe57 | Ni60 | Cu63 | Zn66 | As75 | Cd111 | Hg202 | Pb208 | U238 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Skin Peak height (c) | | | | | | | | | | | | | | |
| min | 2.8E+04 | 3.6E+04 | 2.2E+01 | 3.4E+01 | 6.1E+03 | 7.5E+02 | 6.4E+01 | 3.6E+03 | 1.7E+01 | 0.0E+00 | 5.5E+00 | 5.4E+00 | 7.5E+01 | 2.1E+00 |
| max | 8.3E+05 | 1.1E+08 | 7.4E+05 | 3.4E+05 | 1.3E+07 | 1.3E+07 | 1.4E+05 | 5.2E+06 | 4.1E+05 | 1.0E+04 | 1.8E+03 | 9.5E+03 | 4.3E+05 | 4.9E+03 |
| ave | 2.0E+05 | 1.5E+07 | 4.1E+04 | 5.2E+03 | 7.0E+05 | 5.4E+05 | 8.0E+03 | 1.5E+05 | 3.1E+04 | 7.2E+02 | 1.3E+02 | 1.7E+02 | 2.1E+04 | 5.3E+02 |
| SD | 9.9E+04 | 2.0E+07 | 8.7E+04 | 2.3E+04 | 1.6E+06 | 1.3E+06 | 1.6E+04 | 4.8E+05 | 3.8E+04 | 1.5E+03 | 2.0E+02 | 9.6E+02 | 4.9E+04 | 8.7E+02 |
| | | | | | | | | | | | | | | |
| 'Flesh' mean (c) | | | | | | | | | | | | | | |
| min | 4.0E+02 | 1.0E+01 | 1.0E-01 | 4.6E-01 | 1.0E+01 | 1.1E+02 | 5.5E-01 | 3.5E+01 | 1.0E+00 | 7.7E-02 | 5.9E-02 | 5.6E-01 | 1.0E-01 | 6.0E-03 |
| max | 3.9E+05 | 8.6E+05 | 9.9E+02 | 1.9E+02 | 3.8E+05 | 1.7E+04 | 5.0E+03 | 9.7E+04 | 2.0E+04 | 9.2E+01 | 2.7E+02 | 3.8E+01 | 3.6E+03 | 1.3E+01 |
| ave | 5.0E+04 | 3.3E+04 | 4.5E+01 | 3.8E+01 | 4.0E+04 | 2.1E+03 | 2.6E+02 | 6.9E+03 | 3.0E+03 | 5.4E+00 | 1.6E+01 | 7.4E+00 | 1.3E+02 | 6.9E-01 |
| SD | 4.6E+04 | 7.6E+04 | 8.3E+01 | 3.3E+01 | 5.7E+04 | 2.2E+03 | 5.1E+02 | 9.5E+03 | 3.6E+03 | 9.6E+00 | 3.0E+01 | 4.4E+00 | 4.1E+02 | 1.2E+00 |
| | | | | | | | | | | | | | | |
| Flesh/Skin ratio | | | | | | | | | | | | | | |
| min | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 9.9E-01 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 |
| max | 3.9E+02 | 1.1E+05 | 7.2E+04 | 7.6E+04 | 4.6E+03 | 8.9E+03 | 4.4E+03 | 3.6E+04 | 1.7E+04 | 1.1E+04 | 6.5E+02 | 2.7E+03 | 4.1E+04 | 3.3E+04 |
| ave | 1.4E+01 | 4.2E+03 | 2.6E+03 | 4.9E+02 | 8.4E+01 | 3.2E+02 | 1.1E+02 | 3.1E+02 | 1.3E+02 | 4.1E+02 | 2.3E+01 | 2.5E+01 | 9.7E+02 | 1.7E+03 |
| SD | 4.1E+01 | 1.2E+04 | 8.2E+03 | 5.0E+03 | 3.5E+02 | 8.1E+02 | 3.8E+02 | 2.9E+03 | 1.1E+03 | 1.4E+03 | 5.9E+01 | 2.3E+02 | 3.0E+03 | 3.7E+03 |
| | | | | | | | | | | | | | | |
| FWHM* (mm) | | | | | | | | | | | | | | |
| Min | 0.09 | 0.08 | 0.06 | 0.07 | 0.09 | 0.08 | 0.06 | 0.08 | 0.06 | 0.05 | 0.08 | 0.05 | 0.08 | 0.08 |
| Max | 1.4 | 0.75 | 0.81 | 1.1 | 2.1 | 1.4 | 1.2 | 1.4 | 1.2 | 1.3 | 1.4 | 16.4 | 0.83 | 0.80 |
| Ave | 0.47 | 0.22 | 0.25 | 0.28 | 0.37 | 0.28 | 0.33 | 0.36 | 0.36 | 0.28 | 0.37 | 0.45 | 0.26 | 0.25 |
| SD | 0.27 | 0.14 | 0.15 | 0.18 | 0.23 | 0.18 | 0.20 | 0.22 | 0.24 | 0.19 | 0.26 | 1.40 | 0.16 | 0.17 |
| | | | | | | | | | | | | | | |

Table 3.2. Summary statistics for LA-ICP-MS analysis of vegetables and fruit, showing skin peak heights in correct counts, Flesh average counts, Flesh/skin ratio and corrected FWHM indicating the peak thickness.

No attempt was made during this analysis to calibrate the LA-ICP-MS system and thus provide estimates of the element concentration. This was due to the difficulty in producing suitable matrix-matched calibration standards for the samples. We therefore relied upon physical separation of skin and flesh (i.e. peeling) followed by conventional analysis to determine element concentrations (Part 4).3.5. LA-ICP-MS images of vegetable and cereal grains

Successive measurements of aligned line scans spaced at 250 µm intervals were employed to create images depicting the micrometer scale spatial distribution of elements in two-dimensions. In the case of vegetable sections progressive drying of the sample occurred in the sample chamber due to the argon gas flow, yet comparable data was obtained over 21 lines (8 x 5 mm). Figures 3.15 to 3.18 show the images produced using Origin 9.1 software (OriginLab, Northampton, MA), providing an essentially qualitative illustration of the distribution of the metals within the sample.

As observed with the line scans, elements including Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb and U. There was variation in the magnitude of the skin peak indicating a heterogeneous distribution of elements within the skin. This highlights the difficulty in obtaining quantitative data from LA-ICP-MS as only tiny quantities of skin are samples.
The flesh levels cannot be viewed in most of these, because counts from the flesh are lower than the first level of colour changed. Similarly, a single high point as observed for U in Figure 3.15 can obscure any other features. Flesh can be viewed in the log scale, however.

Cereals grains had lower water content and were thus stable inside the LA sample cell. Multiple line scans (typically 16-18) spaced at 250 µm intervals in the Y plane were performed using the same parameters as described above. The data were converted into. Example data is shown in Figures 3.19 and 3.20, whilst the full sample set is shown in Appendix i (b). In Figures 3.19 and 3.20 C, As, Cd, and Hg are shown in natural scale and the remainder of the elements in log 10 scale to better show the element distribution.

The cereal grains were prepared by hand removal of the husk, leaving the bran intact. A section through the centre of the grain (latitudinal) was prepared by hand using a scalpel. The carbon images show the extent of the cereal grain and was relatively consistent across the grain, though some variation in density would be expected. Many of the other elements were elevated in the outer bran layer or in the cell nucleus. Appendix 1c provides additional images of further samples and compares images made with natural and log scales. It also shows the actual intensity count levels, which can affect the clarity of the image.

The apparent presence of metal beyond the boundaries of the sample to the right of the sample, which is particularly visible in the log scale plots, is caused by the ‘memory effect’ of the analytical determination. When high levels of an element are recorded it will take some time for levels to revert to the baseline in the argon gas flow transporting the analyte to the ICP-MS detector. In other words, the peaks observed in Figures 3.5 to 3.11 can tail substantially. Occasionally we also observed a ‘real signal’ outside the boundaries of the sample. This may be attributed to some contamination on the slide surface, possibly from the sample itself which was transferred during the mounting process.

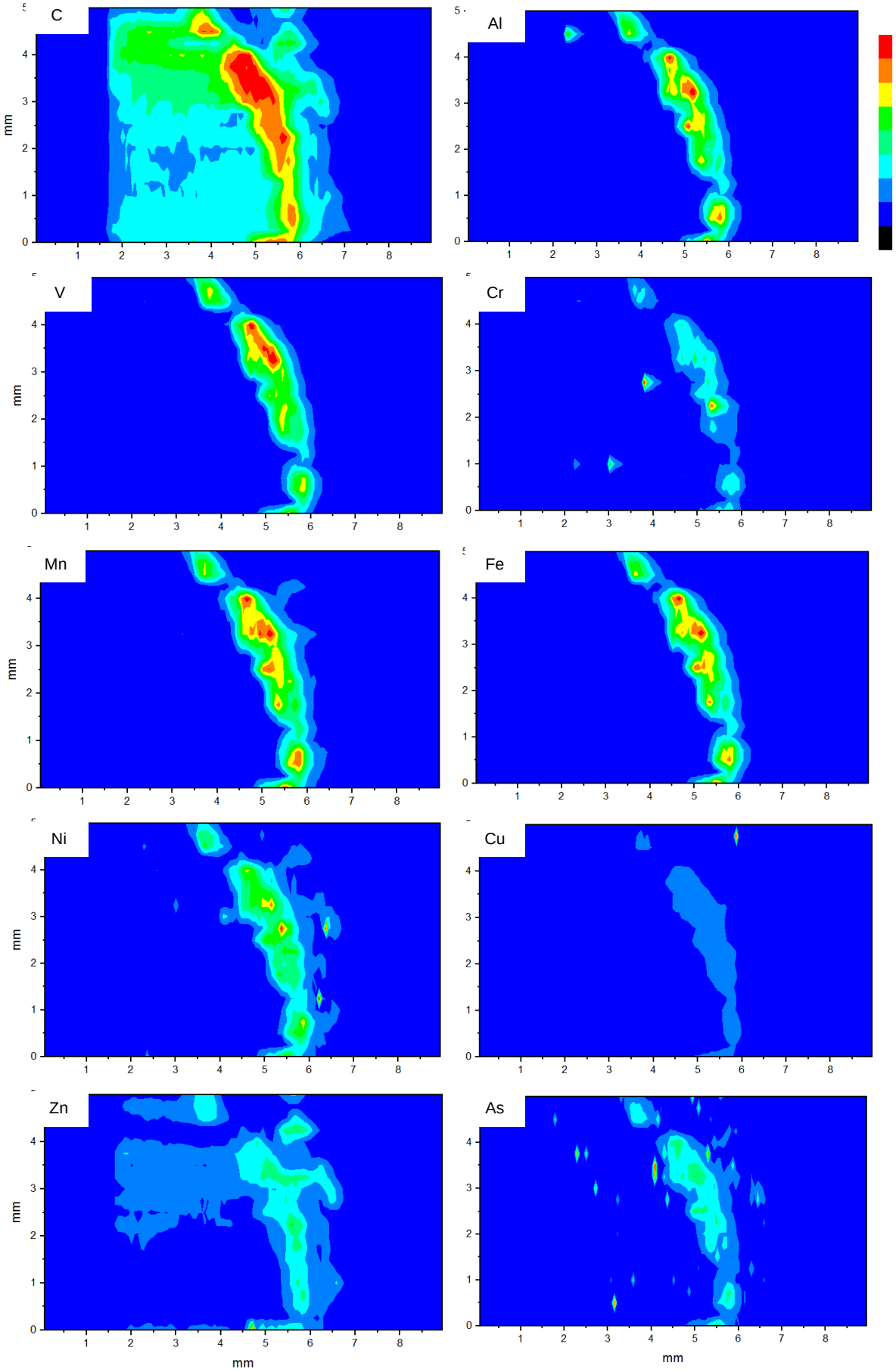


Figure 3.15 LA-ICP-MS imaging of Suffolk Potato (Red King Edward) on a relative scale from 0 to 1

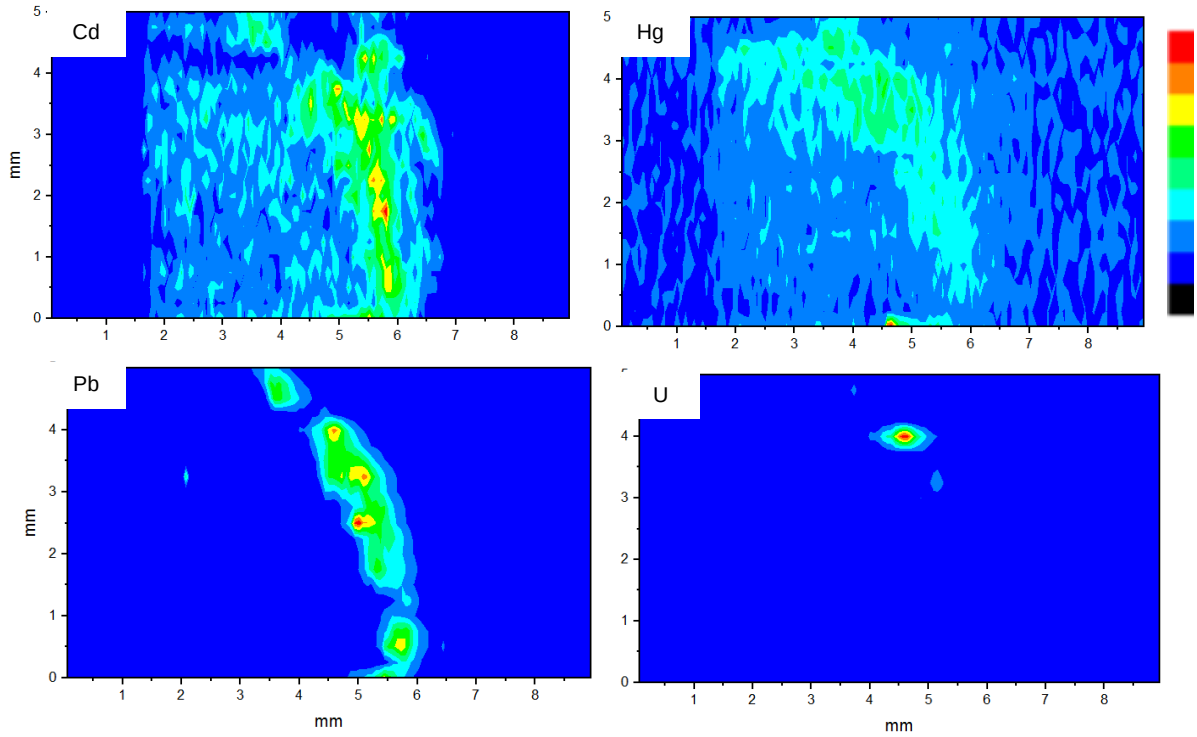


Figure 3.15 LA-ICP-MS imaging of Suffolk Potato (Red King Edward) (cont) on a relative scale from 0 to 1.

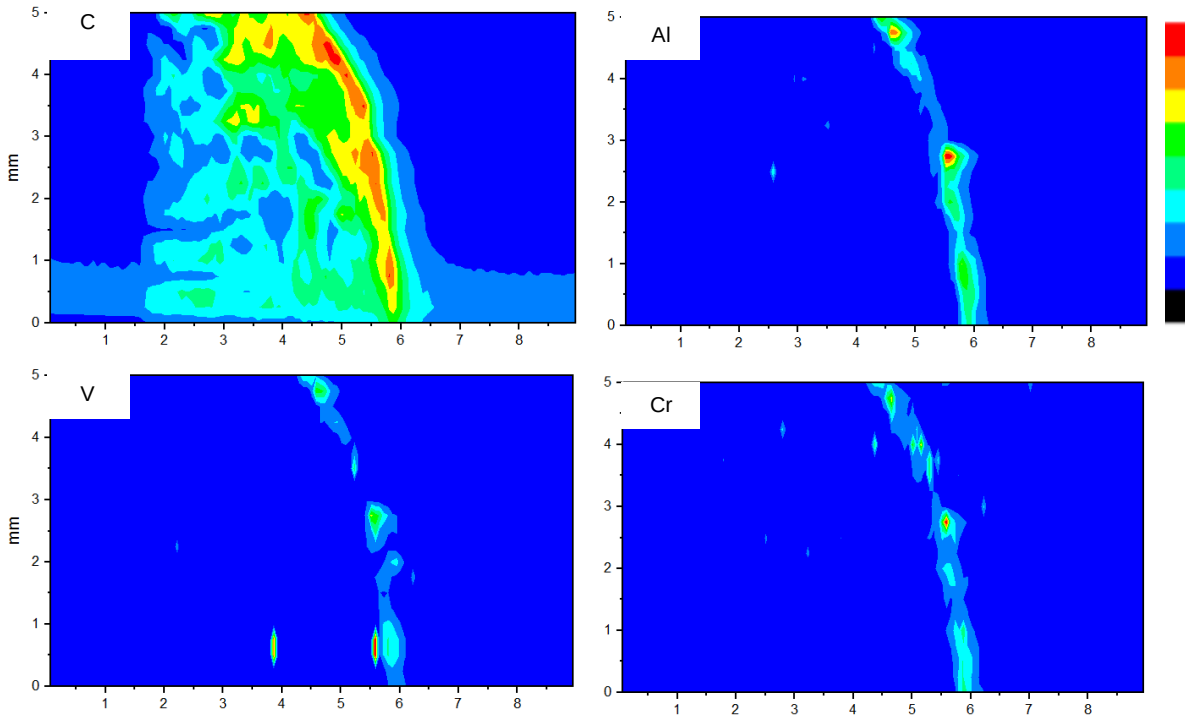


Figure 3.16 LA-ICP-MS image of Leicestershire Carrot section on a relative scale from 0 to 1

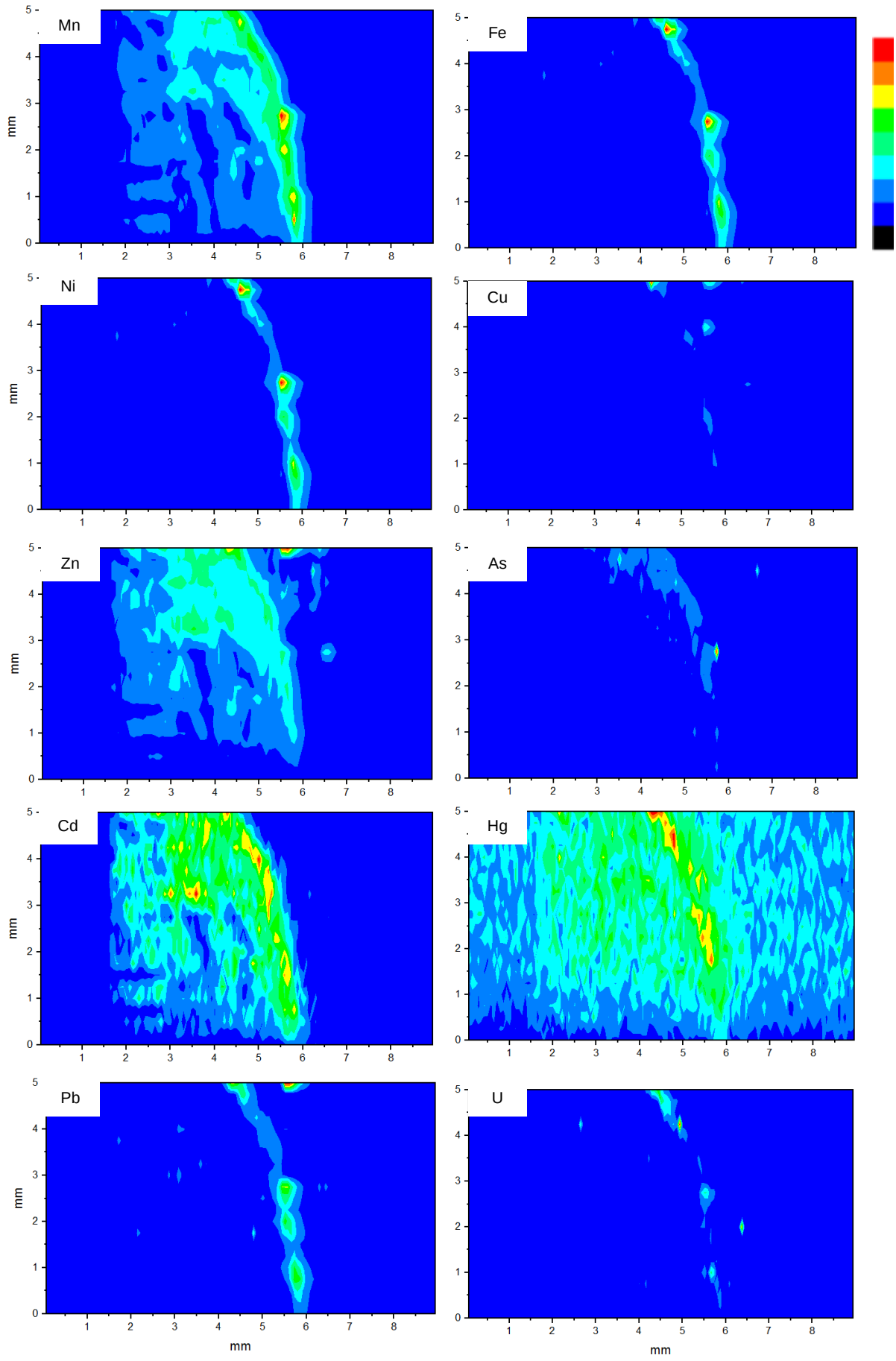


Figure 3.16 LA-ICP-MS image of Leicestershire Carrot section. (cont) on a relative scale from 0 to 1

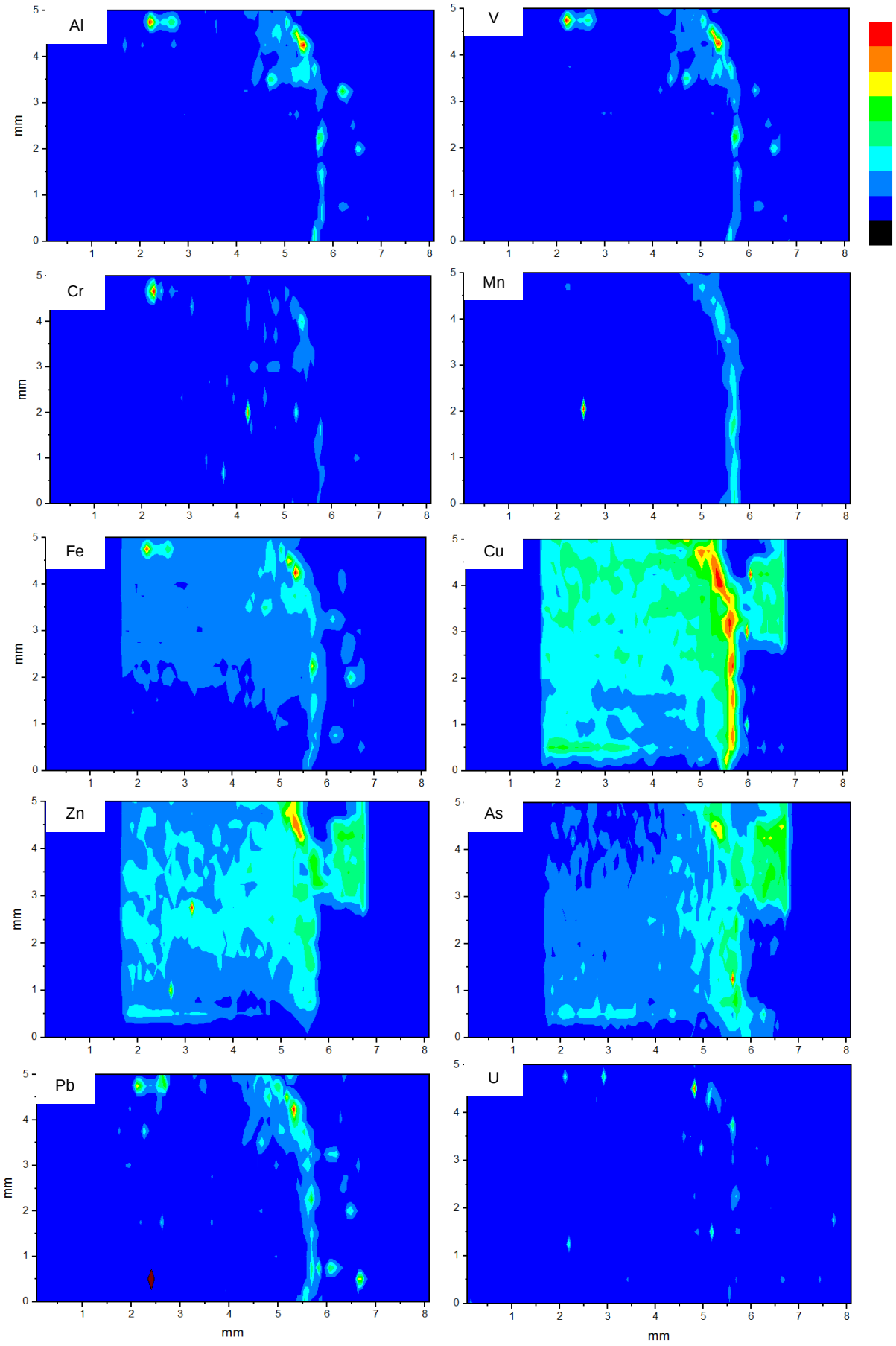


Figure 3.17. LA-ICP-MS image of Kent Potato (King Edward) on a relative scale from 0 to 1

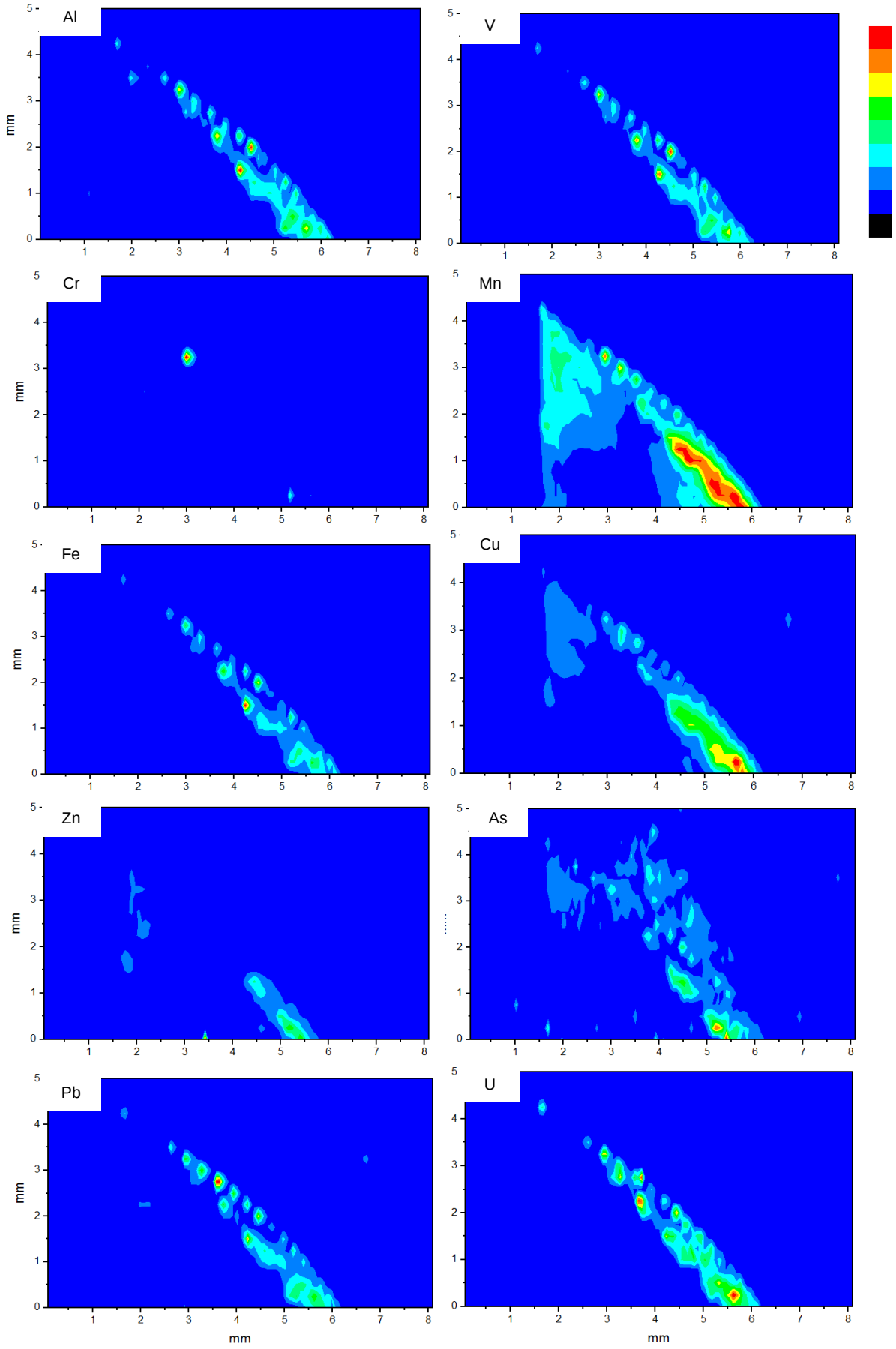


Figure 3.18. LA-ICP-MS image of Lancashire Beetroot (KE) on a relative scale from 0 to 1

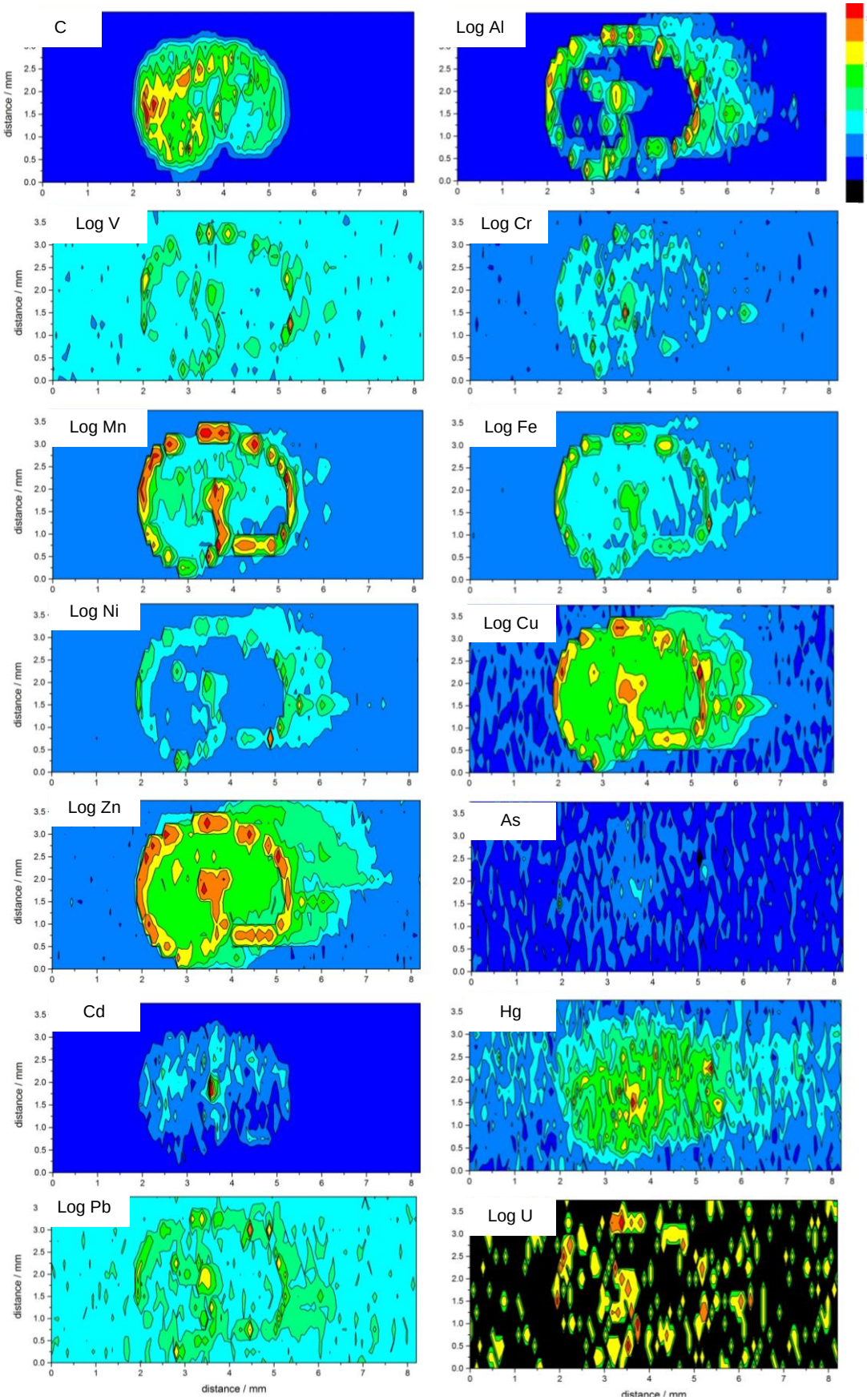


Figure 3.19 LA-ICP-MS imaging of Nottinghamshire Wheat on a relative scale from 0 to 1

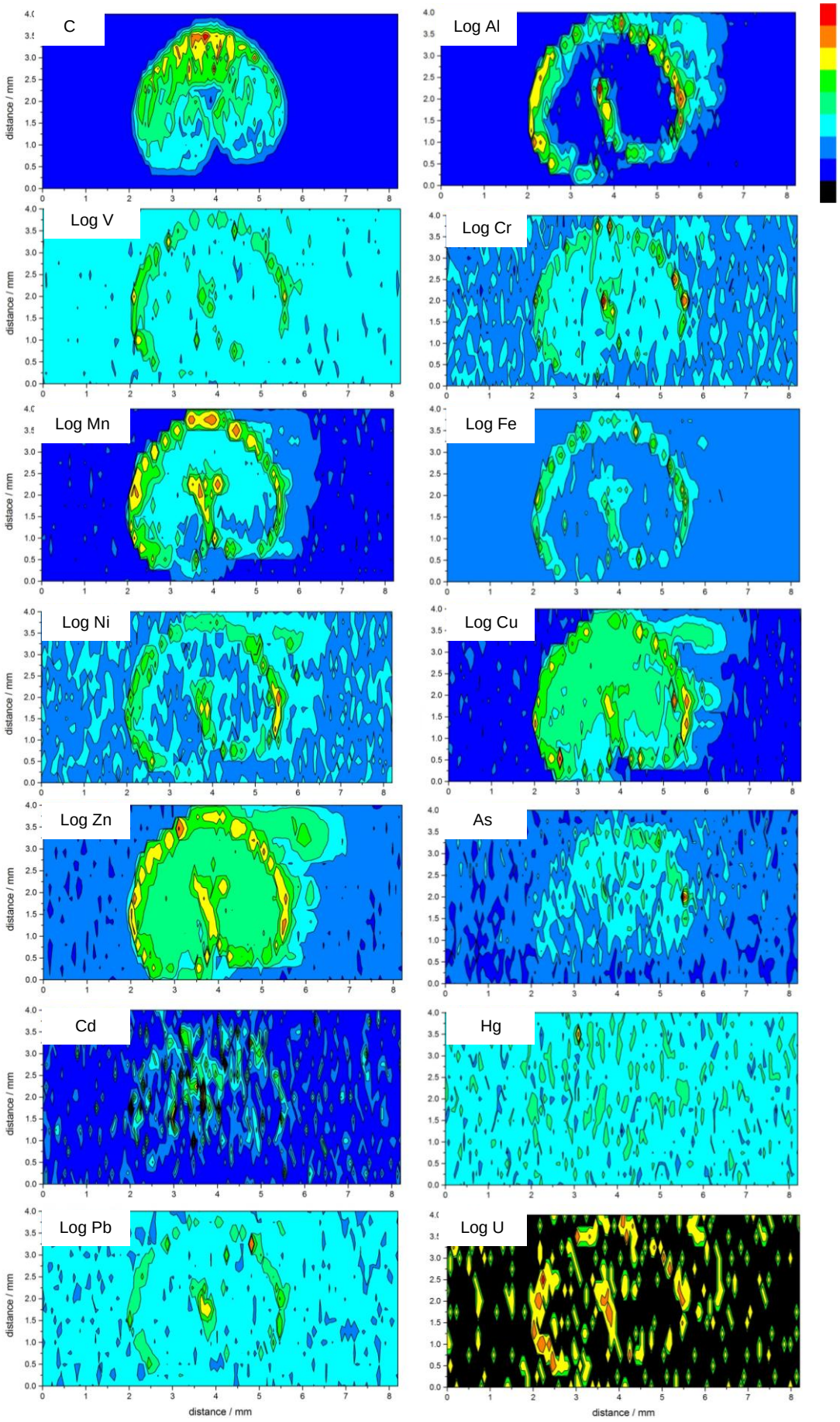


Figure 3.20 LA-ICP-MS imaging of Leicestershire Wheat on a relative scale from 0 to 1

## 4. Quantitative ICP-MS analysis

### 4.1 Introduction

Conventional solution ICP-MS analysis following acid digestion was performed to quantify the concentration of elements present in the peel (skin) and skin fractions of vegetables and fruit, and in the whole grain of cereal samples (see section 4.2). The purpose of these experiments were to confirm the LA-ICP-MS observations and determine whether any of the samples collected in the different geographical locations gave any cause for concern given the established Maximum (permissible) Levels outlined in Table 1.1.

### 4.2 Sample preparation and instrumentation digestion LA-ICP-MS

As described in Section 2 the collected vegetables were prepared by hand washing with tap water, peeling with a commercially available ceramic peeler, homogenised with a small electric domestic chopping device, and frozen at -20°C. Five individual vegetables from each location were prepared. Preparation for ICP-MS analysis was performed using a Mars 5 microwave digestion system (CEM, Buckingham, UK) equipped with HP-500 Plus$^{TM}$ vessels. After thawing, about 1 g wet weight of the flesh or peel samples were accurately weighed into the vessel. Five ml of high purity concentrated nitric acid was added. The vessels were sealed and heated step-wise to 170°C for a total of 40 minutes plus one hour cool down. The digestate was transferred to a 50 ml tube and diluted with doubly-distilled water and accurately weighed.

Calibration standards we prepared from AccuTrace$^{TM}$ Reference Standard ICP-MS Calibration Standard (AccuStandard Inc, New Haven, CT) and supplemented with single element standards of Cu, Zn, and Hg from the same supplier. An internal standard solution for online addition to ICP-MS was prepared from single element standards containing Y, In and Bi. Calibration Standards and Digested samples were analysed by ICP-MS using a nebuliser and cooled double-pass spray chamber. Quality control was assessed through the analysis of in-house reference materials and external certified reference materials. We also participated in the external proficiency testing schemes FAPAS® 07187 achieving z-scores of -0.4 (As) and -0.6 (Cd) within the expected range of $-2 \leq z \leq 2$ and FAPAS® 07188 achieving z-scores of -1.3 (Cd) and -1.2 (Pb) within the expected range of $-2 \leq z \leq 2$

### 4.3 ICP-MS analysis of vegetables, fruit and cereals

Table 1 gives the element concentrations measured in flesh and peel fractions of vegetables and fruit collected in the different locations with full data of the replicates provided in Appendix ii. Summary statistics are provided in Table 4.1. Element concentrations were typically low and within the normal expected range. Ranked concentrations for Cd and Pb showed that some sample exceeded ML's. Element concentrations were consistently higher in the peel than in the flesh, as shown by the Peel/Flesh ratios summarized in Table 4.2, confirming the LA-ICP-MS measurements. It was clear that peeling removes elements concentrated in the skin. We estimate that peeling removes an approximate thickness of 1 mm of skin, which is in excess of the element peak width measured by LA-ICP-MS. Element concentrations in the cereals were typically low (Table 4.2).

Table 4.1 Mean and standard deviation of the amount of elements (µg/kg) in peeled vegetables and fruits

| | Peeled vegetable | V | Cr | Ni | Cu | Zn | As | Cd | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Derby Pot (MP) | 3.6 ± 2.9 | 17.2 ± 5.0 | 280 ±170 | 2180 ± 240 | 8300 ± 2200 | | 108 ± 31 | | 34 ± 37 |
| 2 | Derby Pot (MP) | 7.0 ± 3.1 | 18 ± 12 | 86 ± 56 | 2000 ± 210 | 7400 ± 2000 | 4.0 ± 1.5 | 95 ± 33 | 4.4 ± 3.3 | 130 ± 170 |
| 3 | Derby Pot (MP) | 4.5 ± 0.4 | 11.8 ± 1.3 | 76 ± 28 | 1980 ± 280 | 6900 ± 920 | 2.9 ± 0.2 | 79 ± 17 | 2.4 ± 0.5 | 53 ± 88 |
| 4 | Glouc Pot (Des) | 2.6 ± 1.3 | 11.7 ± 7.1 | 140 ± 130 | 3340 ± 610 | 9100 ± 3000 | 1.6 ± 0.1 | 12 ± 4.9 | | |
| 5 | Glouc Pot (Nic) | | 6.2 ± 2.1 | 39 ± 19 | 2420 ± 250 | 4900 ± 1100 | | 6.9 ± 5.5 | 1.7 ± 0.1 | 0 |
| 6 | Kent Pot (Est) | 4.1 ± 1.3 | 18.8 ± 8.6 | 110 ± 110 | 1470 ± 210 | 6000 ± 2600 | 1.4 ± 0.4 | 10 ± 1.2 | | 3.7 ± 2.8 |
| 7 | Kent Pot (La R) | 6.1 ± 3.0 | 65 ± 98 | 81 ± 51 | 1600 ± 550 | 7300 ± 2500 | 1.5 ± 0.5 | 26 ± 1.2 | 11 ± 10 | 3.2 ± 0.6 |
| 8 | Kent Pot (Wilja) | 1.7 ± 0.3 | 5.8 ± 1.3 | 41 ± 7.4 | 710 ± 160 | 3700 ± 330 | | 9.5 ± 3.5 | | |
| 9 | Kent Pot (DOY) | 2.0 ± 0.8 | 7.0 ± 0.3 | 34 ± 6.7 | 730 ± 120 | 4200 ± 1000 | | 14 ± 2.6 | | 0 |
| 10 | Kent Pot (Yukon) | 3.1 ± 1.4 | 9.3 ± 2.9 | 30 ± 4.0 | 490 ± 120 | 4050 ± 930 | 1.4 ± 0.1 | 14 ± 4.4 | 2.1 ± 1.7 | 5.1 ± 1.0 |
| 11 | Kent Pot (RKE) | 1.9 ± 0.5 | 13.6 ± 2.7 | 58 ± 33 | 800 ± 190 | 5040 ± 630 | | 11 ± 1.9 | 12.2 ± 3.6 | 5.2 ± 1.3 |
| 12 | Kent Pot (MP) | 1.6 ± 0.2 | 4.8 ± 1.5 | 47 ± 23 | 620 ± 320 | 4000 ± 1100 | | 11 ± 3.7 | | 4.5 ± 1.5 |
| 13 | Kent Pot (KE) | 1.4 ± 0.9 | 3.0 ± 1.4 | 26 ± 9.2 | 650 ± 210 | 3050 ± 890 | | 7.8 ± 2.3 | 2.8 ± 1.9 | 4.0 ± 1.3 |
| 14 | Kent Pot (ShBk) | 2.1 ± 0.9 | 18.3 ± 4.8 | 750 ± 340 | 700 ± 230 | 4470 ± 390 | 1.5 ± 0.4 | 9.5 ± 1.7 | 3.9 ± 2.1 | 4.8 ± 1.8 |
| 15 | Kent Pot (SB) | | 15.8 ± 1.9 | 380 ± 270 | 1040 ± 160 | 5300 ± 950 | 1.9 ± 0.5 | 13 ± 1.3 | | 2.7 ± 0.8 |
| 16 | Kent Pot (HBR) | 5.9 ± 3.1 | 17.8 ± 9.2 | 400 ± 220 | 1670 ± 990 | 7610 ± 450 | 1.6 ± 1.0 | 15 ± 8.2 | | 3.8 ± 1.9 |
| 17 | Kent Pot (KP) | 6.1 ± 1.1 | 12.0 ± 2.3 | 32.0 ± 5.1 | 980 ± 220 | 4220 ± 720 | 3.4 ± 0.7 | 13 ± 1.9 | 3.7 ± 1.8 | 9.4 ± 2.3 |
| 18 | Kent Pot (Char) | | 9.6 ± 2.5 | 38 ± 15 | 1800 ± 260 | 5100 ± 1180 | 2.6 ± 1.1 | 5.5 ± 3.1 | | |
| 19 | Kent Pear (Conc) | 3.4 ± 1.0 | | 88 ± 21 | 1500 ± 610 | 950 ± 560 | 2.1 ± 0.4 | 6.2 ± 1.5 | 6.7 ± 2.8 | |
| 20 | Kent Pear (Conf) | 3.3 ± 0.4 | 8.0 ± 9.6 | 66 ± 19 | 883 ± 39 | 450 ± 290 | 2.9 ± 0.5 | 5.1 ± 0.6 | 3.6 ± 1.2 | |
| 21 | Kinross Carrot | 3.3 ± 0.5 | 27 ± 46 | 26 ± 12 | 384 ± 49 | 2880 ± 260 | | 26 ± 5.9 | 2.4 ± 0.6 | 18.2 ± 9.1 |
| 22 | Kinross Carrot | | 8.2 ± 1.8 | 55 ± 14 | 2160 ± 700 | 6220 ± 1240 | 1.7 ± 0.7 | 3.3 ± 1.3 | | |
| 23 | Kinross Pot (MP) | | 8.8 ± 2.2 | 58 ± 12 | 2360 ± 580 | 6840 ± 1190 | 1.7 ± 0.4 | 4.9 ± 1.4 | | |
| 24 | Lancs Carrot | 5.8 ± 1.2 | 8.2 ± 3.1 | 33 ± 7.4 | 410 ± 80 | 4030 ± 750 | | 1.4 ± 0.3 | | 6.2 ± 1.2 |
| 25 | Lancs Beetroot | 18 ± 11 | 37 ± 33 | 270 ± 150 | 2600 ± 1400 | 14900 ± 8000 | 11.3 ± 1.0 | | 4.4 ± 3.0 | 7.3 ± 4.7 |
| 26 | Lancs Swede | 5.0 ± 1.1 | 7.7 ± 2.6 | 64 ± 6.9 | 340 ± 85 | 2770 ± 330 | 9.6 ± 1.2 | | 3.8 ± 2.3 | |
| 27 | Lancs Turnip | 2.5 ± 0.2 | 9.6 ± 1.8 | 57 ± 5.4 | 580 ± 100 | 3200 ± 400 | 10.4 ± 1.7 | | 2.1 ± 0.7 | 3.8 ± 1.8 |
| 28 | Lancs Pot (KE) | | 3.6 ± 2.5 | 71 ± 35 | 1720 ± 480 | 7600 ± 1700 | | | | |
| 29 | Lancs Pot (Est) | | 4.8 ± 2.5 | 30 ± 21 | 1620 ± 310 | 6400 ± 490 | | 4.8 ± 2.4 | | 2.7 ± 1.7 |
| 30 | Leic Carrot | 1.9 ± 1.0 | | 152 ± 21 | 640 ± 140 | 3750 ± 360 | 1.3 ± 0.2 | 28 ± 3.8 | 3.0 ± 0.7 | 10.1 ± 1.6 |
| 31 | Leic Carrot | 1.8 ± 0.4 | | 116 ± 9.0 | 1660 ± 110 | 9640 ± 1000 | 18.4 ± 4.2 | 19.6 ± 1.3 | 3.8 ± 1.4 | 50 ± 18 |
| 32 | Leic Beetroot | | 16.4 ± 4.7 | 248 ± 23 | 1130 ± 160 | 5440 ± 860 | | 30 ± 6.8 | | 9.6 ± 2.0 |
| 34 | Leic Pot (MPe) | 6.5 ± 1.2 | 11.8 ± 2.5 | 40 ± 12 | 1380 ± 190 | 6250 ± 500 | 4.4 ± 0.6 | 16 ± 2.8 | 3.4 ± 0.9 | 11 ± 4.8 |
| 35 | Leic Pot (MP) | | 13.6 ± 5.1 | 69 ± 58 | 1860 ± 150 | 6780 ± 17 | 1.8 ± 0.7 | 6.5 ± 4.0 | | |
| 36 | Leic Pot (KE) | | 19 ± 15 | 640 ± 540 | 3740 ± 520 | 10800 ± 5800 | 1.7 ± 0.4 | 25 ± 7.8 | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 37 | Leic Pot (RKE) | | 13.0 ± 7.9 | 260 ± 110 | 3340 ± 590 | 7300 ± 1500 | 1.6 ± 0.4 | 26 ± 15 | 3.1 ± 2.8 | 2.3 ± 0.8 |
| 38 | Lincs Carrot | 16.5 ± 7.4 | | 81 ± 21 | 1090 ± 170 | 4180 ± 400 | 16.8 ± 1.3 | 12 ± 2.0 | 4.7 ± 3.0 | 19 ± 5.4 |
| 39 | Lincs Beet | 12.1 ± 2.7 | | 68 ± 2.7 | 1780 ± 250 | 4800 ± 1400 | 5.7 ± 1.1 | 17 ± 1.8 | 1.6 ± 0.3 | 12 ± 1.7 |
| 40 | Lincs Beetroot | 12.0 ± 1.9 | | 80 ± 9.0 | 2720 ± 170 | 10600 ± 1100 | 7.3 ± 1.1 | 11 ± 0.6 | 3.1 ± 1.2 | 24 ± 4.5 |
| 41 | Lincs Beetroot | 4.3 ± 0.6 | | 62 ± 11 | 790 ±110 | 3950 ± 230 | 2.5 ± 0.7 | 16 ± 1.6 | 2.9 ± 0.7 | 10 ± 1.9 |
| 42 | Lincs Pot (Wilja) | 1.2 ± 0.3 | 10.6 ± 2.5 | 87 ± 130 | 1210 ± 200 | 4080 ± 1780 | 1.6 ± 0.2 | 9.4 ± 1.1 | 5.3 ± 5.7 | |
| 43 | Lincs Pot (Marf) | | 4.4 ± 1.5 | 16 ± 7.7 | 1400 ± 140 | 3220 ± 540 | | 3.1 ± 2.3 | | 1.2 |
| 44 | Norfolk Apple (Disc) | 3.6 ± 0.3 | | 6.5 | 600 ± 100 | 610 ± 290 | 1.4 ± 0.3 | 3.3 ± 0.4 | 3.3 ± 1.2 | |
| 45 | Norfolk Pear (Conf) | 2.7 ± 0.9 | | 66 ± 47 | 760 ± 500 | 970 ± 500 | 1.7 ± 0.3 | 4.6 ± 0.4 | 3.7 ± 1.2 | |
| 46 | NI Carrot | 5.1 ± 3.1 | 87 ± 149 | 430 ± 140 | 480 ± 260 | 3300 ± 1700 | 3.5 ± 1.2 | 89 ± 29 | | 37 ± 21 |
| 47 | NI Parsnip | 7.2 ± 3.5 | 11.2 ± 1.7 | 143 ± 5.0 | 1250 ± 190 | 3800 ± 620 | 3.4 ± 0.5 | 35 ± 4.0 | | 61 ± 13 |
| 48 | NI Pot (Comber) | 3.2 ± 2.3 | 5.5 ± 3.9 | 97 ± 38 | 1630 ± 710 | 4000 ± 1400 | 1.6 ± 0.4 | 30 ±16 | | 3.5 ± 1.4 |
| 49 | NI Pear (Conc) | | | 68 ± 11 | 388 ± 93 | 920 ± 400 | 1.2 ± 0.1 | | | 16 ± 24 |
| 50 | NI Apple (Disc) | | | 24 ± 9.4 | 450 ± 450 | 1100 ± 1100 | 1.3 ± 0.2 | | | |
| 51 | Perth Beetroot | 1.4 ± 0.3 | 6.3 ± 1.0 | 55 ± 5.7 | 1460 ± 250 | 4180 ± 520 | 7.0 ± 1.7 | | 2.5 ± 1.1 | |
| 52 | Perth Swede | | 3.2 ± 1.4 | 40 ± 10 | 520 ± 110 | 2720 ± 410 | | 7.0 ± 2.5 | 22 ± 23 | |
| 53 | Perth Parsnip | | 25 ± 31 | 330 ± 65 | 2400 ± 510 | 13400 ± 1800 | | 85 ± 2.5 | 22 ± 7.0 | 20 ± 7.9 |
| 54 | Perth Carrot | | 13.8 ± 5.6 | 77 ± 26 | 1100 ± 400 | 4600 ± 1100 | | 32 ± 13 | 19 ± 25 | 13 ± 7.3 |
| 55 | Wales Carrot | 25.3 ± 3.8 | | 125 ± 19 | | 9700 ± 3700 | 49 ± 11 | 55 ± 16 | | 260 ± 70 |
| 56 | Wales Parsnip | 22.8 ± 1.0 | | 405 ± 65 | 2470 ± 790 | 12500 ± 2300 | 27 ± 1.0 | 243 ± 42 | | 178 ± 26 |
| 57 | Wales Swede | 8.0 ± 1.2 | | 78 ± 7.2 | 900 ± 100 | 3660 ± 220 | 7.7 ± 0.8 | 21 ± 2.2 | 3.6 ± 1.5 | 11 ± 2.3 |
| 58 | Wales Pot (MP) | | 5.8 ± 0.3 | 51 ± 19 | 1525 ± 190 | 5300 ± 550 | 3.8 ± 0.9 | 5.3 ± 0.7 | 2.7 ± 0.6 | 2.9 ± 0.9 |
| 59 | Wales Pot (RKE) | 1.7 ± 0.1 | 7.2 ± 4.1 | 68 ± 34 | 1820 ± 270 | 6840 ± 690 | 2.8 ± 0.5 | 5.1 ± 2.6 | 2.9 ± 0.6 | 2.7 ± 1.3 |
| 60 | Suffolk Parsnip | 21.7 ± 2.7 | | 250 ± 49 | 1510 ± 720 | 11250 ± 990 | 31 ± 3.4 | 61 ± 6.8 | | 104 ± 13 |
| 61 | Suffolk Turnip | 43.0 ± 3.3 | | 133 ± 45 | | 2520 ± 440 | 56 ± 1.9 | 43 ± 2.2 | | 52 ± 9.1 |
| 62 | Suffolk Pot (RKE) | 6.0 ± 5.7 | 10.4 ± 3.6 | 23 ± 5.2 | 1500 ± 330 | 4820 ± 660 | 3.0 ± 0.9 | 12 ± 4.7 | 3.2 ± 0.9 | 4.1 ± 4.1 |
| 63 | Suffolk Pot (RKE) | 2.7 ± 0.5 | 6.7 ± 1.6 | 57 ± 47 | 2800 ± 2700 | 5180 ± 920 | 2.1 ± 0.3 | 9.3 ± 1.4 | 2.0 ± 0.9 | 2.0 ± 1.3 |
| 64 | Suffolk Apple (Disc) | | | 8.3 ± 4.8 | 500 ± 100 | | 1.9 ± 0.5 | | | |
| 65 | Suffolk Apple (Bram) | | | 4.2 ± 1.2 | 340 ± 180 | | 1.1 0.1 | | | 4.1 ± 0.8 |

*Pot = potato, Glouc = Gloucestershire, Lancs = Lancashire, Lincs = Lincolnshire, NI = Northern Ireland, MP = Maris Piper, Des = Desiree, Nic = Nicola, Est = Estima, La R = La Ratte, DOY = Duke of York, RKE = Red King Edward, KE = King Edward,ShBk = Shetland Black, SB= Salad Blue, HBR = Highland Burgundy Red, KP = Kerr's Pink,Char = Charlottes, Conc = Concorde, Conf = Conference, Disc = Discovery, Bram = Bramley, MPe = Maris Peer.

Table 4.2 Average amount of elements (µg/kg) in peel fraction (skin) of vegetables and fruits.

| | Peel | V | Cr | Ni | Cu | Zn | As | Cd | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Derby Pot (MP) | 77 ± 41 | 95 ± 34 | 297 ± 84 | 4150 ± 190 | 8000 ±1100 | 13 ±7.8 | 208 ± 55 | | 340 ±180 |
| 2 | Derby Pot (MP) | 58 ± 13 | 59 ± 14 | 108 ± 29 | 3320 ± 410 | 6900 ±1500 | 13 ± 2.5 | 180 ± 57 | 4.7 ± 1.2 | 430 ± 270 |
| 3 | Derby Pot (MP) | 90 ± 62 | 78 ± 44 | 142 ± 16 | 3420 ± 350 | 7600 ± 920 | 16 ± 8.6 | 162 ± 33 | 5.6 ± 1.2 | 454 ± 270 |
| 4 | Glouc Pot (Des) | 92 ± 51 | 80 ± 36 | 143 ± 35 | 3950 ± 940 | 7300 ± 920 | 11 ± 8.6 | 16 ± 33 | 2.3 ± 1.2 | 39 ± 17 |
| 5 | Glouc Pot (Nic) | 59 ± 11 | 47 ± 8.8 | 71 ± 16 | 3660 ± 480 | 5500 ± 950 | 6.6 ± 2.3 | 12 ± 7.7 | 4.2 ± 3.5 | 34 ± 10 |
| 6 | Kent Pot (Est) | 155 ± 50 | 123 ± 31 | 193 ± 87 | 2400 ± 260 | 7730 ± 950 | 26 ± 11 | 23 ± 3.6 | 34 ± 13 | 36 ± 12 |
| 7 | Kent Pot (La R) | 144 ± 48 | 100 ± 22 | 138 ± 22 | 2140 ± 210 | 9800 ± 1300 | 23 ± 8.0 | 31 ± 8.9 | 41 ± 11 | 32 ± 10 |
| 8 | Kent Pot (Wilja) | 138 ± 68 | 102 ± 43 | 82 ± 17 | 1530 ± 140 | 4800 ± 560 | 22 ± 13 | 19 ± 6.0 | 17 ± 1.4 | 37 ± 21 |
| 9 | Kent Pot (DOY) | 167 ± 47 | 85 ± 31 | 104 ± 11 | 1630 ± 230 | 8000 ± 1700 | 19 ± 6.7 | 24 ± 4.5 | | 31 ± 5.5 |
| 10 | Kent Pot (Yukon) | 145 ± 47 | 91 ± 30 | 89 ± 27 | 1230 ± 190 | 5200 ± 1200 | 28 ± 11 | 19.2 ± 2.6 | 4.4 ± 2.7 | 35 ± 13 |
| 11 | Kent Pot (RKE) | 113 ± 68 | 67 ± 34 | 124 ± 57 | 2000 ± 620 | 6500 ± 2300 | 16 ± 9.0 | 16.6 ± 2.1 | 49 ± 23 | 27 ± 10 |
| 12 | Kent Pot (MP) | 57 ± 21 | 35 ± 13 | 84 ± 78 | 890 ± 390 | 3700 ± 1600 | 12 ± 4.7 | 12.8 ± 4.4 | 5.5 ± 1.9 | 19 ± 4 |
| 13 | Kent Pot (KE) | 127 ± 127 | 75 ± 78 | 80 ± 38 | 1320 ± 1060 | 3500 ± 1400 | 21 ± 21 | 10.4 ± 3.7 | 6.2 ± 4.8 | 41 ± 40 |
| 14 | Kent Pot (ShBk) | 168 ± 50 | 97 ± 32 | 510 ± 310 | 1970 ± 280 | 5700 ± 690 | 21 ± 6.4 | 19.3 ± 3.6 | | 24 ± 9 |
| 15 | Kent Pot (SB) | 73 ± 45 | 71 ± 26 | 420 ± 300 | 2580 ± 370 | 7640 ± 650 | 11 ± 5.7 | 26.0 ± 1.4 | | 25 ± 8 |
| 16 | Kent Pot (HBR) | 82 ± 29 | 58 ± 19 | 250 ± 32 | 3100 ± 1500 | 7400 ± 3800 | 7.3 ± 2.2 | 23 ± 12 | | 22 ± 11 |
| 17 | Kent Pot (KP) | 134 ± 34 | 80 ± 19 | 78 ± 12 | 2220 ± 480 | 9900 ± 9100 | 25 ± 10 | 24 ± 2.6 | 4.4 ± 1.1 | 130 ± 200 |
| 18 | Kent Pot (Char) | 157 ± 29 | 103 ± 19 | 118 ± 10 | 3130 ± 370 | 6600 ± 1200 | 32 ± 8.2 | 12 ± 4.5 | | 22.7 ± 3.4 |
| 19 | Kent Pear (Conc) | 5.1 ± 0.4 | 5.2 ± 0.6 | 0 | 3850 ± 71 | | 4.6 ± 0.1 | 7.0 ± 0.8 | 6.8 ± 2.7 | 7.4 ± 0.9 |
| 20 | Kent Pear (Conf) | 6.3 ± 0.4 | 9.2 ± 3.5 | 140 ± 8.2 | 1975 ± 96 | 1300 ± 320 | 4.7 ± 0.7 | 7.9 ± 1.3 | 4.4 ± 0.9 | 12.0 ± 4.8 |
| 21 | Kinross Carrot | 14 ± 3.4 | 11 ± 2.3 | 30 ± 5.4 | 1050 ± 220 | 3180 ± 610 | 2.5 ± 0.8 | 45 ± 16 | 2.4 ± 0.8 | 22.8 ± 2.5 |
| 22 | Kinross Carrot | 36 ± 22 | 34 ± 10 | 200 ± 130 | 4320 ± 810 | 9800 ± 1200 | 7.1 ± 2.4 | 9.0 ± 2.8 | | 15.4 ± 8.9 |
| 23 | Kinross Pot (MP) | 115 ± 102 | 84 ± 91 | 160 ± 150 | 4320 ± 2210 | 8800 ± 3000 | 18 ±11 | 5.5 ± 2.5 | | 45 ± 56 |
| 24 | Lancs Carrot | 274 ± 93 | 184 ± 61 | 151 ± 81 | 2090 ± 1080 | 7000 ± 2200 | 50 ± 16 | 7.2 ± 3.0 | 3.5 ± 0.8 | 115 ± 54 |
| 25 | Lancs Beetroot | 293 ± 118 | 156 ± 57 | 720 ± 490 | 5800 ± 2900 | 22000 ± 12000 | 51 ± 22 | | 3.3 ± 1.7 | 92 ± 27 |
| 26 | Lancs Swede | 108 ± 68 | 148 ± 61 | 151 ± 45 | 1300 ± 810 | 5000 ± 1800 | 30 ± 12 | | 3.8 ± 0.6 | 36 ± 19 |
| 27 | Lancs Turnip | 154 ± 268 | 386 ± 634 | 530 ± 650 | 5100 ± 4600 | 20000 ± 18000 | 48 ± 47 | | 25 ± 28 | 187 ± 184 |
| 28 | Lancs Pot (KE) | 21 ± 10 | 26 ± 18 | 118 ± 30 | 2840 ± 290 | 9900 ± 3200 | 4.5 ± 4.8 | 13 ± 16 | 2.3 ± 1.1 | 31 ± 40 |
| 29 | Lancs Pot (Est) | 122 ± 69 | 24 ± 10 | 51 ± 28 | 2400 ± 1100 | 5400 ± 2800 | 5.5 ± 1.4 | 11 ± 6.8 | 2.8 ± 1.6 | 63 ± 31 |
| 30 | Leic Carrot | 47 ± 12 | 126 ± 15 | 270 ± 100 | 1960 ± 460 | 5780 ± 820 | 18 ± 5.2 | 57 ± 15 | 3.4 ± 0.4 | 31 ± 10 |
| 31 | Leic Carrot | 9.1 ± 3.5 | 130 ± 23 | 170 ± 36 | 2960 ± 790 | 8600 ± 1800 | 20 ± 5.9 | 38 ± 8.2 | 5.5 ± 1.6 | 32 ± 15 |
| 32 | Leic Beetroot | 156 ± 96 | 147 ± 78 | 1220 ± 110 | 4160 ± 710 | 18400 ± 2500 | 36 ± 26 | 94 ± 26 | 2.2 ± 1.7 | 58 ± 28 |
| 34 | Leic Pot (MPe) | 104 ± 38 | 59 ± 16 | 89 ± 24 | 2120 ± 230 | 8400 ± 2300 | 23 ± 6.6 | 27 ± 6.3 | 6.0 ± 1.8 | 71 ± 22 |
| 35 | Leic Pot (MP) | 96 ± 60 | 84 ± 74 | 125 ± 24 | 3000 ± 170 | 9800 ± 970 | 18 ± 11 | 11 ± 5.9 | | 40 ± 26 |
| 36 | Leic Pot (KE) | 109 ± 47 | 91 ± 34 | 358 ± 80 | 5200 ± 640 | 8300 ± 1600 | 14.8 ± 4.8 | 45 ± 14 | 1.2 0.2 | 22 ± 10 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 37 | Leic Pot (RKE) | 96 ± 41 | 82 ± 31 | 330 ± 140 | 4420 ± 870 | 7500 ± 1600 | 13.9 ± 4.8 | 46 ± 27 | 1.8 ± 0.8 | 27.4 ± 8.7 |
| 38 | Lincs Carrot | 41 ± 12 | | 96 ± 15 | 1540 ± 130 | 5000 ± 1800 | 44 ± 7.2 | 13 ± 2.4 | 3.0 ± 0.3 | 47 ± 16 |
| 39 | Lincs Beet | 181 ± 78 | | 260 ± 110 | 3540 ± 810 | 11100 ± 7300 | 84 ± 38 | 28 ± 4.0 | 2.9 ± 0.4 | 91 ± 39 |
| 40 | Lincs Beetroot | | 225 ± 44 | 263 ± 56 | 4200 ± 470 | 21700 ± 1700 | 81 ± 41 | 18 ± 2.2 | 4.2 ± 0.5 | 203 ± 45 |
| 41 | Lincs Beetroot | | 263 ± 52 | 235 ± 46 | 2080 ± 530 | 8800 ± 1900 | 127 ± 33 | 29 ± 8.9 | 3.0 ± 1.3 | 152 ± 40 |
| 42 | Lincs Pot (Wilja) | 149 ± 69 | 131 ± 76 | 170 ± 100 | 3500 ± 2000 | 7300 ± 3800 | 15 ± 6.6 | 17 ± 2.6 | 2.8 ± 1.9 | 42 ± 18 |
| 43 | Lincs Pot (Marf) | 262 ± 160 | 86 ± 50 | 88 ± 34 | 2280 ± 270 | 4500 ± 470 | 48 ± 32 | 8.0 ± 3.2 | | 66 ± 40 |
| 44 | Norfolk Apple (Disc) | 6.1 ± 1.6 | 7.9 ± 6.1 | 33 ± 13 | 1200 ± 410 | 800 ± 530 | 2.4 ± 0.6 | 4.7 ± 0.7 | 3.2 ± 0.4 | 6.1 ± 2.9 |
| 45 | Norfolk Pear (Conf) | 5.0 ± 0.5 | 4.4 ± 2.0 | 240 ± 120 | 2300 ± 1100 | 2200 ± 900 | 2.3 ± 0.6 | 6.3 ± 0.5 | 4.5 ± 1.5 | 8.2 ± 2.2 |
| 46 | NI Carrot | 92 ± 16 | 92 ± 19 | 980 ± 480 | 1380 ± 720 | 4420 ± 190 | 16 ± 2.5 | 163 ± 5 | | 74 ± 16 |
| 47 | NI Parsnip | 46 ± 16 | 52 ± 18 | 373 ± 47 | 3250 ± 260 | 4320 ± 730 | 11 ± 3.3 | 82 ± 16 | | 62 ± 23 |
| 48 | NI Pot (Comber) | 55 ± 5.1 | 52 ± 10 | 198 ± 61 | 2000 ± 690 | 4620 ± 2130 | 12 ± 1.0 | 38 ± 18 | | 53 ± 12 |
| 49 | NI Pear (Conc) | 15 ± 1.3 | 22 ± 9.3 | 160 ± 14 | 1750 ± 58 | 4200 ± 420 | 3.1 ± 0.5 | 5.5 ± 1.3 | | 22 ± 1.7 |
| 50 | NI Apple (Disc) | 7.5 ± 1.0 | 7.9 ± 3.7 | 85 ± 29 | 1168 ± 140 | 2600 ± 1200 | 3.0 ± 0.6 | | | 13 ± 3.0 |
| 51 | Perth Beetroot | 52 ± 35 | 45 ± 28 | 332 ± 34 | 6020 ± 580 | 17300 ± 2700 | 16 ± 5.9 | | 4.5 ± 4.0 | 9.3 ± 7.2 |
| 52 | Perth Swede | 180 ± 140 | 139 ± 99 | 165 ± 42 | 1450 ± 340 | 7900 ± 2400 | 29 ± 17 | 28 ± 6.4 | 28 ± 29 | 57 ± 32 |
| 53 | Perth Parsnip | 151 ± 62 | 110 ± 47 | 600 ± 210 | 5600 ± 1100 | 11400 ± 4200 | 27 ± 10 | 186 ± 52 | 14 ± 15 | 68 ± 46 |
| 54 | Perth Carrot | 110 ± 56 | 105 ± 85 | 183 ± 74 | 3700 ± 610 | 9500 ± 2000 | 14 ± 6.5 | 113.3 ± 8.2 | 10.5 ± 8.4 | 26 ±13 |
| 55 | Wales Carrot | 169 ± 96 | | 200 ± 77 | 2900 ± 1100 | 10100 ± 3900 | 174 ± 82 | 108 ± 39 | | 890 ±700 |
| 56 | Wales Parsnip | 130 ± 28 | | 810 ± 250 | 4500 ± 750 | 11600 ± 1100 | 55.4 ± 7.9 | 398 ± 43 | | 164 ± 46 |
| 57 | Wales Swede | 21 ± 5.1 | | 102.0 ± 5.4 | 1500 ± 290 | 8350 ± 760 | 17 ± 5.4 | 26 ± 3.9 | 3.5 ± 1.0 | 25.0 ± 2.7 |
| 58 | Wales Pot (MP) | 64 ± 33 | 46 ± 17 | 112 ± 28 | 3220 ± 510 | 9130 ± 610 | 12 ± 3.5 | 14 ± 4.9 | 5.0 ± 1.3 | 30 ± 11 |
| 59 | Wales Pot (RKE) | 105 ± 30 | 56 ± 16 | 96 ± 14 | 3900 ± 1000 | 11300 ± 3700 | 13 ± 3.3 | 12.3 ± 4.5 | 5.4 ± 0.5 | 56 ± 17 |
| 60 | Suffolk Parsnip | 94 ± 22 | | 410 ± 120 | 1900 ± 1300 | 7900 ± 2100 | 60 ± 10 | 94 ± 39 | | 139 ± 38 |
| 61 | Suffolk Turnip | 252 ± 123 | | 228 ± 86 | 330 ± 170 | 4300 ± 410 | 137 ± 44 | 51 ± 5.3 | | 360 ± 220 |
| 62 | Suffolk Pot (RKE) | 134 ± 95 | 82 ± 47 | 93 ± 26 | 2680 ± 130 | 7000 ± 1500 | 25 ± 17 | 19 ± 1.5 | 5.4 ± 2.2 | 96 ± 67 |
| 63 | Suffolk Pot (RKE) | 112 ± 27 | 68 ± 21 | 110 ± 32 | 3500 ± 1500 | 8180 ± 600 | 20 ± 4.7 | 12 ± 1.9 | 1.5 ± 0.2 | 61 ± 14 |
| 64 | Suffolk Apple (Disc) | 3.2 ± 0.1 | | 44 ± 24 | 1270 ± 170 | | 3.2 ± 0.7 | | | 30 ± 11 |
| 65 | Suffolk Apple (Bram) | | | 22 ± 3.9 | 893 ± 74 | | 1.7 ± 0.6 | | | 10 ± 1.2 |

*Pot = potato, Glouc = Gloucestershire, Lancs = Lancashire, Lincs = Lincolnshire, Leic = Leicestershire, NI = Northern Ireland. MP = Maris Piper, Des = Desiree, Nic = Nicola, Est = Estima, La R = La Ratte, DOY = Duke of York, RKE = Red King Edward, KE = King Edward,ShBk = Shetland Black, SB= Salad Blue, HBR = Highland Burgundy Red, KP = Kerr's Pink,Char = Charlottes, Conc = Concorde, Conf = Conference, Disc = Discovery, Bram = Bramley, MPe = Maris Peer.

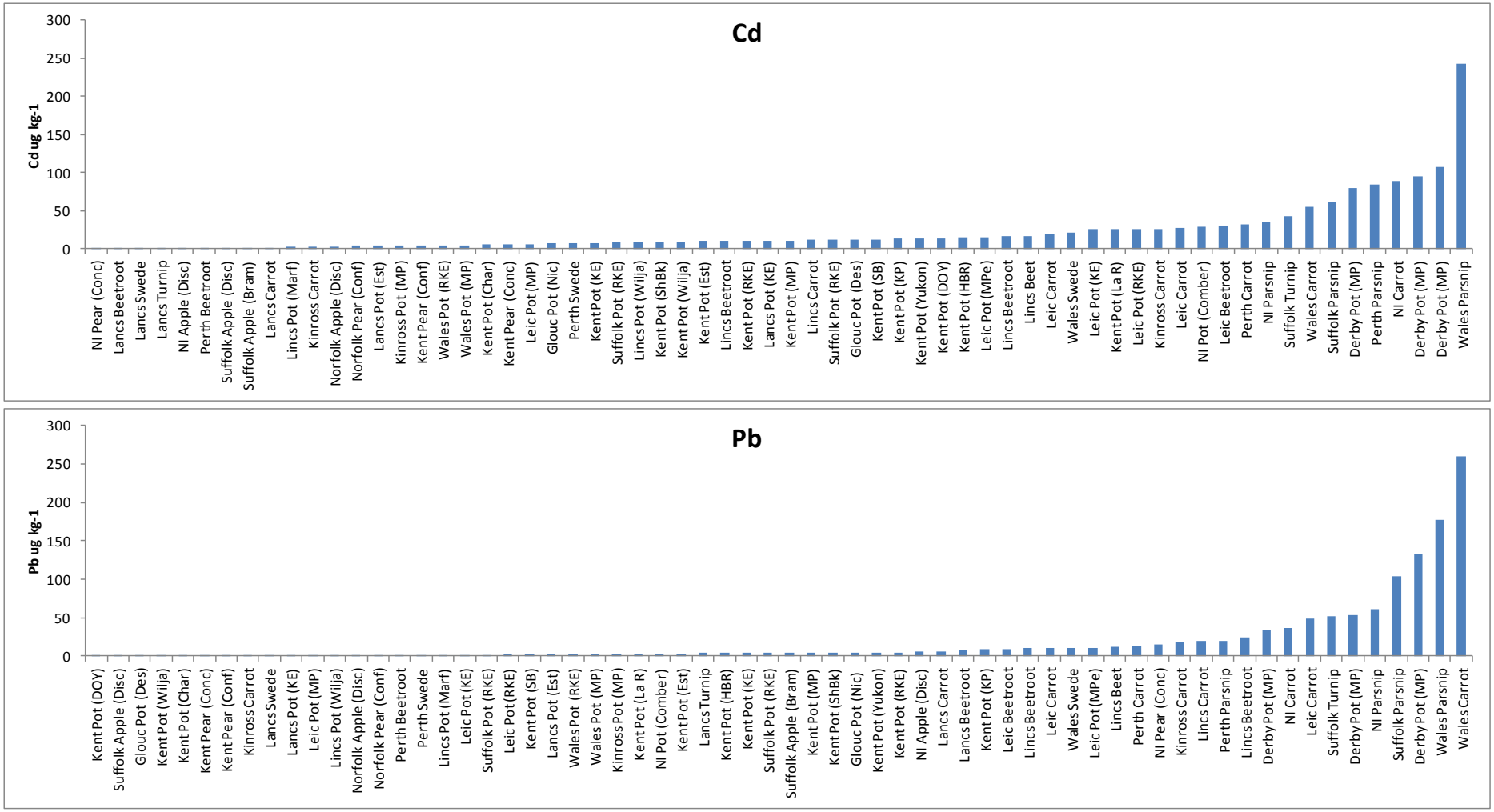


Figure 4.1 Ranked average concentrations of Cadmium and Lead in vegetable and fruits. *Pot = potato, Glouc = Gloucestershire, Lancs = Lancashire, Lincs = Lincolnshire, Leic = Leicestershire, NI = Northern Ireland. MP = Maris Piper, Des = Desiree, Nic = Nicola, Est = Estima, La R = La Ratte, DOY = Duke of York, RKE = Red King Edward, KE = King Edward,ShBk = Shetland Black, SB= Salad Blue, HBR = Highland Burgundy Red, KP = Kerr's Pink,Char = Charlottes, Conc = Concorde, Conf = Conference, Disc = Discovery, Bram = Bramley, MPe = Maris Peer.

Table 4.2 Range and (of average values i Table 2) mean of Flesh and peel in all vegetables and fruits plus average Peel/Flesh Ratios measured digestion ICP-MS

| | V | Cr | Ni | Cu | Zn | As | Cd | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Flesh µg $kg^{-1}$ | | | | | | | | | |
| Min | 3.2 | 4.4 | 22 | 330 | 800 | 1.7 | 3.0 | 1.2 | 6.1 |
| Max | 290 | 390 | 1200 | 6000 | 22000 | 170 | 400 | 50 | 890 |
| Ave | 100 | 90 | 230 | 2800 | 8000 | 30 | 50 | 7.8 | 86 |
| | | | | | | | | | |
| Flesh µg $g^{-1}$ | | | | | | | | | |
| Min | 1.2 | 1.1 | 4.2 | 340 | 130 | 1.0 | 1.0 | 1.6 | 1.0 |
| Max | 43 | 87 | 750 | 3700 | 15000 | 60 | 240 | 22 | 260 |
| Ave | 6.7 | 14 | 124 | 1400 | 5400 | 6.6 | 26 | 6.5 | 25 |
| | | | | | | | | | |
| Peel/Flesh | | | | | | | | | |
| Min | 1.6 | 0.9 | 0.5 | 1.2 | 0.7 | 1.1 | 1.1 | 0.2 | 0.7 |
| Max | 390 | 40 | 9.3 | 8.8 | 6.2 | 290 | 6.5 | 14 | 370 |
| Ave | 55 | 8.2 | 2.7 | 2.4 | 1.7 | 18 | 2.0 | 2.3 | 25 |
| SD | 76 | 8.7 | 1.7 | 1.2 | 1.0 | 42 | 0.9 | 2.5 | 55 |

Table 4.3 Average concentration of elements in cereal crops

| Grain µg $kg^{-1}$ | **V** | **Cr** | **Ni** | **Cu** | **Zn** | **As** | **Cd1** | **Hg** | **Pb** |
|---|---|---|---|---|---|---|---|---|---|
| Kent Wheat | 22 | | 150 | 5400 | 33000 | 9 | 60 | 21 | 7.6 |
| Notts Wheat | 20 | | 45 | 5900 | 28000 | 16 | 110 | 20 | 12 |
| Lincs Wheat | 21 | | 38 | 6600 | 42000 | 10 | 34 | 19 | 4.6 |
| Yorks Wheat | 18 | | 93 | 7400 | 39000 | 6 | 130 | 16 | 2.3 |
| Perth Wheat | 33 | 18 | 120 | 6400 | 23000 | 11 | 57 | 13 | 10 |
| Yorks Barley | 17 | 42 | 120 | 3100 | 20000 | 14 | 38 | 1.6 | 25 |
| Leic Wheat | 15 | 37 | 170 | 5000 | 33000 | 12 | 110 | | 34 |
| NI Wheat | 31 | 65 | 820 | 3400 | 17000 | 17 | 25 | | 47 |

*Notts = Nottinhamshire, Lincs = Lincolnshire, NI = Northern Ireland, Leic = Leicestershire, NI = Northern Ireland.

Tables 4.4 and 4.5 detail the results obtained for samples collected in Derbyshire and Wales where Maximum Levels (Table 1) were exceeded for some specimens. Peel concentrations were higher than those recorded in the flesh and substantially higher than ML's established for peeled potatoes. In Derbyshire, MLs were exceed in peeled potatoes in 4 of the 15 samples measured. Mean values were marginally below ML.s but with high standard deviation. Carrot from South Wales exceeded MLs for Pb whilst parsnip exceeded MLs for both Cd and Pb. Figure 4.1 compares Cd and Pb concentrations in the soil collected during this work, showing the Derbyshire solid was elevated in Cd and Pb. The soil collected at the site in Wales where carrots and parsnips were collected was also elevated in Cd and Pb. The Derbyshire and Wales regions are, known to be hotspots for soil Cadmium and Lead due to historic mining and smelting activities.[19] Neither location was a large scale producer, however, meaning the overall impact to dietary intake would be low.

Suffolk Parsnip (Table 4.2 #60) showed average Pb close to ML, but showed low soil Pb. Turnip and potato from the same location showed lower lead, indicating this was an unusual result.

| | Flesh | | | Peel | |
|---|---|---|---|---|---|
| | Cd | Pb | | Cd | Pb |
| Derby Pot (MP) 1 | 94 | 210 | | 160 | 370 |
| Derby Pot (MP) 2 | 76 | 14 | | 210 | 760 |
| Derby Pot (MP) 3 | 66 | 16 | | 170 | 700 |
| Derby Pot (MP) 4 | 61 | 12 | | 120 | 160 |
| Derby Pot (MP) 5 | 100 | 14 | | 150 | 280 |
| Derby Pot (MP) 6 | 150 | 170 | | 190 | 780 |
| Derby Pot (MP) 7 | 110 | 470 | | 280 | 740 |
| Derby Pot (MP) 8 | 51 | 77 | | 110 | 380 |
| Derby Pot (MP) 9 | 84 | 21 | | 180 | 240 |
| Derby Pot (MP) 10a | 88 | 28 | | 170 | 190 |
| Derby Pot (MP) 10b | 89 | 31 | | 150 | 230 |
| Derby Pot (MP) 11 | 130 | 15 | | 280 | 330 |
| Derby Pot (MP) 12 | 89 | 100 | | 150 | 270 |
| Derby Pot (MP) 13 | 91 | 20 | | 210 | 280 |
| Derby Pot (MP) 14 | 150 | 17 | | 270 | 690 |
| Derby Pot (MP) 15a | 78 | 18 | | 170 | 260 |
| Derby Pot (MP) 15b | | | | 170 | 200 |
| Mean | 94 | 77 | | 185 | 404 |
| SD | 29 | 121 | | 51 | 228 |

Table 4.4 Concentration of Cd and Pb in Peel and Flesh of individual Maris Piper potatoes collected from Derbyshire. Shaded areas indicating specimens exceeding ML's. a and b notations refer to duplicate analysis of one individual vegetable.

| | Flesh | | | Peel | |
|---|---|---|---|---|---|
| | Cd | Pb | | Cd | Pb |
| Wales Carrot 1 | 83 | 160 | | 140 | 1900 |
| Wales Carrot 2 | 54 | 370 | | 98 | 1300 |
| Wales Carrot 3 | 61 | 250 | | 150 | 630 |
| Wales Carrot 4 | 51 | 220 | | 100 | 430 |
| Wales Carrot 5a | 39 | 280 | | 51 | 180 |
| Wales Carrot 5a | 42 | 280 | | | |
| Mean | 55 | 260 | | 108 | 888 |
| SD | 16 | 70 | | 39 | 702 |
| | | | | | |
| Wales Parsnip 1 | 270 | 190 | | 390 | 140 |
| Wales Parsnip 2 | 260 | 180 | | 390 | 160 |
| Wales Parsnip 3 | 260 | 200 | | 460 | 160 |
| Wales Parsnip 4 | 180 | 140 | | 340 | 120 |
| | | | | 410 | 240 |
| Mean | 243 | 178 | | 398 | 164 |
| SD | 42 | 26 | | 43 | 46 |

Table 4.4 Concentration of Cd and Pb Peel and Flesh of individual Carrots and Parsnips from Derbyshire. Shaded areas indicating specimens exceeding ML's. a and b notations refer to duplicate analysis of one individual vegetable.

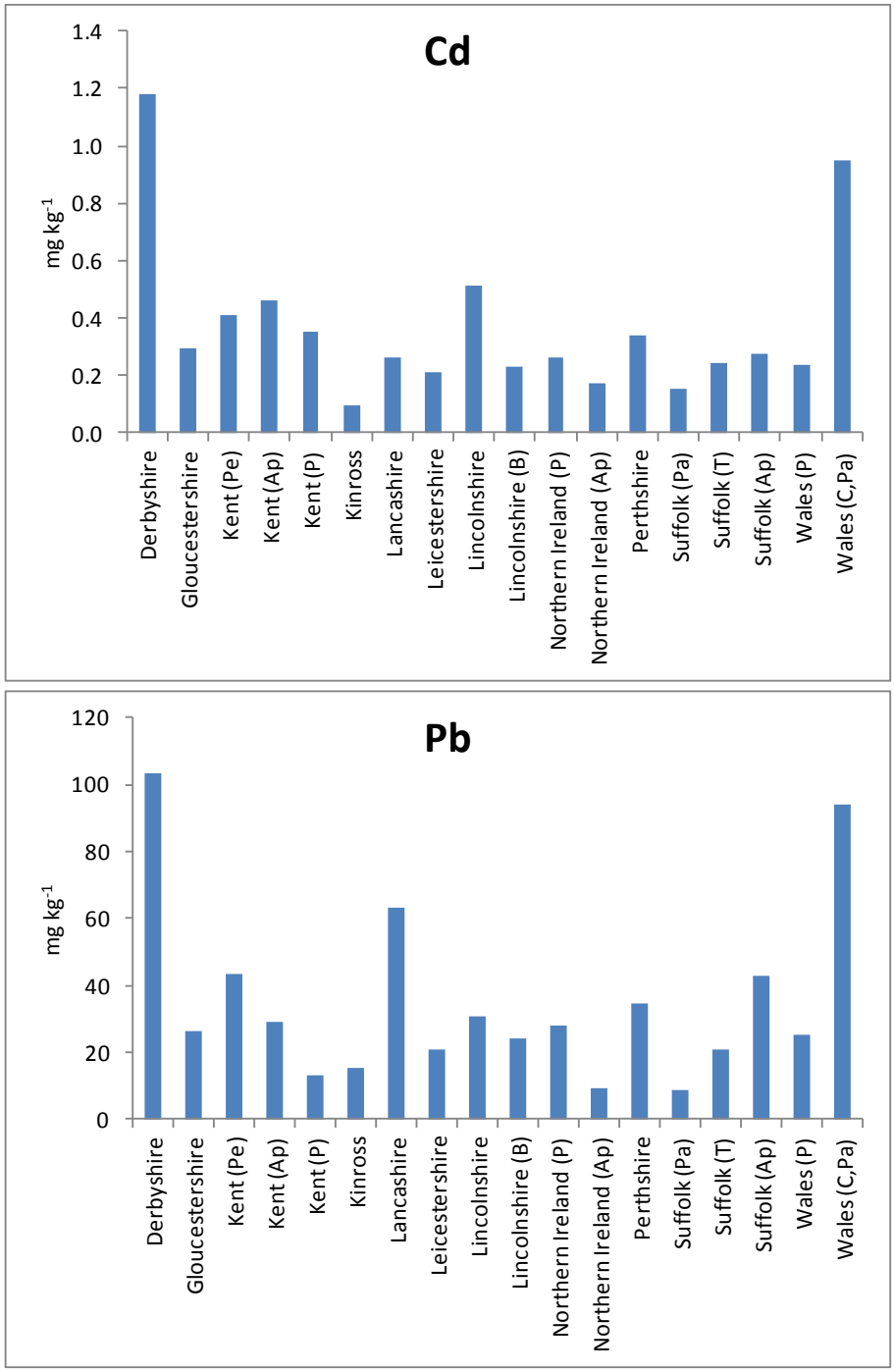


Figure 4.2 Average concentration of Cd and Pb in in soil sorted by location. (P=potato, Pe = Pear, Ap = Apples, B = Beet, Pa = Parsnip, T = Turnip, C = Carrot where >1 samples were taken in each county. Cereal crop data not included).

4.4 LA-ICP-MS image of Derbyshire Potato with 'calibration'.

*A potato* specimen from Derbyshire (Derbyshire potato 11) was selected for laser ablation imaging analysis as described above. An attempt to calibrate the measurements was made via analysis of FAPAS(r) test material 07188 Vegetable Puree using the target values for Cd (245 µg $kg^{-1}$) and Pb (311 µg $kg^{-1}$). Average Cd measured by LA-ICP-MS was about 350 µg $kg^{-1}$ in flesh and 700 µg $kg^{-1}$ in peel compared to digestion ICP-MS values of 130 µg $kg^{-1}$ and 280 µg $kg^{-1}$, respectively. Average Pb measured by LA-ICP-MS was about 50 µg $kg^{-1}$ in flesh and 1000 µg $kg^{-1}$ in peel compared to digestion ICP-MS values of 15 µg $kg^{-1}$ and 330 µg $kg^{-1}$, respectively. These results indicate the LA-ICP-MS calibration overestimated the amount of Cd and Pb present. The overall trend was consistent with the digestion ICP-MS data, however. Cd was elevated in both flesh and peel whilst Pb was substantially lower in flesh than peel. The images show the highly localised nature of Cd and Pb accumulation in the peel. The area of potato sampled was effectively 1 $cm^2$, with an estimated depth of 100 µm, peel forming only a fraction of the whole. 1 $cm^3$ of potato has a weight of about 1.2 g (approx. the amount samples for digestion ICP-MS) indicating the LA samples about 0.012 or less material (and much less for peel), reducing how representative the measurements are. The image took 4 hours to acquire on LA-ICP-MS plus data processing and is thus not suitable for measurement of large quantities of sample. Additional work improving the calibration scheme would be valuable, however, in particular creating several matrix matched calibration standards. Again the use of cryo LA-ICP-MS would likely be advantageous.

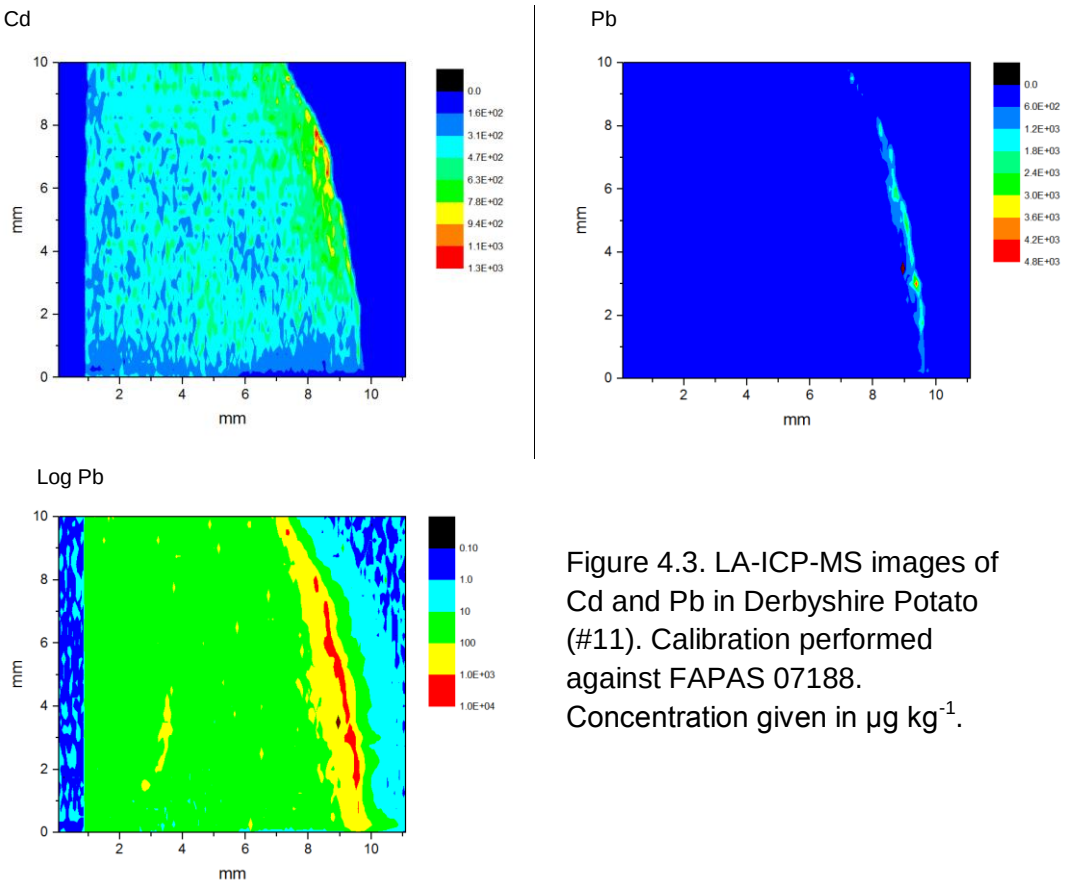


Figure 4.3. LA-ICP-MS images of Cd and Pb in Derbyshire Potato (#11). Calibration performed against FAPAS 07188. Concentration given in µg $kg^{-1}$.

## 5. Overall Conclusions

- Laser ablation – inductively coupled plasma – mass spectrometry measurement of the micrometer scale spatial distribution of trace elements in UK grown root vegetables and fruit showed that Al, V, Cr, Ni, Mn, Fe, Cu, Zn, As, Cd, Hg, Pb and U were frequently elevated in the skin with respect to the flesh.

- The width (depth) of the skin accumulation was less than 0.5 mm. Images of the micrometer scale spatial distribution of elements in vegetable and cereal grains were produced. They showed the heterogeneous nature of elements in the vegetable skin.

- Images of the cereals indicated elevated levels of trace elements in bran and germ.

- LA-ICP-MS is not presently suitable for quantitative analysis as (1) work to create effective matrix matched calibration standards is required and (2) the small sampling area of LA-ICP-MS and slow measurement rate limits the effectiveness of the method.

- The LA-ICP-MS data was confirmed by peeling the vegetables and determining element concentration by solution ICP-MS analysis following acid digestion.

- In most cases the level of heavy metals in vegetables was low and not of cause for concern.

- Of 15 potatoes collected from Derbyshire, 2 specimens exceeded Maximum Levels (0.1 mg $kg^{-1}$) for Cadmium, 2 specimens exceeded ML's (0.1 mg $kg^{-1}$) for Lead, and 2 specimens exceeded ML's for both elements. Neither location was a large scale producer.

- All specimens of carrot (n=5) collected in one site in Wales exceeded ML's for Lead whilst parsnip from the same site exceeded ML's for Cadmium and Lead.

- Soil samples collected in Derbyshire and South Wales were elevated in Cd and Pb and were the likely source of higher vegetable concentrations of Cd and Pb

## 6. Recommendations for future research

- Identify calibration materials and standards reference materials for ICP-MS and investigate if LA-ICP-MS could be used quantitatively (maybe using multiple surface analysis to address heterogeneity). This would avoid need for follow-up ICP MS analysis for quantification.
- Investigate the use of *cryo* LA-ICP-MS (a sample cell held at <0°C) for improved imaging, and quantitative analysis of fruit and vegetables.
- The elevated levels of Cadmium in Lead in root vegetables from Derbyshire and Wales requires further study as the number of samples collected in each location was small.
- Investigation of the levels of metals in fruit, vegetables and crops imported into the UK from overseas.

## Acknowledgements

The authors would like to express their gratitude to Sabine Freitag for project planning, Annika Koch and Shaun Lancaster (University of Aberdeen) for assistance with sample preparation and analysis; and to Paul Jenkins (FSA) for support throughout the project.

**References**


1. G. Norton, A. Mestrot and A. Meharg, Arsenic speciation in fruit and vegetables grown in the UK, Food Standards Agency Final Report, FSA241003 (2012).

2. G. Norton, A. Mestrot and A. Meharg, Total cadmium, copper, lead and zinc in fruit and vegetables grown in the UK, Food Standards Agency Final Report, FSA241003 (2012).

3. G. Norton, C. Deacon, A. Mestrot, J. Feldmann, P. Jenkins, C. Baskaran and A.A. Meharg, Arsenic Speciation and Localization in Horticultural Produce Grown in a Historically Impacted Mining Region, *Environ. Sci. Technol.* 2013, **47**, 6164−6172.

4. B. J. Fryer, S. E. Jackson, H. P. Longerich, The design operation and role of the laser-ablation microprobe coupled with an inductively coupled plasma – mass spectrometry (LAM-ICP-MS) in the Earth Sciences. *The Canadian Mineralogist* 1995, **33**, 303-312.

5. J. Feldmann, A Kindness, P Ek, Laser ablation of soft tissue using a cryogenically cooled ablation cell, *J. Anal. At. Spectrom.* 2002, **17**, 813-818.

6. J. S. Becker, M. Zoriy, A. Matusch, B. Wu, D. Salber, C. Palm, J. S. Becker, Bioimaging of metals by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *Mass Spectrometry Reviews* 2010, **29**, 156-175.

7. J. S. Becker, A. Matusch, J. S. Becker, B. Wu, 1, C. Palm., A. J. Becker, D. Salber. Mass spectrometric imaging (MSI) of metals using advanced BrainMet techniques for biomedical research, *Int. J. Mass Spectrom.* 2011, **307**, 3-15.

8. E. Hoffmann, (2. Liidke, H. Scholze, H. Stephanowitz. Analytical investigations of tree rings by laser ablation ICP-MS, Fresenius J Anal Chem (1994) 350:253-259.

9. D. J. Bellis, K. Satake, C. W. McLeod. A comparison of lead isotope ratios in the bark pockets and annual rings of two beech trees collected in Derbyshire and South Yorkshire, UK, *Sci. Total Environ.* 2004, **321**, 105–113.

10. M. Siebold, P. Leidich, M. Bertini, G. Deflorio, J. Feldmann, E. M. Krupp, E. Halmschlager, S. Woodward. Application of elemental bioimaging using laser ablation ICP-MS in forest pathology: distribution of elements in the bark of Picea sitchensis following wounding, *Anal. Bioanal. Chem.* 2012, **402**, 3323–3331.

11. J. S. Becker, R. C. Dietrich, A. Matusch, D. Pozebon and V. L. Dressler, *Spectrochimica Acta Part B: Atomic Spectros.* 2008, **63**, 1248–1252.

12. B. Wu, M. Zoriy, Y. Chen and J. S. Becker, *Talanta* 2009, **78**, 132–137.

13. K. Baba, E. Watanabe, H. Eun and M. Ishizaka. Direct determination of cadmium in rice flour by laser ablation-ICP-MS, *J. Anal. At. Spectrom,* 2003, **18**, 1485–1488

14. A. A . Meharg, E. Lombi, P. Williams, K. G. Scheckel, J. Feldmann, A. Raab, Y. Zhu, R. Islam. Speciation and Localization of Arsenic in White and Brown Rice Grains, *Environ. Sci. Technol. 2008*, **42**, 1051–1057.

15. I. Cakmak, M. Kalayci, Y. Kaya, A. A. Torun, N. Aydin, Y. Wang, Z. Arisoy, H. Erdem, A. Yazici, O. Gokmen, L. Ozturk, W. J. Horst. Biofortification and Localization of Zinc in Wheat Grain, *J. Agric. Food Chem.* 2010, **58**, 9092–9102.

16. Y. X. Wang, A. Specht and W. J. Horst. Stable isotope labelling and zinc distribution in grains studied by laser ablation ICP-MS in an ear culture system reveals zinc transport barriers during grain filling in wheat, *New Phytologist* 2011 189: 428–437.

17. B. Wu, F. Andersch, W. Weschke, H. Weber, J. S. Becker. Diverse accumulation and distribution of nutrient elements in developing wheat grain studied by laser ablation inductively coupled plasma mass spectrometry imaging, *Metallomics*, 2013, **5**, 1276-1284.

18. D. J. Bellis, R. Santamaria-Fernandez. Ink jet patterns as model samples for the development of LA-ICP-SFMS methodology for mapping of elemental distribution with reference to biological samples, *J. Anal. At. Spectrom.* , 2010, **25**, 957-963.

19. B. G. Rawlins, S.P. McGrath, A. J. Scheib, N. Breward, M. Cave,T. R. Lister, M. Ingham, C. Gowing, S. Carter 2012. The Advanced Soil Geochemical Atlas of England and Wales. (Keyworth, Nottingham: British Geological Survey.)