REDUCING COSTS USING THE FIELD PORTABLE XRF ANALYSER DURING THE ASSESSMENT, REMEDIATION AND VALIDATION OF A 3 HA ORCHARD IN HASTINGS, HAWKES BAY

Drs. Ben Keet and Royston Gillett, Geo & Hydro – K8 Ltd, e-mail: ben@benkeet.com

Abstract

The redevelopment of a 3 Ha Orchard into a 33 lot subdivision in Hastings, Hawkes Bay, posed a number of challenges due to extensive contamination from historic pesticide use in particular lead arsenate. Previous remedial works in the area had shown very limited relation between hot spots and objects visible on old aerial photographs with the exception of spray sheds. Over a century of orcharding, preceded by sheep farming had seen many changes in property use, tree settings, position of auxiliary buildings and boundary adjustments.

A cooperative client, who's life motto 'do it once, do it right' had this reinforced by observing second and third rounds of remediation by soil mixing on surrounding properties. He thus agreed to a thorough site investigation, but on a sharp budget. The resulting quality site data have proved invaluable throughout the project and the remediation was carried out according to plan, on budget and with a minimum of surprises.

The use of a field portable XRF analyser allowed in situ analysis for heavy metals to be completed in 20 seconds per analysis. Directing the remediation process was greatly speeded up while the excavated volume could be greatly reduced. The resulting 'BMX-track' like landscape could be validated with much greater confidence by combining the XRF and laboratory analysis.

Introduction

Reducing costs involved in the site assessment, remediation and validation of contaminated land while improving or at the very least maintaining standards is the ultimate objective of any contaminated land practitioner. However these two objectives are often in conflict with one another. The client demands reduced consulting, laboratory and earthwork costs. Regulatory bodies imposing stricter guideline levels, introducing audit systems while restricting disposal of contaminated soil at land fill sites.

Higher quality at lower cost, it's up to the consultant to deliver.

In Europe as far back as 2002 the NICOLE workshop[i] concluded that for too many years there has been a 'misplaced emphasis' by the contaminated land community on analytical precision of the samples taken for laboratory analysis rather than focusing more on the error involved in sampling which has a far greater effect. The importance of finding a cheaper on site measurement technique and off-site analysis for validation was stressed. Obviously on site screening is preferable whenever possible as it is quicker and cheaper and if numerous samples can be taken it reduces the uncertainty. You can be 90 % wrong if you don't take enough samples. Consequently there is a real demand for a portable, analytical instrument that can be used on site.

In 1997 Ariadni Argyraki of Imperial College, London after using a portable XRF concluded[ii]: "the technique has proved to be a useful and fit-for-purpose, powerful tool, capable of giving precise and very rapid analytical results for the determination of Pb concentrations in soil" The differences between field analysis were investigated and the need to correct for soil moisture and sample compaction / surface roughness identified. Once correction for this was made "the bias for lead measurements was effectively reduced to a statistically insignificant level".
Colleagues of the Open University and Imperial College continued the work with the XRF to study its usefulness[iii] at historically contaminated sites. One of them, Michael Ramsey, working on sampling strategies from the University of Sussex concludes in 2006[iv] "studies have repeatedly shown that it is the sampling phase that generates the highest component of uncertainty." An investigator may also choose to "employ more innovative sampling methods, such as *in situ* measurement strategies that can significantly reduce the overall time taken to complete the survey". He also discusses a new approach "The 'optimized contaminated land investigation' (OCLI) method that can be used to balance the site-specific variables of any given investigation, such as the measurement costs against the level of uncertainty and costs that may arise from misclassification. This provides an objective and traceable judgement of whether the measurements are fit-for-purpose."

At this point he reaches the same conclusion as Deana Crumbling (US EPA) in 2000 who developed the TRIAD methodology[v]. She also worked extensively on the sampling methodology[vi] and sample representativeness[vii].

As in the UK the introduction of field analysis techniques in the US was slow and even in 2003 the debate continued[viii] and the cost-effectiveness of the TRIAD approach was discussed at length[ix].

So even though Argyraki et al in 1997 showed that a high degree of correlation ($r^2 = 0.83$) could be achieved with a XRF during field analysis, a major European study funded by CL:AIRE concluded in 2008: 'the XRF is a powerful tool useful for screening sites for major metal contaminants and acknowledges that it is a rapid and low cost alternative'.
In comparing the field portable XRF against laboratory analysis they defined Pb analysis as 'definitive' meaning that the correlation is statistically similar ($r^2 = 0.89$) [x]. Similar results have been found in New Zealand by Keet[xi].

Over the last 13 years the field portable X-ray fluorescence analyser (FP-XRF) is emerging as an extremely useful tool for analysis of heavy metal concentrations in contaminated land. The XRF analyser works by measuring the florescence spectrum of X-rays emitted when metal atoms are excited by an X-ray source. The energy of the emitted X-rays identify the metal in a sample and the intensity indicates their concentration. In modern instruments each test typically takes 20 seconds, displaying metal concentrations in wet weight immediately. A wide range of elements can be detected from Arsenic to Zinc, all at the same time (20 sec.)

This case study intends to investigate the cost effectiveness of using a XRF analyser in combination with limited laboratory analysis compared to using only standard laboratory analysis.

Site Assessment stage

The maximum budget for the site assessment was negotiated to be $ 30,000.- ex GST.

Evaluating the options the following initial budget calculation was made:

Time and mileage plus disbursement for travel	$ 1,000.-
Meetings with client, the engineers and council	$ 3,000.-
Reporting	$ 6,000.-
Taking samples at objects / hot spots, 10 Lab analysis (Metals, OCPNsc)	$ 4,000.-
Remaining to characterise the diffuse contamination on 3 ha	$ 16,000.-

This equates to less than $ 2.-/m^2.
To get the best results for the money put in a structured approach is required.

Assuming the setting out in open field, taking samples, placing sample in jars, labelling jars, filling out analysis request forms – COC, courier samples to lab, interpreting the results, plotting these on maps and then setting out the resulting contaminant contours in the field takes $ 22.50/sample. Laboratory costs (As, Pb, Cu analysis [screen]) adds $ 57.50/sample. This brings the total to $ 80.-/sample, thus 200 samples can be taken and analysed. The analytical package could be refined, as it does not allow for broad acre OCPN screening, adding costs, and potentially the Cu could be left out of the analytical package, reducing costs. For argument sake we keep the analytical cost at the $ 57.50 as set out above.

This results in 1 sample per 150 m^2 assuming 1 layer sampling or 1 per 300 m^2 for 2 layer sampling. HDC recommendation is to sample 0 -75 as a minimum and the following 75 mm or thicker layer for further characterisation. So leaving the uncertainty wether the base of the contamination can be established by soil colour (the sub-base is yellow, while the soil is generally grey – brown), sampling 2 layers is an absolute minimum (0 – 75, 75 – 200 mm)

One sample per 300 m2 results in a grid size of 17.5 x 17.5 m or rounded off 18 x 18 m. From past experience on other orchards in the area it is known that hotspots with arsenic concentration up to 200 mg/kg may exist anywhere in an orchard. Due to landfill closure for contaminated soil the preferred remedial option in Hawkes Bay is to remediate low level contaminated soil by soil mixing. Using the following table the effect of missing a hot spot and mixing it into the bulk of the soil can be determined.

In this table the 'final concentration' is set at 25mg/kg instead of the guideline concentration of 30 mg/kg (for arsenic) as in practice the aim of a mixing operation is to obtain soil in which the maximum concentration found is to be below the guideline concentration. Even well mixed soil will have a variability of +/- 5 mg/kg.

It is assumed that samples representing layers of 100 mm, which in practice gives 150 mm 'layers' due to sampling variability.
- this is only applicable for near surface related contaminants, arsenic / pesticides (DDT, Dieldrin), where usually 3 - 4 layers are sampled
- for deeper contamination (fuel, central sheep-dip area, farm-tips) the sampling may extend much deeper and is very much site specific.

And finally in the table it is assumed the hotspots are 'square' and equal to one grid area, while in practice they are more likely to be oval and can have an area of up to 1.5 times the area of the grid square.

Calculation of potential contamination capacity of a hotspot when mixed into soil at 'background' concentration							
	grid size :	6 x 6	12 x 12	18 x 18	24 x 24	30 x 30	(m)
	grid area :	36	144	324	576	900	(m2)

hotspot	background concentration	final conc.	mixing	5.4	21.6	48.6	86.4	135	grid volume at 150 mm
mg/kg	mg/kg	mg/kg	factor	volume of background soil required to dilute hotspot to 'below guideline / final concentration' in m3 ?etc					
200	4	25	8	45	180	405	720	1125	
200	8	25	10	56	222	500	889	1390	
200	12	25	13	73	291	654	1163	1817	
200	16	25	19	105	420	945	1680	2625	
200	20	25	35	189	756	1701	3024	4725	
200	24	25	175	945	3780	8505	15120	23625	

Due to the wide application of orchard sprays even non-sprayed areas in the area investigated have topsoil background levels of around 12 – 16 mg/kg arsenic. Using 18 x 18 grid cells missing a hotspot in just a single layer of 150 mm can result in the need to use up to 945 m3 of ‘background’ topsoil to dilute the hotspot to below guideline levels.

At a topsoil thickness of 200 mm this means the topsoil from an area of close to 5,000 m^2 would be needed to dilute such a hotspot down. Thus when all topsoil in the orchard would be at local ‘background’ level of max. 16 mg/kg arsenic, 6 hotspots of this size would cause the total volume of topsoil, after mixing to be over the guideline value.

As the topsoil in orchards contains often more than 16 mg/kg arsenic, this ‘chance’ turns into a reality at most sites. This ‘nightmare’ scenario has occurred on at least 4 of the 6 subdivisions in the area where remediation was completed before this project started.

Clearly a smarter approach was needed to increase the certainty of detecting smaller hotspots.

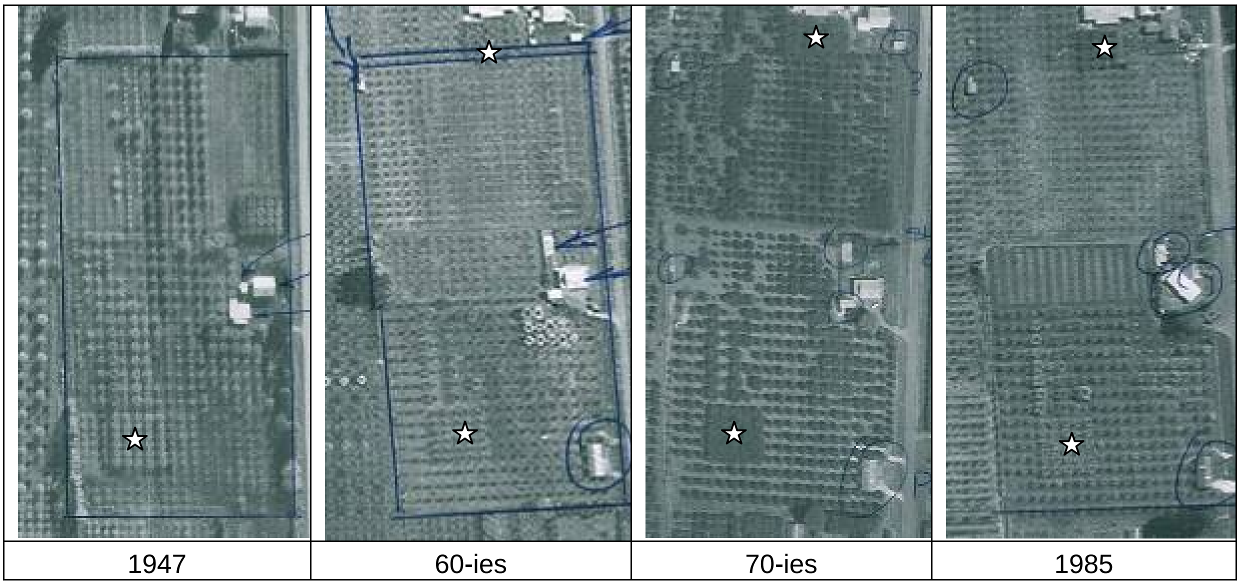
Using the portable XRF analyser, analysis for arsenic and other metals can be carried out in 20 seconds per sample. As the iPAQ computer on the analyser separates the ‘detected’ from the ‘non detected’ metals, a single glance at the screen is sufficient to see As, Cu, Pb, Zn and others if detected at significant levels. Analysis almost keeps pace with the hand augering of the samples.

Based on some trial auger holes it was found at places topsoil extended to 600 mm, likely to coincide with filled in tree stump holes. Sampling depth was determined to be 0 – 700 mm in 4 layers (0 – 75, 75 – 200, 200 – 400, 400 – 700mm). Drilling and analysis of a few boreholes was timed at about 4 minutes per borehole (4 XRF results including entering into data-logger and leaving a colour mark indicating contaminant level). Using a 2 man field crew at approx. $ 200.-/hour, each borehole with 4 analysis would cost $ 13.50.- or $ 3.35 per analysis results ‘plotted directly on the site’.

The $ 16,000.- now allowed well over 1000 sample points down to 700 mm with over 4,000 analysis to be carried out with money left over for delays and some lab analysis to correlate the XRF readings.
It was decided to drill 24 boreholes on each of the 38½ lot sized[1] sections (approximately 800 m^{2}). In total about 924 boreholes were drilled on a grid of just under 6 x 6 m. This brought the total number of samples analysed to 3,696.

The risk of undetected hotspots has been dramatically reduced. Due to the 4 layer system certainty was obtained on the depth of contamination. Maximum undetected hotspot size was deduced from over 100 m^{3} (hotspots in the 2 sample system could be well over 300 mm thick), to about 5 m^{3} a 20 fold, or 2000% decrease.

When the project was awarded the TRIAD approach was followed starting with an assessment of the aerial photographs.



1947 60-ies 70-ies 1985

Figure 1: Aerial photographs. The star indicates the suspected pear trees

Experienced had learned that elevated topsoil readings can be expected near spray sheds, water wells (sprayer filling) and blocks with large trees, such as pear trees. The spray shed appeared outside the subdivision area and based on the determined 6 x 6 m grid the pear block would show up automatically. After the assessment of the orchard the spray shed area was included in the assessment.

Anecdotal evidence was collected from owner, neighbours and previous owners. Besides some water logging problems in an elongated low area located behind the house and sheds on the middle of the photos, very little information was available. Sheep yards and sheep-dip were mentioned, however agreement was reached these were located across the road and demolished prior to the 30-ies.

So a first step conceptual site model was made based on available information.

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[1] 33 lots, 3 reserves (one of 1 ½ lot size) and 4 lot sized road sections results in 38½ lot sized sections.

Figure 2 2005 aerial photo with identified potential hotspots, scale bar = 150 m.

The first step conceptual site model CSM-1 shows object related potential hotspot areas:

S for potential hotspots related to structures
The 2 small structures on the left are pump sheds
The 2 sheds close to the house in the middle are a stable and a garage and possibly a spray shed
The shed at the bottom of the picture was last used as packing shed

P for potential hotspots related to Pear trees

From the historical aerial photographs and this more recent one it is easy to see the significant variability of soil / vegetation colours over the site.

The Heretaunga plain soils are deposited by a breaded river system and soil types can vary significantly at points less than 5 meters apart[xii] (Griffith, 1997 and 1999).

Keeping these hotspots in mind the site assessment has been carried out using a 6 x 6 meter grid.

Sampling and analysis was undertaken during a 2 week period. This resulted in the pattern of contaminant levels sketched on the map on the left. This is the conceptual site model 2 (CSM 2).

On this map there are 4 levels of arsenic indicated:

green shaded :	lower than 20 mg/kg
green cross hatched:	20 – 40 mg/kg
brown intermittent shading:	40 – 95 mg/kg
red shading:	over 95 mg/kg

(figures in red: depth of arsenic contamination)

Comparison with the CSM 1 map (above) shows two hotspots more or less coinciding with the lower pear block.
The upper pear block has likely been much larger in the past (pre-1950), as a large 'square' has arsenic up to 95 mg/kg with 3 hotspots.
The low laying area behind the house in the middle appears to have accumulated fines with attached arsenic and a similar lower strip is found towards the left of the map. Smaller hotspots on lots 32, 34, 6, 13, 14 and 4 may have been missed with a 30 x 30 m sampling grid, while the other hotspots likely would have been poorly defined, requiring a further investigation.

Clearly at this point the XRF has provided a higher quality investigation at comparable or taking the likely need for a further investigation into account, lower cost. In the site assessment report correlation with laboratory analysis of the individual metals As, Cu, Pb and Zn is made and after correction for soil moisture the correlation is within 4 % as has been published elsewhere [xi].

Remediation

Off-site disposal of soil to the local landfill is strongly discouraged in the Hastings District. As an alternative the future council reserves on subdivisions can be utilised as miniature landfill sites. Soil with a significant level of contaminants can be buried in these reserves as can be seen in the following table taken from the Plan Change 28 of Hastings District Council.

Concentrations in mg/kg dw	Residential soils	Parks & Reserves	Suitable for burial within reserve area under 150 mm of 'Parks & Reserves' soil.
Copper	2300	No limit	No limit
Lead	400	400	400
Arsenic	30	95	190
Total DDT	25	50	100

Thus the remediation phase was started by excavating a significant section of the reserve areas to make space for the hotspot soil. Arsenic concentrations over 190 mg/kg had only been found in a few isolated samples, and soil from those areas was mixed before being dumped in the reserve pits.

Next step was to excavate the hotspot areas (marked red on the CSM 2 map.

A number of areas required special attention. On day 3 of the remediation project a pile of ashes was noticed which appeared to have been the wood from some apple crates burned by one of the neighbours in an already excavated area the night before. Extreme arsenic concentrations (> 100,000 mg/kg) were measured (see picture on right).

Fortunately the ashes were discovered before the main site earthworks took place, and were removed by the neighbour effectively.

A quick XRF check revealed extreme copper, chromium & arsenic concentrations in some ashes.

Many of the hotspots marked on version 2 of the CSM were quite accurate, however as can be expected many had small lobes of relatively high contaminated soil at the edges or just a little bit deeper (see pictures on the following page.) The XRF proved itself invaluable in these rapid assessments, which would otherwise cause days of delay (and remobilisation of the contractor).

A lobe with 155 mg/kg As still to be taken out

Here As contamination removed to a depth of 0.7 m

Using the XRF it was made certain the maximum remaining concentration on the site was lower than 95 mg/kg. At this point ‘scraper tracks’ were painted on the surface: solid blue tracks where contaminant levels were 40 – 95 mg/kg As, intermittent blue lines where As levels were 20 – 40 mg/kg (‘neutral’) and white lines indicated tracks over areas with As levels below 20 mg/kg. One 50 ton motor scrapers would pick-up soil over a blue track and lay this out in a 50 mm layer on the mixing pile and the second motor scraper would pick-up a white marked track and overlay the blue marked soil with a 50 mm layer of white marked soil.

After a full layer is laid out over the mixing pile of 120 x 18 m these layers were mixed thoroughly using two disking units. When mixing was deemed complete the surface of the mixing pile was tested with the XRF at 30 – 50 locations per layer. Paint spots indicate ‘acceptable’ a circle means ‘more mixing and a cross means ‘remove from mix pile’. Removal was done with the motor scrapers and that soil was laid out next to the mix pile, inter-bedded with ‘clean’ material and then re-placed on the mix pile. Well over 100 layers were brought onto the mix pile, raising it to 6 – 7 meters height.

Validation with XRF of disked layer in progress. Temporary mix-pad in the background.

During the 3 weeks of excavating the hotspots, followed with scraping of medium contaminated and uncontaminated soil, and placing these in thin layers on the mix-pile to be mixed by disking, approximately 3000 XRF analysis were carried out, about one XRF analysis every 2.5 minutes.
As a result the sub-base validation confirmed the remediation had been successful.
Regardless of the impossibility to have turned around such a large number of samples using a remote laboratory the cost only analysing for arsenic (while the XRF tested for all 4 metals of concern), would have been more than $ 120,000,-. Even analysing only 10% of the samples would have been more than the XRF charges (approx. $ 500.-/day).
The US method 6200 recommends 1 in 10 samples to be checked by a laboratory. This advice was not followed as:

- The method 6200 has been mainly written prior to modern, self-calibrating , X-ray rather than radio-active source type XRF's came on the market
- At regular intervals the XRF was checked against NIST[xiii] soil calibration samples (NIST standards 1944, 2711 and 2710 are most appropriate), of which the results were always within 10 % of the certified value of those calibration samples.

The mix pile was then 'diagonally' excavated, by running the scrapers along a slope on one end, and the soil was laid out on a second mixing pile where further disking and mixing took place.

After this the soil was vertically excavated from the second mix pile and laid out on the sections by scraper, effectively mixing the soil a third time.

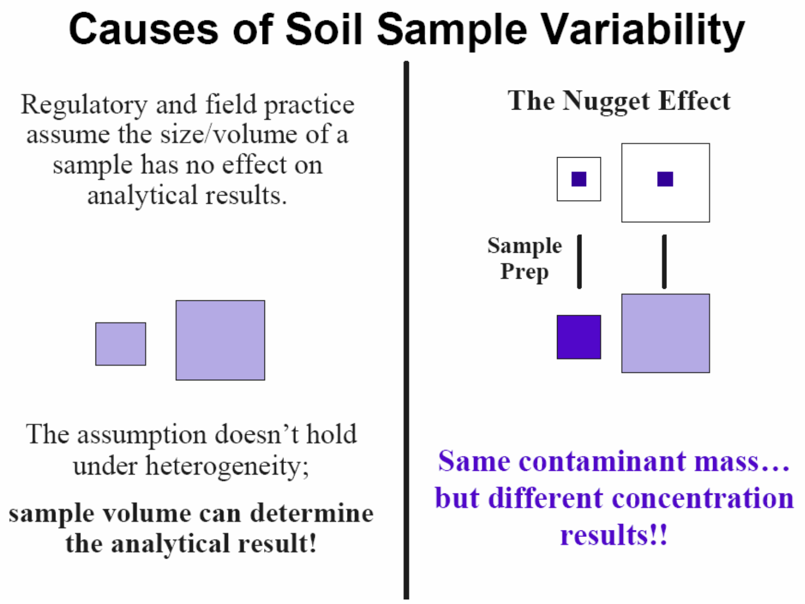
The XRF was used to check the soil as it was layered on the sections, and also for a final check of 9 readings per future lot after the laying out, scraping and contouring was complete. Again around 3000 XRF readings were taken during these mixing and laying out phases of the project.

For the validation one composite per lot was analysed by the laboratory and all samples were well under the guideline levels set by Hastings District Council.

A major cost saving has been not to have to do a re-mix of the soil after it all had been laid out on the lots like in many of the other subdivisions had been the case. A vigilant monitoring program and the abundance of data which the XRF made possible have avoided this expensive (approximately $ 150.000.-) exercise.

A word about sample variability

Soil mixing is worldwide not a very acceptable remediation technique as the result is very dependent on the ability of the soil to be mixed properly. In many soil-types this would be very difficult. Even the silty, friable soils on the Lyndhurst area would only break up to soil-clot size of about 30 - 50 mm, using the scrapers only with larger soil-clots of approx. 40 – 175 gram, sufficient for a lab sample.



Causes of Soil Sample Variability

Regulatory and field practice assume the size/volume of a sample has no effect on analytical results.

The assumption doesn't hold under heterogeneity;

sample volume can determine the analytical result!

The Nugget Effect

Same contaminant mass… but different concentration results!!

When taking such a small single sample it may only contain a soil particle from a previous hotspot. The smaller the soil cloths are made in the mixing process, the smaller these 'nuggets' (see diagram above) will be and the lesser effect they will have of the average of the sample, or for that matter the average of the topsoil on a lot.

The sample size is therefore an important consideration. It is here that the combination XRF and laboratory analysis works very well, because while the average is important, so are potential extreme values. When validating a section with mixed soil, multiple samples are taken from the topsoil layer (0 – 300 mm). Each of these sample bags is XRF analysed individually 5 times at 5 different positions. Should any of these 40 analysis be over the guideline value (24.3 mg/kg ww for arsenic in soil with 20% soil moisture), the bags will be re-analysed, and if still over, the area on site where the sample was taken is checked. When several exceedances are found the section is re-excavated and after filling with fresh topsoil, re-sampled.

Early in this project tests were run on the ease of mixing of the soil and it was decided that disking was essential to break up the soil clots to ensure a fine and homogeneous soil blend. The dry summer conditions made our task a lot easier and our work on site more pleasant.

Conclusion

The availability of the XRF on-site during this project has significantly improved the quality of the final result, while the costs were similar (assessment stage) or lower (remediation and validation stage) compared to only relying on a fixed, remote laboratory.

Compared with the 4 out of 6 ‘other remediation projects’ carried out in the same area, no second remediation phase (after laying out and contouring) was needed and here is where the largest saving is made.

The XRF fits perfectly in every phase of the TRIAD approach to contaminated site work. The conceptual site model (CSM) evolves throughout the assessment, remediation and validations stages of a contaminated site project. Initially little else is known except what can be observed on the surface, from old (aerial) photographs and at times anecdotal information. When more analytical data becomes available the conceptual site model becomes more accurate, however will always remain imprecise. At an early stage using a XRF a general impression can be obtained of the contaminant levels. Such a ‘walk-over’ survey may take only an hour, however with over 100 analysis in an hour, very quickly the range and variability of the contaminant concentration is known.

The XRF proves its cost-effectiveness during the detailed assessment when thousands of analysis are carried out during the sampling and give a full and direct on-site picture of the contaminant distribution in 3 dimensions. This allows the conceptual site model to become far more detailed than would be possible using only laboratory analysis.

During the remediation stage the conceptual model is sharpened up with every segment remediated and hotspot removed. The XRF measurements avoid hotspots being mixed into the mixing pile, and avoids hotspots being overlooked in the sub-base. Direct and simultaneous control of the excavation and the remediation process (here mixing) takes place.

Applying the XRF in a well organised way called the Triad Approach by combining field measurements with the XRF, with laboratory analysis for other compounds and as a regulatory check during validation has resulted in significant savings for the developer. In addition the quality assurance is greatly improved. Like the site owner[2] of this case study says: “do it right; do it once”.

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[2] Permission to use the data of for publication was kindly granted by Nicole & Brian Kelsey part owners of the Frimley Grove Development.

References

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[i] Cost-effective Site Characterisation - Dealing with uncertainties, innovation, legislation constraints 18-19 April 2002 hosted by ISE CNR The National Research Council of Italy, Pisa, Italy. http://www.nicole.org/nicole2/news/ann212a.PDF

ii Ariadni Argyraki, Michael H. Ramsey and Philip J. Potts (1997) 'Evaluation of Portable X-ray Fluorescence Instrumentation for in situ Measurements of Lead on Contaminated Land', Analyst, August 1997, Vol. 122 (743–749) 743

iii Philip J. Potts, Michael H. Ramsey and James Carlisle (2002) Portable X-ray fluorescence in the characterisation of arsenic contamination associated with industrial buildings at a heritage arsenic works site near Redruth, Cornwall, UK, J. Environ. Monit., 2002, 4, 1017–1024.

[iv] Taylor P.D., M.H. Ramsey, 'Sampling strategies for contaminated brownfield sites', Soil Use and Management, Volume 21 Issue s2, Pages 440 - 449

[v] Crumbling, D.M 2004. Summary of the Triad approach, U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Mail Code 5102G 1200 Pennsylvania Ave., NW, Washington, DC 20460

[vi] Crumbling, D.M., J. Griffith, and D.M. Powell. 2003. Improving Decision Quality: Making the Case for Adopting Next Generation Site Characterization Practices. Remediation: The Journal of Environmental Cleanup Costs, Technologies & Techniques. Vol. 13, No. 2, pp. 91-111 (Spring 2003).

[vii] Crumbling. D.M. 2002. In Search of Representativeness: Evolving the Environmental Data Quality Model. Quality Assurance: Good Practice, Regulation and Law, 9:3&4 pp. 179-90. (July-December 2002).

[viii] Interstate Technology and Regulatory Council (ITRC). 2003. Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management (SCM-1). Prepared by the ITRC Sampling, Characterization and Monitoring Team. December

[ix] Woll, B., J. Mack, F. Ellerbusch, and J.R. Vetter. 2003. Facilitating Browfields Transactions Using Triad and Environmental Insurance. Remediation: The Journal of Environmental Cleanup Costs, Technologies & Techniques. Vol. 13, No. 2, pp. 113-130 (Spring 2003).

[x] Field Portable X-ray Fluorescence (FPXRF): A rapid and low cost alternative for measuring metals and metalloids in soils (2008): http://www.claire.co.uk/index.php?option=com_content&task=view&id=167&Itemid=28

[xi] Keet, B. (2008), The Triad Approach to make contaminated sites cleanup projects better and more cost-effective. Case: Complementary laboratory (ICP, etc) and field XRF analysis http://www.tracenz.lab-initio.com/conference2008/papers/NZTEG_2008_026_Keet_paper.pdf

[xii] Griffiths E, 1999. Soils of the Heretaunga Plains: A Guide to their Management. Hawke's Bay Regional Council, Napier. http://www.hbrc.govt.nz/Land/SoilsofHawkesBay/tabid/82/Default.aspx, and Griffiths, E. 1997 Soil Map of the Heretaunga Plains. E,. Hawke's Bay Regional Council, Napier Available at http://www.hbrc.govt.nz/Land/SoilMaps/tabid/81/Default.aspx

[xiii] NIST 2007, reference standards of heavy metals in soils, Available at: https://srmors.nist.gov/tables/view_table.cfm?table=111-7.htm