The Triad Approach to make contaminated sites cleanup projects better and more cost-effective.
Case: Complementary laboratory (ICP, etc) and field XRF analysis

Drs. Ben Keet

Geo & Hydro – K8 Ltd (www.benkeet.com)

Abstract.

The Triad Approach integrates multiple innovations in site assessment, remediation and validation. It does not exclude any of the existing or innovative technologies.
The purpose of the Triad Approach is to provide a framework to integrate new & established characterization and remediation technologies with smart work strategies to achieve "better" cleanups. "Better" means documenting that uncertainties in project decisions are identified & managed, costly decision errors are avoided, decisions are scientifically defensible and yet, lower project costs and improved returns on public & private economic investment (vital to successful site reuse) are achieved.
Triad projects are demonstrably "better, faster, and cheaper" than conventional, however NO ONE is claiming they are easier! Institutional structures often pose barriers and despite a willingness to embrace this new methodology in practice it appears extremely difficult to break from traditional thinking.

A case will be presented illustrating the difficulties encountered during the introduction of field analysis using a handheld XRF analyser. During in In site assessment and remediation earthworks the instrument has been proven invaluable. During site assessment hotspots were detected which if left undetected would have seriously affected the remediation outcome. Even after an intensive investigation, it is only site monitoring with the XRF analyser that ensured hotspots that had a greater depth than common for the area were detected in the sub-base. Given the size of these hotspots and the common grid size of conventional validation sampling these would have been left undetected. Laboratory analysis has proven to be valuable to calibrate the field analysis and to provide analytical data for those compounds that are more difficult to analyse in the field.

However in the peer reviews for the Hastings DC, following traditional methodology, time and again the XRF use was more severely reviewed than the total project methodology. Time and time again the need for 'more reliable' laboratory tests was stressed.

This case will show that the combination of field analysis and laboratory testing have enabled the remediation projects to produce far more reliable results, avoided repeat remedial works (do it right; do it once) all at greatly reduced costs.

Introduction

The Triad approach has been developed since 2000 and is still developing. The main person in the US EPA working on this method is Deana M. Crumbling who works in the Office of Superfund Remediation and Technology Innovation. She has kindly provided permission to use the summary she wrote in May 2004 (Crumbling, 2004) for the introduction to the Triad approach in this paper.

The case study discussed is an application of the Triad method on a site, situated in Hastings, Hawkes Bay.

The Purpose of the Triad Approach

Experienced practitioners from the public and private sectors have pooled their efforts to create the Triad approach. This scientific effort is supported by EPA to foster modernization of technical practices for characterizing and remediating chemically contaminated sites. The goal of the Triad approach is to **manage decision uncertainty,** that is, to increase confidence that project decisions (about contaminant presence, location, fate, exposure, and risk reduction choices and design) are made correctly and cost-effectively. ("Correct" decisions are here defined as the decisions that would be made if fully completely accurate knowledge of contamination nature and extent and receptor exposure were available to decision-makers.) The foundation for site-related decisions that are both correct and optimized (from a cost-benefit standpoint) is the **conceptual site model (CSM)**. A CSM uses all available historical and current information to estimate

- where contamination is (or might be) located,
- how much is (or might be) there,
- how variable concentrations may be and how much spatial patterning may be present,
- what is happening to contaminants as far as fate and migration,
- who might be exposed to contaminants or harmful degradation products, and
- what might be done to manage risk by mitigating exposure.

As a primary Triad product, **an accurate CSM will distinguish and delineate different contaminant populations for which decisions about risk and remediation will differ.** Distinguishing between different contaminant populations improves the quality and interpretation of data, as well as the confidence and resource-effectiveness of project decisions. Triad achieves sufficiently accurate CSMs by proactively identifying and managing decision uncertainties (i.e., those unknowns that stand in the way of making confident decisions) and data uncertainties (sources of variation in data results when decisions are based on data). These tasks are accomplished by incorporating advanced science and technology tools into the project toolbox.

The Triad approach represents an evolution and progression of technical thinking about contaminated sites. Triad serves as a platform to integrate the experiences, lessons learned, and advances in science and technical tools and know-how gained over the past 25+ years of hazardous site investigation, cleanup, and reuse. It was developed through the efforts of practitioners dedicated to perfecting the science and art of site characterization and cleanup, despite recognizing the difficulties posed by the fundamentally **heterogeneous** nature of contaminated sites. Triad supports **second-generation practices** that, although somewhat different from current practices, truly sustain all three benchmarks of "better, faster, and cheaper" projects (Crumbling, et al 2003). The Triad approach is a scientific and technical initiative, not a regulatory approach, although it is hoped that regulatory bodies will take note of advancing scientific knowledge and technical capability and integrate them into their regulatory frameworks.

The Elements of the Triad Approach

"Triad" is not an acronym, and should not be written to appear as one. The word is intended to convey that there are three elements. The most important element of the Triad, **systematic**

project planning (called "strategic planning" by some), supports the ultimate Triad goal of confident decision-making. To ensure high decision confidence and stakeholder satisfaction ("better" projects) Triad encourages developing

- "social capital" (i.e., an atmosphere of trust, transparent, open communication, and cooperation between parties working toward a protective, yet cost-effective resolution of the "problem");
- consensus on the desired outcome (i.e., end goal) for the site/project;
- a preliminary CSM from existing information;
- a list of the various regulatory, scientific and engineering decisions that must be made in order to achieve the desired outcome;
- a list of the unknowns that stand in the way of making those decisions (i.e., decision uncertainties);
- strategies to eliminate, reduce, or "manage around" those unknowns; and
- proactive control over the greatest sources of uncertainty in environmental data (i.e., sampling-related variables such as sample volume and orientation, particle size, sampling density, subsampling, etc.).

The second element, **dynamic work strategies,** is the element that allows projects to be completed "faster" and "cheaper" than ever possible under traditional, static work strategies. Work planning documents written in a dynamic or flexible mode guide the course of the project to adapt in real-time (i.e., while the work crew is still in the field) as new information becomes available. This allows preliminary CSMs to be tested and evolved to maturity (i.e., sufficiently complete to support the desired level of decision confidence) in real-time, saving significant time and money while supporting better resolution of uncertainties. A valuable aspect of dynamic work strategies, focused quality control (QC) that adapt in real-time (a form of "process" QC), makes analytical QC procedures more relevant and powerful than what is possible with traditional work static strategies with the analytical operator far removed from field involvement. Lastly, the third Triad element, **real-time measurement technologies,** makes dynamic work strategies possible by gathering, interpreting, and sharing data fast enough to support real-time decisions. The range of technologies supporting real-time measurements includes field analytical instrumentation, *in situ* sensing systems, geophysics, rapid turn-around from traditional laboratories, and computer systems that assist project planning, and store, display, map, manipulate, and share data. Although field analytical methods are usually less expensive to operate than fixed laboratory analyses, under the Triad analytic budgets will generally be the same or even higher than conventional. Sample densities are increased to manage the various factors contributing to sampling uncertainty.
This allows highly accurate and detailed CSMs to be built as the foundation of confident decision-making. In the big picture, per-sample costs are much less important to the financial bottom-line than are the real-time, confident decisions that so dramatically lower the life-cycle costs of Triad projects. An ideal Triad project would strongly rely on each element. But we do not live in an ideal world, and "the perfect should not the enemy of the good," as the saying goes. Especially when project teams are first learning Triad concepts and attempting to blend technology and strategy tools into a Triad project, it should not be expected that all Triad projects will be equally strong in every element. However, there are a few basic features that define a Triad project:

- consensus on clearly worded project goals and intended decisions (with expressions

- of what decision errors are tolerable and which are not) for field work before it begins, a CSM that anticipates site-specific heterogeneities and contaminant distributions,
- strategies to refine the CSM over the course of the project in relation to the intended decisions, and
- discussions about the mechanisms to manage sampling and analytical uncertainties in data collection.

These features are so fundamental to Triad that if they are lacking from planning or from project documents, a claim for a Triad project is suspect. The advantages offered by dynamic work strategies, high sampling densities and real-time refinement of the CSM to lower costs and increase decision confidence make them highly desirable, and Triad projects will naturally include them to the extent feasible. But the degree to which they are employed is not distinctive, since it will vary depending on many technical and logistical factors, not the least of which include regulatory, budgetary, contracting and legal constraints and the expertise of the project team.

Quality Control is Crucial to the Triad Approach

As mentioned before, QC for all data gathering and processing activities is very important to the Triad approach. Under Triad, QC is designed to aggressively address specific sampling and analytical uncertainties so that **data is of known and documented quality.** Four QC items are of particular note:

1) **Focused QC protocols** increase or decrease the frequency of targeted QC checks in response to fluctuations in the uncertainties that they manage. [Note that the decision logic laying out the rationale for altering QC frequency should be written in planning documents for approval before being implemented.]

2) Real-time evaluation of the **compatibility of incoming data against the current CSM** to detect errors either in the data results OR in the CSM. Discovering discrepancies between the data and the CSM provides valuable feedback, and resolving such discrepancies in real-time supports “better, faster, and cheaper” projects. This incredibly powerful QC check simultaneously evaluates the reliability of both the data and the CSM, and is unique to Triad projects.

3) Split samples (often misleadingly called “confirmation samples”) are used to **establish data comparability** for the performance of field methods that are less selective, more biased and/or imprecise, and/or have higher detection limits than the traditional fixed lab methods used to derive regulatory thresholds. Split samples alone, however, do not provide sufficient information to establish the reliability of field method performance. In-field QC (of a nature appropriate to both the field method and its application) is required. Split sample analysis is an adjunct that supplements, but cannot replace, fully documented in-field QC procedures.

4) **Demonstrations of method applicability** (aka, “pilot studies”) are strongly suggested to establish the appropriateness of all proposed sampling and analytical methods for the actual site and application before full mobilization to the field for project implementation. A single, well-planned study can provide valuable information to guide technology selection and method modification, evaluate QC procedures, and provide initial estimates of site-specific sampling and analytical variability.

Triad embraces a **second-generation data quality model,** where sampling quality is just as important to data quality as analytical quality is. This evolution in thinking about what "data quality" truly means requires adjustment to the typical regulatory view of data produced by screening analytical methods (i.e., those field or lab methods that have higher detection limits, more bias and imprecision, or are more non-specific than available laboratory methods). The first-generation data quality model views data produced by screening methods as automatically of screening (i.e., inferior) quality. Since the term "screening" implies greater uncertainty, regulators have tended to be less accepting of data produced by screening analytical methods. What this view overlooks, however, is the all-important ability of less expensive screening methods to manage sampling variability. The lower operating costs allow sampling density to be increased, permitting tighter delineation of different populations for the purpose of building the CSM. The common phrase "screening a site" actually incorporates the underlying concept of building or testing the CSM, yet current regulatory practice seldom develops this concept to its logical conclusion.

Since the CSM is THE foundation of confident project decisions, building and refining a CSM using less expensive methods to delineate populations and help manage sampling uncertainties powerfully **improves data quality.** The concept of data representativeness is meaningful only in the context of a reasonably mature CSM in the context of the intended project decisions.

Data quality for heterogeneous matrices is achieved by collaborating results between less expensive, more rapid methods (to provide cost-effective high density sampling and build the CSM) and more rigorous (but also more expensive) analyses able to manage any important analytical uncertainty "left over" from the less expensive method. Under this second-generation data quality model, samples for more expensive analyses are chosen once their sample representativeness (i.e., the contaminant population they represent) has been established through the CSM. The ability to mature the CSM to establish **data representativeness** in the context of specific project decisions is not available if expensive fixed laboratory analyses are viewed as the only reliable method options. In contrast, the Triad recognizes that high analytical quality data points are of limited utility if used alone because they are prone to erroneous interpretation if sampling variables are not controlled (Crumbling, 2002). Sampling error occurs when accurate results of tiny samples are erroneously used to represent the concentrations for much larger volumes of matrix. **A Wide Variety of Issues Are Embraced by Triad Systematic Project Planning**
Triad is not a panacea or a "magic bullet." There are issues—legal, regulatory, community relations, toxicological, economic, political—that encompass concerns that Triad does not directly address as a science-based initiative. However, Triad's emphasis on face-to-face systematic planning to manage the full range of uncertainties (i.e., to clarify land use preferences, project goals and concerns through open discussion and documentation) creates an atmosphere **conducive to trust and cooperative negotiations** (i.e., the building of "social capital") among all involved parties. If the technical issues are out in the open and stakeholders are assured that resource limitations and scientific uncertainties are being fairly balanced in relation with their concerns, a strong foundation is laid for negotiating parties to balance the more thorny and value-laden social issues. Environmental insurance and redevelopment economics provide examples of the indirect issues that Triad can impact. Insurance companies have a natural interest in the Triad approach because insurance products are designed and priced through a quantitative evaluation of uncertainty. Insurance premiums assign a dollar value to the benefits of uncertainty management. Premium pricing can help project planners quantify the benefits of investing in the Triad

approach. A case of study illustrating the insurance angle was provided by Marsh, Inc. (a leading risk management and insurance services firm) on an actual Brownfields site (Woll, et al 2003). Despite spending $400,000 to characterize the site using a traditional approach, significant uncertainties remained in the conceptual site model: the actual volume of material requiring remediation and the most appropriate remedial options were still highly uncertain. As a result, the insurance model estimated that, at 98% certainty, the remedial costs could potentially be less than $1 million, but could also be more than $25 million. This large uncertainty caused the Cleanup Cost Cap premium to be priced between $1.58 and $1.89 million. To resolve the lingering CSM uncertainty, an additional investigation using the Triad approach was done at a cost of $30,000. The more refined CSM delineated the contaminant populations to support a much more confident estimate of the volume to be treated and the best remedial design. It became clear that remediation could confidently be expected to cost less than $1 million. This confidence was reflected in the subsequent pricing of the insurance policy. For the $30,000 investment in a Triad investigation, the payoff was a premium reduction of $1.5 to $1.8 million! (The premium was re-priced between $80 and $100 thousand). The decision confidence gained through the Triad approach made the feasibility of remediation more certain, the insurance more affordable, and the site more attractive to a potential buyer. There are also instances where the Triad approach has found more contamination than initially estimated during an investigation to transfer property, but the sale and redevelopment of the property was not adversely affected. The very fact that the degree of contamination was *known* at a high degree of confidence was reassuring to investors. Triad's emphasis on the "management of decision uncertainty" casts a wide net that includes many types of issues in the systematic planning process. But the same concept simultaneously encourages planners to identify and focus on the key issues that must be resolved to have successful, cost-effective, and defensible project outcomes.

Summary

The hazardous waste cleanup arena is changing as a result of 20-30 years of scientific, engineering, and regulatory experience. There are more options for effective remediation than ever before. But a common theme is that accurate site characterization is mandatory for cleanup technologies to perform efficiently. The generation of site data must be designed to produce a CSM that reliably portrays nature and extent of contamination in relation to the intended compliance and cleanup decisions. A data set that is representative of exposure risk probably will not be representative of decisions about remedial design. A data set useful to a remedial design that functions on larger spatial scales (such as thermal oxidation) will probably not be effective for designing a remedy that functions over a smaller spatial scale (such as chemical oxidation). Designs to generate data must take these factors into account from the start, or resources are wasted gathering irrelevant information. Or worse, the non-representative data are not recognized as such and remedial design is based on faulty information, practically guaranteeing that remedial systems will be less than optimally effective. The Triad approach is but one example of the smarter work strategies now available. But coordinated effort and determination will be required to address the multitude of institutional barriers stemming from community inertia and out-of-date regulatory guidance.

Hawkes Bay Case: Complementary laboratory (ICP, etc) and field XRF analysis

Introduction

A 3 ha orchard in Hastings will be subdivided and requires investigation for the presence of horticultural spray residues. DDT is often found wide spread at elevated levels in the area, however the human health based guidelines introduced by Hastings District Council are set at a level where those found in orchards seldom exceed the threshold values. Arsenic, derived from lead arsenate spraying, however, presents a problem. The guideline level for arsenic is relatively low (more in line with international guideline levels compared to the DDT guideline level), which means orchards generally have significant areas with arsenic levels over the threshold level. In addition relatively small (50m3 or less) hot spots are found. These can be related to objects identifiable on old aerial photographs such as spray sheds, however more often are related to:

- incidental occurrences, such as the spray tanker getting stuck and being drained to allow it to be pulled out of the mud,
- run-off of fines to low laying areas,
- burning of tree stumps (and the occasional CCA treated post being added to the pile)
- filling of drains and tree stump holes with topsoil.

Broad acre sampling (10 samples / hectare, composited to 1 sample for analysis as per HDC protocol), will frequently miss these hotspots, so the initial site investigation is often a ‘hit or miss’ operation where many smaller developments will contain undetected hotspots. Hotspots are also a worry when a remediation effort has to be undertaken. Especially when soil mixing as a remedial technique is considered, a few seriously contaminated hotspots even when they are small can seriously upset the end result as can be seen from the following table:

Calculation of potential contamination capacity of a hotspot (arsenic) 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	

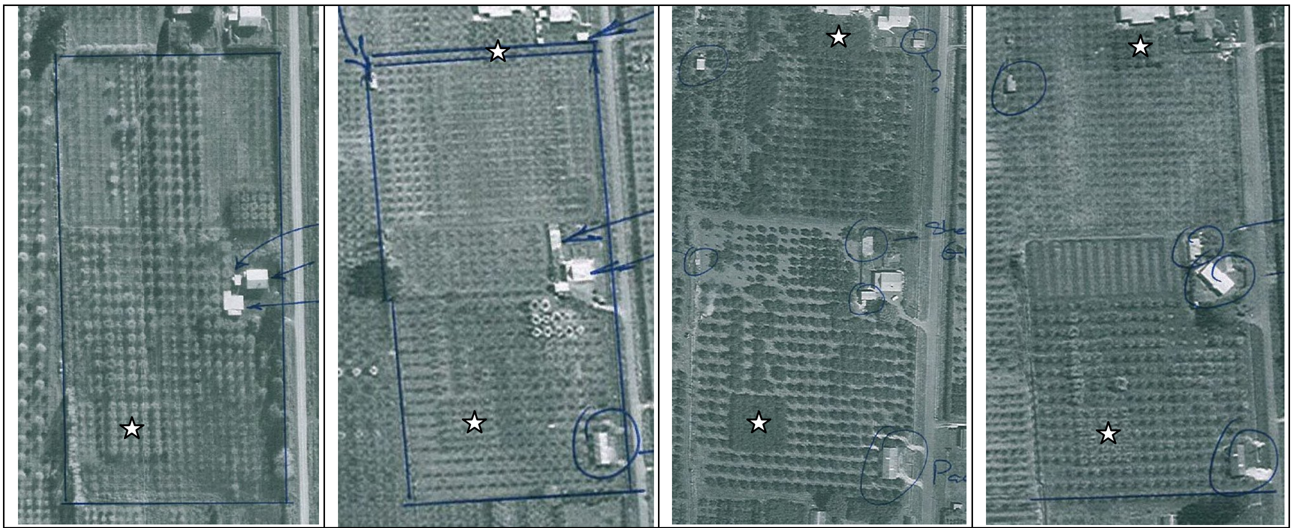
Note 1 'final concentration' is set at 25 instead of at guideline concentration of 30 mg/kg (for arsenic) as in practice the aim of a mixing operation is to obtain soil in which the maximum concentration found is to be below the guideline concentration. Even well mixed soil will have a variability of +/- 5 mg/kg.

Note 2 Assumed is 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 to 5 - 10 m deep and is very much site specific..

Note 3 assumed is a 'square' hotspot equal to one grid area, in practice well up to 1.5 times the area is possible for oval hotspots

Development of the conceptual site model

Our initial conceptual site model was based on the aerial photographs available, which showed a packing shed, several very small pump sheds and a small spray shed close to one of the two house sites. In one area the trees appeared to remain longer on one spot (no replanting) and larger which was interpreted as pear trees. Because of the larger canopy these receive more spray and thus often pesticide residues in the soil are higher.



1947	60-ies	70-ies	1985

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

On neighbouring sites hotspots as small as 5 m^3 had been found. Based on his principle “do it right; do it once”, the client opted for a 6 x 6 meter sampling grid with samples taken every 100 mm over 0 – 300 mm and every 150 mm for deeper layers. In the top layers this gives a resolution of 3.6 m^3 and for the deeper layers 5.4 m^3. Initial sampling was continued well into the yellow sub-base.

Initial Conceptual Site Model (CSM)

In this case the 'surrogate' analytical value to differentiate potentially contaminated soil from non-contaminated soil was chosen to be the colour of the soil. As orchard sprays attach well to organic matter in the soil and the topsoil is often mixed due to ploughing between re-planting this seemed to be an appropriate element in our initial (CSM -1).

Figure 2 2005 aerial photo with identified potential hotspots

On our conceptual site model CSM-1 are marked the 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 (Griffith, 1997 and 1999).

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

Sampling 4 layers on each grid point in total 3,696 samples were collected, sieved, bagged and labelled in 5 days. To set out the grid, use was made of the future sections of the subdivision. On each half section 12 samples were set-out, thus 24 on front and back section combined. Each set of 12 was numbered 'even' or uneven'.

To reduce the amount of analysis required for an initial screening, composites were made using the 6 even and 6 uneven numbered samples taken on half of a future section. All bags with composite samples have been analysed 5 times with the XRF resulting in 3080 analysis, each yielding the result of 20 heavy metals. All were screened for exceedance of a relevant guideline level, which were only found in the arsenic, lead and zinc results. For these metals the average of each composite was calculated.

An evaluation step was introduced to judge the heterogeneity of the soil on each half section: When the even and uneven sample results were more than 20% different a potential hotspot could be present and the individual 6 sample bags of the highest of the two sets were then analysed.

370 individual sample bags were analysed 5 times resulting in a further 1,850 analysis results. 70% of these analysis resulted in an identified hotspot which was mapped per layer investigated. 30% appeared just a general elevated level of one of the contaminants.

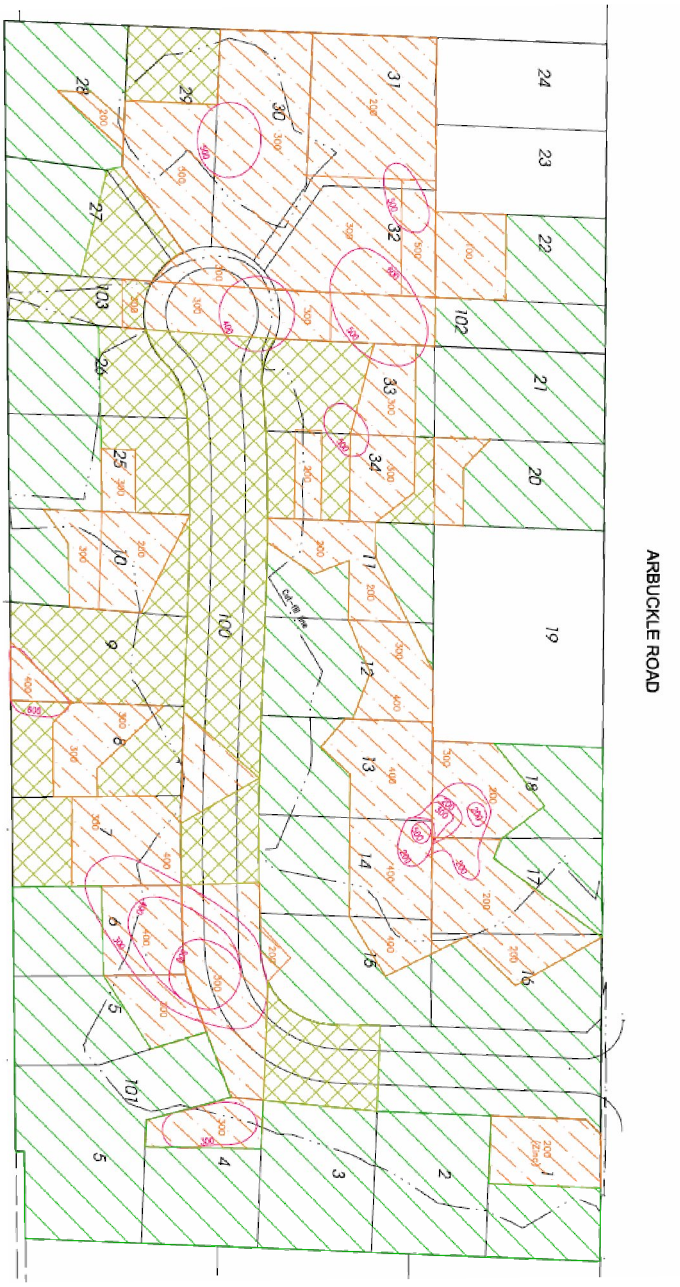


Figure 3 Conceptual site map v 2.1

On the map on the left ,the updated conceptual site model CSM-2 , the actually found hotspots with arsenic over 95 mg/kg are indicated with the red egg-shaped contours, while the areas with arsenic between 40 and 95 is indicated with the red shading. The cross-hatched brown shaded areas have arsenic concentrations between 20 and 40, while arsenic concentration in the green shaded areas is below 20 mg/kg.

Comparison with the CSM-1 map learns that the Pear blocks were correctly classified, while the upper pump shed appears to have only minor arsenic contamination. Both sheds on section 19 were not assessed in this investigation phase, however later the contaminant contours from both neighbouring sections appeared to continue on section 19.

Laboratory testing

Two sets of laboratory tests were now required. Firstly the analytical uncertainty of the field XRF reading of arsenic, copper, lead and zinc needed to be addressed.

Composites have been made from areas with varying arsenic concentration which could double for a screen for Organochlorine Pesticides. The areas composites are shown in figure 4 below.

Ten composite samples (cs) were selected for XRF – Lab comparison (sample points 1 – 10 on figure 4). Important to note is that the XRF readings which are an average of 10 arsenic readings per composite sample are given as As (corr). In order to calculate the average concentration all <LOD have been replaced by a value. When more then 70% of the results are <LOD the value LOD/2 is used when less than 70% results are <LOD the value LOD/1.5 is used. The use of LOD/2 in calculation of averages is quite common when only small data sets are available. In New Zealand the Ministry for the Environment has used this method during the validation of the Mapua remediation. The value requires correlation with work in the Hastings, Lyndhurst area and the LOD/2 appeared to give a good match with low arsenic values, while when less XRF readings of the same sample were <LOD, the 'correction' LOD/1.5 appeared to give a better fit. Clearly this is quite site specific on average a better correlation for the analysis yielding an Arsenic concentration around 25 mg/kg (w.w.), as can be seen here.

	XRF readings (mg/kg ww)					Laboratory results (mg/kg ww)							
Sample number	Av xrf SMC Cu	Av xrf SMC Zn	Av xrf SMC Pb	Av xrf SMC As (corr)	% xrf <LOD	CuTRI Cu	Δ%	ZnTRI Zn	Δ%	PbTRI Pb	Δ%	AsTRI As	Δ%
cs1	240	92	123	33	38	236	2	98	-6	133	-7	43	-22
cs2	107	85	78	25	8	119	-10	87	-3	77	1	24	5
cs3	127	85	215	69	20	132	-4	83	2	221	-3	70	-1
cs4	105	79	150	55	0	98	7	71	11	148	1	46	19
cs5	211	66	159	52	10	251	-16	66	0	199	-20	61	-15
cs6	218	275	53	14	88	176	24	454	-39	46	17	12	17
cs7	182	104	55	19	64	241	-25	123	-16	89	-38	23	-19
cs8	354	107	209	63	0	365	-3	100	7	214	-2	53	19
cs9	228	98	177	51	22	127	79	85	15	156	13	47	8
cs10	112	99	110	27	70	131	-14	111	-11	115	-4	30	-11
average % difference (+ means the XRF reads higher than the lab result)							4		-4		-4		0

Explanation of abbreviations: AV xrf Average XRF reading of 10 – 20 individual XRF readings, SMC = Soil Moisture Corrected, TRI Total Recoverable digest method US EPA 200.2

On each second line in the right hand four columns the difference between the XRF and the laboratory results is given. Even though the average difference for all four metals is between + or – 4 % some larger differences are present at individual samples. These are explained in more detail below.

Looking at Arsenic in particular, the lab found significantly lower concentration than the XRF in samples D4, D6 and D8. In sample D4 and D8 the lead levels are elevated which may have influenced the XRF reading to correct As about 20% upwards as the instrument automatically adjusts the LOD value upwards in case of greater uncertainty, especially in the presence of lead. The difference in D6 is due to the large number of < LOD readings on the XRF which is limited in the low range (see paragraph above the table). Even the replacement of <LOD by LOD/2 still gives a slightly high result.

The lab finds higher levels of Arsenic in samples D1, D5 and D7. D7 has a high % of <LOD readings and the correction by replacement by LOD/1.5 may not be representing the actual concentrations, however no other estimate can be made at these low concentrations.

D1 and D5 both have rather high Arsenic concentrations and the XRF analysis of the individual soil samples within these composites show a wide variation so sample heterogeneity will be the main influence here. It should be noted that despite every effort in field sieving and compositing the homogenising will not be as good as in the lab where samples are sieved after air drying at 35 °C overnight. This is impossible when processing hundreds or in this case thousands of samples in the field.

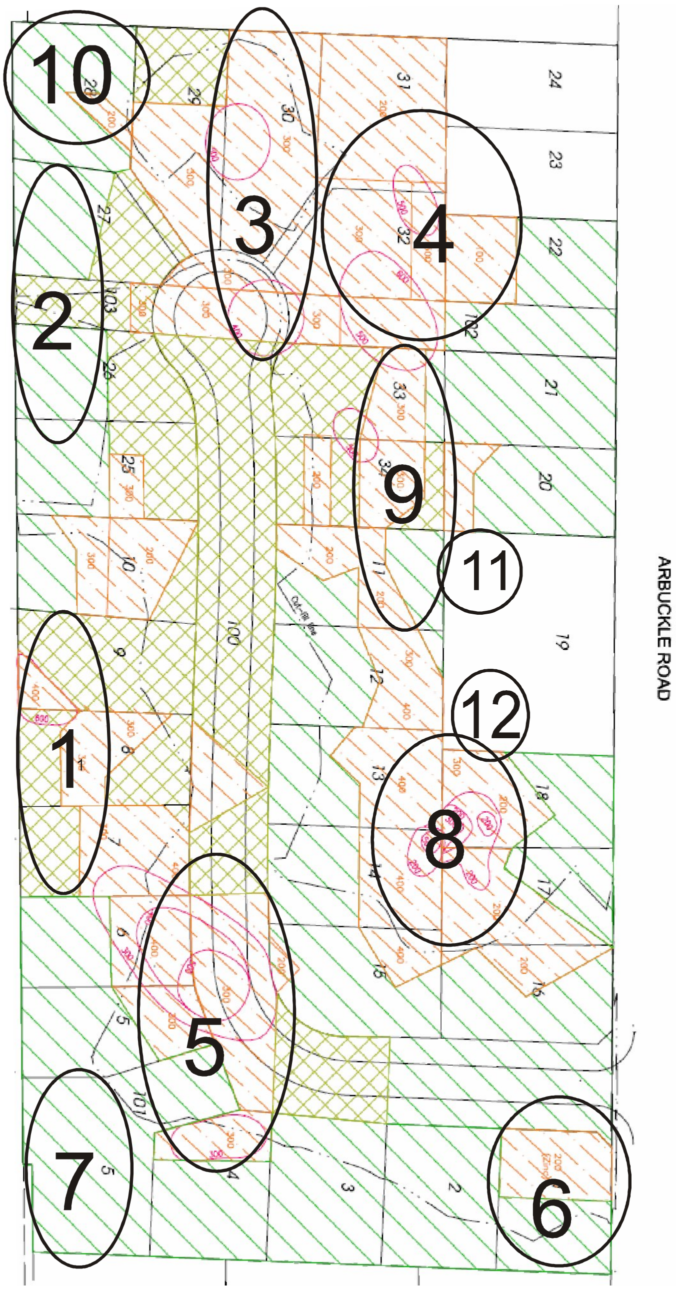


Figure 4 composite sample locations 1 - 12

The 10 composite samples plus 2 composite samples from section 19 have been analysed using an organochlorine Pesticide screen by Hill Laboratories. 11 of the OCP results were well within the Hastings District guidelines for ΣDDT, however sample 12, near the former spray shed had a concentration of ΣDDT of 199 mg/kg dw.

Thus the Laboratory DDT analysis revealed an extra and important hotspot near small spray shed. The addition of the 5 x 5 meter area in the corner of section 19 completed the pre-remediation conceptual site model (CSM-v 2.1).

Remediation

Off-site disposal of soil to the local landfill is discouraged in the Hastings District. As an alternative 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 reserves.

The DDT concentration in the spray shed area was from a composite sample made up out of 5 sub-samples. The maximum concentration in one of the sub-samples could therefore be close to 1000 mg/kg. To be on the safe side all soil from the spray shed area was mixed 1 : 10 with soil low in DDT before burial. All other soil with arsenic concentrations between 95 and 190 was buried in the reserves and the residual areas checked with the XRF to ensure no 'hot soil' remained.

Figure 5 A quick XRF check revealed extreme copper, chromium & arsenic concentrations

Quite some 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 the small pump sheds which had been demolished and burned by one of the site owners the night before. Extreme arsenic concentrations (> 100.000 mg/kg) were measured (see picture above). Fortunately the ashes were removed by the owner, before they could be accidentally mixed into the main soil volume.

Many of the hotspots marked on version 2.1 of the CSM map appeared to be quite accurate, however as can be expected many had small lobes of relatively high contaminated soil at the edges (see picture on the left.)

Figure 6 By continious checking edges and base of the excavated hotspots certainty is gained about the remaining soil which will be brought to the mixing pile.

Using the XRF it was made certain the maximum remaining concentration on the site was lower then 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.

When the arsenic concentrations are all below the site specific limit (here the 'acceptance level was set at 22 mg/kg ww), the next 'sandwich' layer of white over blue would be laid out on top. In case some areas had over the site acceptance level of arsenic this area would either be scraped off and re-layered or overlain by another white layer and disked again.

At times unacceptable hot spots would occur on the mixing pile, probably arising from small burial pits on site. These were scraped off the mixing pile and deposited in one of the reserves. Alternating with the XRF measurements on the mixing pile the scraped areas of the site itself were re-analysed with the XRF and given the blue or white markings, so the scraper drivers would know which areas to pick-up and in which order they were to be laid on the mixing pile.

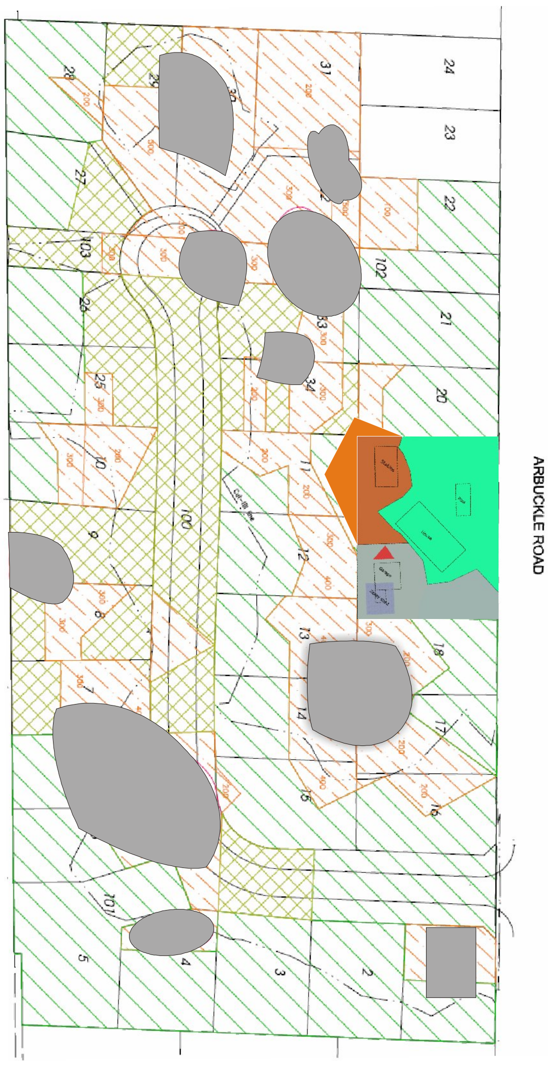
Some hotspots were only discovered by taking auger samples in the 'clean' sub-base. When the XRF readings were low, however discoloration or debris was still present several deeper soil samples were taken to check for any potential contamination. One of those sites discovered had arsenic over the guideline level down to about 2 metres. The excavation process can well be followed when we look at the XRF readings taken on site in relation to the time of the reading.

Cu mg/kg ww	Zn mg/kg ww	As mg/kg ww	As [LOD] [1] mg/kg ww	Pb mg/kg ww	Time
68	107	133	22	183	10:07:14
<LOD	85	120	21	77	10:07:44
48	90	<LOD	30	163	10:08:14
<LOD	52	89	12	28	10:08:44
104	116	44	31	152	10:09:54

51	111	80	25	150	10:10:37
65	177	<LOD	33	184	10:12:31
With mainly red marks the excavator is instructed to take out 0.5 meter from floor and widen the holes by taking back the walls by 1 m					
<LOD	44	77	16	<LOD	10:34:42
<LOD	46	91	16	<LOD	10:35:51
<LOD	27	74	15	<LOD	10:38:28
<LOD	32	52	16	20	10:39:03
<LOD	33	121	17	31	10:39:36
<LOD	56	61	24	60	10:40:09
<LOD	56	62	16	<LOD	10:40:42
Despite all the walls and floor looking mainly yellow, values are still high so a further .5 m will be taken off the floor and 0.5 off the walls. The shape becomes triangular deepening towards the NE as if the lead-arsenate fluid has soaked in coming from the back of the garage					
<LOD	38	49	15	<LOD	11:11:13
<LOD	45	51	15	<LOD	11:11:46
<LOD	52	51	9	61	11:12:20
73	44	<LOD	27	83	11:12:52
61	80	33	10	125	11:13:31
<LOD	48	46	17	<LOD	11:14:09
<LOD	43	44	17	25	11:14:44
<LOD	64	45	11	114	11:15:18
<LOD	50	43	18	23	11:15:47
<LOD	29	36	18	23	11:16:21
<LOD	58	42	22	48	11:16:52
<LOD	68	21	19	<LOD	11:17:27
<LOD	38	41	18	38	11:18:01
<LOD	32	32	14	<LOD	11:19:11
Excavator removes the marked 'red' areas and the surface of walls and floor is checked again					
<LOD	61	39	15	<LOD	11:23:08
<LOD	115	33	18	23	11:23:52
<LOD	178	32	24	103	11:24:25
<LOD	86	31	15	21	11:24:54
53	84	31	19	38	11:25:25
<LOD	60	<LOD	24	94	11:25:56
<LOD	100	27	17	29	11:26:26
<LOD	78	25	17	36	11:26:55
<LOD	72	21	16	<LOD	11:27:31
<LOD	65	24	18	27	11:28:06
<LOD	37	26	16	24	11:28:49
<LOD	28	23	15	<LOD	11:30:41
Ater last scrape-out the walls and floors are checked for remaining contamination					
52	87	21	16	23	11:53:49
<LOD	54	<LOD	17	<LOD	11:54:49
<LOD	42	21	16	<LOD	11:55:18
<LOD	50	21	17	25	11:55:53
52	69	20	16	19	12:01:45
<LOD	85	<LOD	15	<LOD	12:02:12

<LOD	63	<LOD	16	18	12:02:38
<LOD	78	<LOD	16	22	12:03:05
<LOD	48	<LOD	15	<LOD	12:03:34
<LOD	39	<LOD	15	<LOD	12:04:01
<LOD	40	19	14	<LOD	12:04:27
<LOD	41	<LOD	15	<LOD	12:04:53
<LOD	63	<LOD	17	28	12:05:20
<LOD	47	<LOD	15	<LOD	12:05:46
<LOD	88	<LOD	17	<LOD	12:06:12
<LOD	79	<LOD	17	<LOD	12:06:38
No more contamination found; validation samples taken					

[1] This value represents the accuracy of the XRF reading and thus <LOD (less than the limit of detection) indicates the maximum level of arsenic present.



The hotspot mentioned above is marked as the red triangle on the final CSM map pictured left. The other removed hotspots are given in grey. Their surface is not flat as areas where contamination was found to go deeper have been excavated further.

It is important to note that when working in a new area or an area with large variations in soil composition, more samples will require laboratory analysis to check / calibrate the XRF than when XRF results are available from properties surrounding the site, or as in this case from the assessment phase.
During the 3,5 weeks of remediation approximately 5,500 XRF analysis have been carried out.

Figure 7: Final CSM (v3.1) after hotspot removal; solid green is only area not excavated; topsoil from brown and all other areas taken to the 11.400 ton mixing pile. The spray shed soil was diluted 1 : 10 before burial.

In this project the excavated sub-base has not been covered for several weeks, therefore there was plenty of time to do the sub-base validation and select samples for lab analysis. When tighter time constraints are encountered, more frequent calibration samples need to be sent to the laboratory. Making several site standards is a good idea and is recommended in the US EPA Method 6200 guideline. However modern XRF's (produced after method 6200 was developed have internal calibration procedures, prompt the operator that re-calibration is required, and are calibrated at the start of each measurement session against known standards made by NIST or a similar institute. A suite of a low, medium and high concentration standard in combination with a pure SiO2 sample to check the surface contamination of the instruments window, is a useful set to have on site (NIST standards 1944, 2711 and 2710 are most appropriate, ref. NIST 2007)

After the sub-base is validated clean, it gets graded to adjust the contours to those required for the new subdivision. Sub-base will be taken off some areas and brought on and compacted on others. The distance between sub-base level to final level multiplied with the quantity of top soil available in the mixing pile determines the final level of the sections. In this case the mixing pile held sufficient soil to provide a 300 mm top-soil layer (mixing pile volume was 8,200 m^3 or 11,400 ton of soil).

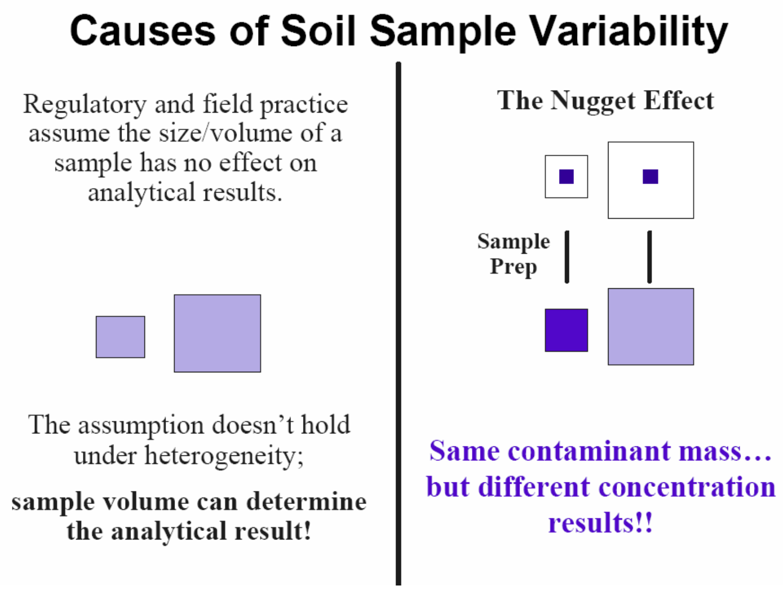
Validation

At the validation stage the ratio of XRF analysis to laboratory analysis is reduced again to low levels. For several projects Hastings District Council has accepted 1 laboratory control analysis for every 20 XRF analyses. This seems a practical approach as in practice the XRF analysis is already an average of 5 readings taken from the same sample. These are averaged mathematically. The laboratory does the averaging mechanically by drying, sieving and grinding the sample.

The soil mixing process reduces the soil-clot seize to about 30 - 50 mm and smaller. The larger soil-clots weight 40 – 175 gram, sufficient for a lab sample. When taking such a small single sample it may only contain soil from a contaminated segment of the site[1]. 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, 8 samples are taken from the topsoil layer (0 – 300 mm). Each of these 8 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 is taken is checked. When several exceedances are found the section is re-excavated and after filling with fresh topsoil, re-sampled. In this project only 3 very minor areas (10 m^2 or less) have been given this 'polishing' treatment, testifying to the success of the soil mixing operation. When all 40 readings are below the guideline value a composite of the 8 samples is sent to the laboratory. All 8 samples combined gives a volume of about half a bucket (5 litres). So this sample is well mixed before the composite sample of 50 – 100 grams is taken out and sent to the lab. In the lab further mixing and homogenising assures the analytical values represent the sample received.

[1] This is one of the reasons that outside New Zealand soil mixing is generally considers an inappropriate remediation 'technology'

All this is carried out to avoid 'the nugget effect'. The nugget effect graphically presented on the right, is often responsible for two totally different outcomes of investigations even when the investigators took their samples 'almost in each others sampling holes'.
However when engineer A uses a 30 mm pastural sampler to take soil plugs while engineer B has used a 100 - 150 mm auger to take samples at the same locations the outcomes may be totally different.



This effect is of course far stronger when sampling recently mixed soils. Thus for the validation stage taking adequate sample volumes ensures a better representation of the average potential health risk of the residual contamination.

However peak values at the surface of the remediated section should certainly not be ignored. About 50 XRF analyses, which can be carried out in less than 30 minutes, will provide a far more detailed picture and ensures the soil mixing process has adequately homogenised the soil.

Conclusion

A conceptual site model evolves throughout the assessment, remediation and validations stages of a contaminated site project. Initially little else is known than 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. During the remediation stage the conceptual model is sharpened up with every segment remediated and hotspot removed. Field measurements are very important as significant hotspots may remain buried, or may get mixed into the mixing pile, which may cause the total soil volume to remain above the set guideline levels. This may require expensive measures such as re-mixing, importing uncontaminated topsoil for further dilution or off-site disposal. All three 'salvaging' operations have been carried out on other projects in the Hastings, Lyndhurst area.

Applying the Triad Approach by combining field measurements with the XRF with laboratory analysis has avoided this, resulting in significant savings for the developers. In addition the quality assurance is greatly improved. As the site owner[2] of this case study says: "do it right; do it once".

[2] Permission to use the data of this case was granted by Nicole & Brian Kelsey part owners of the Frimley Grove Development

References

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 Paper available at http://www.triadcentral.org/ref/doc/triadsummary.pdf

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). Paper available at http://cluin.org/download/char/spring2003v13n2p91.pdf

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). Paper available at http://cluin.org/download/char/dataquality/dcrumbling.pdf

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

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

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. Available at http://www.itrcweb.org/SCM-1.pdf

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

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). Access through http://www3.interscience.wiley.com/cgi-bin/abstract/104520300/ABSTRACT