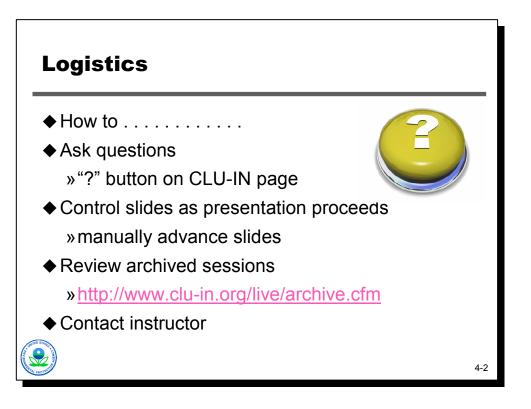




Stephen Dyment, U.S. EPA Office of Solid Waste and Emergency Response; Office of Superfund Remediation and Technology Innovation - Stephen Dyment is a chemist with more than 15 years experience including 4 years in a commercial analytical laboratory and 8 years in environmental consulting. He joined EPA in 2005 with a focus towards enhancing acceptance and use of emerging analytical technologies and sampling strategies. His perspective draws upon years of practical laboratory and field experience to apply EPA's Triad approach at sites in Superfund, Brownfields, RCRA, UST and State programs. Mr. Dyment's efforts have resulted in the development of numerous EPA case studies, profiles, and training courses that outline successful strategies for the use and understanding of collaborative data sets, adaptive QC programs, and real time analytics. He holds a B.S. in Environmental Science/Toxicology from the University of Massachusetts at Amherst.

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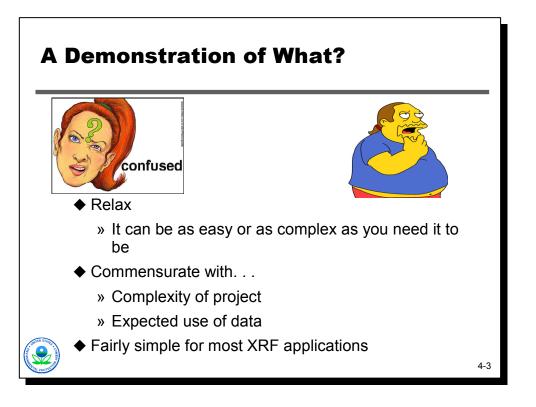
- When you registered, you were directed to this seminar's specific URL, which is the front page of today's seminar. The Front Page of the Web cast contains a short abstract of today's session. We have also included pictures and short biosketches of the presenters. Please note the presenters' email addresses are hotlinked on that page in case you have any questions for one of them after today's presentation.
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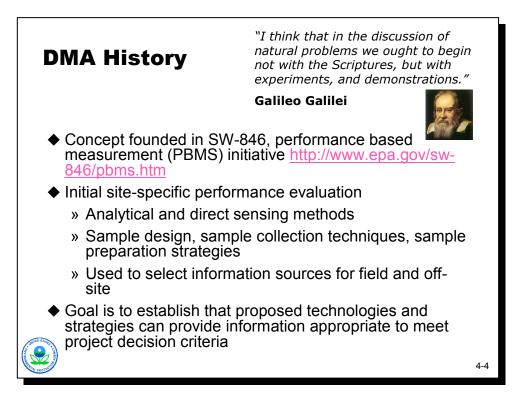
Robert Johnson, Argonne National Laboratory Phone: (630) 252-7004 Fax: (630) 252-3611 E-mail: <u>rli@anl.gov</u>

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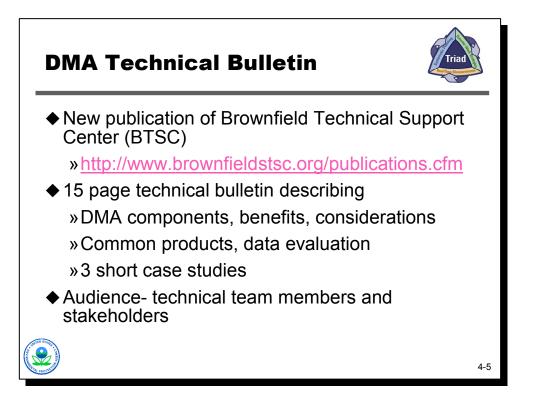


- The term DMA in the mind of some people implies a lengthy and complex assessment of an analytical technology. Field portable XRF (FP XRF) has been in use for over 15 years. Instrumentation, software, electronics, and peripherals have all greatly improved but the physics and theory of operation are the same. XRF has been evaluated under a variety of programs like ETV, ITVRs and has a promulgated method in the form of SW-846 6200.
- In the case of most XRF applications a fairly simple DMA is all that is needed but even a simple DMA can provide critical information for how the instrument will be deployed, QC design, collaborative relationships, field based action levels, etc.



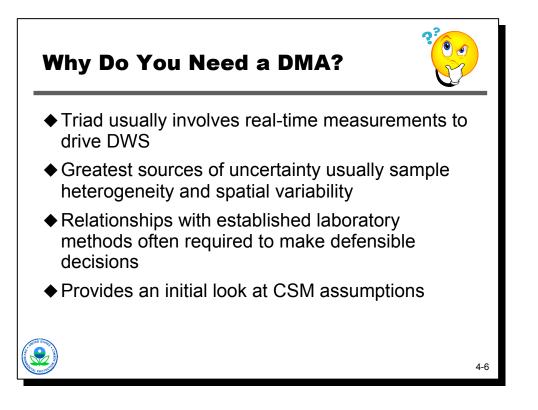


- Concept founded in SW-846: Even with well understood technologies like XRF, MIP, and LIF stakeholders will not rely on these tools and strategies without site-specific demonstrations to understand how tools or approaches can be used to effectively manage uncertainty and be used collaboratively with other information sources. The performance based measurement (PBMS) initiative fits nicely with Triad because PBMS conveys "what" needs to be accomplished, but not prescriptively "how" to do it. EPA defines PBMS as a set of processes wherein the data needs, mandates, or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner.
- Initial site-specific performance evaluation: Under a performance-based approach, EPA would specify:
  - » Questions to be answered by monitoring.
  - » Decisions to be supported by the data.
  - » Level of uncertainty acceptable for making decisions.
  - » Documentation to be generated to support this approach in the monitoring program.
- Goal: Data should be collected to meet project specificity, sensitivity, and reliability requirements.



## Notes

- New publication: The DMA helps overcome pre-conceived notions about what can and cannot be achieved through the use of field analytics, direct sensing, tools, and innovative sampling strategies. Through the use of DMAs and other Triad best management and technical practices, EPA shows how to move beyond "screening and definitive" definitions to demonstrate that all information sources have value, and, that when used collaboratively, they create powerful and persuasive data sets. EPA also recognizes that many of the commonly used analytical methods/sampling designs are not without inherent problems or difficulties. EPA hopes to achieve a broadening of knowledge, expansion of the toolbox, and establishment of a bridge to harmonious existence of field analytics, direct sensing tools, and laboratory methods.
- 15 page technical bulletin: This seminar sets the stage for the upcoming Brownfield Technical Support Center (BTSC) technical bulletin on DMAs. EPA is currently finalizing the document and it's expected release date is in August 2008. Watch for it at <u>http://www.brownfieldstsc.org/publications.cfm</u>.
- Audience: These bulletins are intended for technical project managers and team members. Non-technical managers or stakeholders may also present these bulletins to consultants and service providers to ensure appropriate implementation of Triad best management and technical practices at their site. These bulletins provide sufficient information for less technical project managers and team members to request critical Triad project elements in scope of work and planning documents.





Triad usually involves real-time measurements to drive dynamic work strategies (DWS): Because XRF has been used for the past 15 years, performance of a DMA may seem, on the surface, to be unnecessary. However, Module 2 of this series, on basics, illustrated why site-specific regression must be used carefully, and Modules 3.1 and 3.2 showed the importance of understanding sample heterogeneity and developing strategies to deal with those uncertainties. Modules 3.1 and 3.2 also introduced the concept of tailoring sample support to the decision at hand. A DMA can help do that.

- Greatest sources of uncertainty usually sample heterogeneity and spatial variability: The issues associated with heterogeneity and spatial variability cannot be managed if they are not recognized until after demobilization from the field. DMAs provide an early look at the significance of these issues and allow establishment of effective strategies (QA/QC) to deal with them. Many technologies still struggle with the "screening" stigma. XRF is a good example of a very well established technology for which many regulators still require fixed laboratory "confirmation" and stakeholder acceptance often requires this.
- Relationships with established laboratory methods often required to make defensible decisions: The relationship of XRF and laboratory methods allow the user to have confidence in the program. By establishing this relationship, the project team can develop field based action levels, ranges (clean, dirty, unsure), target collaborative samples, and monitor decision error rates. The relationship can also help highlight the fact that "gold plated fixed laboratory" results suffer from the same sampling sub-sampling issues that innovative or field methods do. By establishing these relationships, the project team can demonstrate why stakeholders cannot expect field methods to compare any better than two laboratories or even the same laboratory.

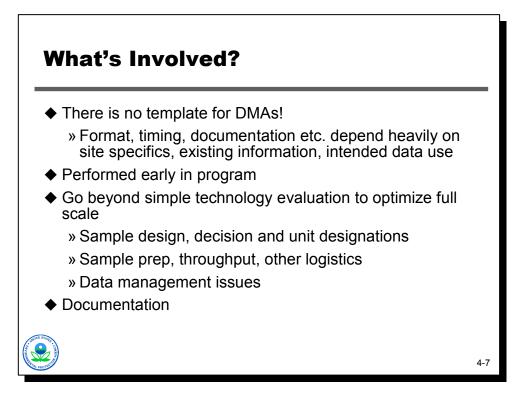
Provides an initial look at CSM assumptions: Most technologies and approaches requiring a DMA result in increased information density. The DMA should be used to determine if the preliminary CSM assumptions are true.

Some components of investigation and cleanup such as the Site Inspection (SI) step within the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) or Superfund, where guidance suggests collection of 20 or fewer samples, may not be appropriate for conducting a DMA. Similarly, some Brownfields sites, with grants that have very limited funding, may not be appropriate to accommodate a DMA. Projects with adequate resources to employ established mobile or fixed laboratory methods at sufficient density may be inappropriate, while those requiring method modifications or careful examination of sampling and spatial uncertainties may benefit significantly from DMAs. Even if only fixed laboratory methods are used, a DMA should be considered for a fixed laboratory method if there is any question about matrix interference effects. Just a few pilot samples could save millions of dollars of wasted analyses by detecting extraction or other problems at the start.

In should be noted however, that for most applications a DMA is beneficial precisely because a particular field analytical technique, direct sensing tool, or innovative strategy is identified as applicable to cost effectively increase data density, refine the CSM, or address small scale variability and matrix heterogeneity. In some cases, selection of sampling locations for an SI are obvious (for example: visual staining, product, lagoons, discharge points) while other cases are more complicated, making determination of appropriate sampling locations for those 20 samples problematic. Depending on the nature of suspected contamination some sample material can be archived and potentially used later as part of a DMA for an expanded SI or additional work.

In the case of Brownfields applications, most assessment grants are in the range of \$200,000 where it is reasonable to assume that resources allow for data densities greater than 20 samples. At sites with elevated expenditures associated with collection of subsurface samples, adding limited additional cost for analysis of field analytical methods, direct sensing tools, or other innovative technologies does not significantly raise project expenses. In these cases, inexpensive analytics and direct sensing tools can provide greater vertical density and help target locations for more expensive traditional laboratory samples.

Finally, the very definition of a Brownfield- "a property, redevelopment, or reuse which may be complicated by the presence or potential presence, of a hazardous substance, pollutant, or contaminant" underscores the need for higher data density and collaborative data sets that often accompany DMAs. Regardless of whether significant contamination or the perception of contamination is present at such a property, DMAs and associated innovative tools allow for a higher data density that facilitates timely re-vitalization. These data sets are particularly helpful to address stakeholder concerns and provide a level of comfort that allows developers, insurance partners, risk partners, public stakeholders, state agencies, local agencies and others to be involved, invested, and reassured with a project outcome.



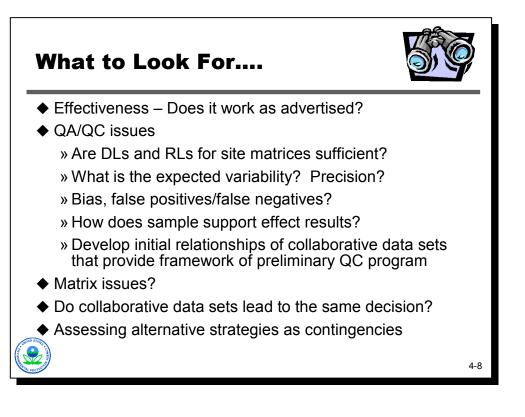


There is no template for DMAs: DMAs can be performed easily and affordably before mobilization, or as an early component of a field program. It does not necessarily require a separate mobilization. The complexity of the DMA should be commensurate with the expected complexity and scope of the project and with the expected data use and decisions being made.

Existing information and archived samples are often extremely valuable.

- Performed early in program: It is best to identify potential issues and design strategies early in the sampling program. The DMA process also allows planning for contingencies.
- Go beyond simple technology evaluation to optimize full scale: Effective DMAs go beyond simple "does it work at my site" questions to look at sampling, logistical, and data management issues. Communication, data sharing, visualization, collaborative data needs, staffing, project sequencing can all be optimized prior to full-scale implementation.

Documentation: Documentation is a critical component of the effort. A variety of formal and informal means have been used to document DMAs. Informal methods, such as memoranda of understanding, meeting notes, project Web sites, E-rooms, and E-bulletin boards, serve to document the DMA process. These informal methods are particularly useful to document stakeholder participation and buy-in for Triad investigations. Informal discussions with stakeholders subsequent to the DMA can also be very useful to accelerate document comment, revision, and submission. Regardless of the method used to document a DMA, good records are essential to scientifically validating and legally defending the selection and use of analytical methods, and ultimately, the conclusions made based on data generated in the field. Project teams are strongly encouraged to plan for and complete DMA documentation.



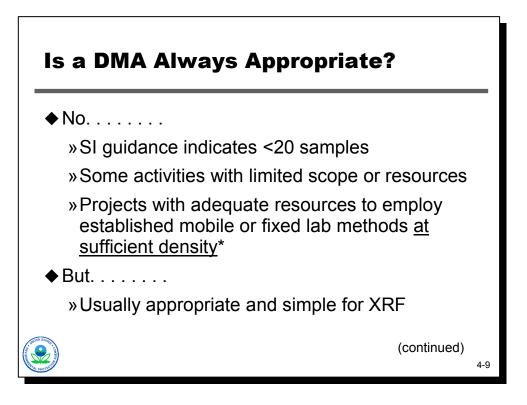


- ► Effectiveness: A DMA can assess whether or not the technologies to be used will perform as advertised by the vendor. Sites can benefit from even simple DMAs. For example, on several sites, DMAs were not performed for technologies such as GPR, EM, and resistivity. The project teams encountered depth issues with GPR, interferences with EM, and data processing/interpolation and surveying with resistivity. A DMA and performance-based contracting mechanism would have saved project resources because the data from these technologies was collected, but could not be used.
- QA/QC issues: A DMA can provide valuable information that can be used to optimize procedures to address variability. Variability effects statistically based sampling designs and tolerable uncertainty. For example, if a 95 UCL is being used to make decisions and there is significant variability, often times the 95 UCL is pushed above the action level. In such a case, some resources put toward understanding and controlling variability due to small scale or matrix heterogeneity will benefit a sampling design. With a high density real time tool it may be possible to isolate problem areas within a decision unit and address them separately, rather than taking action on the entire decision unit.

Sample support is the size, shape and orientation of the sample. A DMA can assess if the level of effort required for advanced sample preparation is worth the higher precision, accuracy, or bias control achieved.

QC samples are collected and analyzed to evaluate which uncertainties are the largest contributors to total measurement error. Project resources can then be allocated to control for those activities with the highest impact.

- Matrix issues: Some direct sensing tools have direct push limitations that can be evaluated and addressed during a DMA. Typical matrix issues include, XRFlead arsenic peak overlap, moisture >20%, and high concentration of unexpected metals.
- ◆ Assessing alternative strategies as contingencies: By conducting a DMA, alternative strategies can be assessed as contingencies that can be implemented should the performance of intended methods prove to be inadequate.





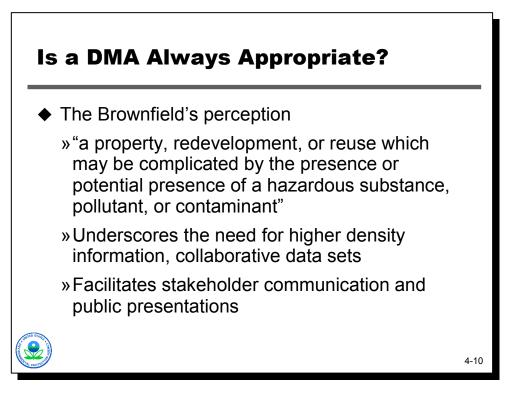
**No:** During the development of the DMA technical bulletin one commenter noted that some projects cannot support the level of effort for a DMA. This may be true, but for most applications, a DMA is beneficial precisely because a particular field analytical technique, direct sensing tool, or innovative strategy is identified as applicable to cost effectively increase data density, refine the CSM or address small scale variability and matrix heterogeneity. A DMA is a consideration if the site in question may have some of these issues. In addition, at sites with elevated expenditures associated with collection of subsurface samples (deeper contamination), adding limited additional cost associated with field analytics, direct sensing tools, or other innovative technologies may not significantly raise project expenses. Yet these tools can provide greater information density and help target locations for collection of fixed lab samples, placement of monitoring wells, optimizing screen depths/length and so on.

A DMA may not be appropriate for an SI. In some cases the selection of these locations is obvious (visual staining, products, lagoons, discharge points) while others situation are more problematic for determining appropriate locations for these samples. Depending on the nature of the contamination (for example, metals) some material may be archived for later DMA activities should expanded SI or additional site work be warranted.

Projects using mobile or fixed laboratory methods requiring modifications (shortened run times on GCs, different QC sample frequencies, different reporting packages) or careful examination of sampling and spatial uncertainties may derive significant benefit from a DMA.

It should be noted that even projects that are using only fixed laboratory methods may benefit from a very limited DMA if there are questions regarding matrix interference effects. Just a few pilot samples can help save project resources by detecting extraction, cleanup, or dilution issues at the start of a program.

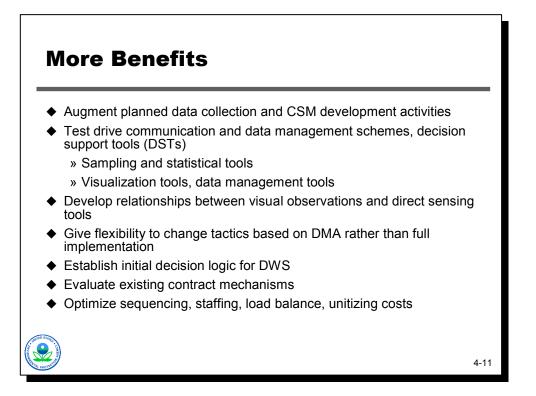
But: A DMA is usually appropriate and relatively simple for XRF. A DMA will help to optimize instrument operation, sample preparation, and decision rules or logic, and will help identify key uncertainties that will need to be managed.





**The Brownfield's perception:** Another DMA bulletin comment indicated that a DMA was of limited value at Brownfields (BF) sites and was more appropriate for larger more complex Superfund-type site activities. In reality, DMAs are used on sites across a variety of regulatory programs SF, BF, RCRA, UST, VCUP. In fact many of our BF tech support sites have completed DMAs.

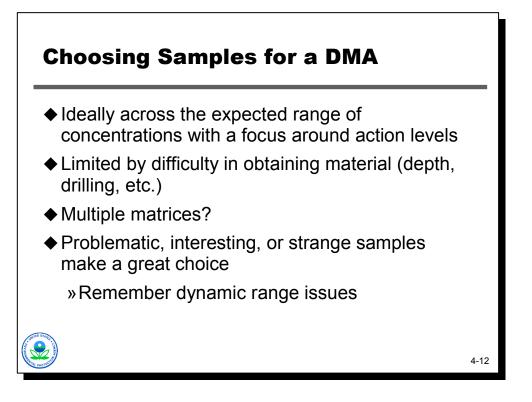
In general sites are evaluated under the BF program because they have an industrial history and the perception of contamination is there in the minds of many stakeholders, particularly concerned citizens groups. Regardless of whether the presence of contamination is real or perceived at such a property, DMAs and the use of a real time, high density tool like XRF help facilitate timely revitalization. The data sets, CSMs, and visualizations associated with DMAs and tools like XRF have helped to address stakeholder concerns at many sites. DMAs provide a level of comfort with the process that allows developers, insurance partners, risk partners, public stakeholders, state and local agencies, and other others to be involved, invested, and reassured with a project outcome.





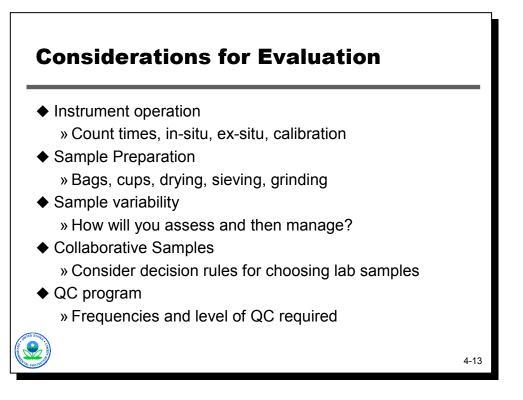
- Augment planned data collection and CSM development activities: The DMA data has additional use other than just to evaluate and optimize how the XRF will be used. The DMA data will augment the future data collection and CSM development activities.
- Test drive communication and data management schemes: The DMA allows the project team to test the communication and data management schemes that are available. These include sampling and statistical tools and visualization and data management tools.
- Develop relationships between visual observations and direct sensing tools: The DMA can be used to develop standard descriptions for visual observations. Although this can be extremely beneficial for things like MIP and LIF, it also applies to XRF. Things like tailings, high moisture, or matrix differences like ash layers, can be visually obvious and can warrant special consideration.
- Give flexibility to change tactics based on DMA rather than full implementation: The DMA provides the flexibility and opportunity to change tactics based on the results. This is much easier to accomplish with the smallerscale DMA rather than during full implementation of a sampling program.
- Establish initial decision logic for DWS: It is difficult to develop decision logic without some knowledge of how analytical tools or sampling strategies will work in the field. The DMA provides the information necessary to develop site-specific decision logic.

- Evaluate existing contract mechanisms: The results of the DMA are useful for evaluating existing contract mechanisms to determine if they are suitable for a dynamic work strategy.
- Optimize sequencing, staffing, load balance, unitizing costs: A DMA gives insight into logistical requirements. Understanding throughput and other logistics will allow the project team to balance personnel and optimize field efforts.



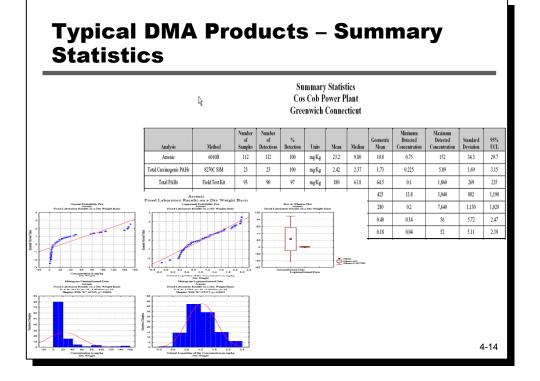


- Ideally across the expected range of concentrations with a focus around action levels: Determining which samples to split or analyze in the laboratory is a critical question. In addition, the method for splitting samples is just as important (for example, cups for XRF and then sent to a laboratory). If the XRF is mobilized to the site, it is best to collect a large number of samples that span the range of concentrations and focus around the action level.
- Limited by difficulty in obtaining material (depth, drilling, etc.): XRF sampling is only limited by the difficulty in obtaining samples but the project team can conceivably evaluate 100 samples to choose the best 20, that span the expected range of concentrations, for analysis at the laboratory (for example, 5 high, 5 low, 10 around action levels). In most cases, some percentage of samples will still be required or collected (5-20%, to confirm excavation, etc).
- Multiple matrices: In the case of applications with obviously different matrices (sand, soil, sediment, tailings), it is wise to evaluate each separately.
- Problematic, interesting, or strange samples make a great choice: The advantage of the real time information that XRF supplies is that as the sampling program progresses the project team can identify problematic, interesting, or strange samples for additional XRF measurements or targeted collaborative laboratory analysis. Remember the linearity issues associated with the instrument that were explained in Module 2; at percentage levels (10,000 ppm or greater) the XRF will have a low bias.



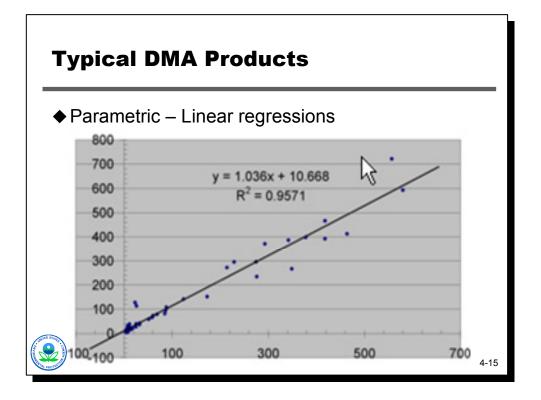


- Instrument operation: Count times generally range from 30 seconds to 600 seconds. A rule of thumb is that a 4X increase in count time equals ½ detection limit or 50% reduction in error but consider the time implications and more importantly where the greatest variability is coming from. EPA has evaluated many DMA XRF data sets where shorter count time 30 seconds was recommended, and more shots across the sample support area (bags or in-situ) to get a better estimate of the average concentration.
- Sample preparation: Evaluate the improvements derived from various preparation methods. EPA has had great success with bags. Cups are also good because of the limited sample size (<5g) that can also be sent for ICP to limit within sample variability. In-situ offers great speed and flexibility but can be limited by moisture, depth, repeatability, and particle size considerations.</p>
- Sample variability: The sample variability is critical in optimizing SOPs, considering QC options, and developing decision rules or decision logic. The impact of matrix and potential interferences must be evaluated.
- **Collaborative samples:** Those decision rules can be translated into methods for determining the best samples for collaborative analysis (most often ICP).
- QC program: QC is discussed in Module 5 in greater detail, but the ease of repeating measurements if "out of control" situations are identified is one consideration when evaluating the frequency and level of effort for QC samples.



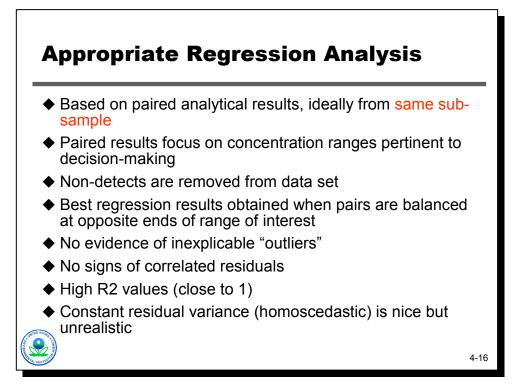
## Notes

Summary statistics from a DMA can provide an indication of expected DLs/RLs, detection frequencies, mean, median, minimum/maximum concentrations, expected SD, 95UCL, and more. DMA summary statistics are used to develop the QC program. Control charts, for example, can be based on DMA summary statistics. DMA results can be used to develop scatter plots, box and whiskers, histograms, etc. The results will indicate if population distribution (normal, lognormal, other). The results can also indicate if there are multiple populations. When detections are compared to locations on a map, distinct populations related to historical use may be evident. The project team should use the DMA information to better design CSM refinement, delineation etc. These products are not just something for chemists and statisticians to play with. These evaluations have real implications for QC sampling decisions.





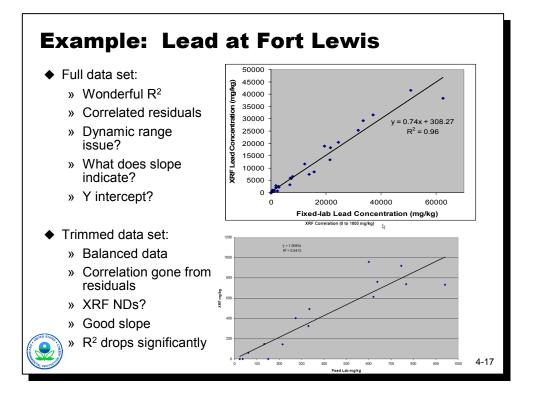
- Linear regressions are the most common parametric techniques and often the "gold standard" of method comparison. They are very powerful tools but can be misleading (next series of slides illustrates some potential pitfalls).
- Parametric statistical methods use assumptions about the data's underlying shape of the statistical distribution (normal, lognormal, other). If those assumptions are invalid, the statistical conclusions may not be reliable.
- Non-parametric techniques do not require as many assumptions to be true, so they are more broadly applicable to the properties of environmental data.
- Comparability is quantified by establishing the frequency with which results from different techniques agree with each other with respect to a declared reference point. Different points of reference can be used, but the most common strategy used in Triad projects is establishing comparability with respect to the decision being made on the data. These data may require quantitative comparability (such as if or when two data sets are combined to calculate risk assessment parameters) or qualitative comparability for agreement at the compliant/noncompliant decision threshold.





- Based on paired analytical results, ideally from same sub-sample: Such an analysis would be based on paired results, ideally with the analytical work done on the same sub-sample where possible to minimize the effects of sample preparation. It should not be expected that XRF will compare better than ICP.
- Paired results focus on concentration ranges pertinent to decision-making: The paired results should focus on the concentration range pertinent to decisionmaking. Often times field analytical methods have a more limited dynamic range within which they provide accurate results. This means that it is unreasonable to expect a good, strong linear relationship for two methods over the complete range of concentrations (which may span several orders of magnitude) present at a site. What is important is to determine whether such a relationship exists over the range in which making decision is important.
- Non-detects are removed from the data set: Non-detects should be removed from a regression analysis because they will skew regression results. Forcing the instrument to report values <DL or using appropriate substitution methods is better.
- Best regression results obtained when pairs are balanced at opposite ends of the range of interest: The best regression results are obtained when the data used are balanced, i.e., half are at the lower end of interest, and half are at the higher end of interest.
- No evidence of inexplicable "outliers": There should be no evidence of outliers. Outliers are points that clearly fall well away from the regression line and appear to be different than the rest. Data sets should be balanced.

- No signs of correlated residuals: There should be no signs of correlated residuals. Correlated residuals refer to the situation where a group of points consistently fall above or below the regression line.
- High R2 values (close to 1): A good regression should have a high R2 value, preferably close to 1 (will range between 0 and 1).
- Constant residual variance (homoscedastic) is nice but unrealistic: A good regression should have constant residual variance across the concentration range, or in other words the data should be homoscedastic. Unfortunately for environmental collaborative data sets, this is rarely the case.

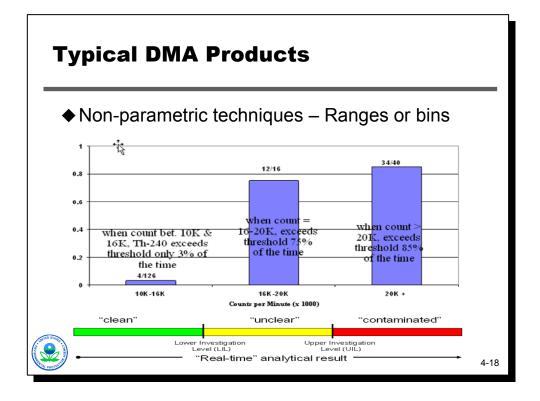




This is a preview of the case study that I'll quickly touch on at the end of this module, but here is another example of linear regression cautions. The top graphic shows a scatter plot based on the complete data set collected. The regression line has a wonderful R2 value but other problems.

The second data set has had its data trimmed to include only those concentrations that fall within the range truly of interest from a decision-making perspective. These data are balanced across the concentration range of interest. The correlations are gone from the residuals. The slope corresponds to what one would expect from a calibrated XRF. Note that the R2 value is actually less, though, than the first example, even though the second regression is clearly superior. This example underscores the problems with simply using R2 values as a measure of regression performance and hence field analytic data quality and usability.

There is something else to note in the second scatter plot. Notice how the spread of the data around the line increases as concentrations increase. This is called heteroscedasticity...a big word that simply means the variance of our data is not constant over the range of observed concentrations. However, this did not effect the project because some loss of linearity in the % range was acceptable because all action levels were <1,000 ppm.



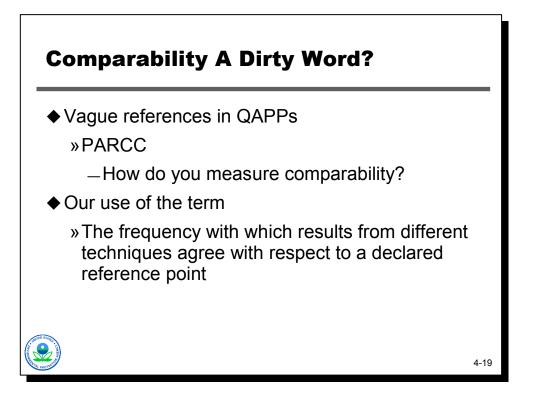


 Non-parametric methods do not make assumptions about underlying distribution of contaminants or use the estimation of parameters such as mean or standard deviation.

Non-parametric methods were developed to be used in cases when the researcher knows nothing about the parameters of the variable of interest in the population (hence the name *nonparametric*). In more technical terms, nonparametric methods do not rely on the estimation of parameters (such as the mean or the standard deviation) describing the distribution of the variable of interest in the population. Therefore, these methods are also sometimes (and more appropriately) called *parameter-free* methods or *distribution-free* methods.

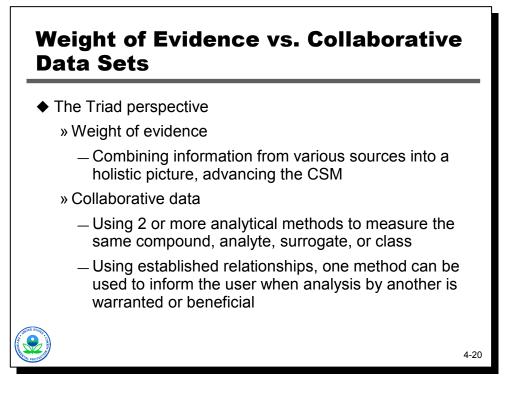
The contaminant is Th-230. It was collocated with radium, which was amenable to field screening by gamma walkover, however the radium was not at levels that posed health concerns (or where it was, its health concerns were dominated by Th-230 concerns).

There was no way to measure Th-230 directly at its action levels with real-time techniques. That required ex situ laboratory analysis by alpha spec, a technique that is fairly complicated and expensive requiring significant sample preparation/extractions/etc.





- Vague references in QAPPs: It is important to establish that the use of field analytics, direct sensing tools, and other information sources are appropriate for expected decisions. One technique is comparability. With XRF this is fairly straight forward because we are comparing apples to apples (in other words As to As or Cr to Cr). Although a more appropriate metaphor may be comparing Gala apples to granny smith, because we are looking at a total value that XRF sees (postage stamp / 2 mm) to a digested value of approx 1 gram, both of which are meant to represent a larger sample size and decision unit. But the advantage of XRF is that it's relatively inexpensive to overcome concerns regarding sample and decision unit variability. More samples, more shots, for a better average concentration.
- Our use of the term: In this course, the term comparability means establishing the frequency with which results from different techniques agree with each other with respect to a declared reference point. Different points of reference can be used, but the most common strategy used in Triad projects is establishing comparability with respect to the decision being made on the data, such as action levels, decision thresholds, etc. These data may require quantitative comparability (such as if or when two data sets are combined to calculate risk assessment parameters) or qualitative comparability for agreement at the compliant/non-compliant decision threshold.





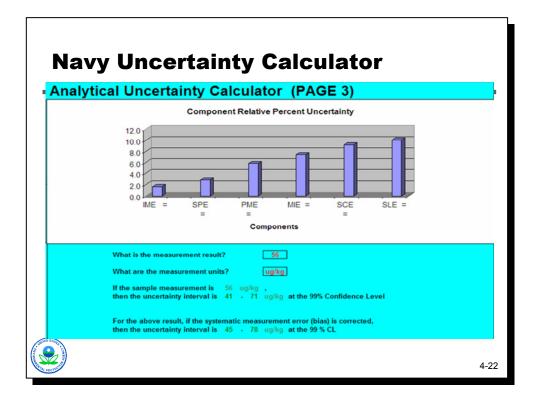
- **The Triad perspective:** Many DMAs are looking at issues of comparability, but all information sources have value and can be used to address a site's problem. This requires an understanding of some definitions.
  - Weight of evidence Terms such as "weight of evidence" or "multiple lines of evidence" and "collaborative data sets" have been developed to describe these layered data sets. From a Triad perspective, there is a distinction between the two. "Weight (or "lines) of evidence" refer to combining information from various different sources into a holistic picture (i.e., a conceptual site model). For example, historical information may be used in conjunction with geological, hydrogeological, chemical, and geophysical data to predict contaminant fate and transport.
  - » Collaborative data "Collaborative data sets" or "collaborative methods" refer specifically to the strategy of using two (or more) analytical methods to measure the "same" analyte or a surrogate of an analyte. For example, total uranium can be measured by X-ray fluorescence (XRF), gamma spectroscopy and alpha spectroscopy. Or PCBs by IA and spectrophotometer, bioassays, GC/ECD, HRGC/MS. Collaborative methods are paired so that the strengths of one method can compensate for limitations of the other. Frequently, a field method is selected for its ability to provide a much higher density of data points than an expensive laboratory method. However, the laboratory method will generally achieve better detection limits and accuracy than the field method. A DMA should be designed to guide the "marriage" of the techniques to produce reliable information that is not biased by the effects of heterogeneity or analytical inaccuracy.

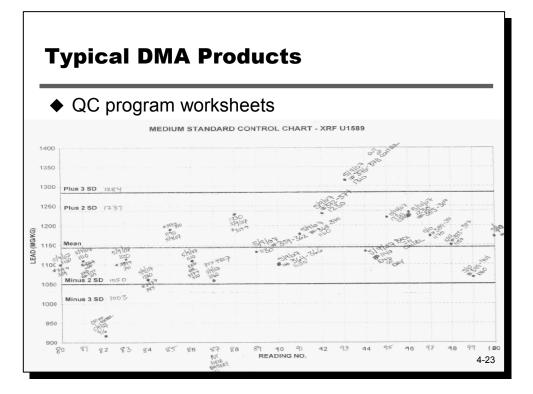
Additionally, alternative analytical methods, particularly those that provide results in "real time" can be used to optimize the decision making process. For example, the real-time decisions and high data density possible with field methods can reduce the volume of material removed during cleanup by more precisely defining and confirming the actual contamination footprint. Real-time data can in this way improve decision confidence and limit surprises after a project is complete.

<ul> <li>Uncertainty evaluations – Example: Navy Uncertainty Calculator <u>http://www.navylabs.navy.mil/Archive/Uncertainty-Calc.xls</u></li> </ul>			
Intrinsic (Instrumental) Measurement Effects	IME	Instrument Calibration Standard	ICS
Spike Preparation Effects	SPE	Initial Calibration Verification Standard	ICV
Preparation Method Effects	PME	Laboratory Control Sample	LCS
Matrix Interference Effects	MIE	Matrix Interference Sample Matrix Spike/ Duplicate Sample	MIS MS/MSD
Sample Collection Effects	SCE	Field Replicate (Duplicate) Sample (Collected from same location and during same sampling event time)	FSR
Sample Location Effects	SLE	Co-Located (Same Location) Sample (Collected 0.5 – 3 feet away from field sample)	CLR
Sampling Site Population Effects	SSE	Site field sample collected from the environmental site for the study	SFS



The Navy Uncertainty Calculator was developed by Bill Ingersoll at the Navy. It can be accessed at <u>http://navylabs.navy.mil/Archive/Uncertainty-Calc.xls</u>.





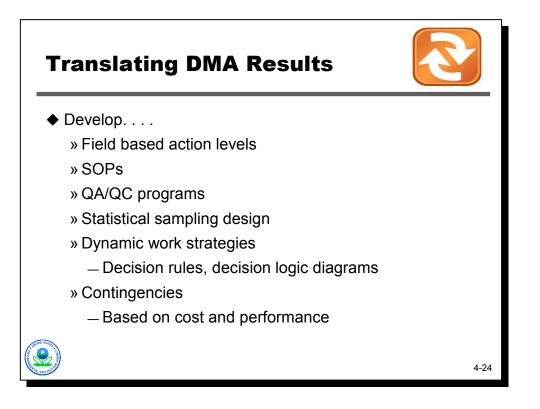


• With a good DMA control charts for SRMs and SSCS can be established which are essentially the initial and continuing calibration standards.

DMAs control charts should have 30 or more results but that does not take a whole lot of time since they are needed as part of the DMA. In addition NIST standards like 2709, 2710, and 2711 will be incorporated into the program. The project team should also include spiked samples or well characterized samples from the site.

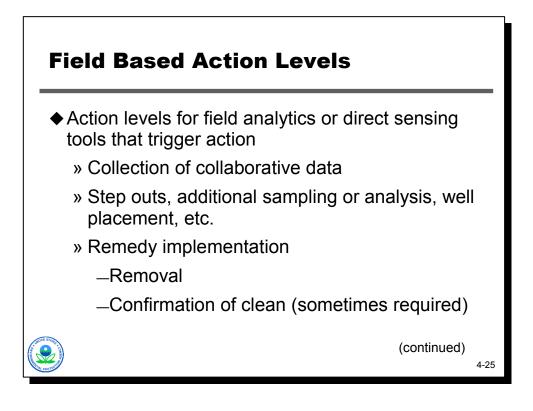
Monitor analytes of concern using SRM or standard checks with these control charts. Trends in instrument drift can be spotted and "out of control" situations can be identified. Generally the DMA can provide a sufficient number of SRM measurements (30 or more) to develop summary statistics for analytes of concern. Based on the DMA values and summary statistics, specify an expected mean and standard deviation for each analyte. Specifying an expected mean and standard deviation is considered better because determining these values as the data set progresses can be difficult since outliers can dramatically increase 2 SD and 3 SD values and mask potentially "out of control" situations.

Again, the value in doing this is that out of control situations can be identified as they happened limiting the number of samples that may need to be re-run. If it is done only at the start and end of each day, and for example, one of your analytes is >3SD at the end of the day, all samples for that day will need to be re-run. This is the most problematic with in-situ applications.



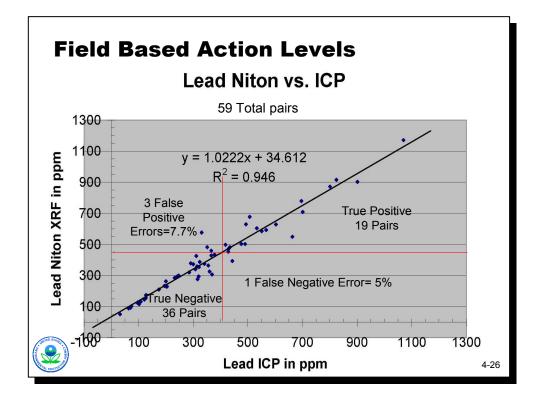


Develop: The term "actionable intelligence" fits nicely in this context. That term used in military and counter insurgency circles, but this is where the rubber hits the road. This is where we are taking those valuable lessons learned and translating them into a plan for how to implement or operate the XRF, develop sampling strategies, data management plans, QC programs, etc. as the site or program progresses. This is an iterative process, so the data relationships that are established and corresponding sampling and analysis implications can be refined as the program continues. The DMA provides a solid platform from which to do this.

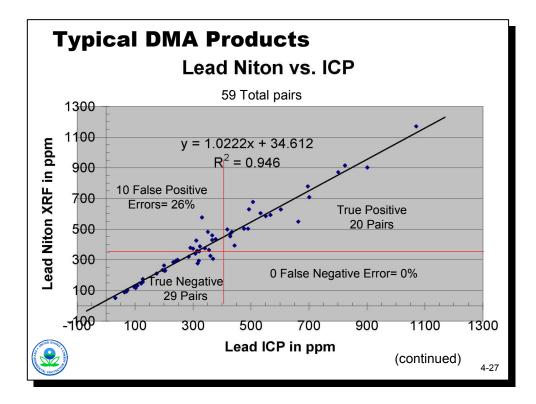




Action levels for field analytics or direct sensing tools that trigger action: The DMA results should be used to develop action levels that trigger action. The action may include collection of collaborative data, stepping out to conduct additional sampling and analysis or well placement, or implementing a remedy by identifying material to be removed or confirming adequate cleanup.

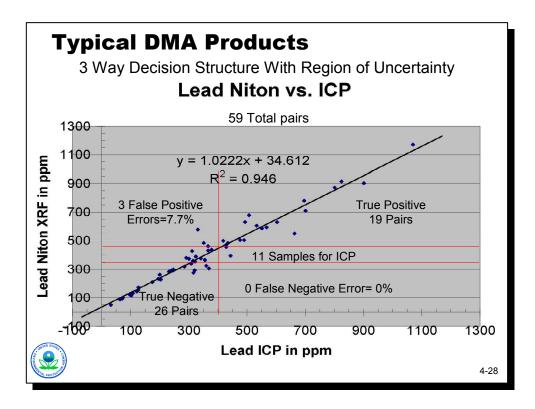


- Notes
- The graph above is another typical DMA product. EPA uses this for its technical support sites to develop field based action levels for XRF. This is a well correlated data set but the concept holds true for less "well behaved" data sets. The XRF action level is at 400 ppm.

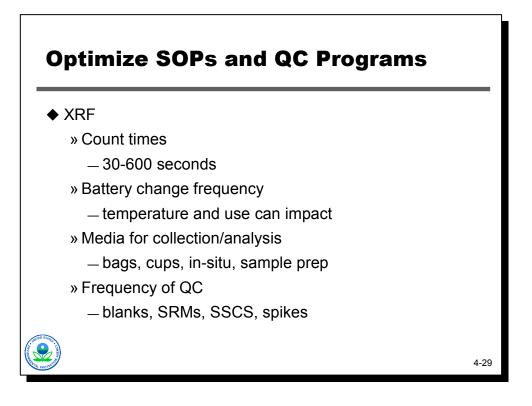




If there is more concern about a Type I or false negative error, the XRF field based action level could be reduced to 350 ppm and decrease the false negative or "false clean" to 0. This would however result in a higher false positive or "false dirty" rate of 13 false positive errors or 22%. The project team has to weigh the consequences of a false negative vs. the costs associated with excavation or clean up at a rate of 17% false dirty. Many sites default to 5% error for false negative and 10% for false positive.



- Notes
- The graph shows the structure of a 3 way decision. There are 19 true positives, 26 true negatives, 3 false positives, and 11 samples for ICP. The region of uncertainty is 350-450 ppm. Below 350 is definitely clean, above 450 is definitely dirty (with 5% false positives).

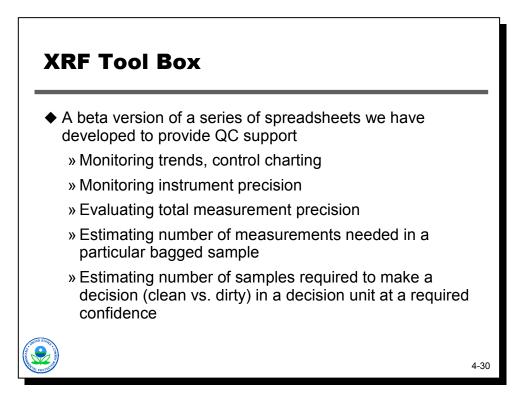




## XRF:

- » Count times For most applications, count times between 30-120 seconds are sufficient but they can be increased to lower DLs and variability. In the case of bags, the majority of variability exists across the sample support (the bag). By decreasing count times and increasing the number of measurements systematically across the bag, better control over the variability is achieved for the whole measurement system. In other words 4/30 sec shots (2 then flip bag/ 2 more) may be better than 1/ 2 minute shot at 1 location.
- » Battery change frequency Module 5 will look at an example of what can happen to XRF results from the battery. Unfortunately the impact can be obvious (such as the instrument won't let you continue until you change the battery and re-initialize) or subtle (changes that can go unnoticed but can effect results).
- » Media for collection/analysis Sample type and sample support must be selected.

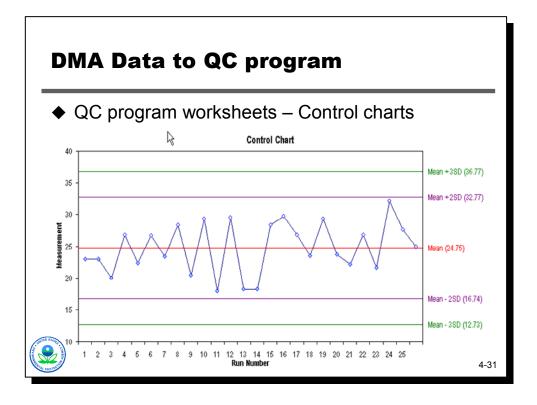
Frequency of QC – The DMA should help you determine an appropriate QC frequency. Ultimately it becomes a balance of "how easy and quickly can QC sample analysis be completed vs. what are the consequences of being out of control". When a laboratory encounters an issue with continuing calibration, it is forced to re-run those samples that have been analyzed since the last initial or continuing calibration. The same is true for XRF. Depending on how samples are being collected and analyzed, a higher or lower frequency of checks will be required. The frequency can range from as few as twice a day (beginning and end) to as many as every 10 samples. With the in-situ method, it is difficult to re-analyze so checks are likely more frequent. Bags or cups are already prepared and stored and XRF is non-destructive so re-analyzing isn't too problematic. At the same time, the analyses should not fall behind the collection speeds and the need for real time information because of QC analyses.





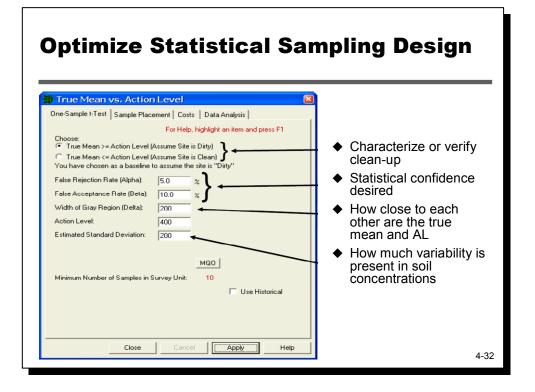
One of the tools EPA has developed to support SOP and QC optimization is the XRF tool box. This is a series of spreadsheets developed mostly by Bob Johnson and Deana Crumbling that we are currently adjusting and using at some sites. EPA hopes to release this as a tool to help XRF users in the future. Module 5 will provide more examples of the XRF tool box.

EPA is trying to use and test these tools and get feedback from users. The XRF tool box is not available to the public, but if you are interested you can contact us regarding helping us through the testing and optimization procedures. In return, EPA asks that you share data and provide feedback.



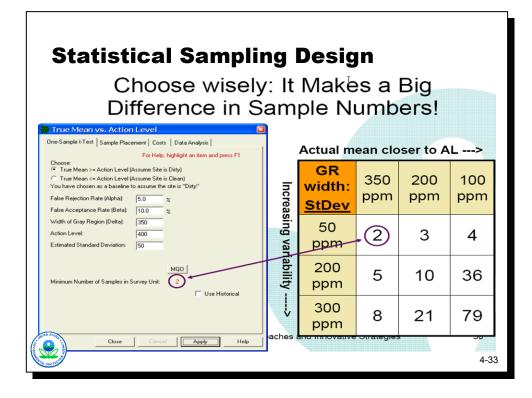
- Notes
- This is an example of a spreadsheet from the XRF toolbox. Essentially, DMA summary statistics provide the inputs. The user can monitor the behavior of key metals (COCs) that are present in the QC samples. The user can spot trends in instrument drift and identify "out of control" situations. The trend issue is important with regard to potential battery issues.

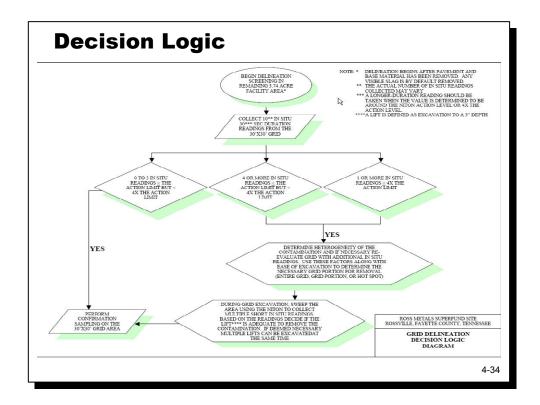
In general, if one measurement exceeds 2 SD, take it again (using a 95 UCL you would expect 5 out of 100 readings to be outside the <u>+</u>2SD value). If the second reading is within the 2SD of the mean, continue and monitor for trends. If the second reading is still outside the 2SD window, initiate corrective action (change battery, re-initialize, re-run SRMs and QC). Likewise, any one reading outside the 3SD window would require corrective action. Again, the value in doing this is that out of control situations can be identified as they happen and limit the number of samples that may need to be re-run.





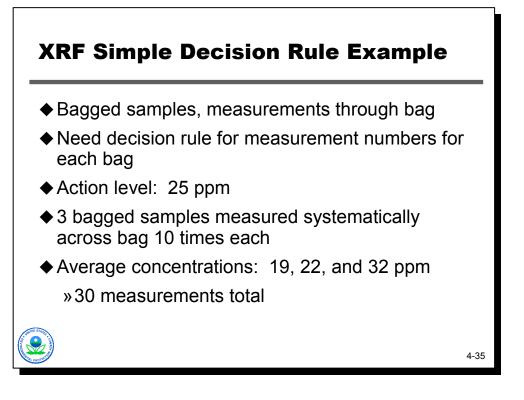
There are many sampling design tools available, such as visual sampling plan. One of the acknowledged pitfalls associated with using classical statistical tools in sampling design is that project teams seldom have a sound estimate of total measurement error for use in establishing sample quantities, grid sizes, etc. With results from a DMA, project teams can use classical statistical tools (such as the Visual Sample Plan software, <u>http://vsp.pnl.gov/</u>) more effectively in sampling design because they have generated site-specific method error information.

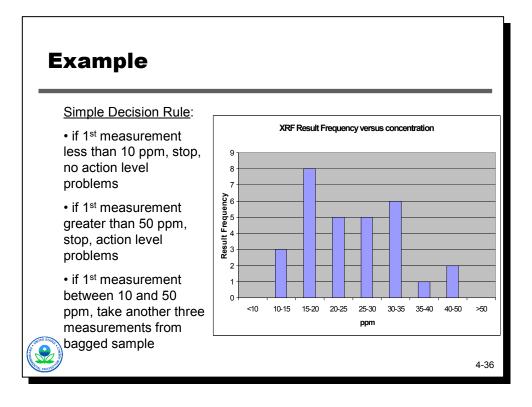




## Notes

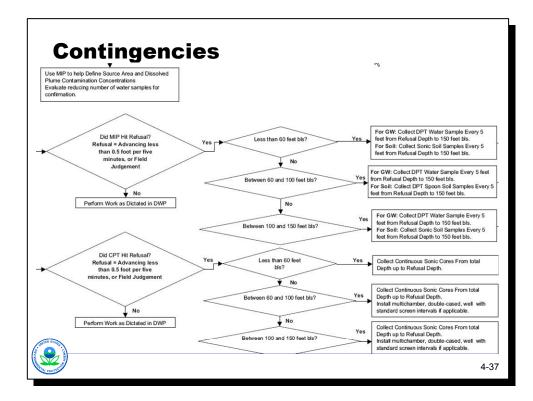
The DMA provides critical information to develop decision logic. There are many advantages to using XRF but one of the greatest is the real-time information. To maximize the benefits of that real time information, Triad practitioners develop decision logic for field teams. In this case, there are clear and easy instructions for how results will be interpreted and how decisions or subsequent actions are triggered. At this site there were 2 XRF-specific decision logic diagrams, one for delineation and one for confirmation. The instrument was being operated in the in-situ mode with multiple readings across each decision unit (in this case a 30'X30' grid to a depth of 3 inches). The grid sizes and depths were determined from DMA data and practical considerations (a back hoe couldn't remove on a finer scale than 3 inch lifts). Depending on the number of values that exceeded the action level and the degree to which they did, grids were further assessed for removal of hot spots; additional in-situ readings; excavation; or the grid moved to a confirmation logic, ex-situ readings, and laboratory analyses.







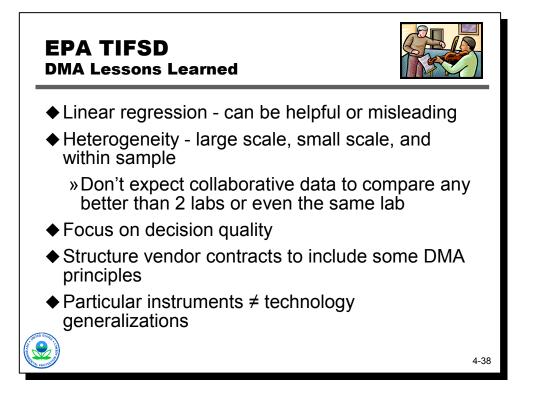
• Modules 6.1 and 6.2 will discuss adaptive decision rules in more detail.



## Notes

DMAs also support development of contingencies for technologies and drilling platforms. This graphic above is a subset from a much more comprehensive decision logic diagram from some Triad work completed at Hurlburt Field. This portion of the decision logic focused on contingencies whose necessity was determined during a DMA. The concern was to have drilling platform contingencies should the MIP (on a direct push platform) have issues with refusal. The contingencies included options for sonic drilling, core analyses (in lieu of CPT information), laboratory analyses, well placement, well screen intervals, etc.

A DMA can often provide information on the likelihood of field analysis or drilling issues that would in turn necessitate the need to plan for contingencies. This is particularly helpful for dynamic work strategies where the goal is to meet project objectives in one or limited mobilizations while maximizing real time information.





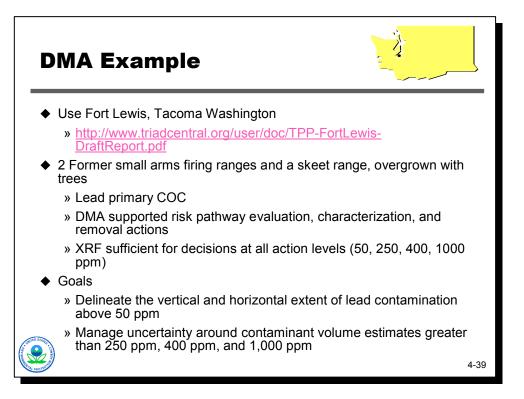
These lessons are based on experiences from our technical support sites.

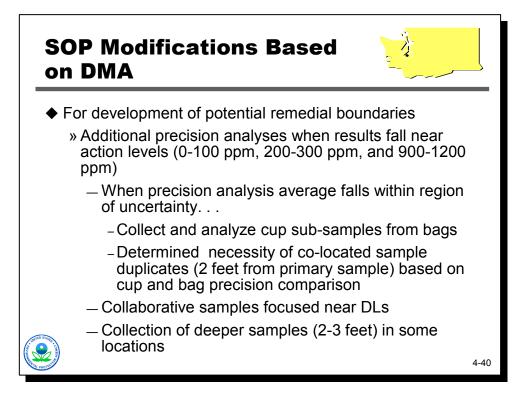
Linear regression: Do not just focus on the R2 value. If you are planning on using linear regression: 20 or more paired samples is a good rule of thumb. The regression should be based on paired analytical results, ideally from same sub-sample. The paired results should focus on concentration ranges pertinent to decision-making (dynamic range over which calibrations hold).

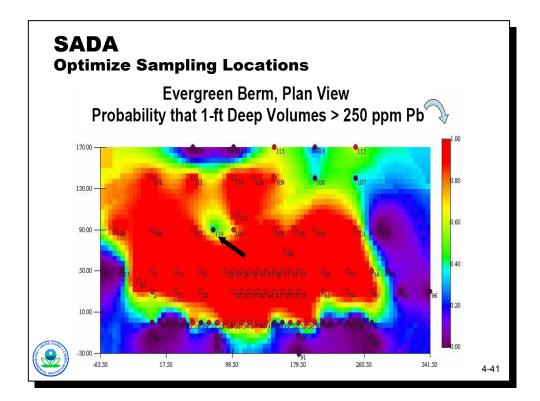
Non-detects are removed from data set. XRF can force instruments to report values <DL or use appropriate substitution methods. Best regression results are obtained when pairs are balanced at opposite ends of range of interest. Good regressions should have no evidence of inexplicable "outliers." There should be no signs of correlated residuals. In general, there should be high R2 values (close to 1). Constant residual variance (homoscedastic) is nice but unrealistic. Watch out when using UCLs UTLs.

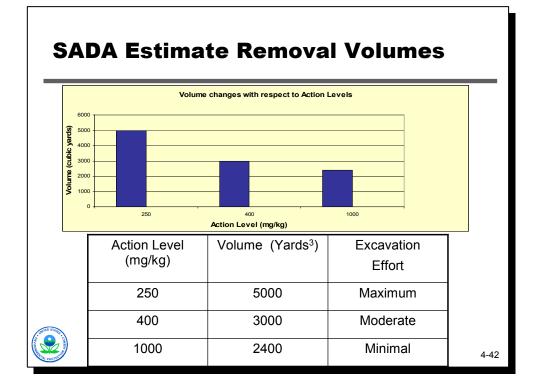
Heterogeneity: Standard laboratory data can be "noisy" and are not necessarily an error-free representation of reality. In fact, a DMA may identify laboratory issues based on comparability with field analytics. A DMA can identify laboratory issues or mistakes, sampling issues, sub-sampling issues etc. that have far greater project impacts than solely focusing on field analytics.

- Focus on decision quality: Focus on decision quality not necessarily laboratory method comparability. Determine if collaborative data sets or multiple lines of evidence are supporting the same decision. Evaluate if data can be used to determine an area is clean, dirty, or that more information is needed (in real time of course). Remember parametric and non-parametric techniques are available, so some DMA data sets with weaker correlations may still be useful for decision support. They can also be indicative of other sampling, matrix heterogeneity, or small scale variability issues.
- Structure vendor contracts to include some DMA principles: Some vendors may participate for free, such as sending material to vendors to see if it fluoresces. Ask to see what outputs you will be getting and using to make decisions. As an example, there are varying degrees of complexity for MIP vendor outputs. There can be a big difference in spreadsheets vs. real-time 3D visualizations. In fact one of the advantages of a technology like MIP is the ability to drive DWS and facilitate stakeholder discussions in real time. That can be difficult when the out put is a spreadsheet, or the information is provided in days or weeks such that it cannot be used effectively in the field. When used in a static fashion, a tool like MIP or LIF becomes less effective. Contract language can really help avoid issues of paying for services that don't work as advertised. Ask vendors to demonstrate technologies (example GPR).
- ◆ Particular instruments ≠ technology generalizations: Not all XRFs, MIPS, LIFs, vendors are created equal.











 In the end they ended up using the 1,000 ppm action level, excavated and reused the material elsewhere at the base.

