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THE LEADER IN ENVIRONMENTAL TESTING

Producing Defensible Environmental Data using Modified and Non-Standard Methodology

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Abstract

Purpose and Objective - To demonstrate the need in project design to establish data quality objectives to ensure that environmental data generated is defensible and able to support the needs of the data user community.

Approach or Experimental Design - Identify fundamental aspects of environmental laboratory quality systems. We will also identify potential gaps that may exist in standard quality systems when performing modified or non-standard methodology that should be considered in experimental design and execution. Discussion on how these systems and considerations are being applied to evaluate coal ash and Kingston specific studies to provide data of known quality to the user community. .

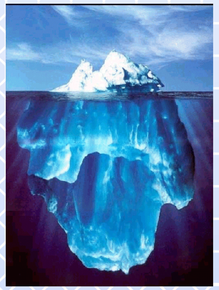
Results or Findings to date - Utilizing a Kingston coal ash project specific sequential extraction method for metals, we will provide examples of how quality systems were adapted to conform to industry standards and what supplemental information should be considered in project design.

Significance or Benefit to Kingston Ash Recovery Program - Data generated from this program will have many uses and users. It will be utilized for a variety of purposes. Significant decisions will be made from data generated to investigate this site and incident. The data underlying these decisions must be of known quality and able to provide support to assist in appropriate evaluation and decision making.

Future Studies - Continued emphasis to increase awareness of project communication in advance during project design to ensure that all appropriate measures are considered and in place prior to data generation.

Introduction

The coal ash release that occurred in Kingston TN in December 2008 was unprecedented in scope and is unique in many aspects. As such we do not have significant experience to draw upon to understand all of the potential impacts of this event. Many investigations are being and will be conducted to both characterize the site to understand the immediate and potential long term effects of the release. The data being generated by these various investigations are being conducted for specific purposes. The data quality may be sufficient for the purposes generated. However, it is likely that as our understanding of the situation evolves we will be looking to the entire body of data generated to help us better understand other related aspects of the event for other than its originally intended purpose. We should ensure that we fully understand the nature of the data, assumptions that may have been used in experimental design, and uncertainty of the data itself to understand how it may or may not be able to be utilized for other purposes than its original intended use. Due to the unique nature of the investigations and recovery efforts, both routine methodology are being utilized as well as novel investigative techniques. We are presenting here for discussion purpose an example of a study performed that employed an adaptation of a published research investigation combined with routine USEPA methodology to better characterize the metal content of the ash. It should be noted that while we focus on the laboratory aspects, similar considerations should be given to field activities as they have significant impact on the overall project data quality, usability and defensibility.

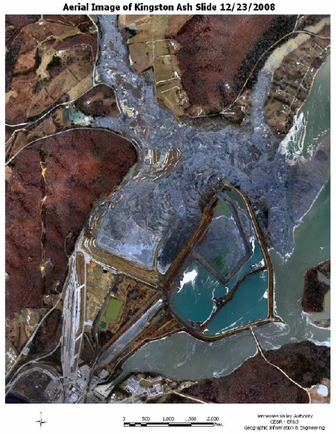


Establishing Data Quality Objectives

Importance

Data quality objectives (DQOs) are qualitative and quantitative statements that are developed to clarify study objectives, define the appropriate type of data and specific potential decision errors and uncertainty. These are used for establishing the quality and quantity of data needed to support decisions. One of the challenges that investigations being conducted in association with the TVA Kingston Coal Ash release that should be considered, is that while DQOs may be understood for the initial study, much of this data may be used for other purposes later as the data are generated, the investigation evolves and new questions develop. Understanding the limitations of the data will assist in determining how this data are or are not able to support current and later evaluations and decisions. Projects that do not initially define these objectives may be unable later to asses the usability of contributed data. Data quality indicators such as precision, bias, representativeness, completeness, comparability and sensitivity should routinely utilized to assess project data.

Aerial Image of Kingston Ash Slide 12/23/2008



Laboratory Quality Systems

Fundamentals for Environmental Laboratories

As a base to support all environmental measurements, fundamental components of quality systems should exist to support the data and provide the user community confidence in the data. The National Environmental Laboratory Accreditation Program (NELAP) has established extensive quality systems criteria that address many of these aspects. We will not exhaustively review all of these components in this presentation but we do want to highlight major areas that should be considered when utilizing modified and non-standard testing protocols. Quality systems that ensure the defensibility of the data must be in place to provide the foundation from which modifications are made to address the specific needs of the project investigation. This defined starting point then allows that deviations and modifications are able to be identified and documented. These deviations and modifications need to be associated with the data generated to understand how they may affect the usability of the data for its intended purposes as well as future potential uses.

1. Documentation - Written procedures, SOPs, bench sheets and project narratives are essential components of defining data quality. By clearly recording what was done, what modifications to existing methodology or studies were made and what assumptions were considered in the experimental design it will serve both to provide defensibility of the data as well as help frame the data for future users.

2. Sample Management - Ensure that sample identity, validity and integrity are able to be tracked and documented throughout the entire process including subsequent aliquots of the sample that may result from various extractions, digestions or sample manipulations. As data may be drawn into future litigation or utilized by other researchers, it is critical that these criteria define a traceability of sample custody and conditions to provide confidence in data presented.

3. Analytical procedures employed - This may involve any of the following individually or a combination of them.

a. Defined and accepted methodology that has known precision, accuracy and quality criteria.

b. Modifications to defined methodology to address project specific needs or conditions.

c. Unique and innovative project specific studies conducted

Laboratory Quality Systems

Fundamentals (continued)

4. Accuracy and Precision - define and understand the performance of the methodology, the impact of the modifications or verification that known methods performed as expected on the material being investigated. The measurements and criteria used to define these aspects will help the data user understand potential uncertainty of the data set. Some aspects to consider relative to these characteristics are identified below

a. Instrument calibration - acceptance criteria, calibration technique employed, source material used, second source verification of standard material, traceability of standards, frequency of calibration, dynamic range of measurement system.

b. Precision/Reproducibility - replicate analyses, control levels

c. Matrix effect - fortified sample analysis, monitoring for known interferents to the methodology

d. Method performance - Laboratory Control Samples (known values), Standard Reference Material.

e. Sensitivity - verification of lowest levels of detection to evaluate potential of false positives or negatives. Demonstrate and verify the level of detection reported.

f. Interference evaluation - understanding known and potential limitations of the methods employed. Demonstration of impact of levels of potential interferents.

g. Contamination controls - method and process blanks, understanding and defining limitations of quantitation relative to levels of measurements being conducted.

5. Record retention - Due to the historic and significant nature of this event it is possible that data generated from these investigations will be reviewed and utilized for years to come as we learn more from the various studies. It is essential that we maintain and retain adequate documentation of what was actually performed, especially in situations where we are modifying or employing project specific methodology as part of these investigations.

Example Non-Standard, Modified Method

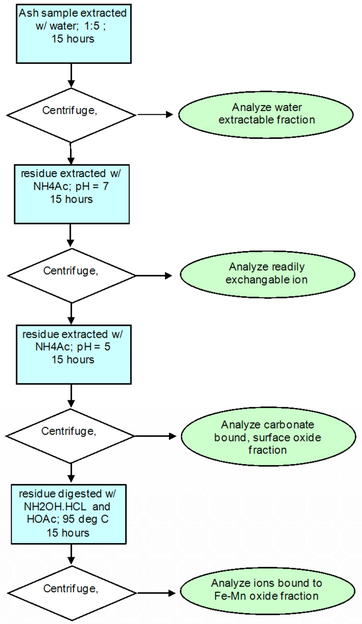
Kingston Coal Ash Investigation Usage

Traditionally samples are analyzed for total metal content to characterize them for comparison to known values for decision making in routine application. As we try to better understand and predict the impact of this material release, we need to understand more fully the form in which these metals exist to better predict their behavior in various situations. To evaluate the potential mobility of metals in fly ash and combustion by-products based upon speciation of the metals and metal complexes present, a modification of a method presented by Querol et. al[1] was conducted. While the article referenced provided adequate detail for utilization, local interpretations may and were made. These should be adequately documented for understanding when reviewing and interpreting data generated. This process employed a sequential extraction procedure which was designed to evaluate mobility in coal and combustions wastes for the following fractions followed by ICP/MS analysis.

1. Water extractable
2. Readily exchangeable ions
3. Carbonate bound, surface oxide bound ions
4. Ions bound to Fe-Mn oxides

Fractions were generated using the sequential extraction procedure. The water extractable, readily exchangeable, carbonate and surface oxide bound fractions were preserved to a pH < 2 following collection and analyzed directly by ICP/MS by USEPA method 6020 following centrifugation without subsequent filtration or digestion. Water samples analyzed by 6020 would normally be digested and paired with a method blank and laboratory control sample that would be digested prior to analysis. In this study we modified this to include these without associated digestion to evaluate any contribution or effect of the reagents used in the extraction procedure.

The Fe-Mn oxide bound ions were extracted from the residue by digesting using hydroxylamine hydrochloride and acetic acid prior to analysis. A special method detection limit study that is different from that routinely used for water samples in the laboratory was conducted to evaluate the effect of this non-routine digestion reagent system on method performance. Additionally process and method blanks were evaluated to assess contamination. A laboratory fortified sample was also digested and processed through the reagent system and analysis process to evaluate overall method performance on the metals of interest. Routine production benchsheets and LIMS utilized by commercial laboratories do not adequately document these variances and modifications Supplemental laboratory notes and documentation are required to ensure the process was adequately documented to allow for use in the evaluation, validation and defensibility of the data generated. Project communication before, during and after project execution are critical between the laboratory and project staff to ensure any modifications or observations made are communicated.



Conclusion

This study identified the need to understand that data being generated must meet its intended purpose to answer the scientific questions that it is being conducted to address as well as be defensible to withstand potential future challenges. It should also be sufficiently documented and characterized to detail its limitations, modifications and assumptions so that data users may understand its suitability for use. We have identified the need for additional documentation of conduct of these investigations that are not included in routine production laboratory processes that have been demonstrated to meet industry standard by State agencies and Industry programs and organizations such as NELAC. As many investigations are being conducted by a variety of, commercial, academic and regulatory organizations we want to identify the need to adequately document all aspects of quality systems and data generation so that the data collected may be appropriated utilized and understood to address this incident and potential future incidents.

References

1. Querol, et.al. ; Mobility of trace elements from coal and combustion wastes. Fuel, 75, 7, 821-838, 1996

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