Background Comparisons for Inorganic Chemicals

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REVISION HISTORY

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EP-ERSS-SOP-5086, R0	02/09/07	Reformatted and renumbered, supersedes SOP-15.12	E
SOP-5245, R0	10/06/09	New number sequence assigned. Supersedes EP-ERSS-SOP-5086. Added process for performing statistical comparisons and conducting background comparisons for essential nutrients	T
SOP-5245, R1	8/26/2010	Deleted references to data review appendix and other editorial changes; Revised approach for addressing essential nutrients per NMED comments; Updated organization change.	T/E
EP-SOP-10071, R0	1/6/2015	Major changes on how to eliminate or retain COPCs Editorial changes. Supersedes SOP-5245. Reformatted to new template.	T/E

CONTENTS

1.0 PURPOSE

This standard operating procedure (SOP) describes the process for performing background comparisons on inorganic chemicals for the Los Alamos National Laboratory (LANL) Environmental Programs (EP) Directorate. This procedure integrates the criteria of the Quality Assurance Plan for the EP Directorate.

2.0 SCOPE

All EP Directorate participants and subcontractors shall implement this procedure when identifying inorganic chemicals of potential concern (COPCs) for sites investigated by the Corrective Actions Project, Technical Area 21 Closure Project, and Technical Area 54 Closure Project.

3.0 BACKGROUND AND PRECAUTIONS

3.1 Background

The purpose of this procedure is to describe the process for performing background comparisons on inorganic chemicals at sites investigated by EP Directorate projects. The procedure involves the comparison of site data sets to background data sets established for the Pajarito Plateau and associated canyons. The Laboratory has received informal approval from the New Mexico Environmental Department's (NMED's) Hazardous Waste Bureau to use the soil, sediment, and tuff background values (BVs) and data from the Laboratory background document "Inorganic and Radionuclide Background Data for Soils, Canyon Sediments, and Bandelier Tuff at Los Alamos National Laboratory," LA-UR-98-4847 (LANL 1998, 059730).

3.2 Precautions

In addition to the process described herein, there is a need to apply professional experience and judgment in determining whether inorganic chemicals are eliminated or retained as COPCs. The intent of the procedure is to be **inclusive rather than exclusive** so that the nature and extent of contamination and the potential risks are representative. However, it is recognized that for some site data sets, there may be a basis for eliminating inorganic chemicals as COPCs if concentrations are interpreted as being equivalent to background and no statistical or nonstatistical methods can be used to justify the elimination. In these cases, lines of evidence must be presented as the bases for eliminating the inorganic chemical as a COPC. The key component is consistency and NMED's acceptance of this process.

4.0 REFERENCES

- "Inorganic and Radionuclide Background Data for Soils, Canyon Sediments, and Bandelier Tuff at Los Alamos National Laboratory," LA-UR-98-4847 (LANL 1998, 059730)
- SOP-5250, *Selection and Use of Annotated Outlines/Templates for Consent Order Investigation Work Plans and Investigation Reports,* Attachments 3 and 4
- EP-DIR-SOP-4004, *Records Transmittal and Retrieval Process*

5.0 DEFINITIONS AND ACRONYMS

5.1 Definitions

Background concentration — Naturally occurring concentrations of an inorganic chemical or radionuclide in soil, sediment, or tuff.

Background data — Data representing naturally occurring concentrations of inorganic and radionuclide constituents in a geologic medium. LANL's background data are derived from samples collected at locations that are either within or adjacent to LANL. These locations (1) are representative of geological media found within LANL boundaries and (2) have not been affected by LANL operations.

Background value (BV) — A statistically derived concentration (i.e., the upper tolerance limit [UTL]) of a chemical used to represent the background data set. If a UTL cannot be derived, either the detection limit or maximum reported value in the background data set is used.

Chemical of potential concern (COPC) — A chemical compound or radionuclide with the potential to adversely affect a receptor as a result of its concentration, distribution, and toxicity.

5.2 Acronyms

ALLH	all horizons (soil)
BV	background value
COPC	chemical of potential concern
DL	detection limit
EP	Environmental Programs
LANL	Los Alamos National Laboratory (Laboratory)
NMED	New Mexico Environment Department
Qbt	Quarternary Tshirege Member of the Bandelier Tuff
SED	sediment
SOP	standard operating procedure
UTL	upper tolerance limit

6.0 TOOLS AND EQUIPMENT

Essential equipment and tools required to implement this SOP include the following:

- the U.S. Environmental Protection Agency ProUCL computer program containing statistical methods or other statistical packages, as appropriate;
- the Laboratory background document "Inorganic and Radionuclide Background Data for Soils, Canyon Sediments, and Bandelier Tuff at Los Alamos National Laboratory," LA-UR-98-4847 (LANL 1998, 059730);
- Microsoft Excel;
- the current version of NMED's risk assessment guidance; and
- the annotated outline for the investigation report (see SOP-5250, Attachments 3 and 4).

7.0 STEP-BY-STEP PROCESS DESCRIPTION

Note: See Attachment 1 for overall process flow.

7.1 Prepare for Background Value Comparisons

Project Members

1. Obtain the current list of BVs from the Laboratory background document "Inorganic and Radionuclide Background Data for Soils, Canyon Sediments, and Bandelier Tuff at Los Alamos National Laboratory," LA-UR-98-4847 (LANL 1998, 059730).
2. Determine the sample preparation and analytical methods used to generate results from the background samples from the background data sets.
   NOTE: Background data sets are available from the data stewards upon request.
3. Obtain the site data set (i.e., solid waste management unit, area of concern, and consolidated unit being evaluated) from the data steward, including at least the following information:
   - sample concentration results
   - reporting units of the sample concentrations
   - final sample result qualifiers
   - sample analytical methods
   - sample preparation methods
4. Determine the comparability of the methods used to prepare and analyze the site samples and the background samples.
   NOTE: If site sample methods differ from the LANL background sample methods, consult a chemist.

7.2 Select Appropriate BVs

Project Members

1. For samples collected from soil, compare with LANL's soil BVs.
   NOTE: In this context, "soil media" includes any soil or fill material. Soil is designated as all horizons [ALLH], and fill is designated as FILL.
2. For samples collected from tuff identified as Qbt 2, Qbt 3, Qbt 4, Qbt 1v, Qbt 1g, Qbo, and/or Qct, compare with the appropriate BV(s).
3. For sediment samples, compare with the sediment BVs.
   NOTE: Sediment is designated as SED.

7.3 Comparing Site Data with BVs and Background Data

Project Members

1. If the inorganic chemical is detected but has no BVs, identify the inorganic chemical as a COPC.
2. If the maximum result for an inorganic chemical is less than or equal to the BV(s) for that inorganic chemical and all media sampled, do not identify the inorganic chemical as a COPC.
3. If there are only nondetects in the site data set and detection limits (DLs) are above the BV(s), either provide lines of evidence why the inorganic chemical is not a COPC or retain as a COPC. The lines of evidence include the following:

- comparison of the maximum detection limit to the maximum background concentration;
- the amount the DLs are above the BV(s) and below the maximum background concentration;
- the number of times the inorganic chemical was detected or not detected in the other samples of the same medium;
- the number of times the inorganic chemical was detected below/above the BV or not detected at the site; and
- assume that all of the DLs above the BV(s) are detects, and run statistical tests to see if data sets are or are not statistically different.

Example Text

Cadmium was not detected above the soil BV (0.4 mg/kg) but had DLs (0.503 mg/kg to 0.615 mg/kg) above the BV in 11 soil samples. The DLs were only 0.103 mg/kg to 0.215 mg/kg above the soil BV and were approximately 2 mg/kg to 2.1 mg/kg below the maximum soil background concentration (2.6 mg/kg). Cadmium was not detected in the 11 soil samples and was not detected above BVs in the 48 samples (detected in 5 samples below the Qbt 2,3,4 BV). The detected concentrations of cadmium (0.014 mg/kg to 0.107 mg/kg) are well below all BVs and indicate that cadmium, when present, is below BVs. If an assumption is made that all of the DLs above the soil BV are detects, the quantile test ($p = 0.1347$) and slippage test ($p = 1$) indicate that the data sets are not statistically different (p-values >0.05). Based on these lines of evidence, cadmium is not a COPC.

4. If there are only nondetects in the site data set and detection limits (DLs) are above the BV(s) and the maximum background concentration, retain the inorganic chemical as a COPC.

5. If there are fewer than 8 samples and/or fewer than 5 detected sample results for the environmental medium and the inorganic chemical being evaluated and the maximum result is greater than the BV, either provide lines of evidence why the inorganic chemical is not a COPC or retain as a COPC. The lines of evidence include, but are not limited to, the following:
   - comparison of the maximum result to the maximum background concentration;
   - the amount the maximum concentration is above the BV and below the maximum background concentration;
   - whether the inorganic chemical was detected or not detected above the BV in the other samples of the same medium as well as all samples and the number of times this occurred; and
   - indicate whether the inorganic chemical was detected at a higher concentration in other media sampled but was below the BV for that medium.

   Example Text

   Copper was detected above the Qbt 2,3,4 BV (4.66 mg/kg) in 1 sample at a concentration of 7.06 mg/kg. The concentration was 3.6 mg/kg above the BV and only 0.86 mg/kg above the maximum Qbt 2,3,4 background concentration (6.2 mg/kg). Copper was not detected above BVs in the other 15 samples. Copper is not a COPC.

   Lead was detected above the Qbt 2,3,4 BV (11.2 mg/kg) in 3 samples with a maximum concentration of 12.8 mg/kg. The concentrations were only 0.1 mg/kg, 1.4 mg/kg, and 1.6 mg/kg above the BV and below the maximum Qbt 2,3,4 background concentration

		(15.5 mg/kg). Lead was not detected above BVs in the other 13 samples (detected at higher concentrations in 2 soil samples below the soil BV). Lead is not a COPC. NOTE: This exercise should be confined primarily to inorganic chemicals with only one or two concentrations above the BV and below or only slightly above the maximum background concentration unless all concentrations are below the maximum background concentration or are all barely above the maximum background concentration. Evaluate on a chemical-by-chemical basis, and obtain guidance from a subject matter expert before proceeding.
	6.	For the conditions in section 5 above, present the site data and background data being compared in a box plot(s) and provide the box plot(s) in an appendix in the investigation report (see Attachment 2 for examples of box plots). When constructing the box plot(s), plot the concentrations as points overlying the box plot. When a data set contains both detected concentrations and nondetected concentrations (i.e., detection limits), the detected concentrations are plotted as Xs, and the nondetected concentrations are plotted as Os. Define Xs and Os in the figure caption for each box plot presented. NOTE: Although ProUCL produces box plots, the box plots are not report quality. The ProUCL box plots also do not plot the concentrations on the graph. Use another statistical package or program to construct box plots for the report.
	7.	If there are at least 8 samples <u>and</u> 5 detected sample results for the environmental medium and the inorganic chemical being evaluated and the maximum result is greater than the BV, conduct statistical comparisons of the site data set with the background data set (see Step 7.4).
	8.	Report the detected concentrations or DLs of all inorganic chemicals with DLs and/or detected concentrations above BVs and detected concentrations (if no BVs) at each site in a table. In addition, present all detected concentrations (if no BVs) and detected concentrations above BVs at each site in the data figures for inorganic chemicals.
	9.	Clearly state the conditions of the comparisons being conducted in the text of the data review. For example, state that there were fewer than 8 samples and/or fewer than 5 detected concentrations for the environmental medium (soil, sediment, and tuff unit) and the inorganic chemical evaluated so statistical analyses cannot be conducted.
7.4	**<u>Statistical Comparisons of Site Data to Background Data</u>**	
Project Members	1.	If statistical comparisons are appropriate and warranted as stated above, consult a statistician on how to proceed and which statistical tests to run. The preferred tests are the Gehan, Quantile, and Slippage tests (these are the tests historically used for background comparisons).
	2.	Run all three statistical tests or explain why a test is not applicable, i.e., too many nondetects in the data sets so Gehan test is not possible. The Gehan test requires more than 50% detects in the background or site data sets. (The Gehan test is not recommended if either of the two data sets has more than 50% nondetects.) If more than 50% detects, use only the Quantile and Slippage tests (Quantile test cannot be performed if more than 80% of the combined data are nondetected values). To eliminate as a COPC, the inorganic chemical must pass 2 of 3 tests (i.e., p-value >0.05); if fail two tests (p-value <0.05), then retain as

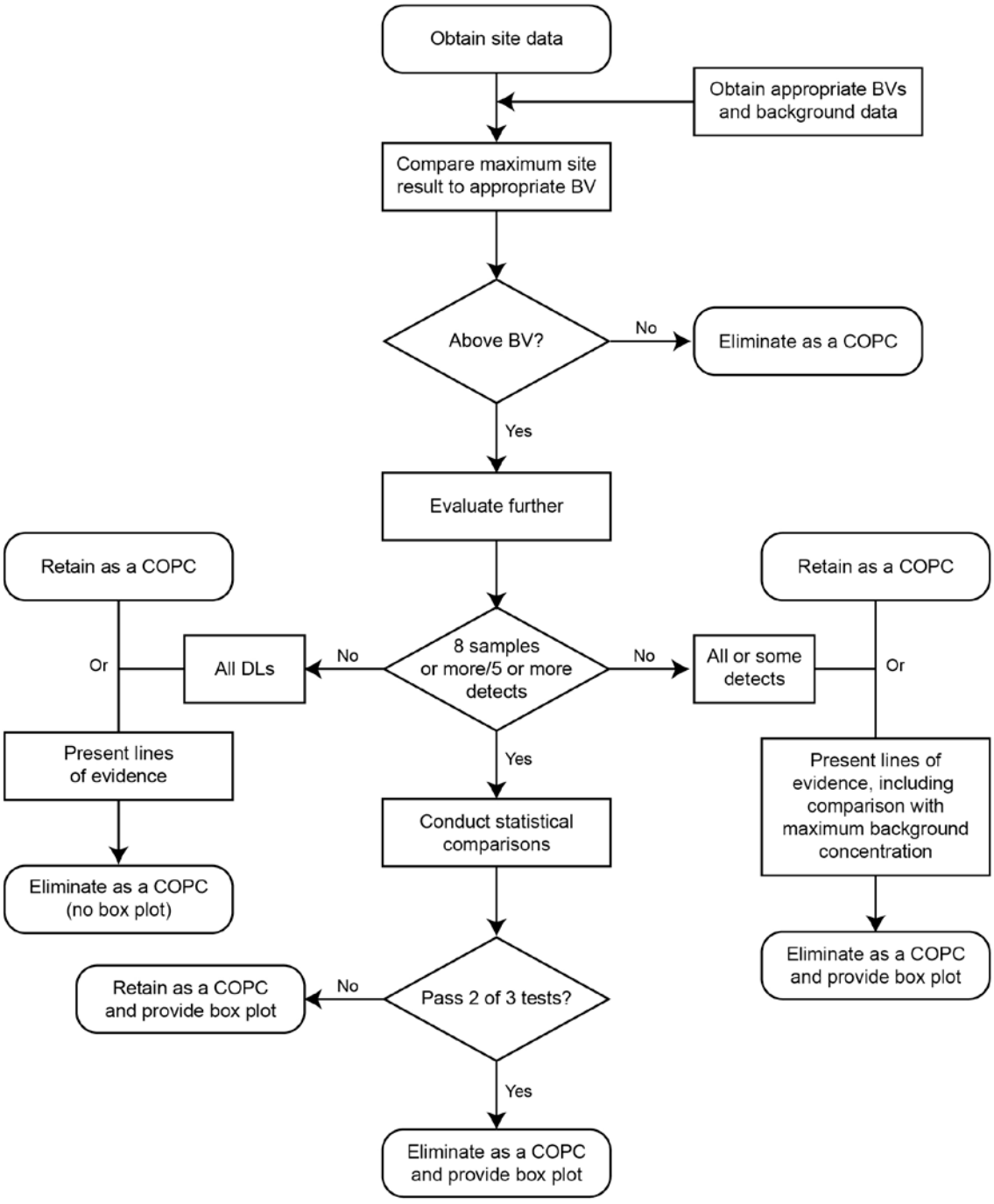
		COPC. Run the Slippage test as the third test; if the Gehan and Quantile both pass or both fail, there is no need to perform the Slippage test. NOTE: ProUCL contains several statistical tests, including the Gehan and Quantile tests. ProUCL or other statistical programs can be used to run these tests. The Slippage test is not included in ProUCL and requires a different statistical package (e.g., download the freeware "R" at http://www.r-project.org/ and follow instructions) or an alternative approach such as using the Excel function =HYPGEOMDIST(n.exceed,n.site,n.exceed,n.total) for the Slippage test (Attachment 3). The statistical ProUCL programs are commercial programs that have been validated to run on the platform used. Before running the program, a test verification calculation that exercises all necessary subroutines should be run to ensure that the program is operating properly.
	3.	Present statistical results for each inorganic chemical statistically evaluated in a table (see Attachment 4 for example of the table) for each medium in an appendix (see previous reports for examples). Present the p-values for each statistical test conducted, and indicate whether inorganic chemical is retained as a COPC. If a test was not performed, indicate so by "n/a" (not applicable).
	4.	Construct box plots for all inorganic chemicals included in the statistical comparisons, and provide the box plots in the same appendix of the investigation report as the statistical tests above (see previous reports for examples). NOTE: Although ProUCL provides box plots, the box plots are not report quality. The ProUCL box plots also do not plot the concentrations on the graph. Use another statistical package or program to construct box plots for the report.
	5.	When constructing the box plots, plot the concentrations as points overlying the box plot. When a data set contains both detected concentrations and nondetected concentrations (i.e., detection limits), the detected concentrations are plotted as Xs, and the nondetected concentrations are plotted as Os. Define Xs and Os in the figure caption for each box plot presented.
7.5	**Essential Nutrients and Background**	
Project Members	1.	Compare the maximum result for the essential nutrients (i.e., calcium, magnesium, potassium, and sodium) with the BVs for the environmental medium being evaluated.
	2.	If there are fewer than 8 samples and/or fewer than 5 detected sample results for the environmental medium and the maximum result is less than the maximum background concentration, see Step 7.3.
	3.	If there are at least 8 samples and 5 detected sample results for the environmental medium, perform statistical comparisons between the site data and background data for calcium, magnesium, potassium, and sodium (Step 7.4).
	4.	In an appendix in the investigation report, provide box plots showing the comparison of site data and background data for calcium, magnesium, potassium, and sodium in all cases.
	5.	If retaining calcium, magnesium, potassium, and/or sodium as COPCs, present the recommended daily allowances in the risk assessment for the site.

7.6	**Records Management**
Project Members or Project Leaders	1. Maintain and submit records and/or documents generated to the Records Processing Facility according to EP-DIR-SOP-4004, *Records Transmittal and Retrieval Process*.

8.0 ATTACHMENTS

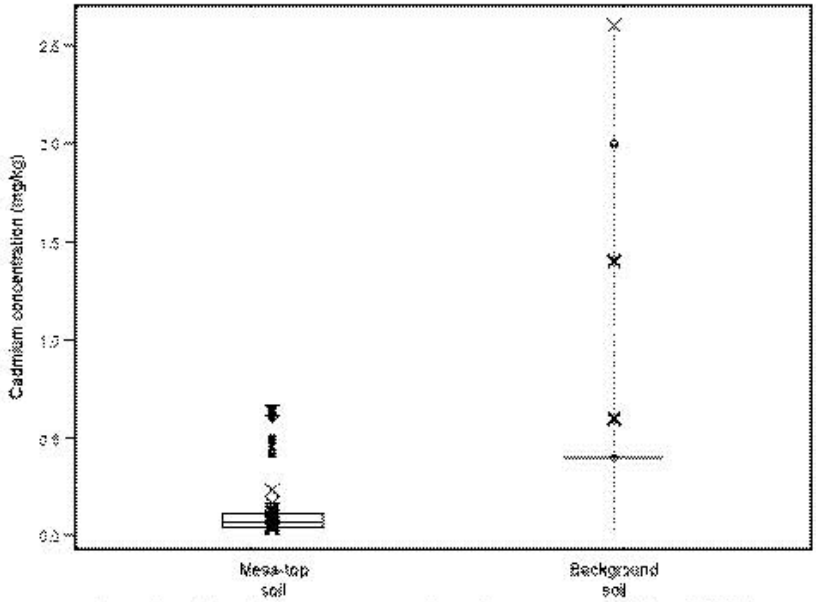
- Attachment 1 Process Flow Chart
- Attachment 2 Examples of Box Plots
- Attachment 3 Example of Excel Function HYPGEOMDIST
- Attachment 4 Example of Table Summarizing Statistical Results

Attachment 1
Process Flow Chart

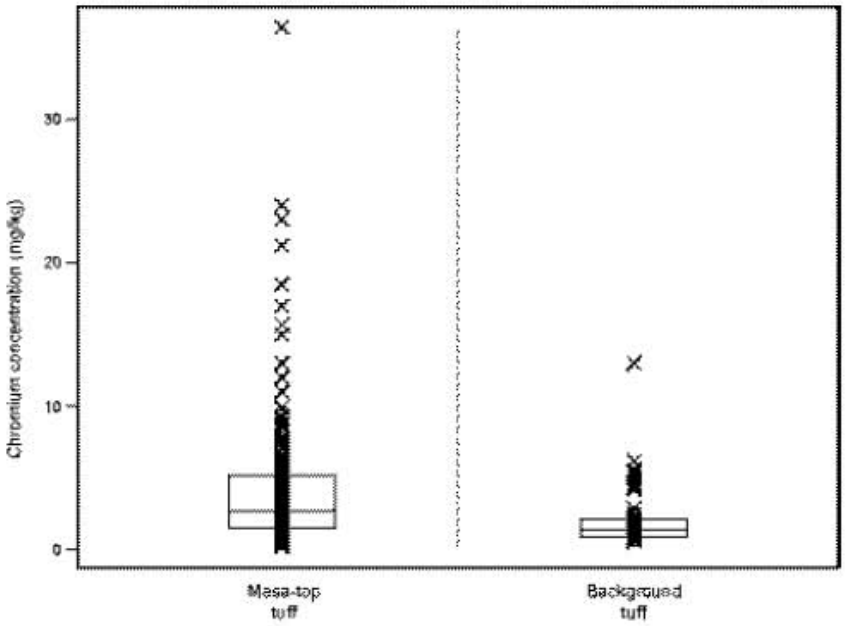


Flow diagram for the COPC identification process.

Attachment 2
Examples of Box Plots



Box plot of cadmium concentrations in mesa-top soil and ALLH background (x's indicate detected concentrations and o's indicate nondetects)



Box plot of chromium concentrations in mesa-top tuff and Qbt 2, 3, and 4 background data (x's indicate detected concentrations and o's indicate nondetects)

Attachment 3
Example of Excel Function HYPGEOMDIST

Slippage test. This test is based on the maximum observed concentration in the background data set and the number (*n*) of site concentrations that exceed the maximum concentration in the background set. The result (p-value) of the slippage test is the probability that *n* site samples (or more) exceed the maximum background concentration by chance alone. The test accounts for the number of samples in each data set (number of samples from the site and number of samples from background) and determines the probability of *n* (or more) exceedances if the two data sets came from identical distributions. This test is similar to the BV comparison in that it evaluates the largest site measurements. It is more useful than the BV comparison because it is based on a statistical hypothesis test, not simply on a statistic calculated from the background distribution.

p-value of slippage test via Excel function =HYPGEOMDIST(n.exceed,n.site,n.exceed,n.total)

where n.exceed = number of site samples>maximum background concentration
n.site = number of site samples
n.total = combined number of samples for site and background

Examples For 10 site samples and 15 background samples, the probability that 2 site samples will exceed the maximum result in background is 0.15; =HYPGEOMDIST(2,10,2,25)=0.15

For 12 site samples and 23 background samples, the probability that 3 site samples will exceed the maximum result in background is p = 0.034; =HYPGEOMDIST(3,12,3,35)=0.034

Attachment 4
Example of Table Summarizing Statistical Results

Results of Statistical Tests for Inorganic Chemicals above the BV

Analyte	Gehan p-value	Quantile p-value	Slippage p-value	COPC?
Aluminum	1	1	n/a*	No
Arsenic	1	0.964	n/a	No
Barium	<0.001	0.023	n/a	Yes
Beryllium	1	1	n/a	No
Calcium	0.005	0.055	n/a	Yes
Chromium	<0.001	0.003	n/a	Yes
Cobalt	n/a	1	0.947	No
Copper	0.040	0.150	n/a	Yes
Lead	0.022	0.074	n/a	Yes
Magnesium	0.988	0.977	n/a	No
Nickel	n/a	0.051	0.037	Yes
Zinc	1	1	n/a	No