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# Environmental Programs Directorate Engineering & Technology

# **Standard Operating Procedure**

# for BACKGROUND VALUE COMPARISONS—INORGANIC CHEMICALS

**APPROVAL SIGNATURES:** 

Subject Matter Expert:	Organization	Signature	Date
Richard Mirenda	ET-ER	Rihadmann	8/18/10
Responsible Line Manager:	Organization	Signature	Date
Patrick Nakagawa	ET-ER	Mazz	8118 400

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# 1.0 PURPOSE AND SCOPE

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

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.

# 2.0 BACKGROUND AND PRECAUTIONS

# 2.1 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).

# 2.2 Precautions

In addition to the process described herein, there is a need to apply professional experience and judgment in determining whether inorganic chemicals are 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 adequately presented. 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 slightly above background and no statistical or nonstatistical methods can be used to justify the elimination. In addition, some background data sets are small, the maximum background concentration is less than the BV, and/or the BV is based on detection limits. If detected concentrations or detection limits are interpreted to be only slightly and infrequently above the BV, the inorganic chemical may be eliminated on this basis. The key component is consistency among all investigation reports and NMED's acceptance of this process.

# 3.0 EQUIPMENT AND TOOLS

Essential equipment and tools required to implement this SOP include the following: the U.S. Environmental Protection Agency (EPA) 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; and the annotated outline for the investigation report (see SOP-5250, Attachments 3 and 4).

# 4.0 STEP-BY-STEP PROCESS DESCRIPTION

4.1 Prep	are 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).

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Project Members (cont.)	2.	Determine the sample preparation and analytical methods used to generate results from the background samples from the background data sets. <b>NOTE</b> : Background data sets are available upon request from the data stewards.
-	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 fields of information:
		sample concentration results
		reporting units of the sample concentrations
		final sample result qualifiers
		sample analytical methods
		sample preparation methods
		<b>NOTE</b> : The site data set may be provided to the user in the same format as it is recorded in the Sample Management Database. Data dictionaries and code definitions are available from the data stewards.
_	4.	Determine the comparability of the methods used to prepare and analyze the site samples and the background samples.
		<b>NOTE</b> : If site sample methods differ from the Laboratory background sample methods, consult a chemist.
4.2 Select	Appro	opriate BVs
4.2 Select Project	Appro	For site samples collected from soil media, compare with the Laboratory's soil BVs.
Project		For site samples collected from soil media, compare with the Laboratory's soil BVs. <b>NOTE</b> : In this context, "soil media" includes any soil or fill material. Soil is designated as
Project	1.	<ul> <li>For site samples collected from soil media, compare with the Laboratory's soil BVs.</li> <li><b>NOTE</b>: In this context, "soil media" includes any soil or fill material. Soil is designated as all horizons [ALLH] and fill is designated as FILL.</li> <li>For site samples collected from tuff identified as Qbt 2, Qbt 3, and/or Qbt 4, compare with</li> </ul>
Project	1. 2.	<ul> <li>For site samples collected from soil media, compare with the Laboratory's soil BVs.</li> <li><b>NOTE</b>: In this context, "soil media" includes any soil or fill material. Soil is designated as all horizons [ALLH] and fill is designated as FILL.</li> <li>For site samples collected from tuff identified as Qbt 2, Qbt 3, and/or Qbt 4, compare with the BVs for Qbt 2, 3, and 4.</li> <li>For site samples collected from tuff identified as Qbt 1v, compare with the BVs for Qbt</li> </ul>
Project	1.       2.       3.	<ul> <li>For site samples collected from soil media, compare with the Laboratory's soil BVs.</li> <li><b>NOTE</b>: In this context, "soil media" includes any soil or fill material. Soil is designated as all horizons [ALLH] and fill is designated as FILL.</li> <li>For site samples collected from tuff identified as Qbt 2, Qbt 3, and/or Qbt 4, compare with the BVs for Qbt 2, 3, and 4.</li> <li>For site samples collected from tuff identified as Qbt 1v, compare with the BVs for Qbt 1v.</li> <li>For site samples collected from tuff identified as Qbt 1g, Qbo, and/or Qct, compare with</li> </ul>
Project Members	1.       2.       3.       4.       5.	<ul> <li>For site samples collected from soil media, compare with the Laboratory's soil BVs.</li> <li><b>NOTE</b>: In this context, "soil media" includes any soil or fill material. Soil is designated as all horizons [ALLH] and fill is designated as FILL.</li> <li>For site samples collected from tuff identified as Qbt 2, Qbt 3, and/or Qbt 4, compare with the BVs for Qbt 2, 3, and 4.</li> <li>For site samples collected from tuff identified as Qbt 1v, compare with the BVs for Qbt 1v.</li> <li>For site samples collected from tuff identified as Qbt 1g, Qbo, and/or Qct, compare with the BVs for Qbt 1g, Qbo, and Qct.</li> <li>For site sediment samples, compare with the sediment BVs. (NOTE: Sediment is</li> </ul>

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Project Members (cont.)	2.	If the maximum result for an inorganic chemical is less than or equal to the BV for that inorganic chemical, do not identify the inorganic chemical as a COPC.
	3.	If the maximum result for an inorganic chemical from a site is greater than the BV and exceeds the maximum background concentration in the background data set for that inorganic chemical, and the site data are interpreted as being substantially above background, identify the inorganic chemical as a COPC.
		<b>NOTE</b> : If this is the case, there is no need to perform statistical comparisons and construct box plots.
	4.	If there are only nondetects in the site data set and detection limits are above the BV, compare the maximum detection limit with the maximum background concentration. No box plots are necessary.
		<ul> <li>If the maximum detection limit is less than the maximum background concentration, do not identify the inorganic chemical as a COPC.</li> </ul>
		<ul> <li>If the maximum detection limit is greater than the maximum background concentration, identify the inorganic chemical as a COPC.</li> </ul>
	5.	If there are fewer than 10 sample results for the environmental medium and the inorganic chemical being evaluated, the maximum result is greater than the BV, and the site data are not interpreted as being substantially above background, compare the maximum result with the maximum background concentration.
		<ul> <li>If the maximum result is less than the maximum background concentration, do not identify the inorganic chemical as a COPC.</li> </ul>
		<ul> <li>If the maximum result is greater than the maximum background concentration, identify the inorganic chemical as a COPC.</li> </ul>
	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 the investigation report (see Attachment 1 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 x's, and the nondetected concentrations are plotted as o's. Define x's and o's in figure caption for each box plot presented.
		<b>NOTE:</b> 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 10 sample results for the environmental medium and the inorganic chemical being evaluated, the maximum result is greater than the BV, and the site data are not interpreted as being substantially above background, conduct statistical comparisons of the site data set with the background data set (see Step 4.4).
	8.	Report the concentrations of all inorganic chemicals above BVs (detected and nondetected) for all samples collected for each site in a table.
		In addition, present all detected concentrations above BVs for each site in the data

figures for inorganic chemicals.

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Project Members (cont.)	Clearly state the conditions of the comparisons being conducted in the text of the data review. For example, state that there were fewer than 10 sample results for the environmental medium (soil, sediment, and tuff unit) and the inorganic chemical evaluated and, therefore, the site data were compared with the maximum background
	concentration.

#### 4.4 Statistical Comparisons of Site Data to Background Data

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 include the Gehan, Quantile, and Slippage tests (these are the tests historically used for background comparisons).

- 2. Choose two statistical tests to run—paired as either the Gehan and Quantile tests, or the Quantile and Slippage tests. 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 less than 50% detects, use the Quantile test as the primary test (this 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 both tests (i.e., p-value >0.05); if fail one test (p-value <0.05) and pass the other, then retain as COPC. Therefore, if the first test fails, there is no need to perform the second test. However, if the first test passes then the second test must be conducted.</p>
  - **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 <u>http://www.r-project.org/</u> 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 2).

The Statistical ProUCL programs are commercial programs that have been validated to run on the platform used. Prior to running the program a test verification calculation, that exercises all necessary subroutines, will be run to ensure the program is properly operating.

- 3. If the number of nondetects prevents the use of the statistical tests even though there are an adequate number of samples, compare the maximum result with the maximum background concentration as described in Step 4.3, section 4 above.
- 4. Present statistical results for each inorganic chemical statistically evaluated in a table (see Attachment 3 for example of the table) for each medium in an appendix (see SOP-5250, Attachment 9). Present the p-values for each statistical test conducted and indicate whether inorganic chemical is retained as a COPC.
- 5. Construct box plots for all inorganic chemicals included in the statistical comparisons and provide the box plots in an appendix of the investigation report (see SOP-5250, Attachment 9).
  - **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.

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Project Members (cont.)	6.	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 x's, and the nondetected concentrations are plotted as o's. Define x's and o's in figure caption for each box plot
		presented.

#### 4.5 Site Data Slightly above BVs

1.

Project Members When only a comparison to BV is applicable because the BV is equal to or exceeds the maximum concentration of the background data set, professional judgment or experience may be used to eliminate inorganic chemicals as COPCs if the site data are interpreted as being slightly and infrequently above the BV.

2. Slightly above background is defined as equivalent to or less than 20% above the BV (after rounding). Infrequently above BV is defined as one to five samples of the total number of samples, <u>depending upon the number of samples in the data set</u>. (NOTE: If the number of samples in the data set is 100 then infrequently detected above BV may be as many as 10 samples. In addition, EPA's Risk Assessment Guidance for Superfund, Part A, section 5.9.3, pages 5-22 uses a frequency of detection of 5% as an example of infrequent detection. However, the exact number of samples used to define infrequently above BV is dependent on the data set and the data assessor and is entirely subjective.)

For example, selenium is detected (or has detection limits) above the tuff BV of 0.3 mg/kg in 3 of 20 samples. The concentrations (or detection limits) range from 0.31 to 0.35 mg/kg. Another example is zinc in sediment detected above the sediment BV of 60.2 mg/kg in 5 of 40 samples. The concentrations range from 60.9 to 71.7 mg/kg. In both cases, professional judgment or experience may be used to eliminate inorganic chemicals as COPCs as not being different from background.

3 If the site data meet the conditions described above for slightly and infrequently above background, the inorganic chemical may be eliminated as a COPC. The rationale must be presented for each inorganic chemical eliminated in this fashion along with associated box plot.

Alternatively, the inorganic chemical is retained as a COPC, regardless of how slight and infrequent the concentration is above the BV (if only comparing to BVs no box plots are necessary). The basis for all decisions must be presented in the report to clearly explain assumptions made in identifying COPCs. (**NOTE**: Consult the subject matter expert and the project leader before implementing this process.)

#### 4.6 Essential Nutrients and Background

Project Members	1.	Compare the maximum result for the essential nutrient (i.e., calcium, magnesium, potassium, and sodium) with the BVs for the environmental medium being evaluated.
	2.	Do not identify calcium, magnesium, potassium, and sodium as COPCs if the maximum results are less than the BVs.
	3.	If there are fewer than 10 sample results for the environmental medium and the maximum result is less than the maximum background concentration, do not identify calcium, magnesium, potassium, and sodium as a COPC (see Step 4.3).

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Project Members (cont.)	4.	If there are at least 10 sample results for the environmental medium, perform statistical comparisons between the site data and background data for calcium, magnesium, potassium, and sodium (see Step 4.4).
	5.	Provide box plots in the investigation report (see SOP-5250, Attachment 9) showing the comparison of site data and background data for calcium, magnesium, potassium, and sodium in all cases.
	6.	If retaining calcium, magnesium, potassium, and/or sodium as COPCs, discuss the recommended daily allowances in the risk assessment for the site.
4.7 Reco	ords Ma	anagement
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.

# 5.0 DEFINITIONS

<u>Background Concentration</u>—Naturally occurring concentrations of an inorganic chemical or radionuclide in soil, sediment, or tuff.

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

<u>Chemical of Potential Concern (COPC)</u>—A detected chemical compound or element that has the potential to adversely affect human receptors as a result of its concentration, distribution, and toxicity.

#### 5.1 ACRONYMS

- ALLH all horizons (soil)
- BV background value
- COPC chemical of potential concern
- EP Environmental Programs
- EPA Environmental Protection Agency (U.S.)
- 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

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#### 6.0 PROCESS FLOW CHART

Flow diagram for the COPC identification process – Figure 1

# 7.0 ATTACHMENTS

- Attachment 1 Example of Box Plot
- Attachment 2 Example of Excel function HYPGEOMDIST

Attachment 3 Example of Table Summarizing Statistical Results

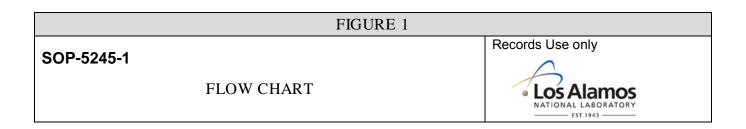
Using a CRYPTO Card, click here for "Required Read" credit.

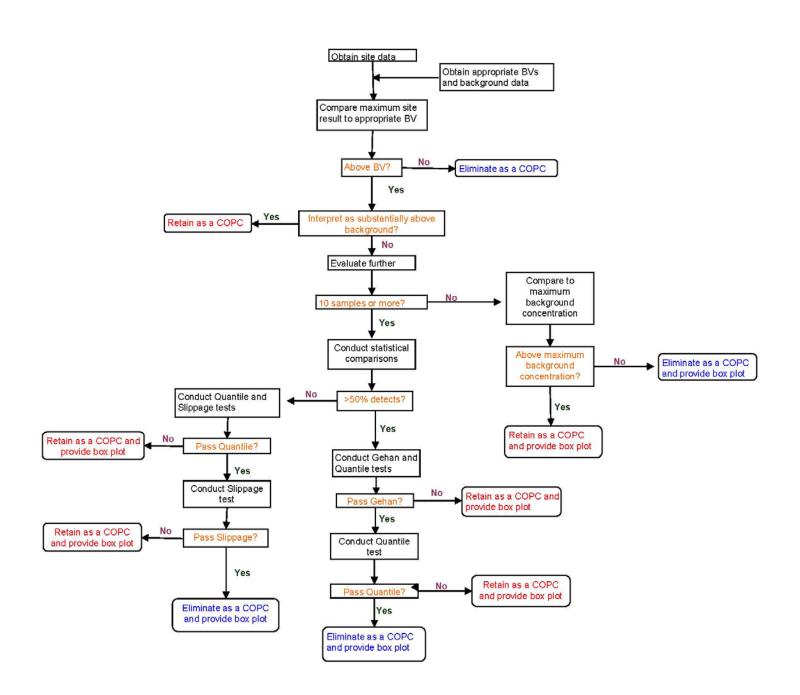
If you don't have a crypto card with A-level access, contact creichelt@lanl.gov for instructions on getting credit

#### 8.0 **REVISION HISTORY**

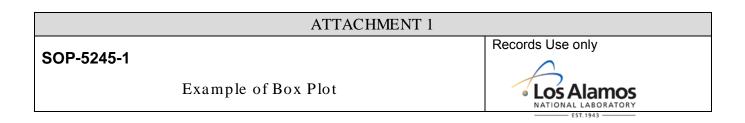
Revision No. [Enter current revision number, beginning with Rev.0]	Effective Date [DCC inserts effective date for revision]	Description of Changes [List specific changes made since the previous revision]	Type of Change [Technical (T) or Editorial (E)]
0	02/09/07	Reformatted and renumbered, supersedes SOP-15.12	E
0	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	т
1	8/26/2010	Major revision. Deleted references to data review appendix and other editorial changes; Revised approach for addressing essential nutrients per NMED comments; Updated organization change.	T/E

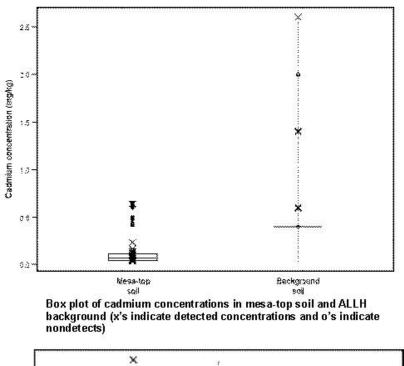
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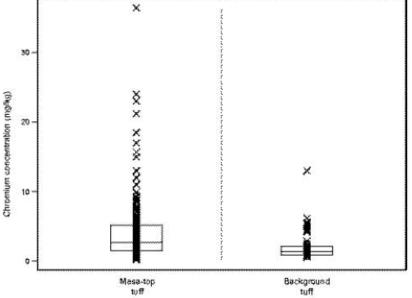




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Box plot of chromium concentrations in mesa-top tuff and Qbt 2, 3, and 4 background data (x's indicate detected concentrations and o's indicate nondetects)

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ATTACHMENT 2		
SOP-5245-2 EXAMPLE OF EXCEL FUNCTION HYPGEOMDIST	Records Use only	

*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)

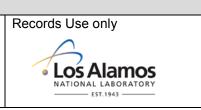
where n.exceed=number of site samples>maximum background concentration n.site=number of site samples n.total=combined number of samples for site and background
 Examples For 10 site samples and 15 background samples, the probability that 2 site samples will exceed the maximum result in background is 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

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# ATTACHMENT 3

# SOP-5245-3

# 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

\*n/a = Not applicable.