Housekeeping

- This event is being recorded; Training will be available On Demand after the event at the main training page
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Advancing Environmental Solutions

Soil Background & Risk Assessment (SBR-1, 2021)

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Soil Background & Risk Assessment (SBR)

Trainers

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Bonnie Brooks, M.S. — Department of Ecology State of Washington

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Training Development

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J. Rocco & L. Hay Wilson — Sage Risk Solutions

Advancing Environmental Solutions

Overview & Soil Background Definitions

BRADY JOHNSON, M.S.

Training Development:

CHRISSY PETERSON EHS Support

CLAUDIO SORRENTINO, PH.D. DTSC Department of Toxic Substances Control

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SBR Guidance

- Section 1 – Introduction
- Section 2 – Soil Background Definition
- Section 3 – Establishing Soil Background
- Section 4 – Using Soil Background in Risk Assessment
- Section 5 – Geochemical Evaluations
- Section 6 – Using Geochemical Evaluations in Risk Assessment
- Section 7 – Environmental Forensics Related to Soil Background

https://www.needpix.com/photo/340338/earthworm-soil-dirt-macro-free-pictures-free-photos-free-images-royalty-free-free-illustrations

SBR Guidance

- Section 8 – Conceptual Site Model and Data Quality Objectives
- Section 9 – Sampling
- Section 10 – Analytical Methods
- Section 11 – Statistics
- Section 12 – Regulatory Framework
- Section 13 – Existing Guidance and Studies
- Section 14 – Case Studies
- Flowcharts

Image source Utah State Analytical lab, © Julija Sapic https://bit.ly/3AJVXNL; Image source Extension, University of Missouri, https://bit.ly/3FP9t6r

Limitations of the SBR Guidance

- Does **not** provide specific soil background values for individual chemicals
- Does **not** replace existing regulatory guidance (check with oversight agency)
- Does **not** provide in-depth details on sampling, and lab analytical methods, statistics, geochemistry or forensics

SBR Training Videos

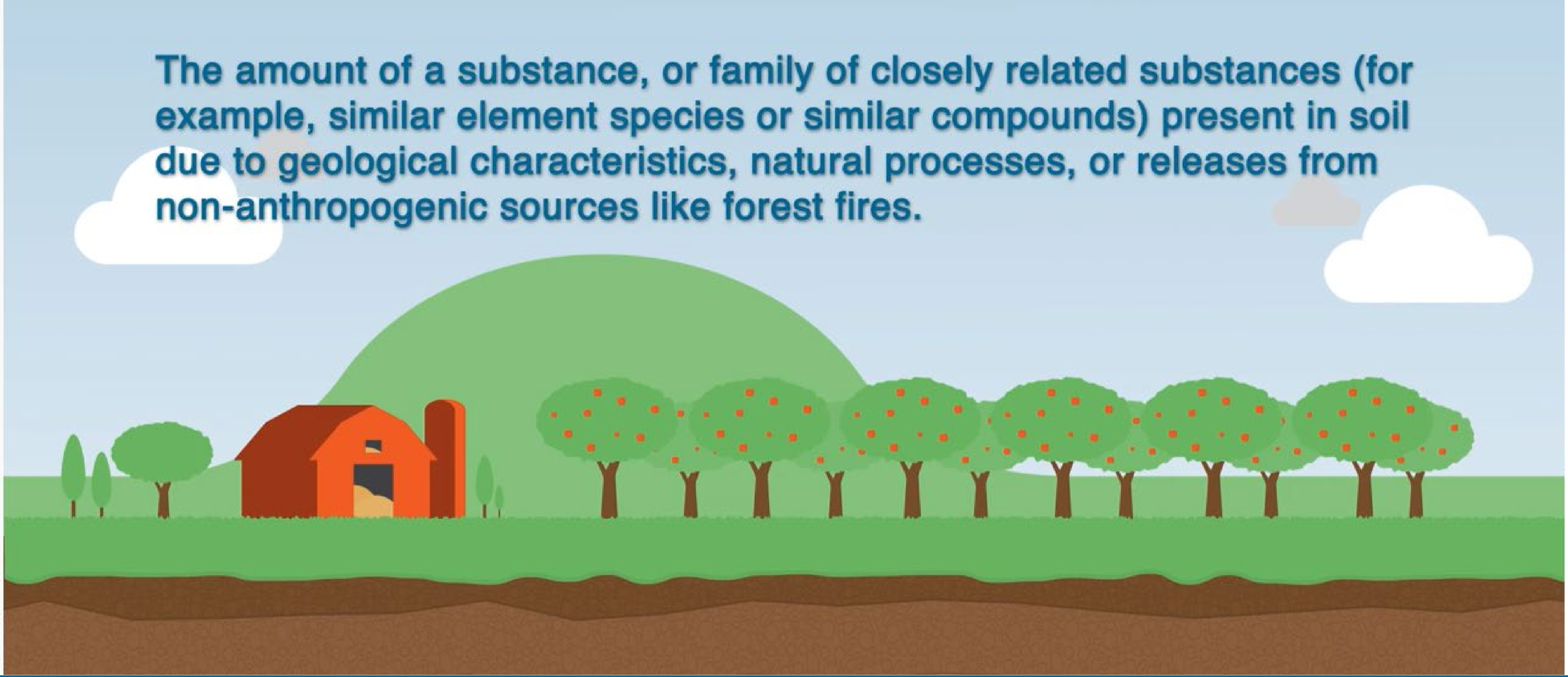
Training Topics

- Introduction
- Soil Background Definition
- Establishing Soil Background
- Using Soil Background in Risk Assessment
- Geochemical Evaluations
- Environmental Forensics

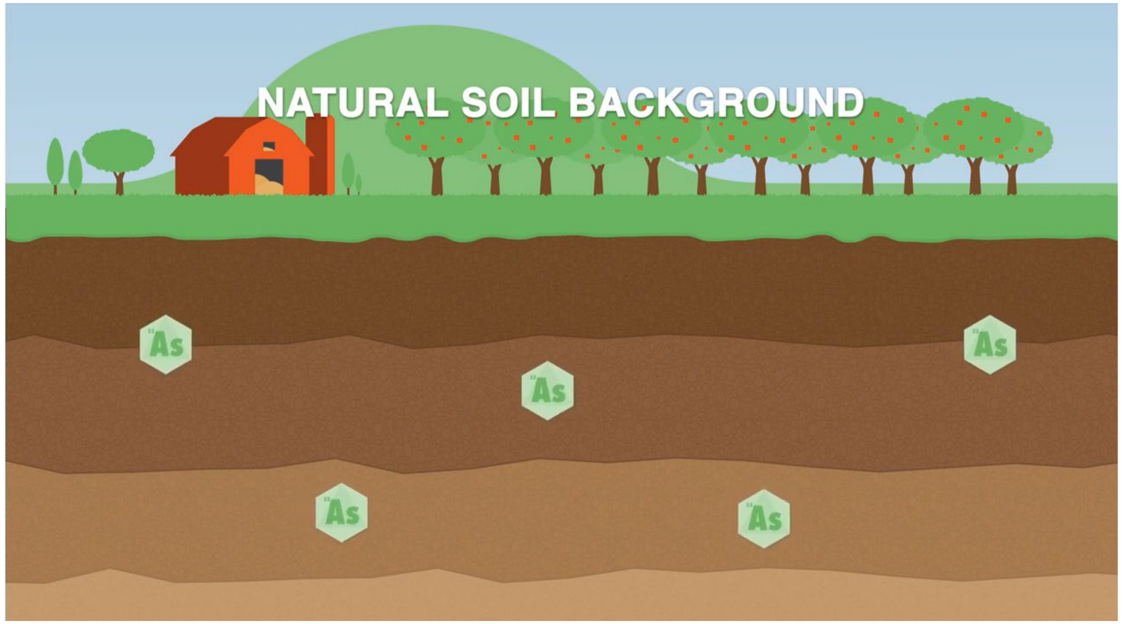
Definitions

- Natural Soil Background
- Anthropogenic Ambient Soil Background
- Default Soil Background
- Site-Specific Soil Background
- Soil Background Reference Area

Natural Soil Background



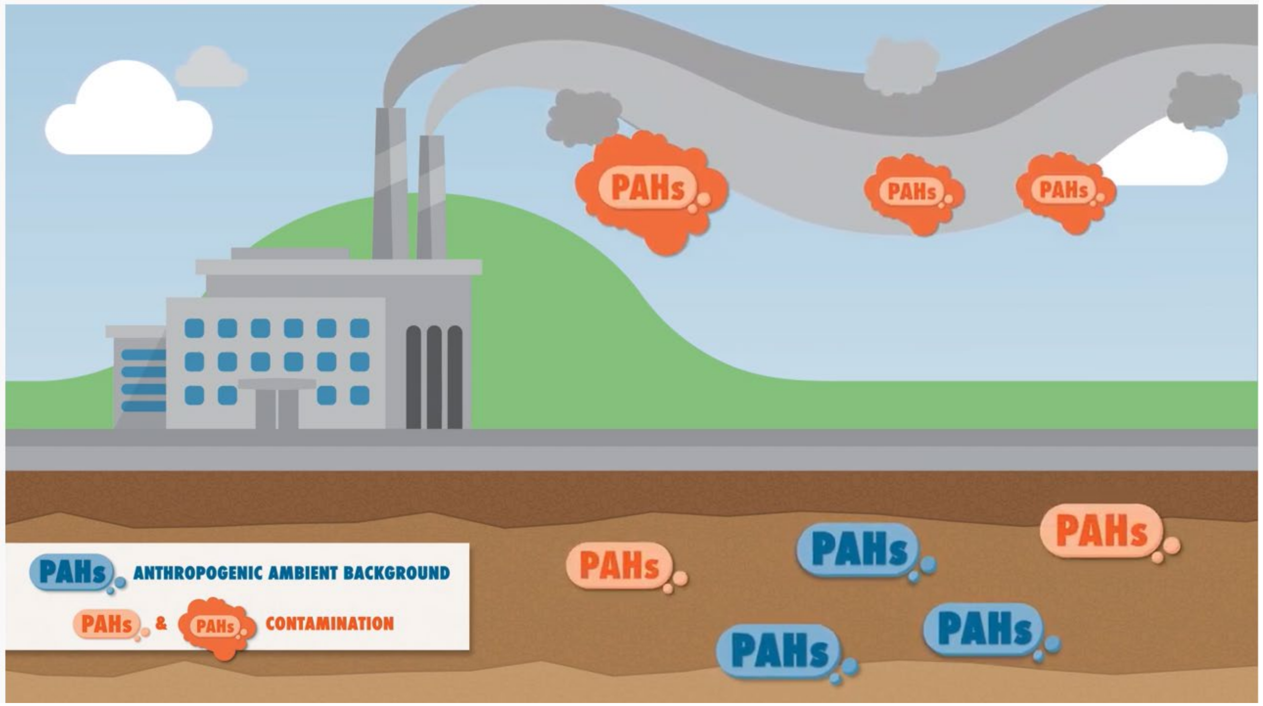
Natural Background and Contamination



Anthropogenic Ambient Background

The amount of a substance, or family of closely related substances (for example, similar element species or similar compounds), present in soil due to anthropogenic non-point sources or due to their ability to be transported long distances.

Anthropogenic Ambient Background and Contamination



Definitions – Default Soil Background

Established by **regulatory agencies** for a larger area (e.g., state, region or unique geological area) that generally shares similar physical, chemical, geological, and biological characteristics

~Section 2.3.1

- Generally established to be conservative; intended to be used to evaluate **a large number** of sites
- Can be established for both natural and anthropogenic ambient soil background concentrations

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Definitions – Site-specific Soil Background

Generally established by a **responsible party** for an area of limited geographic scope that represents one specific site (e.g., an incinerator cleanup site, a railroad yard cleanup site)

~Section 2.3.2

- Generally, a more accurate way to evaluate whether site chemical concentrations are representative of background since it is relevant to a specific site in **a limited geographical area**.
- Can be established for both natural and anthropogenic ambient soil background.

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Definitions – Soil Background Reference Area

Areas identified as appropriate for collection of samples used to ultimately determine a soil background concentration or range and are also used in ecological risk assessment

~Section 2.3.3

- CSM provides context
- Should be conducted in a location similar to the site being assessed.
- Ecological background reference area:
  - Evaluate impacts on community composition
  - Selection of COPCs

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Poll Question

Does the state regulatory agency you work (most) in have a definition for natural and/or anthropogenic ambient soil background?

- Yes, both natural and anthropogenic ambient
- Yes, for natural only
- No

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Advancing Environmental Solutions

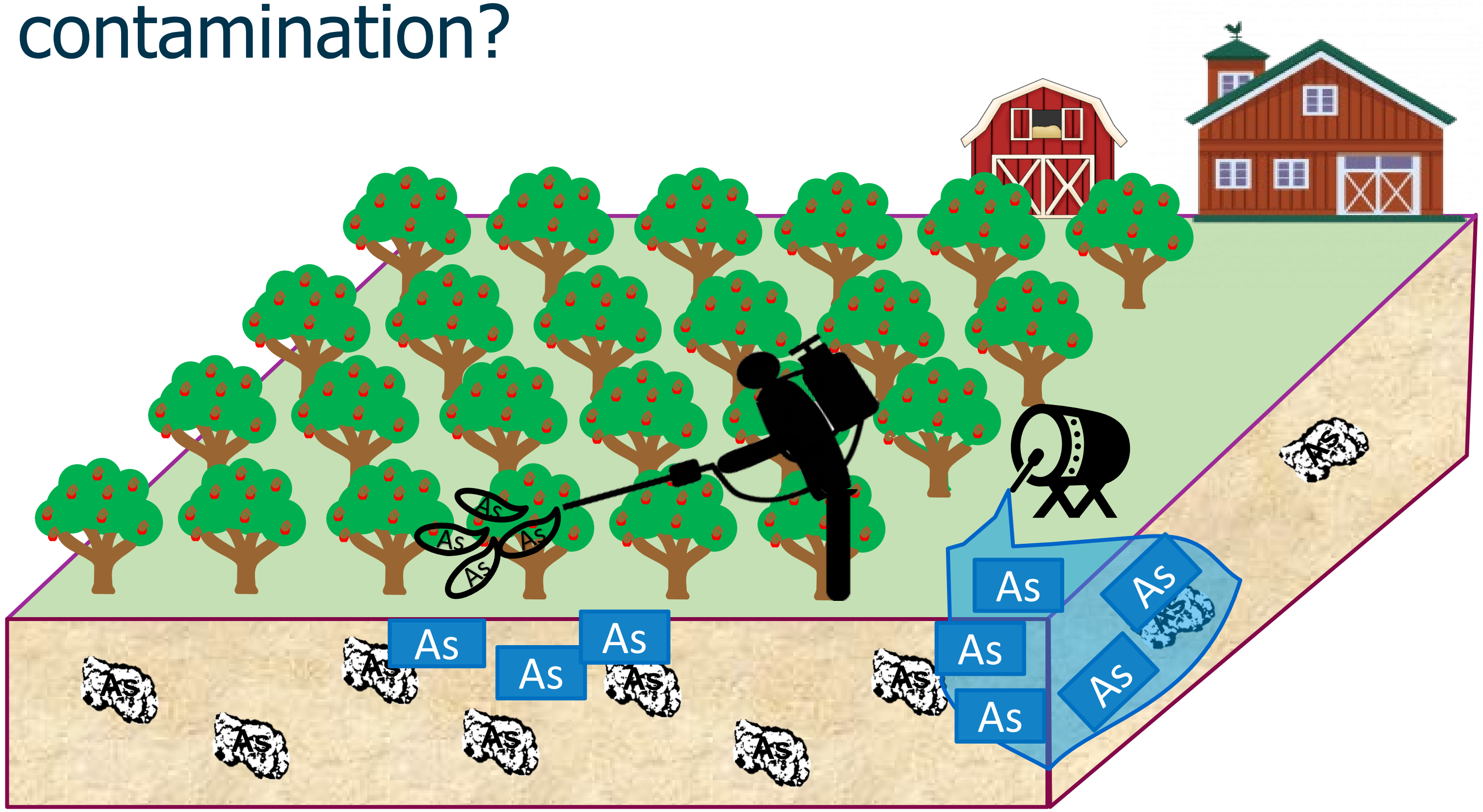
Establishing Soil Background

CHRISSY PETERSON

EHS Support

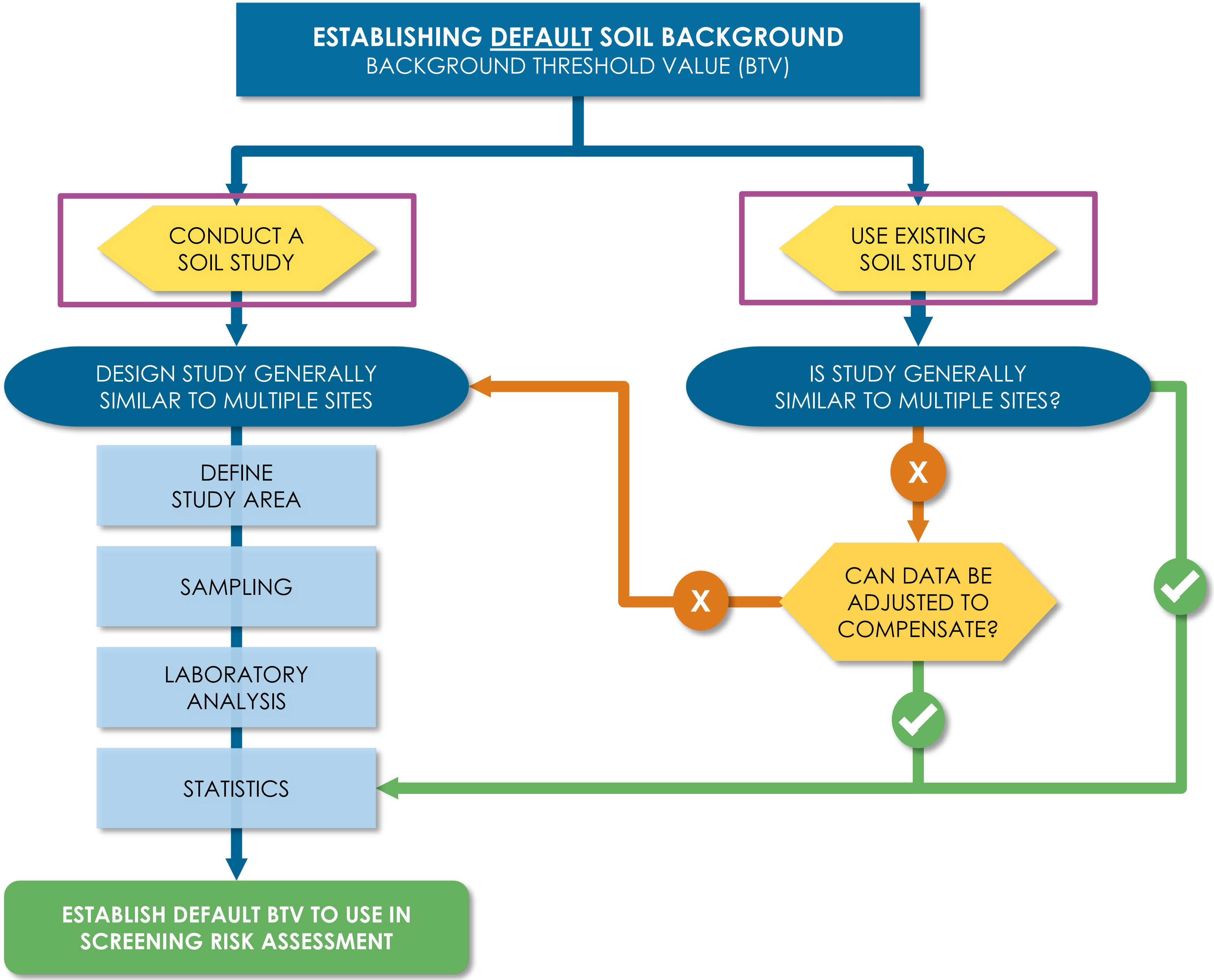
Establishing Soil Background

- Background or contamination?



Framework 1

- Establishing **Default** Soil Background



Establishing Soil Background

- Options
  - Conduct a background study
  - Use existing study
- Background study and sites to be evaluated should be similar
  - Physical
  - Chemical
  - Geological
  - Biological

Image source Guam EPA https://epa.guam.gov/guam-epa-samples-soils-off-base-for-agent-orange/

Considerations

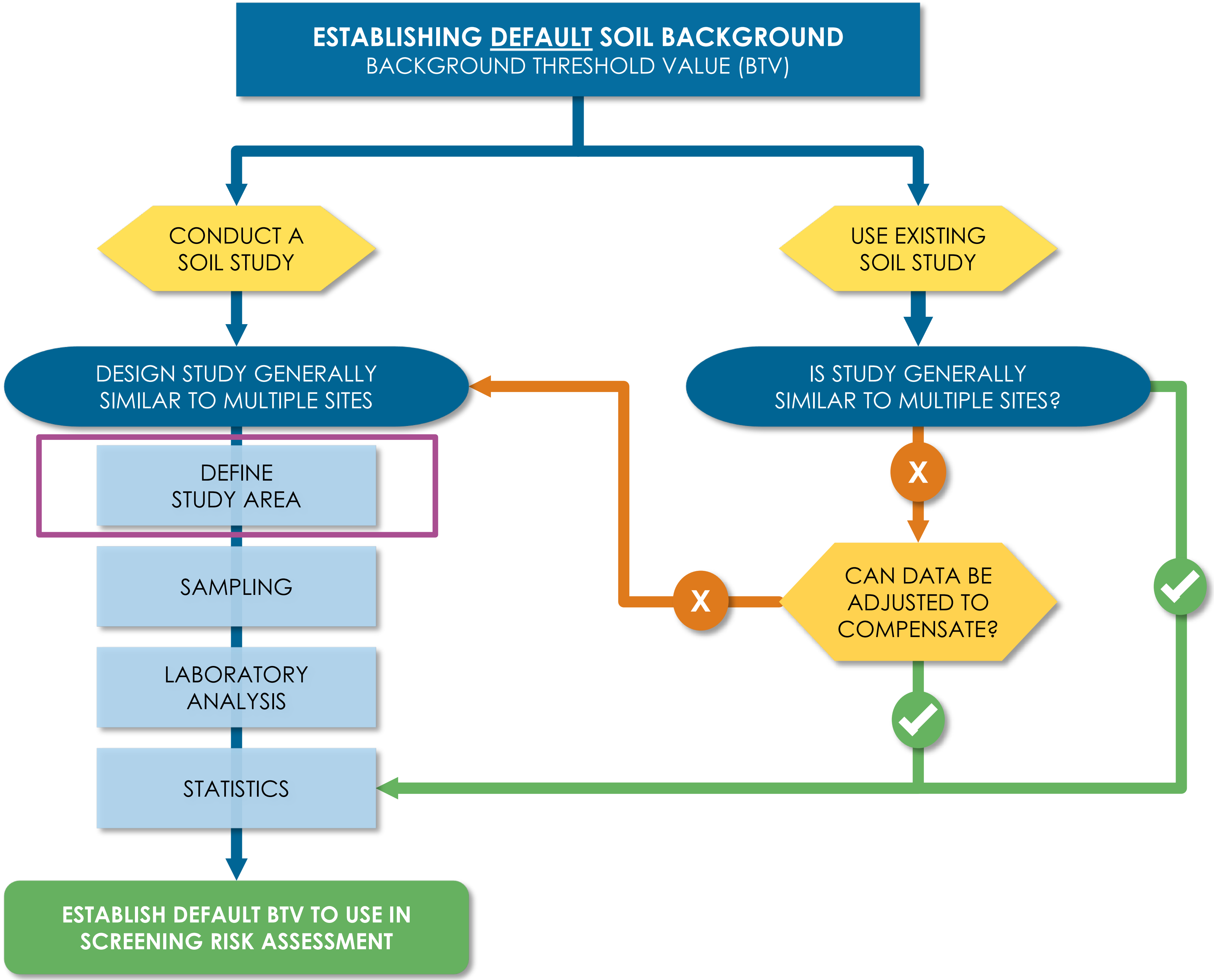
- Section 3.2 – Conducting Background Study
- Section 3.6 - Established soil background study
  - Section 13 - Table 13-2 – Established Soil Studies

Table 13-2: Studies Summary Table

Date	Author	Title	Hyperlink
Federal Agencies			
March 2020	US EPA Region 4	Region 4 Urban Background Study - Inorganic Data	https://semspub.epa.gov/src/document/04/11143730
April 2020	US EPA Region 4	Region 4 Urban Background Study - PAH Data	https://semspub.epa.gov/src/document/04/11149437
July 2007	USEPA	Guidance for Developing Ecological Soil Screening Levels (Eco-SSLs)	https://www.epa.gov/sites/production/files/2015-09/documents/ecossl_attachment_1-4.pdf
10/25/2013	USGS	Geochemical and Mineralogical Data for Soils of the Conterminous United States	https://pubs.usgs.gov/ds/801/
2003	USGS	Concentrations of Polynuclear Aromatic Hydrocarbons and Inorganic Constituents in Ambient Surface Soils, Chicago, Illinois: 2001-02	https://pubs.usgs.gov/wri/2003/4105/report.pdf
3/15/2012	USGS	Distribution and Variation of Arsenic in Wisconsin Surface Soils, With Data on Other Trace Elements	https://pubs.usgs.gov/sir/2011/5202/pdf/sir2011-5202_022412.pdf
1995	USGS	Background Concentrations of Metals in Soil from Selected Regions in the State of Washington	https://pubs.usgs.gov/wri/1995/4018/report.pdf
1988	USGS	Element Concentrations in Soils and Other Surficial Materials of Alaska	https://pubs.usgs.gov/pp/1458/pdf/pp1458.pdf
1984	USGS	Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States	https://pubs.usgs.gov/pp/1270/pdf/PP1270_508.pdf
1984	USGS	Geography of Soil Geochemistry of Missouri Agricultural Soils	https://pubs.usgs.gov/pp/0954h-i/report.pdf
1975	USGS	Background Geochemistry of Some Rocks, Soils, Plants, and Vegetables in the Conterminous United States	https://pubs.usgs.gov/pp/0574f/report.pdf
State Agencies			

Framework 1

- Establishing **<u>Default</u>** Soil Background



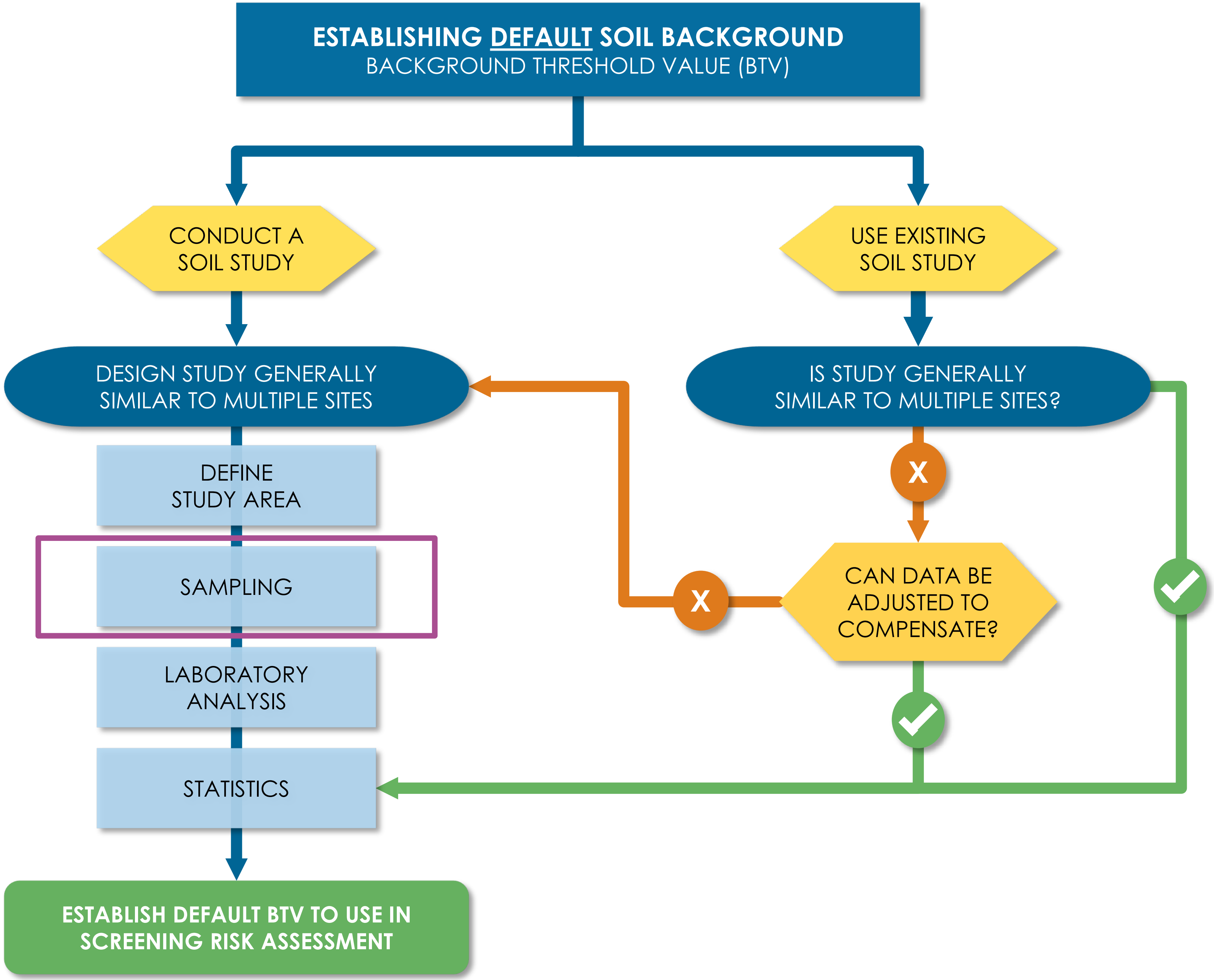
Define Study Area

- Selection of soil background reference area
  - Natural background – area not affected by human activities
  - Anthropogenic ambient background - areas that have not been impacted by local releases
  - Upgradient/upwind
  - Clearly document selection rationale
  - Section 3.3

Image source Extension, University of Missouri, https://bit.ly/3FP9t6r

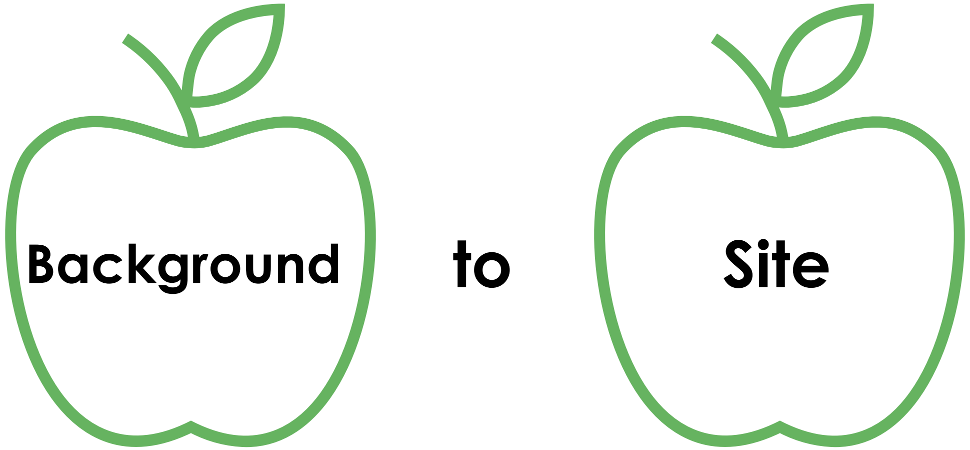
Framework 1

- Establishing **Default** Soil Background



Sampling

- Sampling – Section 9
  - Sample depth – Section 9.2
  - Sample size – Section 9.3
  - Sampling methods – Section 9.4
  - Sampling design – Section 9.5
  - Sample collection methods – Section 9.6
  - Sample handling – Section 9.7



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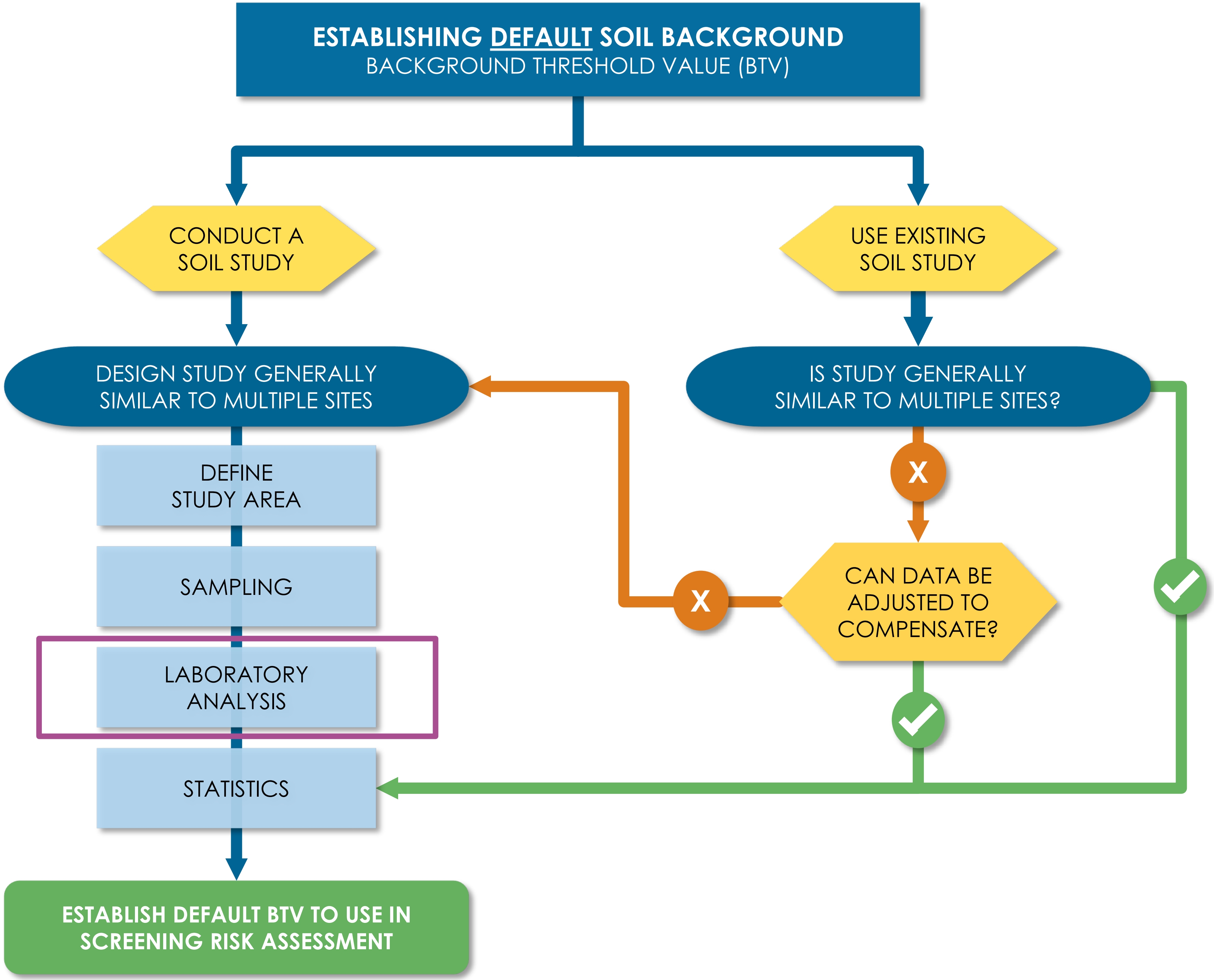
Framework 1

- Establishing **Default** Soil Background



Laboratory Analysis

- Same laboratory analysis between background site and site being evaluated
- Section 10
  - Obtaining Reliable Analytical Data 10.2
  - Analytical Limits – 10.3
  - Preparation and digestion – Section 10.4
  - Analytical test method – Section 10.5

Table 10-2. Analytical methods

Sources: (USEPA 2020 [166]), (Taggart 2002 [463]).

Chemical	Analytical Method(s)	Summary	Comments
Metals	USEPA Method 6010 USGS T01 (ICP/AES)	A digested sample is nebulized into an ICP, where the metal atoms are ionized. The metal ions are quantitated using AES.	**Suitable for soil background studies if RLs are low enough.** ICP/AES analysis is marginally less expensive than ICP/MS but has elevated RLs for some metals (for example, silver, thallium, and mercury).
	USEPA Method 6020 USGS T20 (ICP/MS)	A digested sample is nebulized into an inductively coupled plasma (ICP), where the metal atoms are ionized. The metal ions are quantitated using mass spectrometry (MS).	**Suitable for soil background studies.** ICP/MS typically has lower RLs than ICP/AES, so use of ICP/MS is preferred for soil background studies (to lower the nondetect frequency for some trace metals).

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Example - Analytical Methods

- Section 10.4 - USGS vs USEPA Preparation Methods for Metals
  - All digestion methods are not created equal!
    - Total metals or environmentally available metals?
  - May result in different concentrations depending upon the geological characteristics and chemical nature of each analyte
  - Results are generally not comparable

Table 10-1. Sample preparation

Sources: (USEPA 2020 [166]) and (Taggart 2002 [463]).

Chemical	Reference Method	Summary	Comments
	USEPA Method 3050 (Heating Block Digestion)	Soil is preprocessed using a number of options (see the text of Section 10.4 for a full discussion). The preprocessed soil is digested at 90–95°C on a hot plate or heating block. Digestion uses nitric acid, hydrogen peroxide, and typically hydrochloric acid (HCl always used for ICP/AES and can be used with some ICP/MS systems).	**Suitable for soil background studies**. Will dissolve all environmentally available metals, but not aluminosilicate-bound metals that are not environmentally available.

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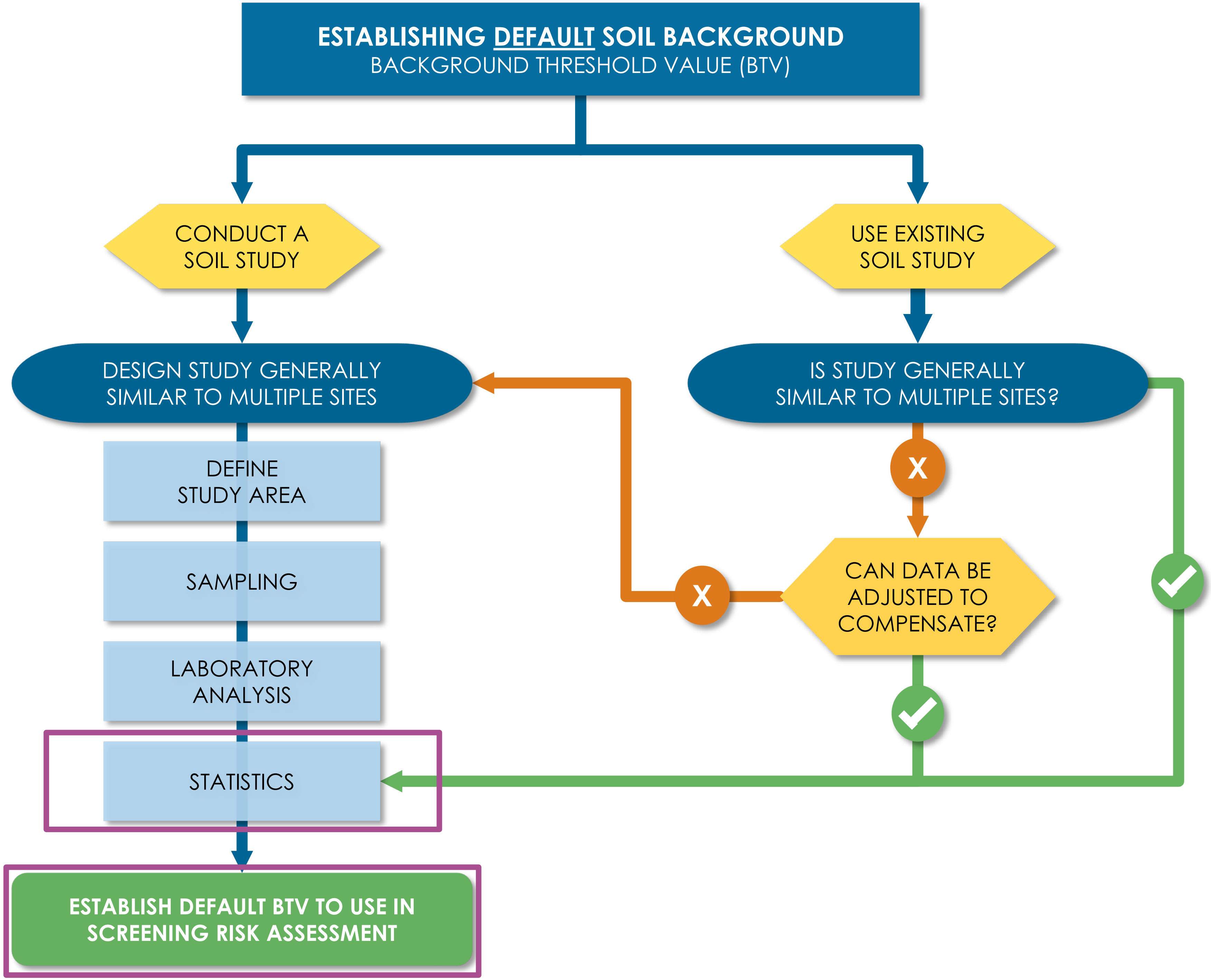
Framework 1

- Establishing **Default** Soil Background



Default Background Threshold Value (BTV)

BTV is defined as a measure of the upper threshold of a representative background population, such that only a small portion of background concentrations exceed the threshold value.

- Dataset distribution – Section 11.2
- Handling nondetects – Section 11.3
- Graphical displays (Q-Q Plot) – Section 11.4
- Identify & remove outliers – Section 11.5
- Statistical software – Section 11.9
- BTV value – Section 11.7

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Default Background Threshold Value (BTV)

- Section 11.7 & Appendix A
  - Description of statistical values used as BTVs
  - Potentials for false negatives and false positives

Table 11-3. Summary of values used to represent BTV

Value	Acronym	Description
Upper percentile	Not applicable	Value below which a specified percentage of observed background concentrations would fall
Upper confidence limit	UCL	Upper limit of 95% confidence interval
Upper prediction limit	UPL	The value below which a specified number of future independent measurements (k) will fall, with a specified confidence level
Upper tolerance limit	UTL	The UCL of an upper percentile of the observed values
Upper simultaneous limit	USL	Value below which the largest value of background observations falls with a specified level of confidence

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Default Background Threshold Value (BTV)

- Upper percentile
  - High false positive error rates when a large number of comparisons are made; generally, not used for default BTVs
- Upper confidence limit (UCL) of the mean
  - High false positives Generally, not appropriate to use for BTVs; generally, not used for default BTVs
- Upper prediction limit (UPL)
  - High false positive error rates when a large number of comparisons are made; generally not used for default BTVs
- Upper tolerance limit (UTL)
  - Appropriate to use when a large number of comparisons are made; most often used to establish default BTVs
- Upper Simultaneous limit (USL)
  - High false negative rates since USLs are an upper limit of the maximum value; generally not used for default BTVs

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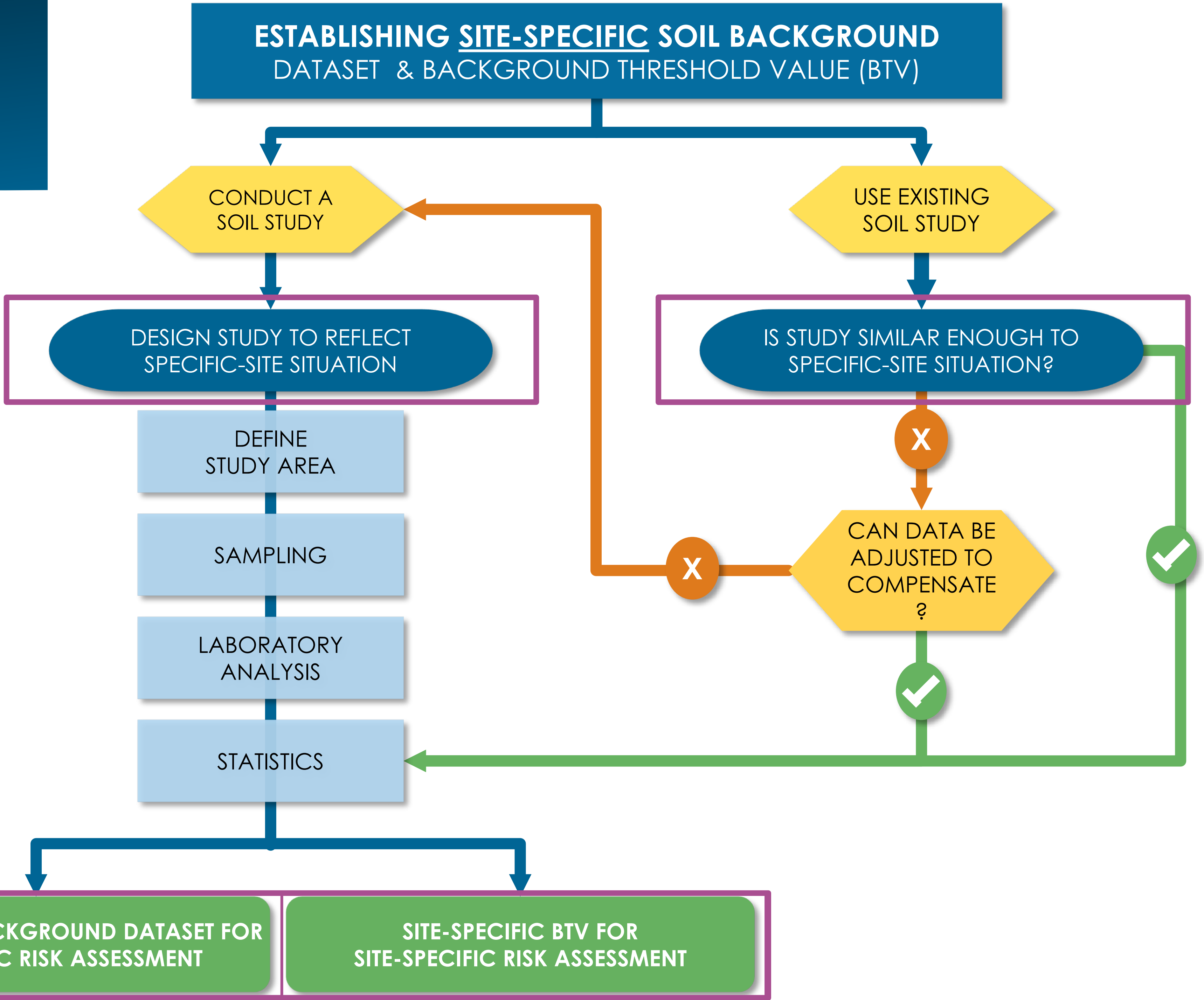
Framework 2

- Establishing **Site-Specific** Soil Background



Site-specific Soil Background

- Site-specific soil background dataset
  - Central tendency
  - Is there slight but pervasive contamination?
  - Statistical tests to compare datasets – Section 11.8
- Site-specific background threshold value
  - Upper end
  - Are maximum concentrations within the range of background?

Table 11-5. Assumptions, advantages, and disadvantages of common two-sample tests

Source: ASTM E3242-20 (ASTM 2020 [146]), Table X4.2.

Test Statistic	Objectives/Assumptions	Advantages	Disadvantages
Quantile test	• Objective is to test for differences in the right tail (largest values) of the site and background concentration distributions. • Nondetects are not among the right tail (largest values) in the pooled set of site and background concentrations.	• Nonparametric: No assumption is required regarding the distributions of the site and background concentrations. • Relatively simple to conduct the test. • No distribution assumptions are necessary. • May be used in conjunction with tests that focus on detecting differences in the mean or median of site and background concentrations.	• May require a large number of measurements to have adequate power to detect differences in site and background concentrations. • Test may be inconclusive if nondetects are present among thelargest data values in the pooled set of site and background data.

~Section 11.8

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Site-specific Background Threshold Value (BTV)

BTV is defined as a measure of the upper threshold of a representative background population, such that only a small portion of background concentrations exceed the threshold value.

- Dataset distribution – Section 11.2
- Handling nondetects – Section 11.3
- Graphical displays (Q-Q Plot) – Section 11.4
- Identify & remove outliers – Section 11.5
- Statistical software – Section 11.9
- BTV value – Section 11.7

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Site-specific Background Threshold Value (BTV)

- Upper percentile
  - High false positive error rates when a large number of comparisons are made
- Upper confidence limit (UCL) of the mean
  - Generally not appropriate to use for BTVs
- Upper prediction limit (UPL)
  - High false positive error rates when a large number of comparisons are made
- **Upper tolerance limit (UTL)**
  - Appropriate to use when a large number of comparisons are made
- Upper Simultaneous limit (USL)
  - High false negative rates since USLs are an upper limit of the maximum value

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Poll Question

Is it appropriate to use the UCL of the mean as the BTV ?

a) Yes
b) No

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Advancing Environmental Solutions

Using Soil Background in Risk Assessment

BONNIE BROOKS

DEPARTMENT OF ECOLOGY
State of Washington

Training Development:

SHUKLA ROY-SEMMEN, PH.D.

DTSC
Department of Toxic Substances Control

Outline

- Default soil background & risk assessment
- Site-specific soil background & risk assessment
- Soil background & remedial goals

Regulatory Agency

- **Coordinate with the regulatory agency**
- Each regulatory agency has
  - Definitions for soil background
  - Requirements (may differ from what is in the guidance)

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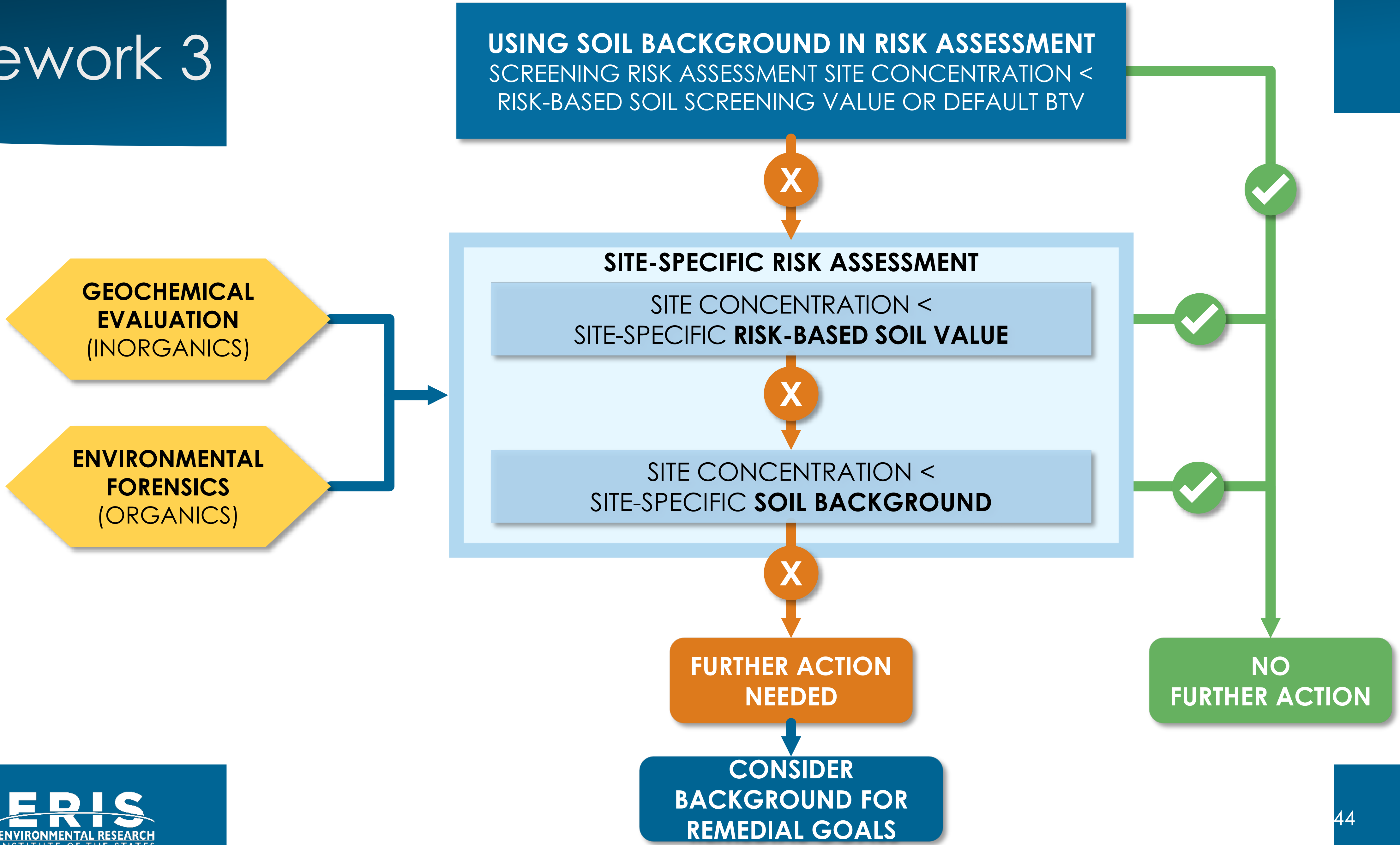
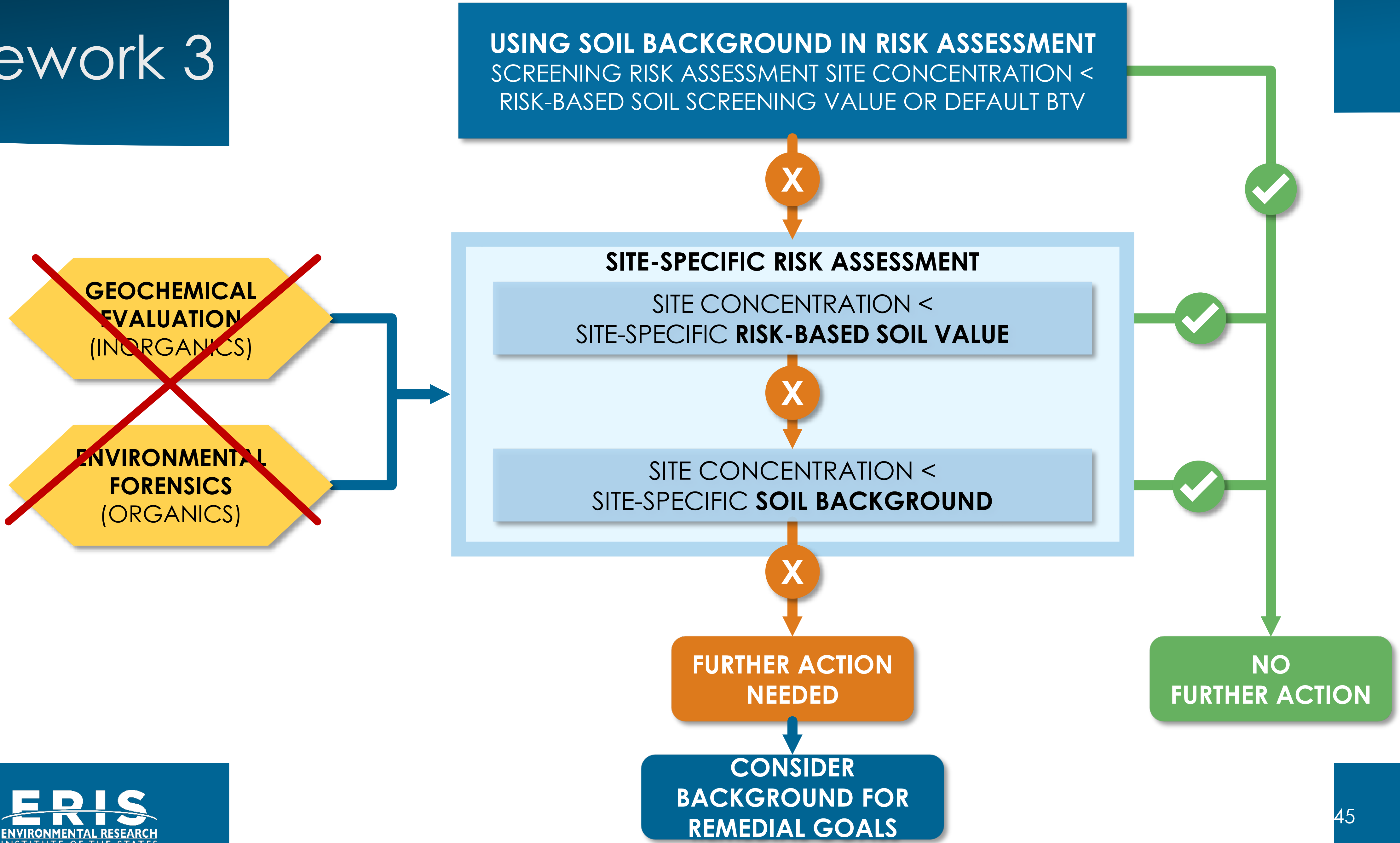
Framework 3



USING SOIL BACKGROUND IN RISK ASSESSMENT
SCREENING RISK ASSESSMENT SITE CONCENTRATION < RISK-BASED SOIL SCREENING VALUE OR DEFAULT BTV
X
SITE-SPECIFIC RISK ASSESSMENT
SITE CONCENTRATION < SITE-SPECIFIC RISK-BASED SOIL VALUE
X
SITE CONCENTRATION < SITE-SPECIFIC SOIL BACKGROUND
X
GEOCHEMICAL EVALUATION (INORGANICS)
ENVIRONMENTAL FORENSICS (ORGANICS)
FURTHER ACTION NEEDED
CONSIDER BACKGROUND FOR REMEDIAL GOALS
NO FURTHER ACTION

Framework 3



USING SOIL BACKGROUND IN RISK ASSESSMENT
SCREENING RISK ASSESSMENT SITE CONCENTRATION < RISK-BASED SOIL SCREENING VALUE OR DEFAULT BTV
X
GEOCHEMICAL EVALUATION (INORGANICS)
ENVIRONMENTAL FORENSICS (ORGANICS)
SITE-SPECIFIC RISK ASSESSMENT
SITE CONCENTRATION < SITE-SPECIFIC RISK-BASED SOIL VALUE
X
SITE CONCENTRATION < SITE-SPECIFIC SOIL BACKGROUND
X
FURTHER ACTION NEEDED
CONSIDER BACKGROUND FOR REMEDIAL GOALS
NO FURTHER ACTION

Representative Site Concentration

- **Site concentration vs.** background threshold value (BTV)
  - **Maximum**
    - **If the BTV is a USL, the maximum must be used (upper boundary of datset maximum)**
    - Sample size is inadequate
    - Large variability in site data
  - **95th percentile**
    - **Not appropriate to use with a BTV based on a USL**
    - In some cases, appropriate to use instead of maximum, but only if the BTV was calculated using a similar statistic
    - Large datasets representing a single population

https://www.needpix.com/photo/340338/earthworm-soil-dirt

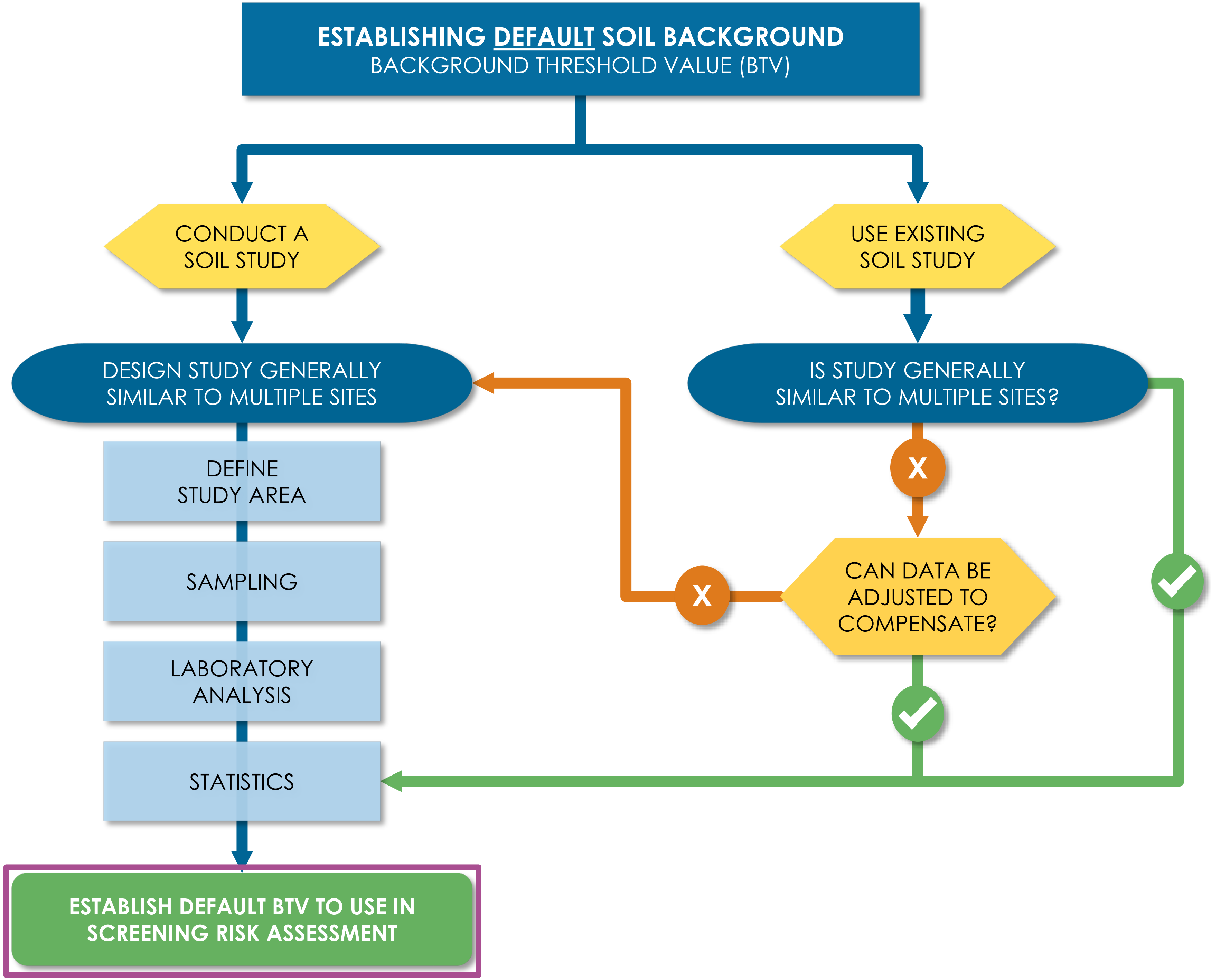
Representative Site Concentration

- **Site concentration vs. background threshold value (BTV)**
- Similar statistics for the site concentration and BTV
  - 95^{th} percentile site concentration vs. 95-95 UTL BTV
- **Not appropriate to compare a 95 UCL of the mean site concentration to BTV**

https://www.needpix.com/photo/340338/earthworm-soil-dirt

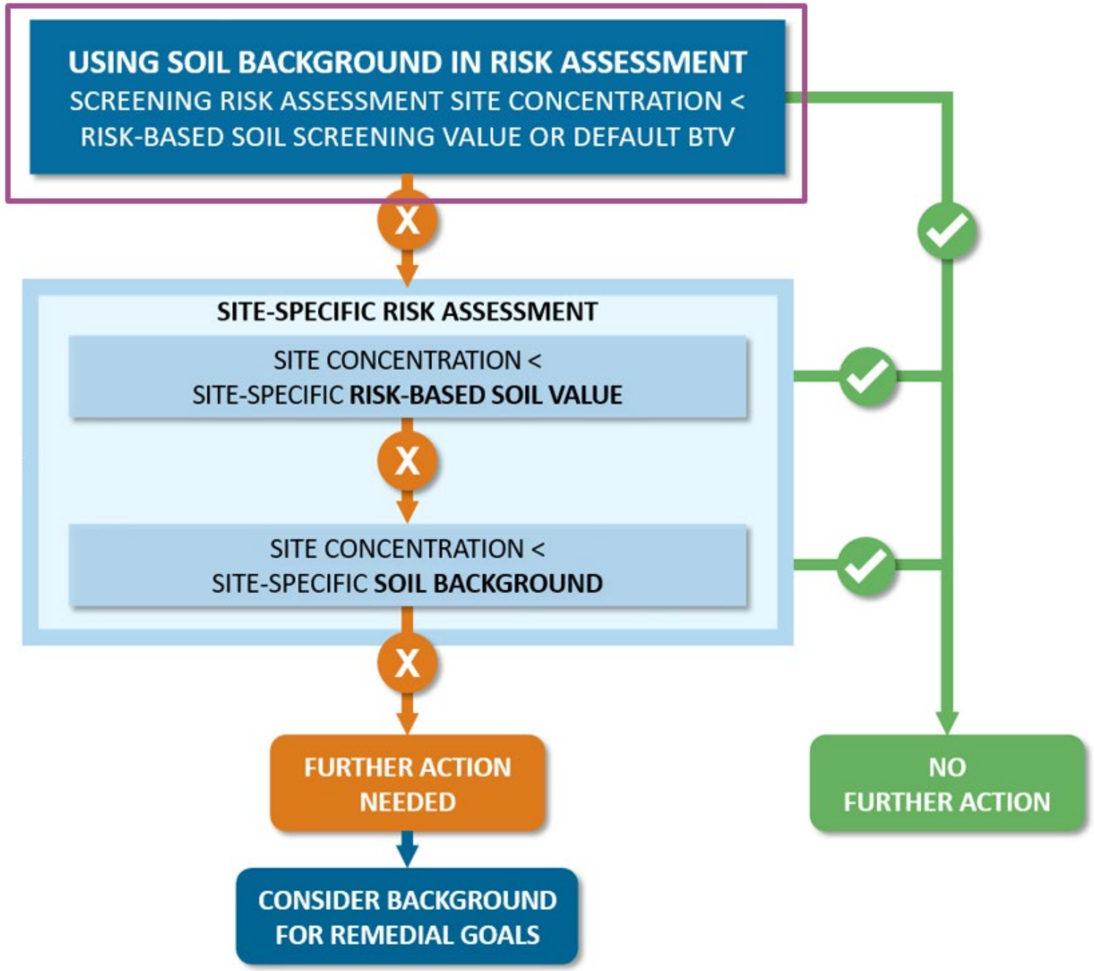
Framework 1

- Establishing **Default** Soil Background



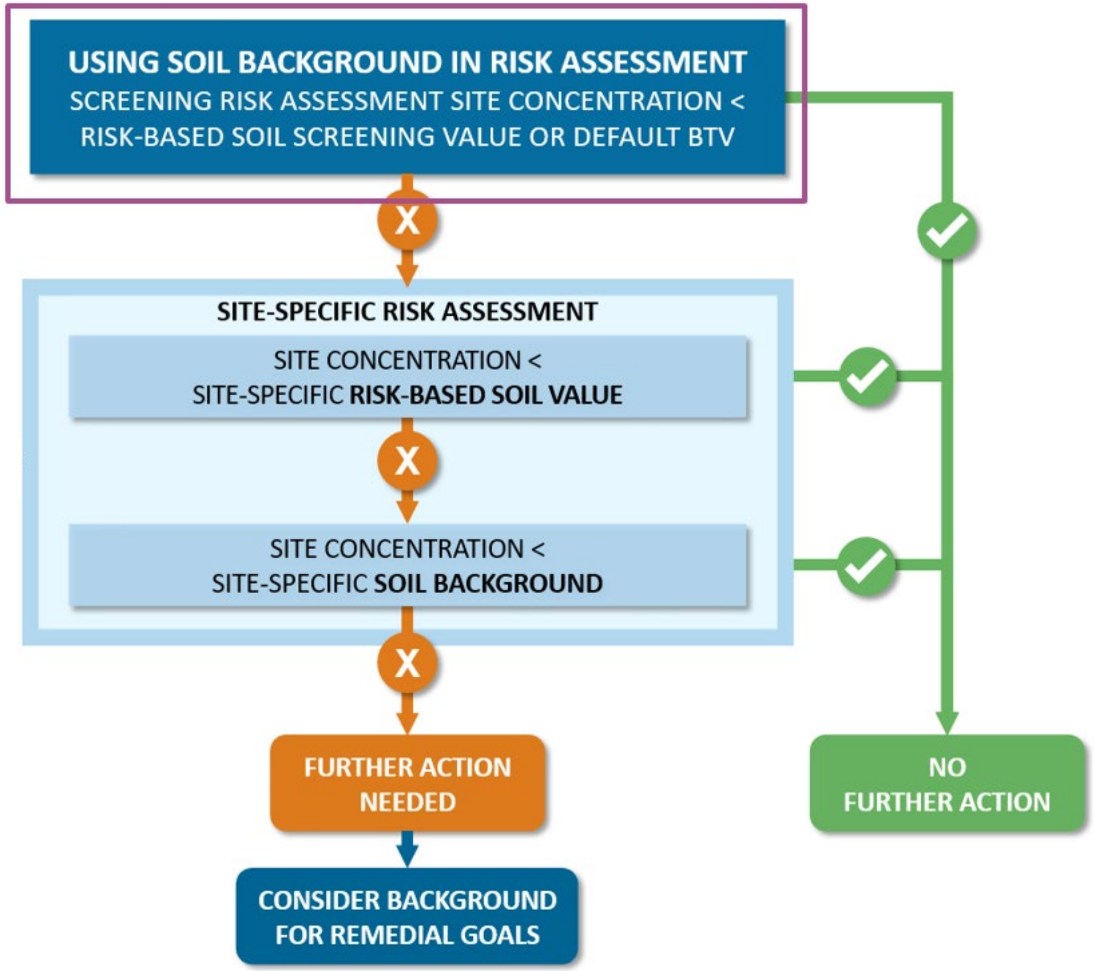
Screening Risk Assessment

- **Default soil background**
  - Site concentration vs. risk-based soils screening values
  - Site concentrations vs. default BTV



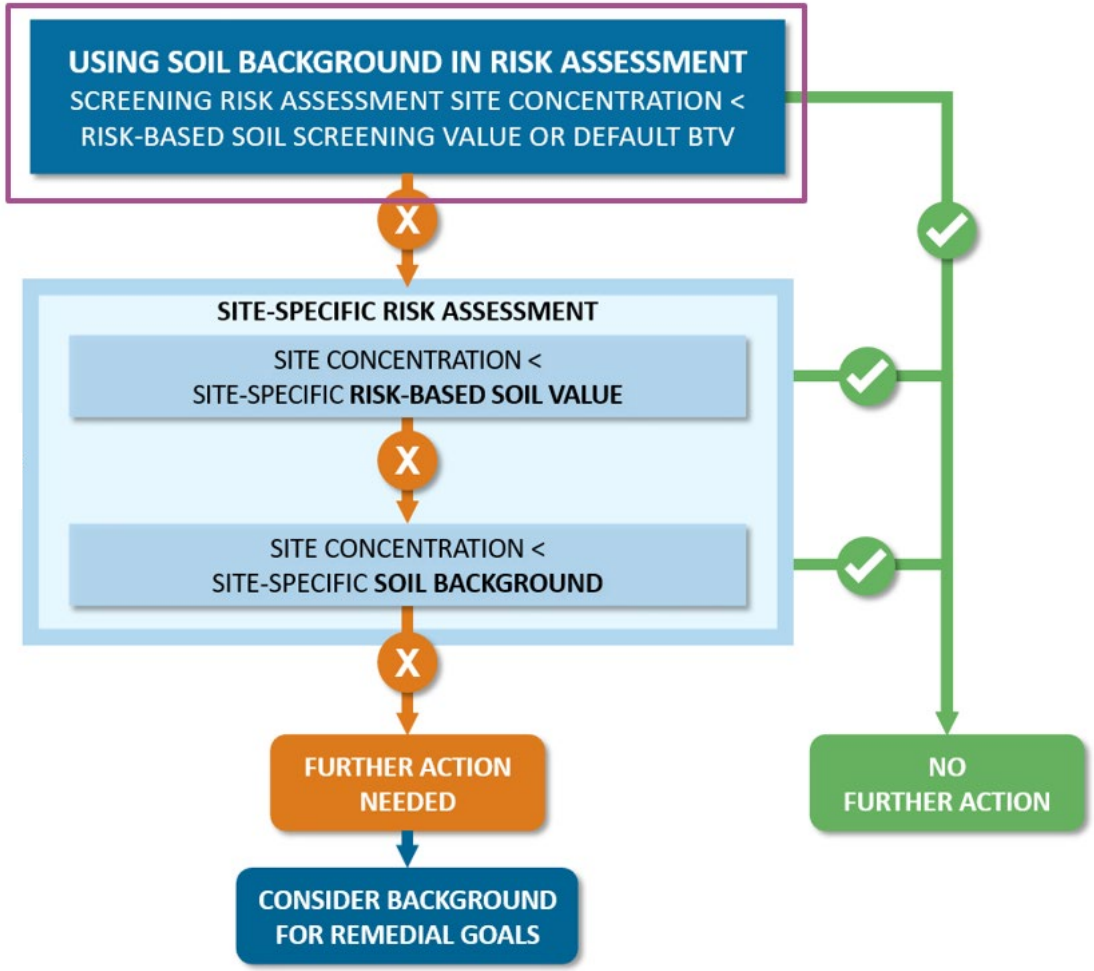
Screening Risk Assessment

- **Site concentrations vs. Default BTV**
  - Representative site concentration - generally maximum
  - Point by point basis
- Site concentrations ≤ default BTV
  - No further action
- Site concentrations > default BTV
  - Move on to Test for Proportions



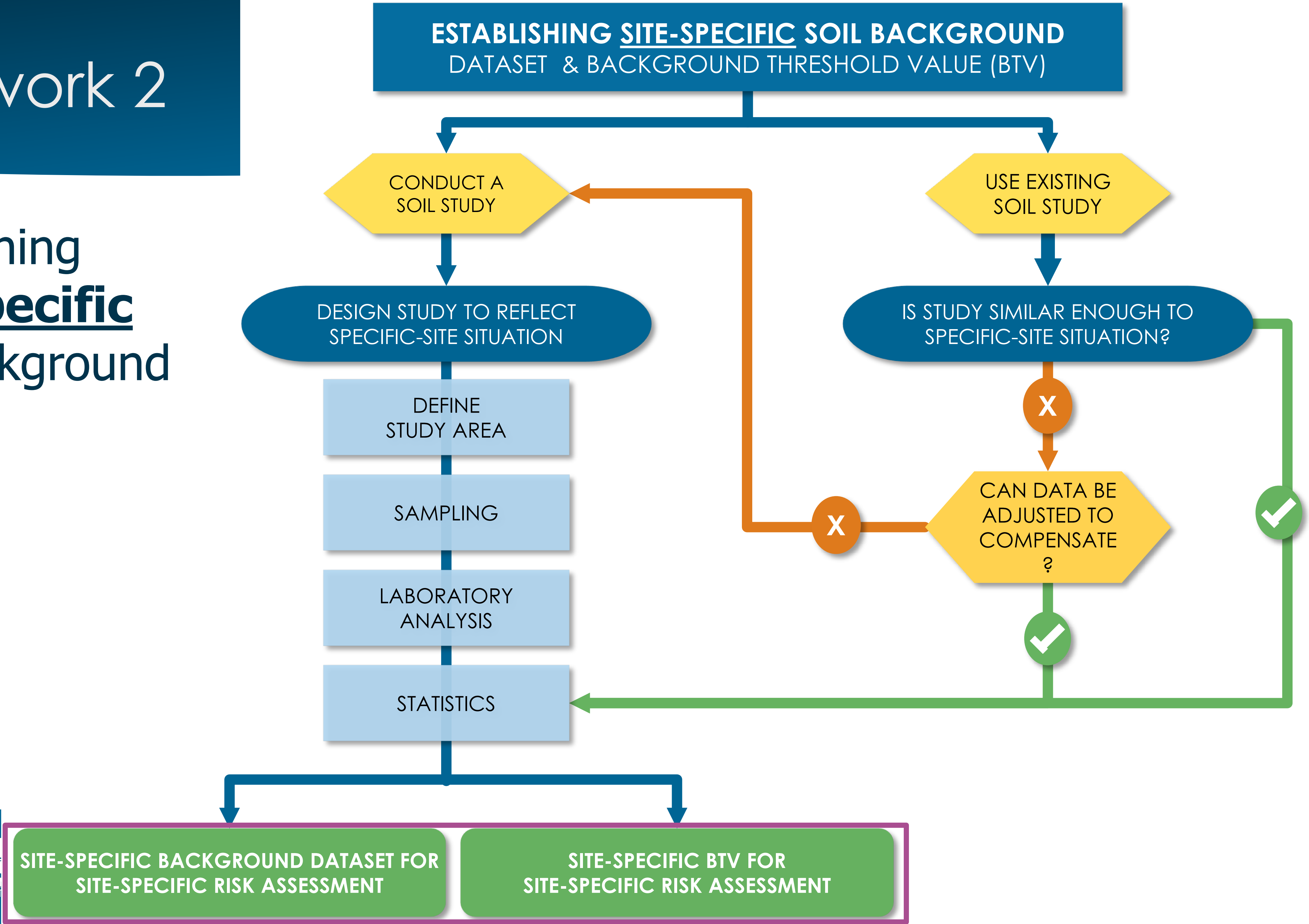
Screening Risk Assessment

- **Test for proportions**
  - U.S. EPA's ProUCL software
  - Rate of exceedances of default BTV significantly different than zero?
    - No, dataset represents background; no further action
    - Yes, dataset does not represent background; move to site-specific risk assessment



Framework 2

- Establishing **<u>Site-Specific</u>** Soil Background

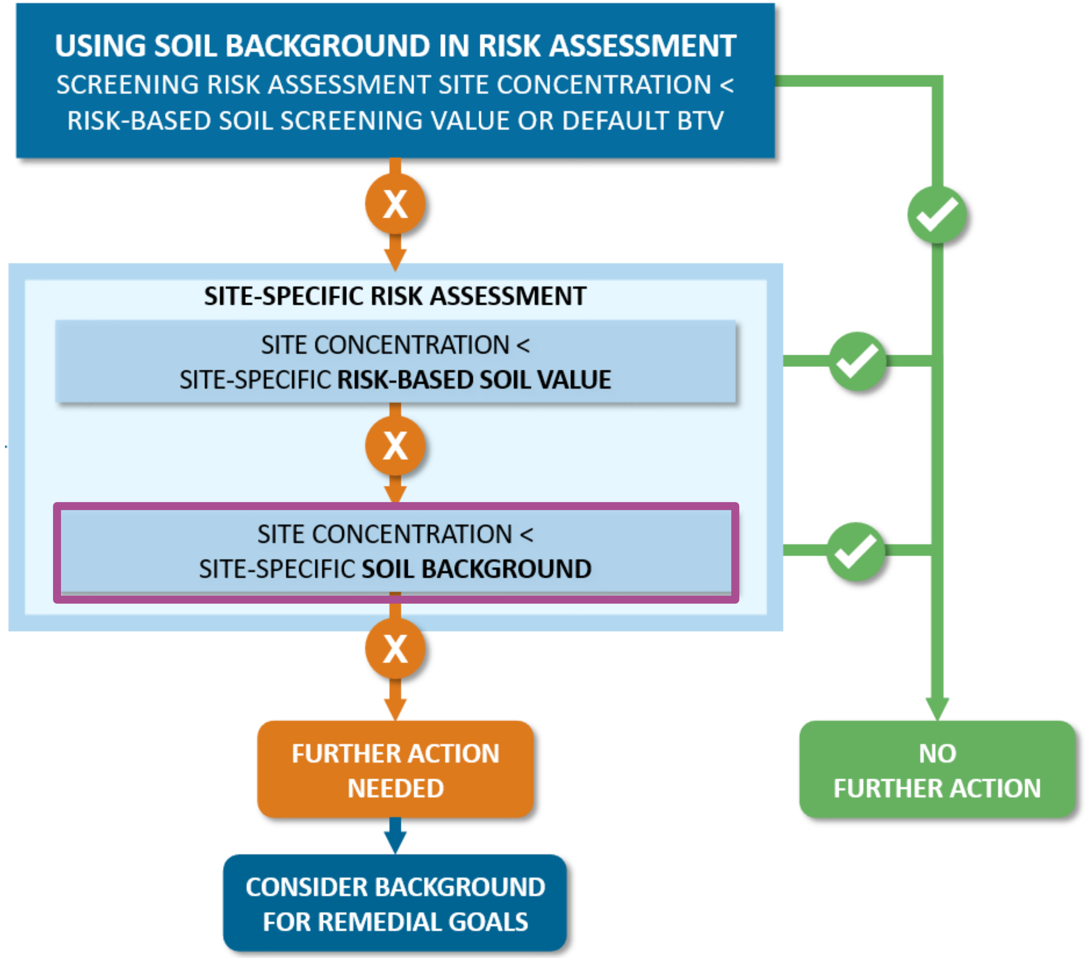


Site-specific Risk Assessment

- **Complementary tests – both should be performed**
  - Test for presence of different types of contamination
- **Site-specific soil BTV**
  - Upper end comparison
  - Are site concentrations within the distribution of soil background?
  - Is there localized contamination (hotspots)?
- **Site-specific soil background dataset**
  - Central tendency comparison
  - Is there slight but pervasive contamination?

Site-specific BTV

- **Site concentrations vs. site-specific BTV**
  - Representative site concentration - generally maximum
  - Point by point basis
- Site concentrations ≤ site-specific BTV
  - Compare site dataset to site-specific soil background dataset
- Site concentrations > site-specific BTV
  - Move on to Test for Proportions



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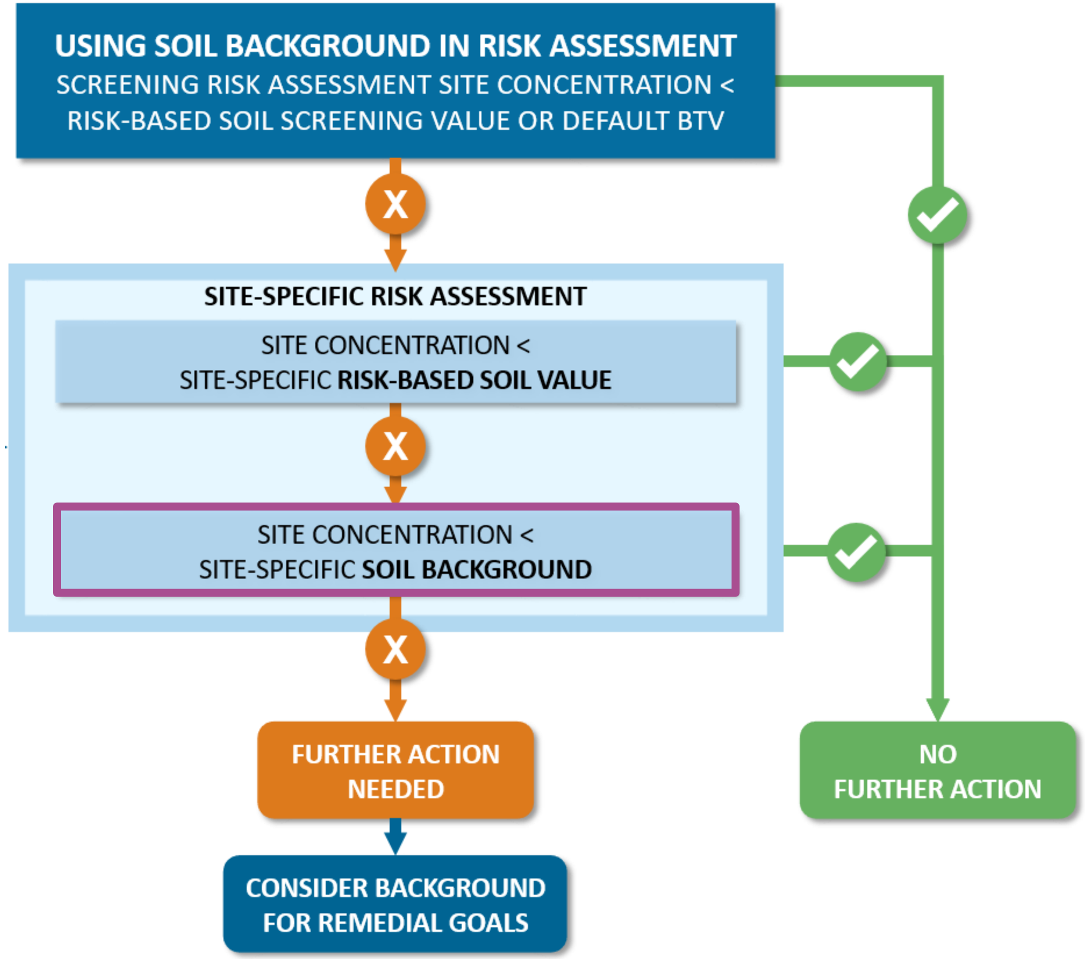
Site-specific BTV

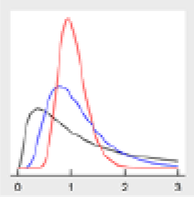
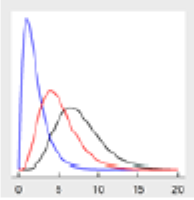
- **Test for proportions**
  - US EPA's ProUCL software
  - Rate of exceedances above site-specific BTV significantly different than zero?
    - No, dataset represents background; Compare site dataset to site-specific soil background dataset
    - Yes, dataset does not represent background; geochemical evaluation & environmental forensics



Site-specific Soil Background Dataset

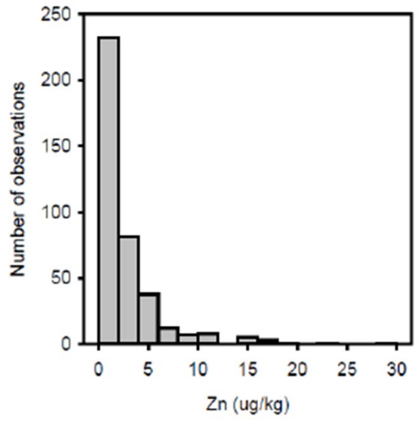
- **Site dataset vs. site-specific background dataset** (Table 11-1)
  - Compare dataset distributions

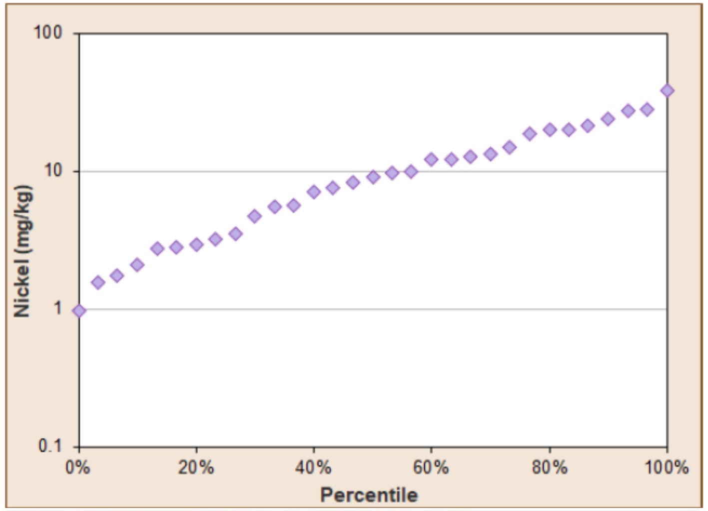
Table 11-1. Common distributions of environmental data

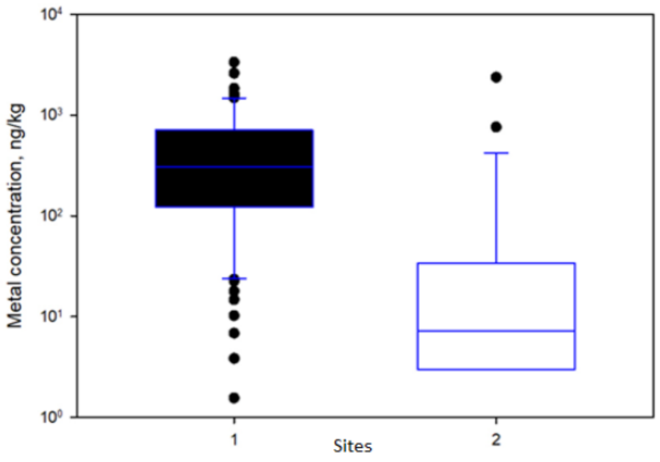
	Distribution Curve	Basic Properties	Statistical Analysis Methods
	Normal	Data distribution is not skewed and centered around the mean	Analyze data set using parametric statistical methods
	Lognormal	Data distribution is skewed and log transforming the data produces a normal distribution	Analyze data set using lognormal statistical methods only if data cannot be modeled by the normal or gamma distributions and the data set is not small (<15-20 samples) and highly skewed
	Gamma	Data distribution is skewed and modeled by the gamma distribution	Analyze data set using gamma statistical methods

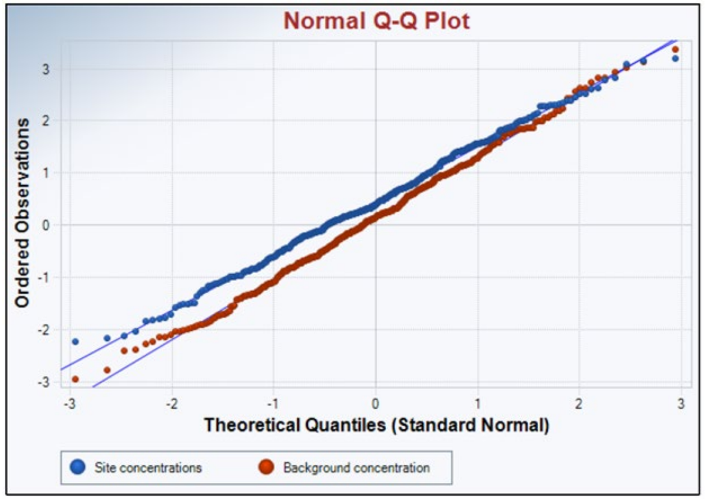
Site-specific Soil Background Dataset

- **Site dataset vs. site-specific background dataset** (Sect. 11.4)
  - Compare datasets using graphical plots
    - Quantile-Quantile (Q-Q Plots)
    - Histogram
    - Box plot
    - Percentile plot
    - Probability plot









Site-specific Soil Background Dataset

- **Site dataset vs. site-specific background dataset** (Table 11-2)
  - Outliers

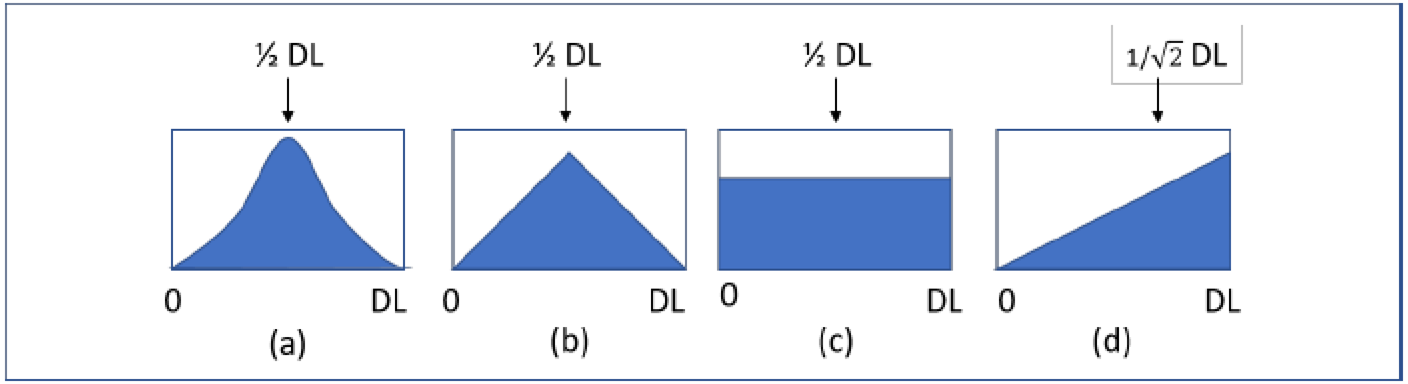
Table 11-2. Outlier tests

Source: Developed from (USDON 2002)[36], Table B-3, and ASTM E3242-20 (ASTM 2020)[146], Table X4.1.

Statistical Test	Assumptions	Advantages	Disadvantages
Dixon's test	• Sample size ≤ 25. • Measurements without outliers are normally distributed. • There is only a single suspected outlier, which can be either the smallest or largest value.	• Available in commonly used software, including USEPA's ProUCL. • Recommended in many guidance documents, including USEPA's ProUCL.	• The user must consider the highest or the lowest measured value as a potential outlier prior to the test. • Assumption of normality is rarely applicable to environmental field data. • In cases of skewed or asymmetric data distributions, the test has a tendency to falsely flag the tail value as an outlier.
Discordance test	• 3 < Sample size ≤ 50. • Measurements without outliers are normally distributed. • There is only a single suspected outlier, which can be either the smallest or largest value.	• Available in commonly used software.	• The user must consider the highest or the lowest measured value as a potential outlier before the test. • Assumption of normality is rarely applicable to environmental field data. • In cases of skewed or

Site-specific Soil Background Dataset

- **Handling non-detects** (Sect. 11.3)
  - Substitution
  - Kaplan-Meier Method
  - Regression on order statistics (ROS)
  - Maximum Likelihood Estimate (MLE)



Symmetric distributions = (a), (b), and (c); right-triangular distribution = (d).

Figure 11-1. Examples of assumed nondetect distributions and their corresponding substitution values.

Image source Extension, University of Missouri, https://bit.ly/3FP9t6r

Site-specific Soil Background Dataset

- **Site dataset vs. site-specific background dataset** (Table 11-5)
  - Two sample hypothesis testing

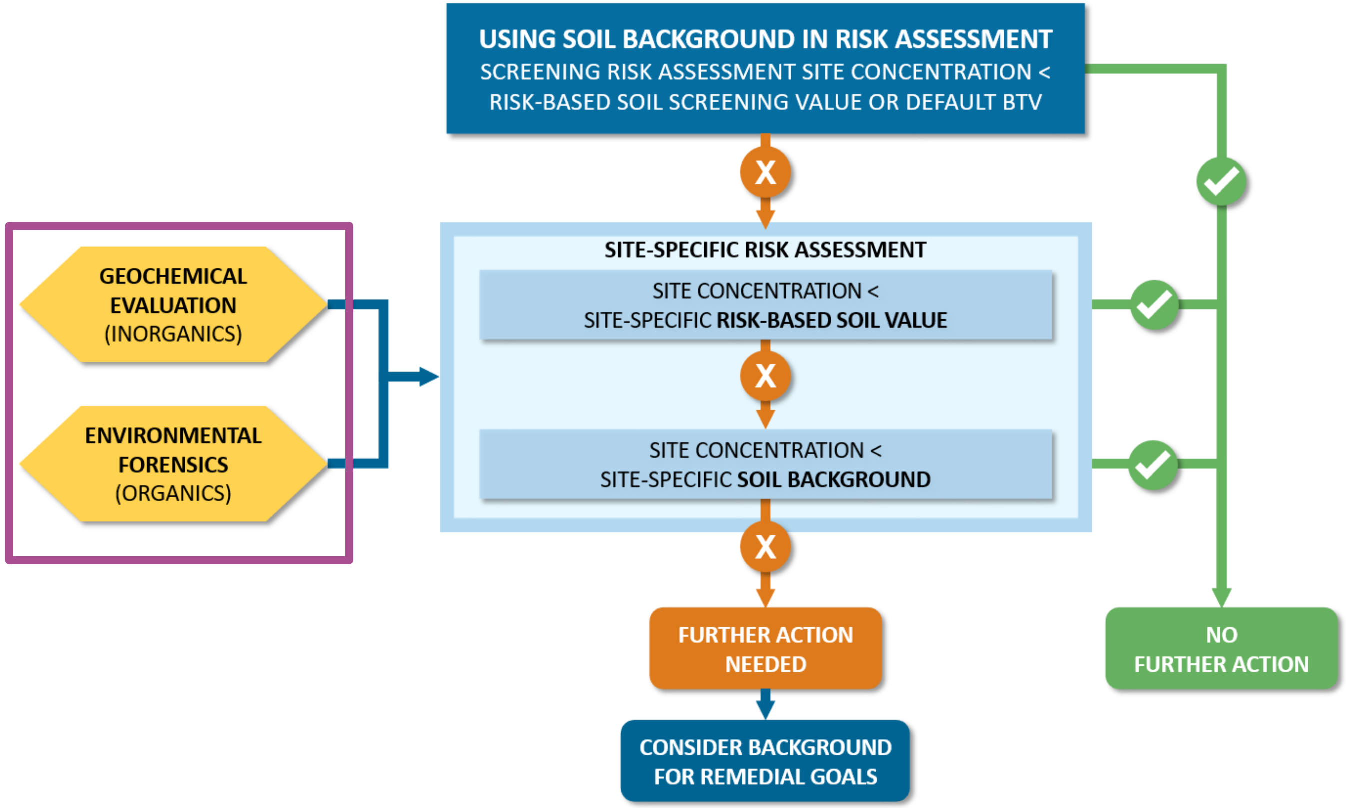
Table 11-5. Assumptions, advantages, and disadvantages of common two-sample tests

Source: ASTM E3242-20 (ASTM 2020)[146], Table X4.2.

Test Statistic	Objectives/Assumptions	Advantages	Disadvantages
Quantile test	• Objective is to test for differences in the right tail (largest values) of the site and background concentration distributions. • Nondetects are not among the right tail (largest values) in the pooled set of site and back-ground concentrations.	• Nonparametric: No assumption is required regarding the distributions of the site and background concentrations. • Relatively simple to conduct the test. • No distribution assumptions are necessary. • May be used in conjunction with tests that focus on detecting differences in the mean or median of site and background concentrations.	• May require a large number of measurements to have adequate power to detect differences in site and background concentrations. • Test may be inconclusive if nondetects are present among the largest data values in the pooled set of site and background data.
Wilcoxon rank sum (WRS) test also referred to as the "Wilcoxon-Mann-Whitney test" or "Mann Whitney U test")	• Objective is to test for differences in the medians of the site and background concentration data. • All nondetects are associated with a single detection limit. • The detection limit is less than the smallest detected concentration. • At least 50% of both the site and background concentrations	• Nonparametric: No assumption is required regarding the type of distributions of the site and background concentrations. • Can be applied to datasets with less than 50% nondetects. • More robust with respect to outliers than parametric two-sample tests, such as Student's *t*-test. • May be used in conjunction with	• Not applicable to cases with less than 50% of detected values. • May conclude that site and background concentrations are derived from the same population when concentrations in right tail differ significantly, so it is important to complement the test with tests that focus on

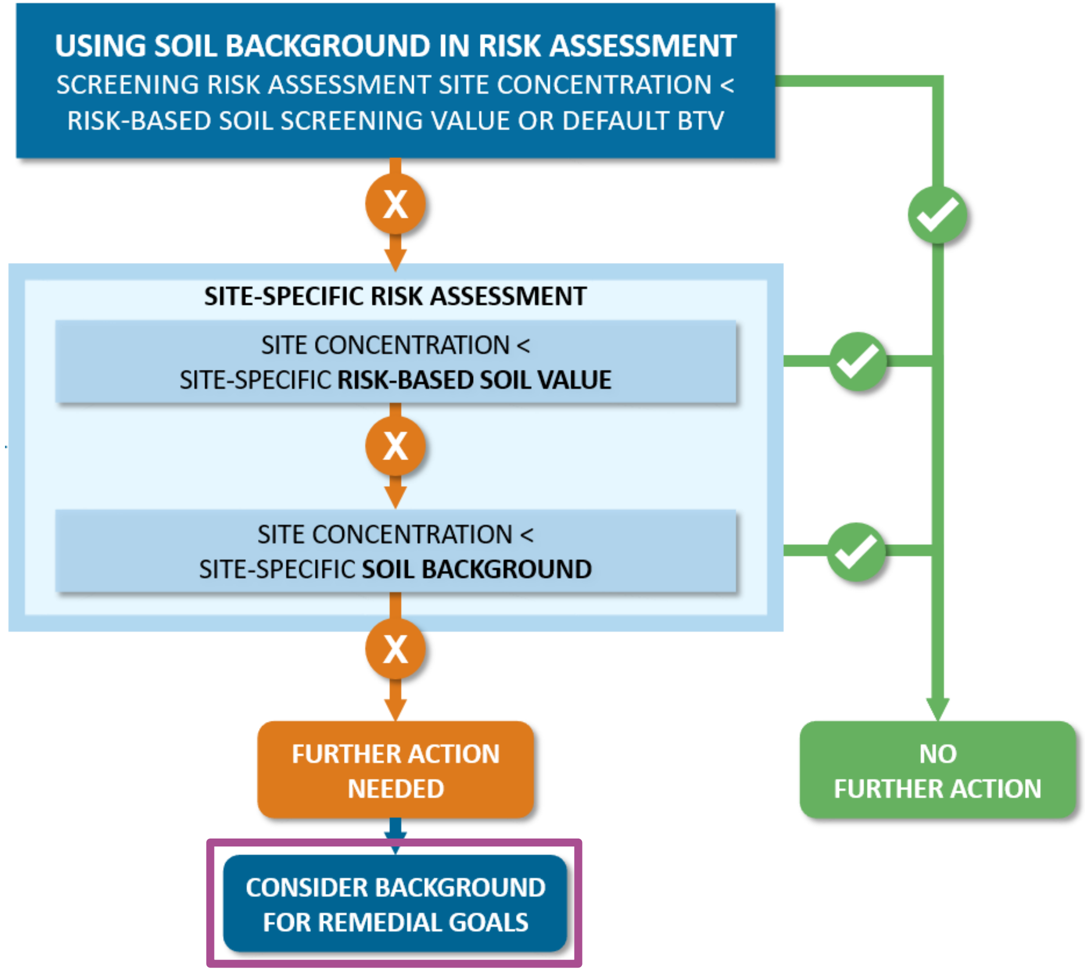
Site-Specific Risk Assessment

- **Site concentrations ≤ site-specific BTV and site-specific dataset**
  - No further action needed
- **Site concentrations > site-specific BTV or site-specific dataset**
  - Geochemical evaluation or environmental forensics



Remedial Goals

- Site concentrations not representative of soil background (Section 4.4)
  - **Establish remedial goals**
    - Site-specific BTV
    - Compare site dataset and site-specific soil background dataset to determine areas that require a response action



Poll Question

What site concentration is most often used to compare to a BTV?

If the BTV you are using to compare to site concentrations is a USL, what site concentration is appropriate to use?

a) Minimum
b) Maximum
c) 95 UCL of the mean
d) 95th Percentile

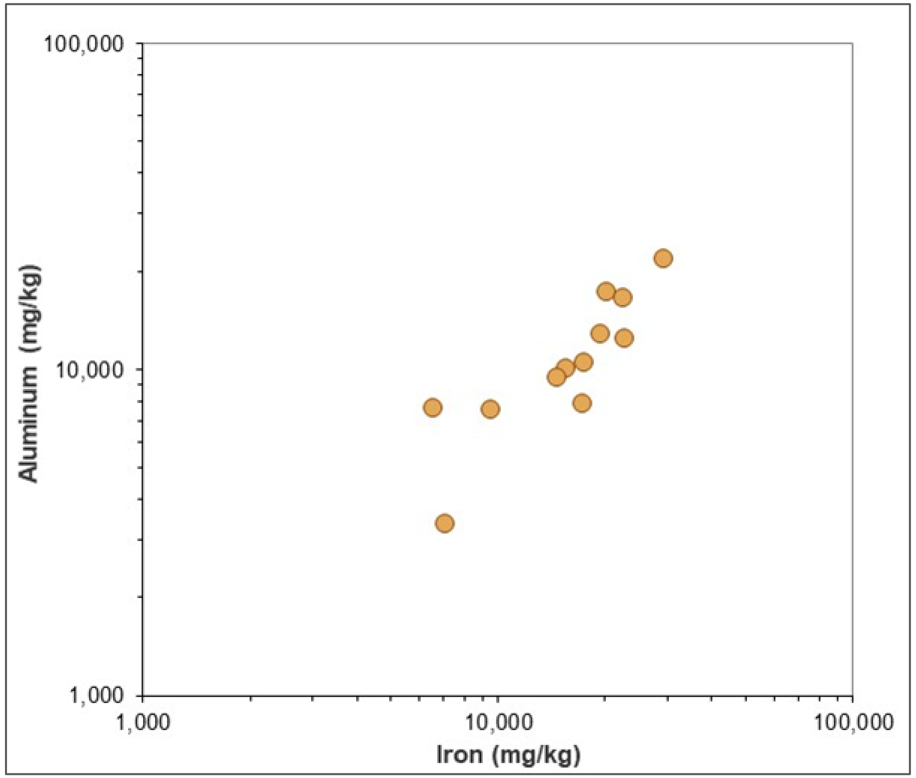
https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Advancing Environmental Solutions

Geochemical Evaluations as a Line of Evidence

KAREN THORBJORNSEN, M.S., P.G.

APTIM



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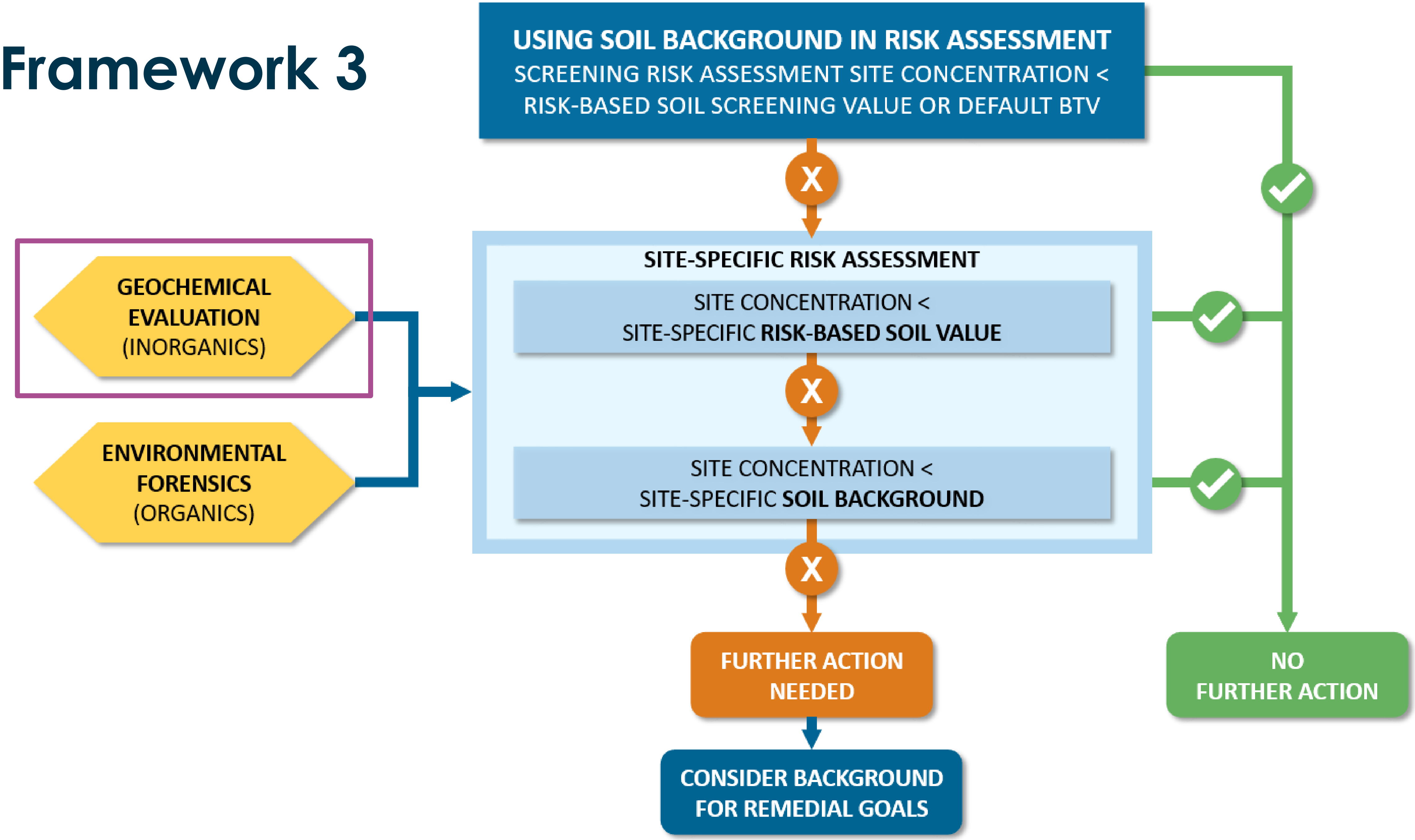
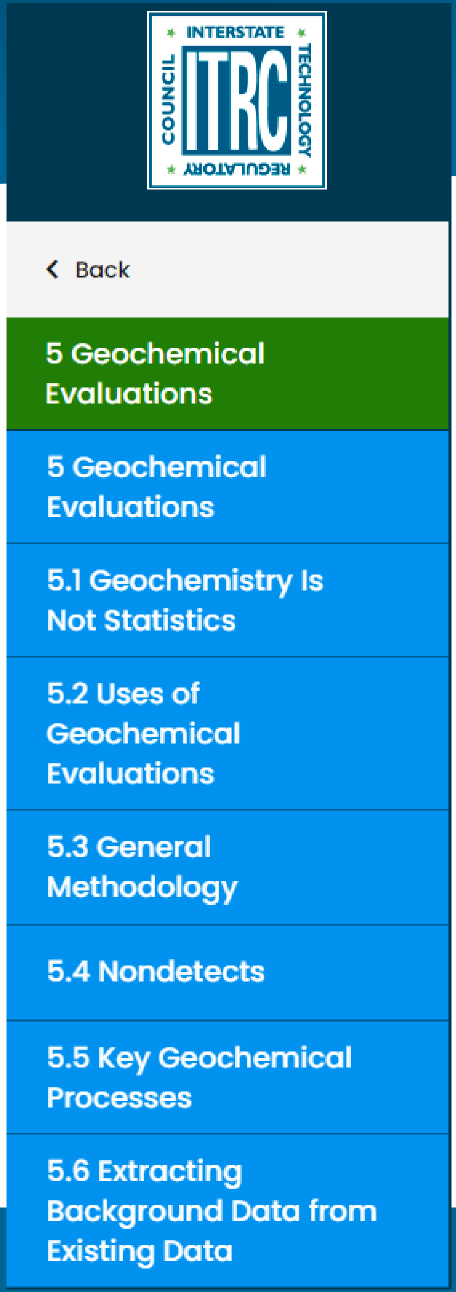


USING SOIL BACKGROUND IN RISK ASSESSMENT
SCREENING RISK ASSESSMENT SITE CONCENTRATION <
RISK-BASED SOIL SCREENING VALUE OR DEFAULT BTV
X
GEOCHEMICAL EVALUATION (INORGANICS)
ENVIRONMENTAL FORENSICS (ORGANICS)
SITE-SPECIFIC RISK ASSESSMENT
SITE CONCENTRATION <
SITE-SPECIFIC RISK-BASED SOIL VALUE
X
SITE CONCENTRATION <
SITE-SPECIFIC SOIL BACKGROUND
X
FURTHER ACTION NEEDED
CONSIDER BACKGROUND FOR REMEDIAL GOALS
NO FURTHER ACTION

Geochemical Evaluations

- Section 5 provides an overview of geochemical evaluations.
- Case studies in Sections 14.4, 14.5, and 14.6 highlight the different ways that geochemical evaluation can provide a reality check during the development of a background data set.



Geochemical Evaluations

- Section 14.4: Statistical outlier = naturally elevated concentration; retained.
- Section 14.5: Statistical outlier = potentially impacted concentration; removed.
- Section 14.6: No statistical outliers. Max. lead concentration potentially impacted; removed.

Geochemical Processes Controlling Element Concentrations in Soil

- Adsorption on clay, iron oxide, manganese oxide minerals
- Solubility
- Presence of evaporite minerals (arid soils)
- Presence of mineralized zones
- Effects of bioconcentration
- Physical weathering of rock (vs. chemical weathering products)
- Effects of low redox in hydric soils

Adsorption on Mineral Surfaces

- Clays (Al)

  Ba^{2+}, Cd^{2+}, Zn^{2+}

- Iron Oxides (Fe)

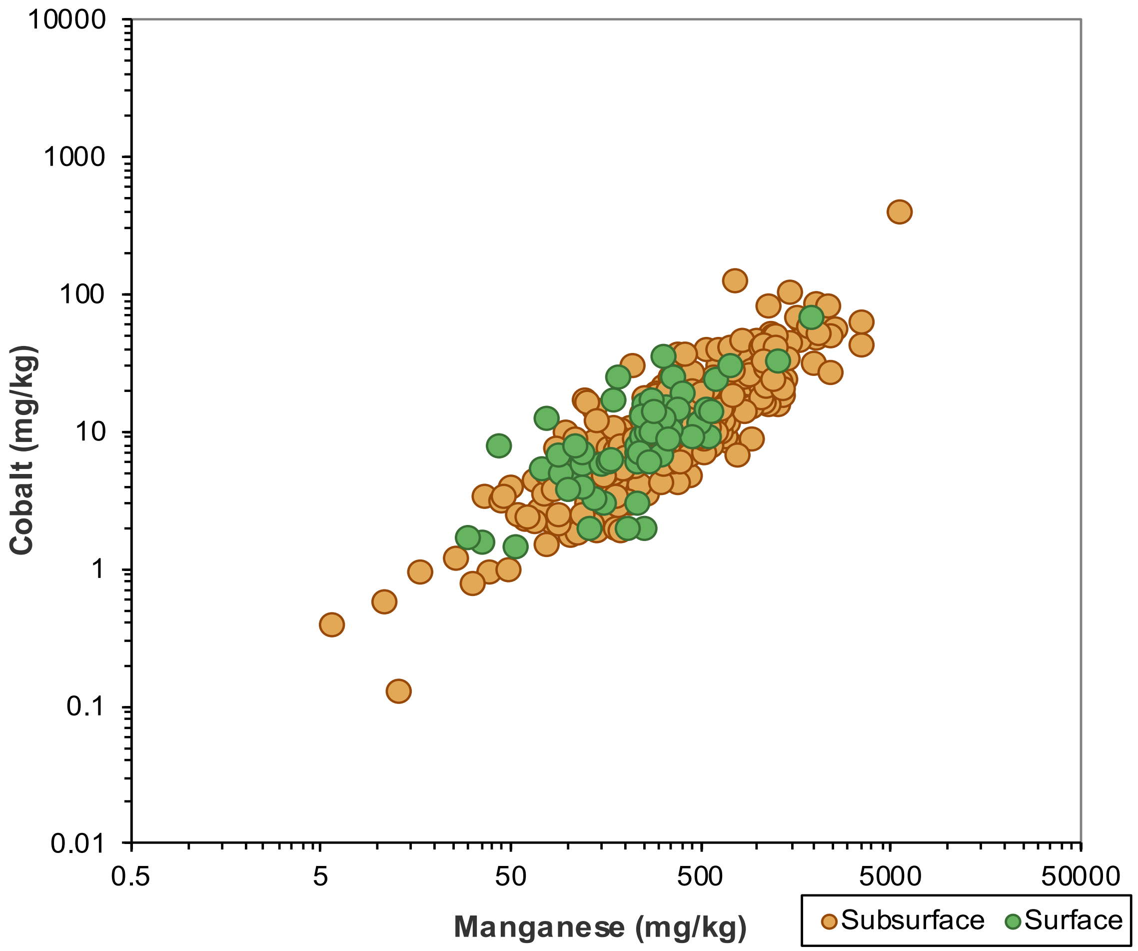
  $HAsO_4^{2-}$, $H_2AsO_4^{-}$

  $H_2VO_4^{-}$, HVO_4^{2-}

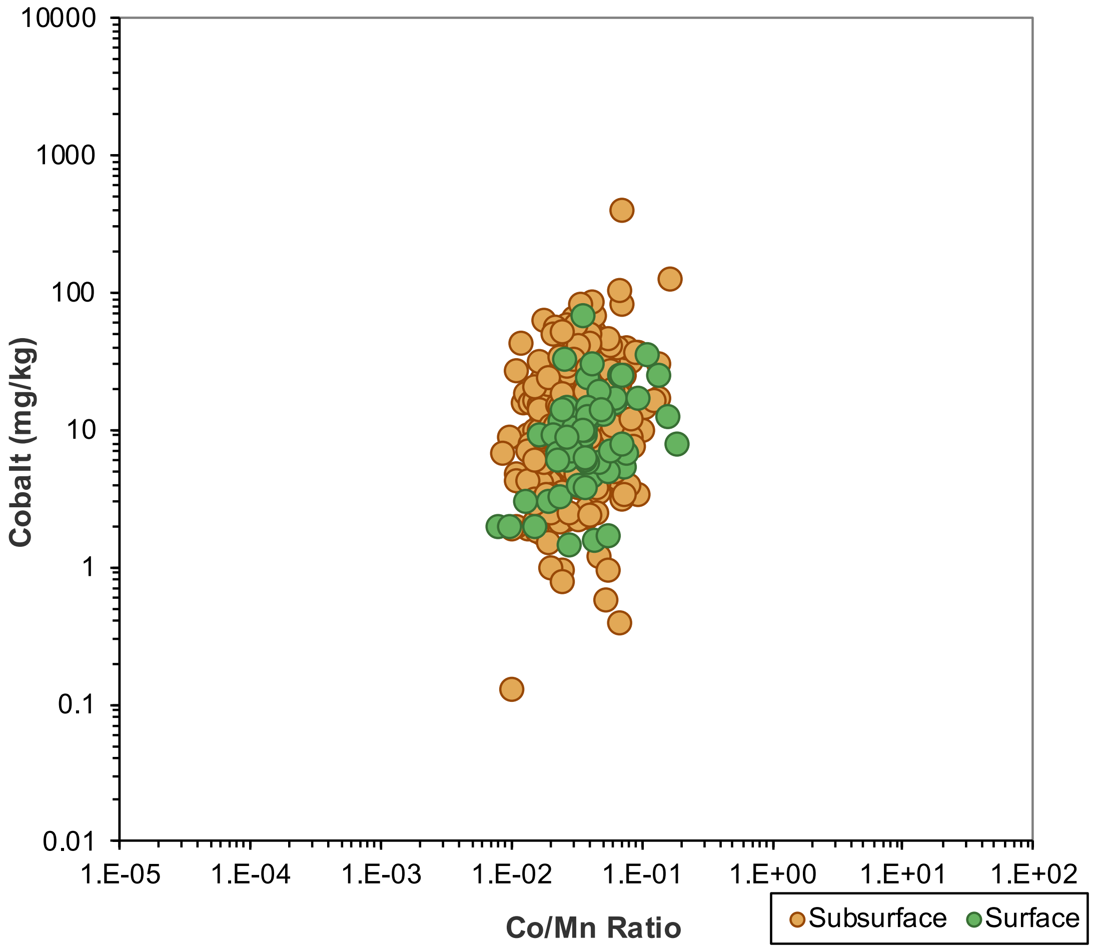
- Manganese Oxides (Mn)

  Co^{2+}, Pb^{2+}

Geochemical Evaluations



Geochemical Evaluations



Geochemical Evaluations

- Section 6 of the SBR guidance describes the use of geochemical evaluations during risk assessment:
  - During COPC selection
  - During risk characterization.
- In either case, the geochemical evaluation is typically provided as its own stand-alone chapter or as an appendix to the main report.

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6 Using Geochemical Evaluations in Risk Assessment

6 Using Geochemical Evaluations in Risk Assessment

6.1 Using Geochemical Evaluations During COPC Selection

6.2 Using Geochemical Evaluations During Risk Characterization

6.3 Considerations

Geochemical Evaluations

- When should geochemical evaluations (and environmental forensics) be considered during your project?
  - *EARLY* in the project life cycle – e.g., when the CSM and DQOs are being developed.
- Be sure to analyze your background and site samples for the reference (major) elements, in addition to the trace elements of concern.

Poll Question

Which are potential geochemical mechanisms controlling element concentrations in soil?
(choose all that apply)

- Adsorption on clay, Fe oxide, Mn oxide minerals
- Physical weathering of rock
- Effects of bioconcentration
- Solubility
- Effects of low redox in hydric soils
- Presence of mineralized zones
- Presence of evaporite minerals (arid soils)

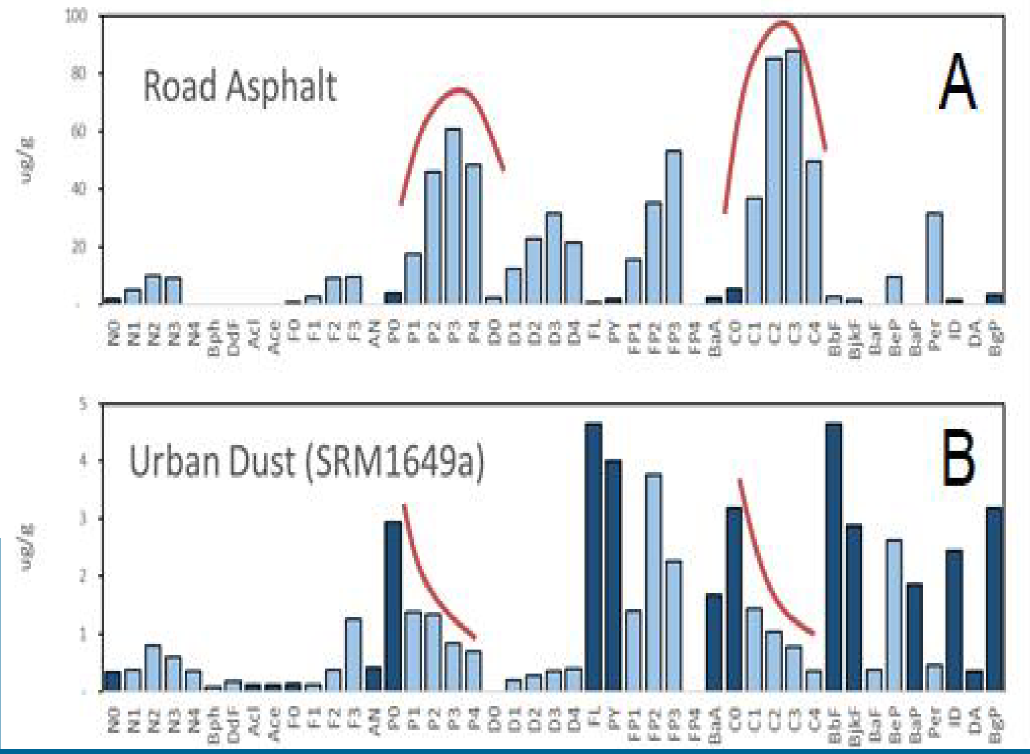
https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

Advancing
Environmental
Solutions

Environmental Forensics as a Line of Evidence

CHARLES P. DEWOLF, PH.D., PG

Trihydro



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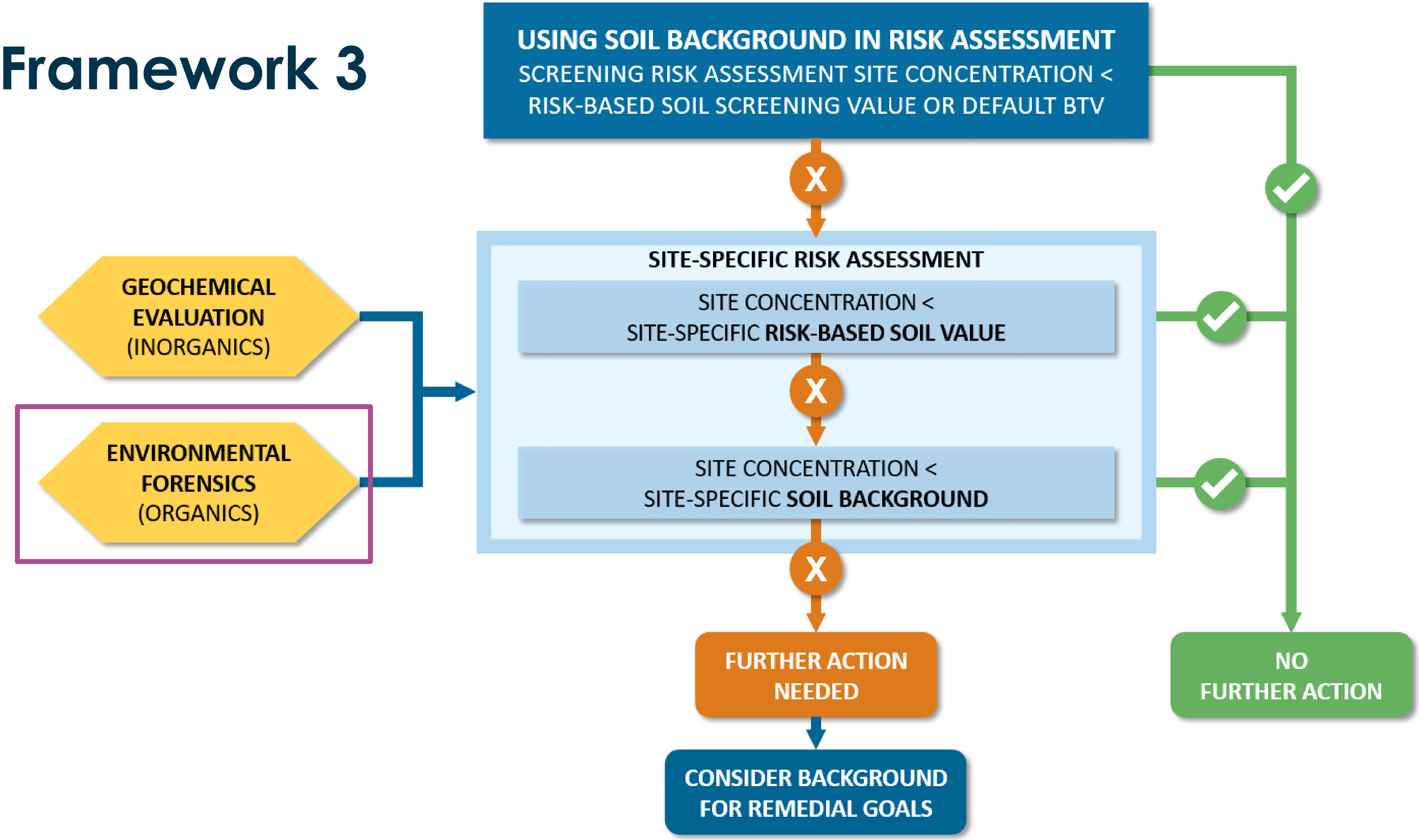
USING SOIL BACKGROUND IN RISK ASSESSMENT
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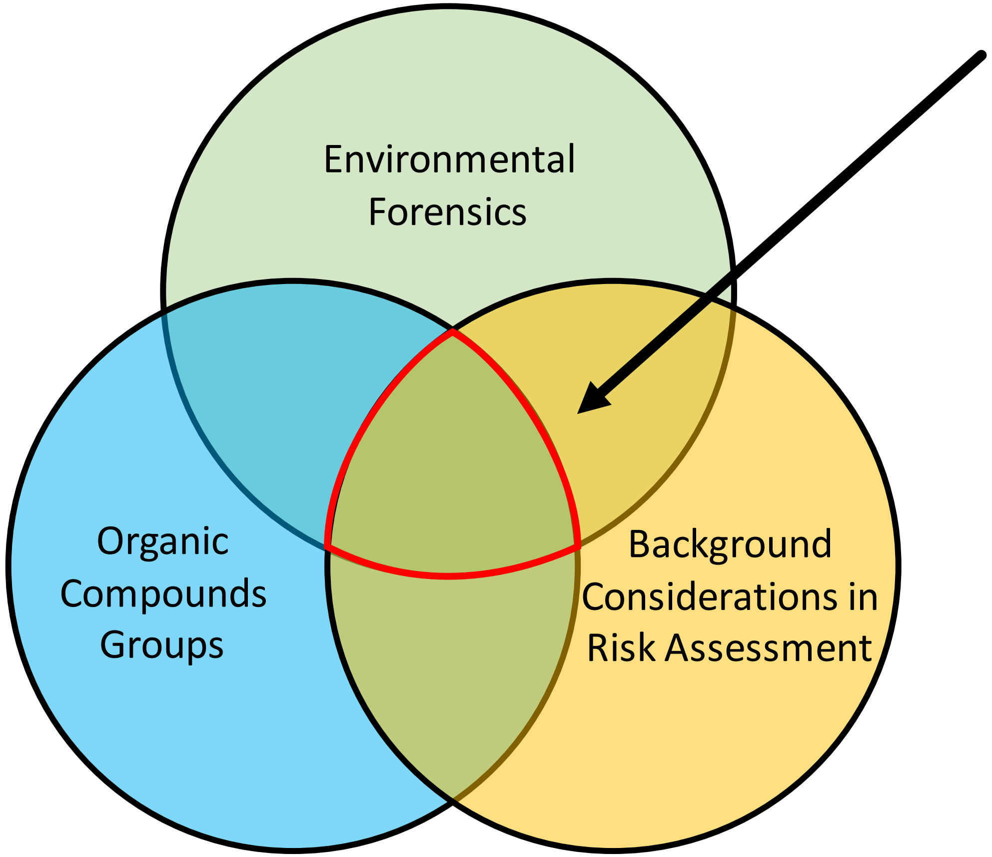
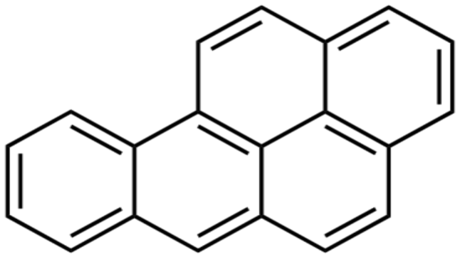
X
SITE-SPECIFIC RISK ASSESSMENT
SITE CONCENTRATION <
SITE-SPECIFIC RISK-BASED SOIL VALUE
X
SITE CONCENTRATION <
SITE-SPECIFIC SOIL BACKGROUND
X
GEOCHEMICAL EVALUATION (INORGANICS)
ENVIRONMENTAL FORENSICS (ORGANICS)
FURTHER ACTION NEEDED
CONSIDER BACKGROUND FOR REMEDIAL GOALS
NO FURTHER ACTION

Environmental Forensics Definition

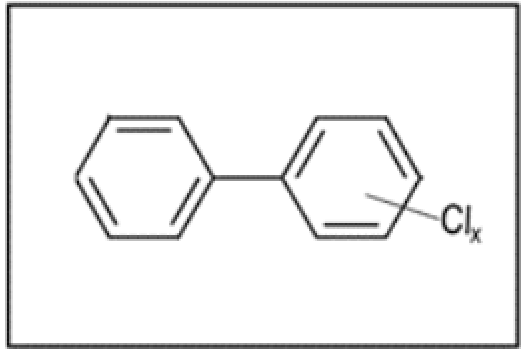
- " A well-established discipline that considers scientific and nonscientific information to interpret the potential sources and ages of certain chemical compounds detected at a site, typically at anomalous concentrations"



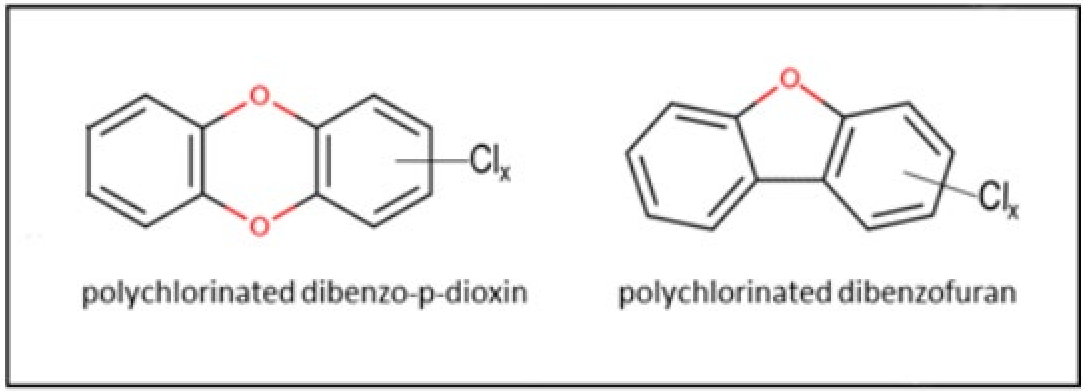
Principles of Environmental Forensics Application



PAHs



PCBs



Apply to "forms of contamination that are compositionally complex, being comprised of scores of different chemicals, some with related chemical structures and similar but not identical chemical properties."

"the complexity of these contaminants not only provides a basis to distinguish among different sources of the same contaminant but also, and of relevance herein, to distinguish contamination from background, particularly at low contaminant concentrations."

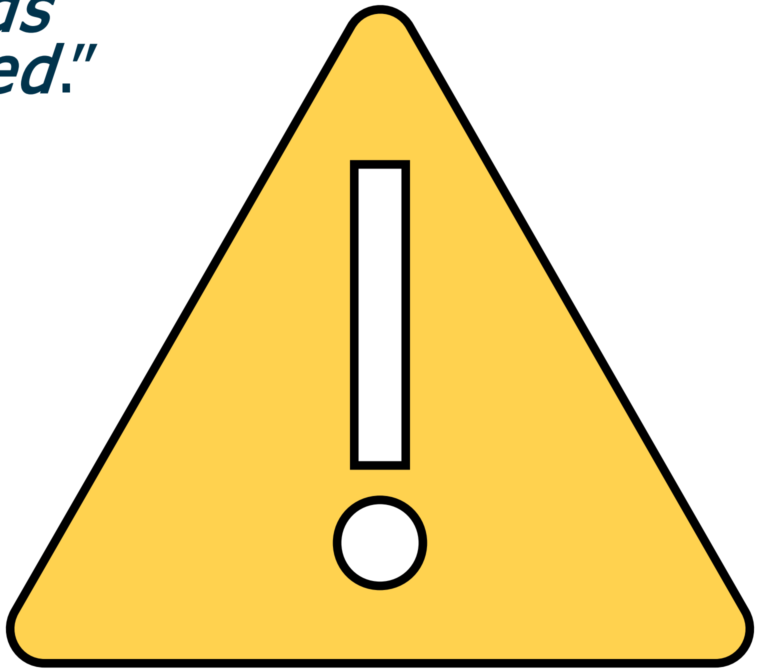
~*Section 7.1*

Dioxins (PCDDs) and Furans (PCDFs)

Don't try this at home…

"Using environmental forensics to determine whether a contaminant is representative of background requires an expert who is knowledgeable about these methods and the chemistry of the contaminant being evaluated."

~ *Section 7.1*



No single approach applies to all sites.

No two datasets are the same

No two sites are the same

What and Where? – Chapter 7

- Chapter 7 – Environmental Forensics Related to Soil Background
  - 7.1: Introduction
  - 7.2: PAHs (detailed, focus; 4-5 pp)
  - 7.3: TPH (brief; <1p)
  - 7.4: PCBs (detailed; 4-5 pp)
  - 7.5: PCDDs/PCDFs (detailed; 4-5 pp)
  - 7.6: PFAS (emerging; ~1p)
  - 7.7: Remote Sensing (brief; ~1p)

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7 Environmental Forensics Related to soil Background

7 Environmental Forensics Related to soil Background

7.1 Introduction

7.2 Polycyclic Aromatic Hydrocarbons

7.3 Total Petroleum Hydrocarbons (TPH)

7.4 Polychlorinated Biphenyls (PCBs)

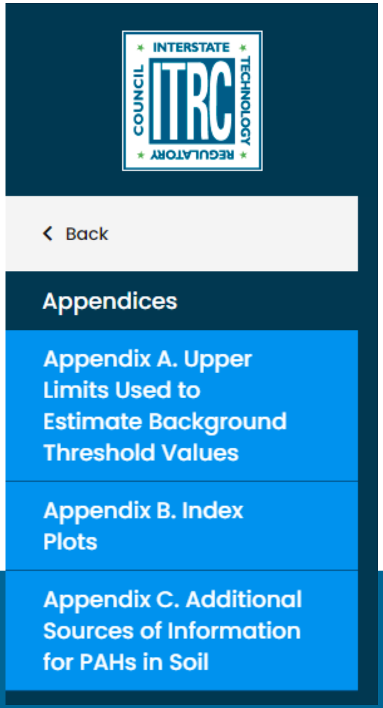
7.5 Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/F)

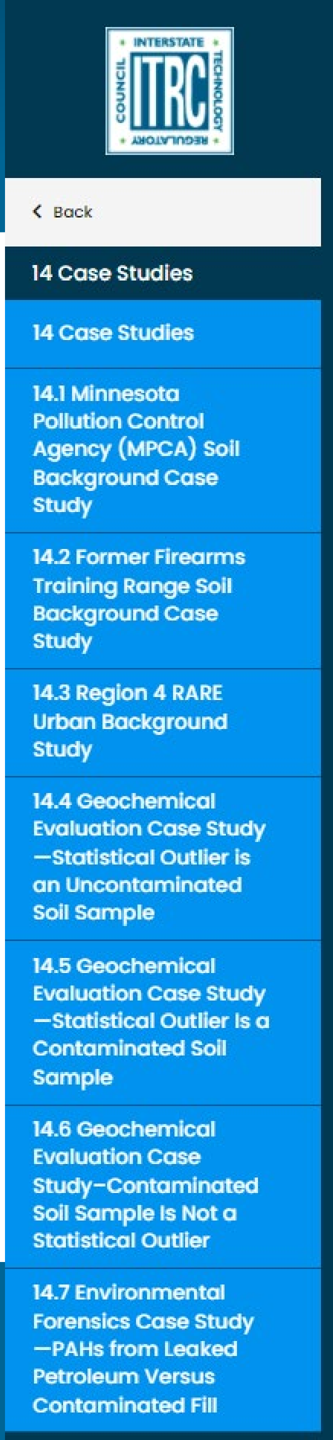
7.6 Perfluoroalkyl Substances (PFAS)

7.7 Remote Sensing

What and Where? – Chapter 14 and Appendix C

- Chapter 14- Case Studies
  - 14.7: PAHs from leaked petroleum versus contaminated fill (~1p)
- Appendix C
  - (~50 references on PAHs and PAH forensics)

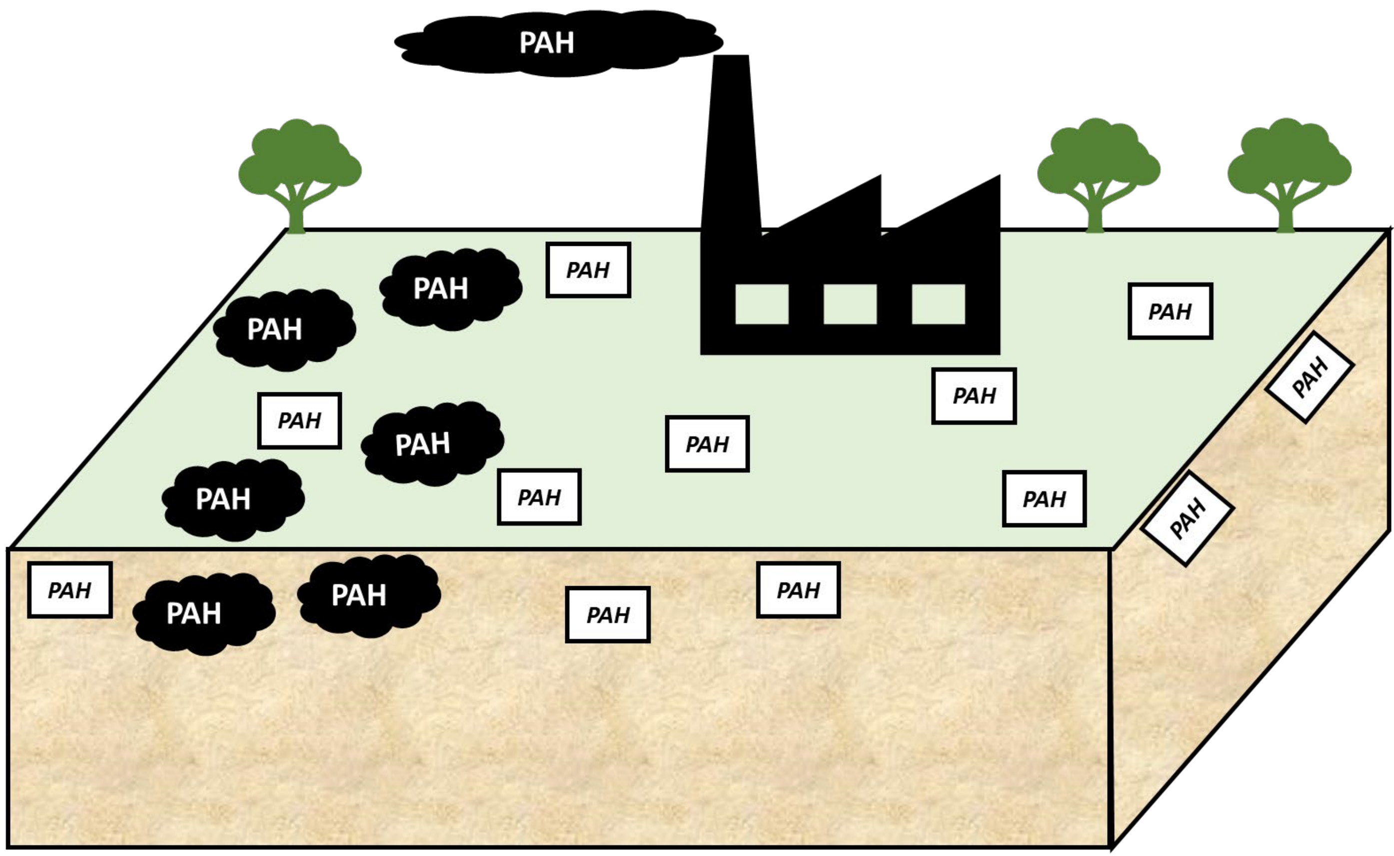




"Background Issues" that Might Require Application of Environmental Forensics

- Assessment of sites in **urban areas with historical regional impacts** (e.g., PAHs)
- Three hypothetical scenarios

1. Concentrations below risk-based screening levels
2. Concentrations generally uniform but straddle/exceed risk-based screening levels
3. Both a site release and regional/background "haze" of same COPCs at concentrations above risk assessment threshold

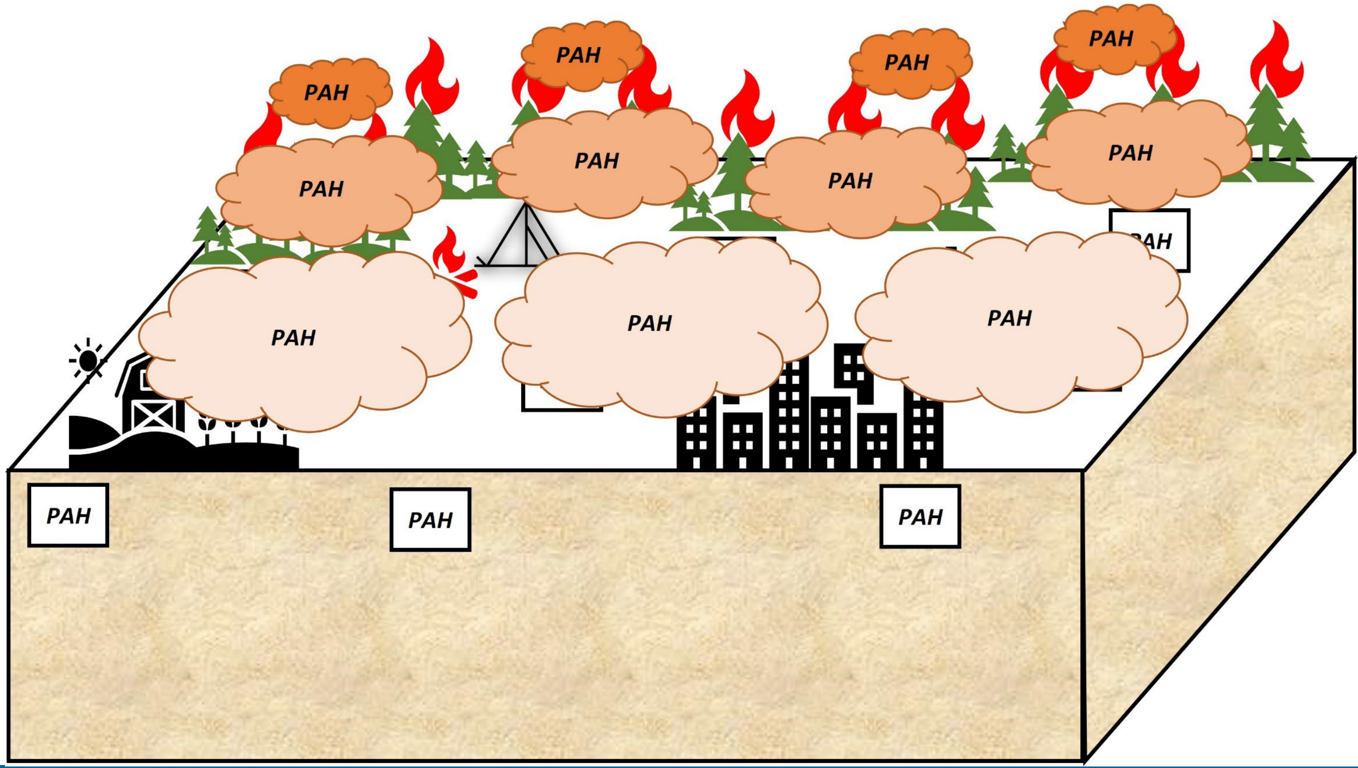


"Background Issues" that Might Require Application of Environmental Forensics

- Assessment of sites in areas **impacted by wildland fire** (e.g., PAHs)

- Three hypothetical scenarios

1. Concentrations below risk-based screening levels
2. Concentrations generally uniform but straddle/exceed risk-based screening levels
3. Both a site release and regional/background "haze" of same COPCs at concentrations above risk assessment threshold



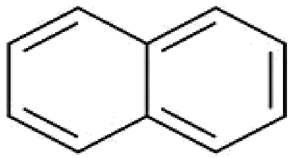
Four "Forms" for Forensic Analyses (e.g. for PAHs)

- Diagnostic Ratios
- Pattern Recognition
- Spatial/Temporal analysis of PAH patterns/ diagnostic ratios and/or concentrations
- Quantitative Source Apportionment
  - PCA, CMB, PMF

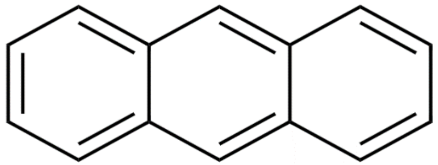
- Guidance briefly describes each of these applied to PAHs and provides references to literature (Appendix C)

Environmental Forensics- PAHs – Chemistry Overview: Low and High Molecular Weight

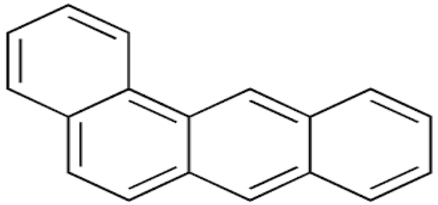
- Polycyclic Aromatic Hydrocarbons
- Contain more than 1 benzene ring structure
- 2-3 rings – low molecular weight
- 4 or more rings – high molecular weight



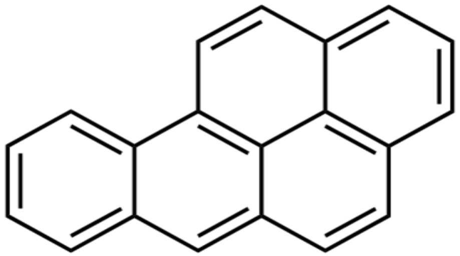
naphthalene



anthracene



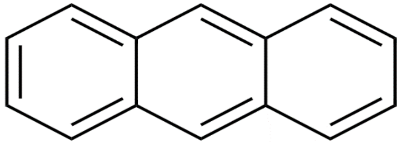
benzo(a)anthracene



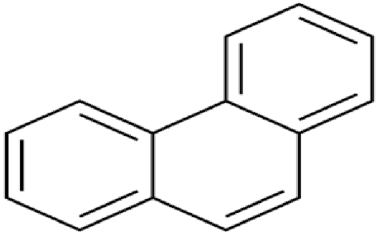
benzo(a)pyrene

Environmental Forensics- PAHs – Chemistry Overview: Isomers

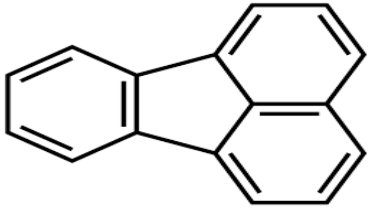
- Examples of pairs used for diagnostic ratios
- Isomers –
- Same molecular formula, slightly different structure
- Similar environmental fate
- Differences in ratios attributed to source



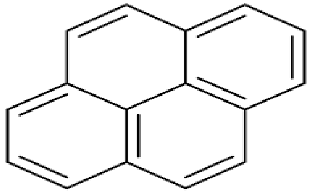
anthracene



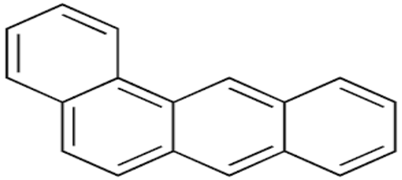
phenanthrene



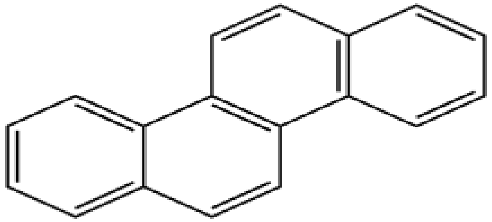
fluoranthene



pyrene

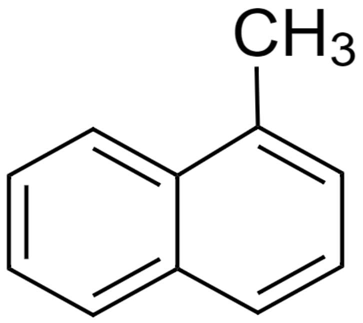


benzo(a)anthracene

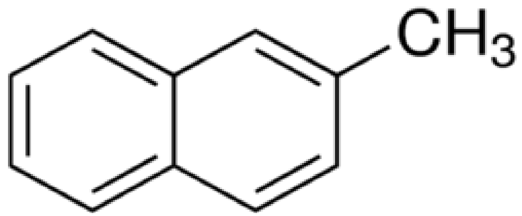


chrysene

Environmental Forensics- PAHs – Chemistry Overview: alkyl groups



1-methyl naphthalene



2-methyl naphthalene

TABLE 2. List of PAHs Recommended for Analytical Measurement to Quantify "Total PAHs" (from U.S. EPA, 2003a)

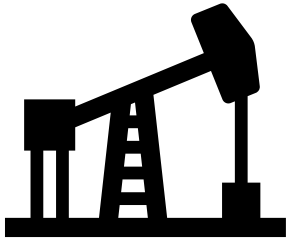
PAH	CAS*	Molecular Weight (μg/mol)
Naphthalene	91203	128.17
C1-Naphthalenes	-	142.20
Acenaphthylene	208968	152.2
Acenaphthene	83329	154.21
C2-Naphthalenes	-	156.23
Fluorene	86737	166.22
C3-Naphthalenes	-	170.25
Anthracene	120127	178.12
Phenanthrene	85018	178.23
C1-Fluorenes	-	180.25
C4-Naphthalenes	-	184.28
C1-Phenanthrene/anthracenes	-	192.26
C2-Fluorenes	-	194.27
Pyrene	129000	202.26
Fluoranthene	206440	202.26
C2-Phenanthrene/anthracenes	-	206.29
C3-Fluorenes	-	208.30
C1-Pyrene/fluoranthenes	-	216.29
C3-Phenanthrene/anthracenes	-	220.32
Benz(a)anthracene	56553	228.29
Chrysene	218019	228.29
C4-Phenanthrenes/anthracenes	-	234.23
C1-Benzanthracene/chrysenes	-	242.32
Benzo(a)pyrene	50328	252.31
Perylene	198550	252.31
Benzo(e)pyrene	192972	252.32
Benzo(b)fluoranthene	205992	252.32
Benzo(k)fluoranthene	207089	252.32
C2-Benzanthracene/chrysenes	-	256.23
Benzo(ghi)perylene	191242	276.23
C3-Benzanthracene/chrysenes	-	270.36
Indeno(1,2,3-cd)pyrene	193395	276.23
Dibenz(a,h)anthracene	53703	278.35
C4-Benzanthracene/chrysenes	-	284.38

* For C# PAHs CAS is not available.

Environmental Forensics- PAHs – Sources

Pyrogenic (high temperature combustion)
Can dominate particulates/ ash, soot in urban areas
anthropogenic background

Petrogenic (oil/geologic)



Biogenic (low temperature)
Decomposition of plant debris)

Environmental Forensics: PAHs- Diagnostic Ratios

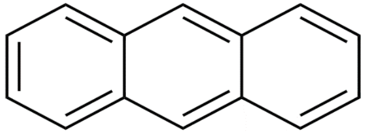
Table 7-1. Diagnostic ratios used to assess PAH sources

Source: Scott A. Stout, NewFields Environmental Forensics Practice, LLC.

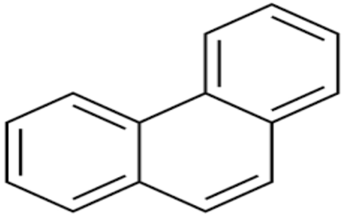
Ratio	Value/Range	Reported Source
AN/(P0+AN)	<0.1	Petrogenic
	>0.1	Pyrogenic
FL/(PY+FL)	<0.4	Petrogenic
	0.4-0.5	Petroleum combustion
	>0.5	Coal & biomass combustion
BaA/(C0+BaA)	<0.2	Petrogenic
	0.2-0.35	Coal combustion
	>0.35	Petroleum combustion
IND/(GHI+IND)	<0.2	Petrogenic
	0.2-0.5	Petroleum combustion
	>0.5	Coal & biomass combustion

See text for cautions regarding use of diagnostic ratios. PAH abbreviations: AN-anthracene; P0-phenanthrene; FL-fluoranthrene; PY-pyrene; BaA-benz[*a*]anthracene; C0-chrysene; IND-indeno[*1,2,3-cd*]pyrene; GHI-benzo[*g,h,i*]perylene.

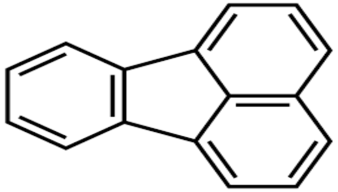
Relatively more abundant in petrogenic source



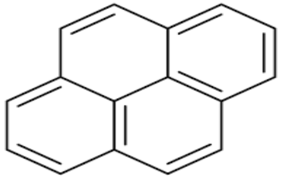
anthracene



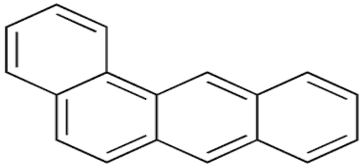
phenanthrene



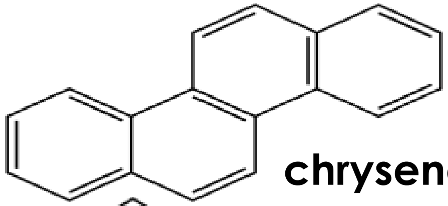
fluoranthene



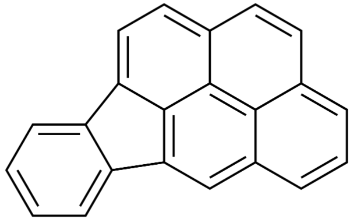
pyrene



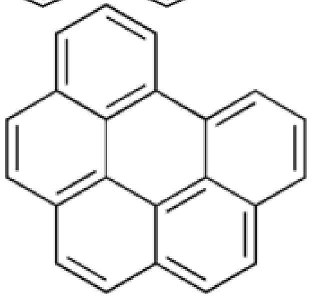
benzo(a)anthracene



chrysene



indeno(123-cd) pyrene



benzo(ghi) perylene

Environmental Forensics: PAHs- Diagnostic Ratios

Table 7-1. Diagnostic ratios used to assess PAH sources

Source: Scott A. Stout, NewFields Environmental Forensics Practice, LLC.

Ratio	Value/Range	Reported Source
AN/(P0+AN)	<0.1	Petrogenic
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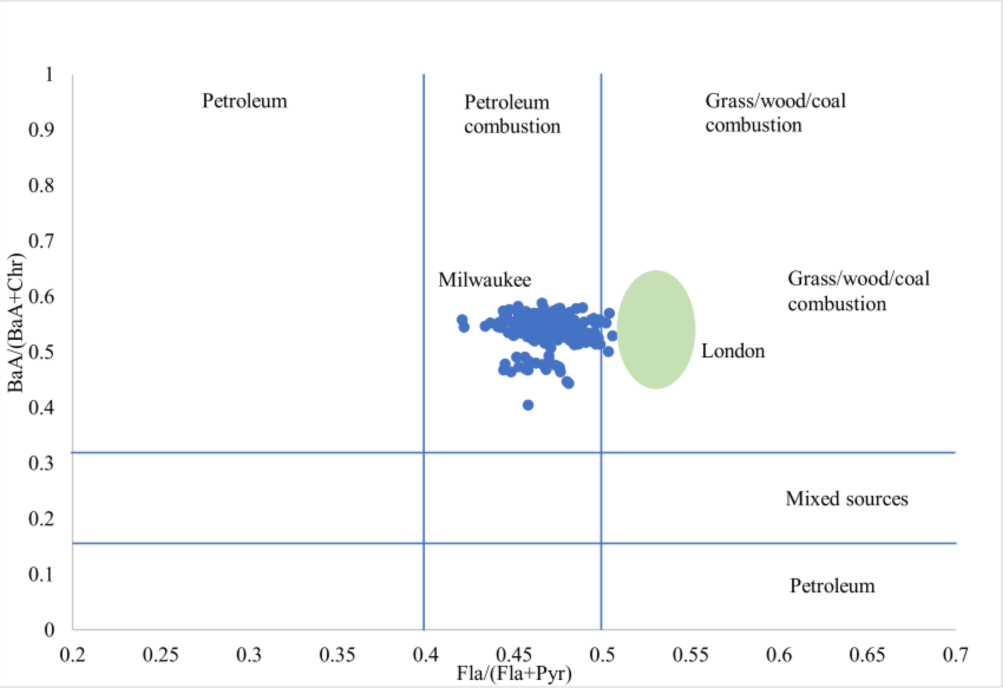
	0.4-0.5	Petroleum combustion
	>0.5	Coal & biomass combustion
BaA/(C0+BaA)	<0.2	Petrogenic
	0.2-0.35	Coal combustion
	>0.35	Petroleum combustion
IND/(GHI+IND)	<0.2	Petrogenic
	0.2-0.5	Petroleum combustion
	>0.5	Coal & biomass combustion

See text for cautions regarding use of diagnostic ratios. PAH abbreviations: AN-anthracene; P0-phenanthrene; FL-fluoranthrene; PY-pyrene; BaA-benz[*a*]anthracene; C0-chrysene; IND-indeno[*1,2,3-cd*]pyrene; GHI-benzo[*g,h,i*]perylene.



Note: London data from Vane et al. (2014) for comparison only.

Fig. 3. Isomeric ratio plot of BaA/(BaA + Chr) and Fla/(Fla + Pyr).

(Siemering & Thiboldeaux, 2021)
(discussed in Section 3.3)

Environmental Forensics: PAHs -Pattern Recognition

- To Look for:
  - Relative abundance of 4-6 ring PAHs vs 2-3 rings
  - Pattern of alkyl homolog groups (skewed vs. hump)

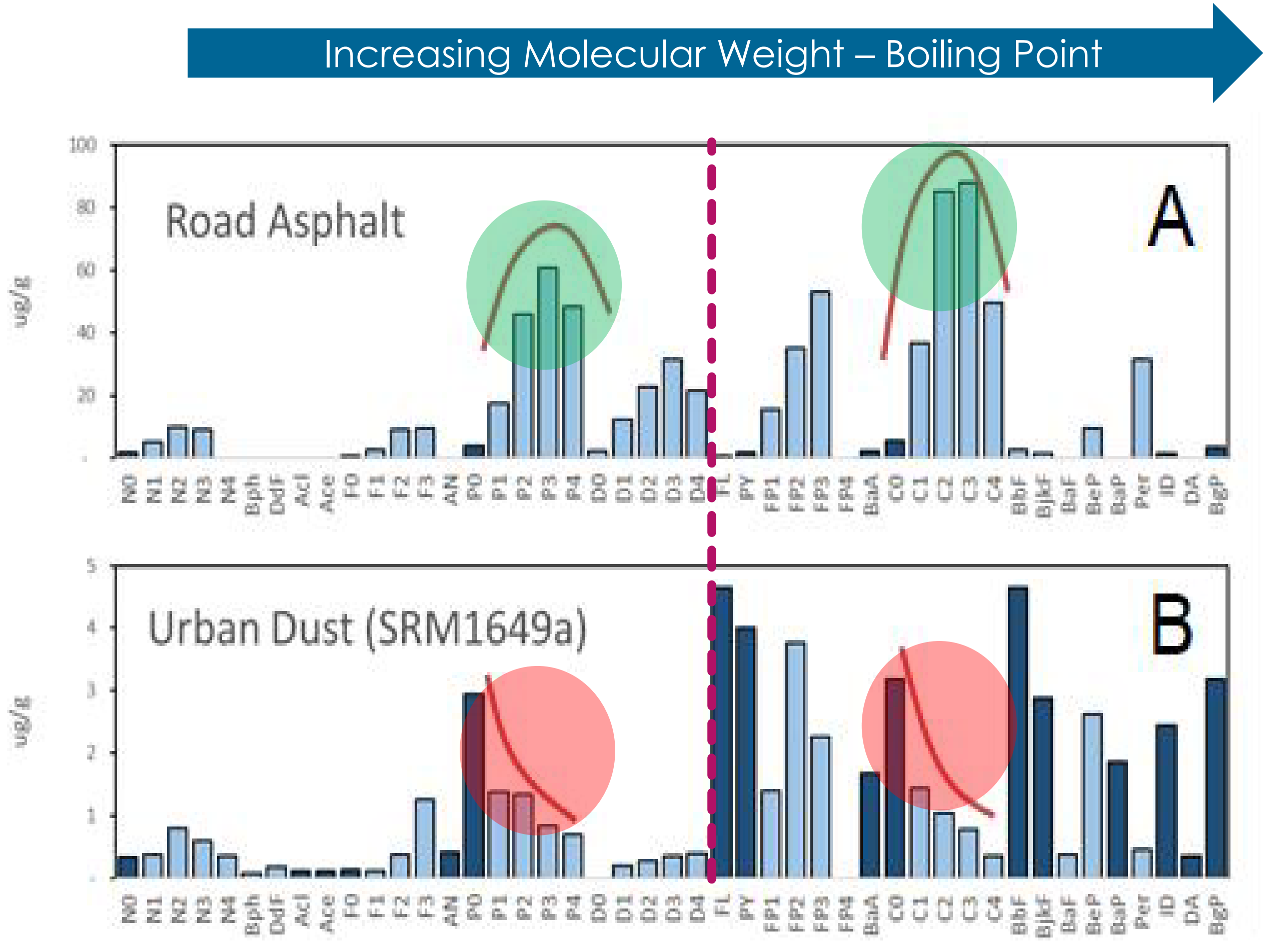
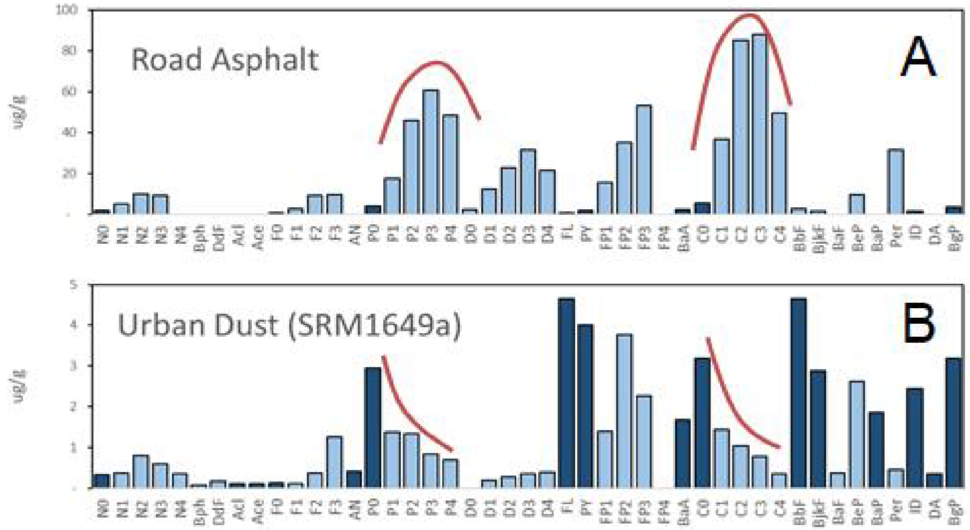


Figure 7-1. PAH histograms for materials that can contribute to anthropogenic ambient soil background.

Environmental Forensics: PAH Pattern Recognition Example

"Skewed" versus *"Bell-shaped"* PAH homolog profiles can be easily recognized through qualitative inspection if alkylated PAH data are available (Section 7.2.1.1)

Asphalt dominated by alkyl homologs
Dust (soot) dominated by 4-6 ring parent PAHs



(A) road asphalt and (B) urban dust (NIST SRM1649a). Dark blue bars represent USEPA priority pollutant PAHs; light blue bars represent alkylated PAHs often used in forensic assessments; red lines depict (A) bell-shaped and (B) skewed homolog profiles (see (Stout et al. 2015)[369] for additional details).

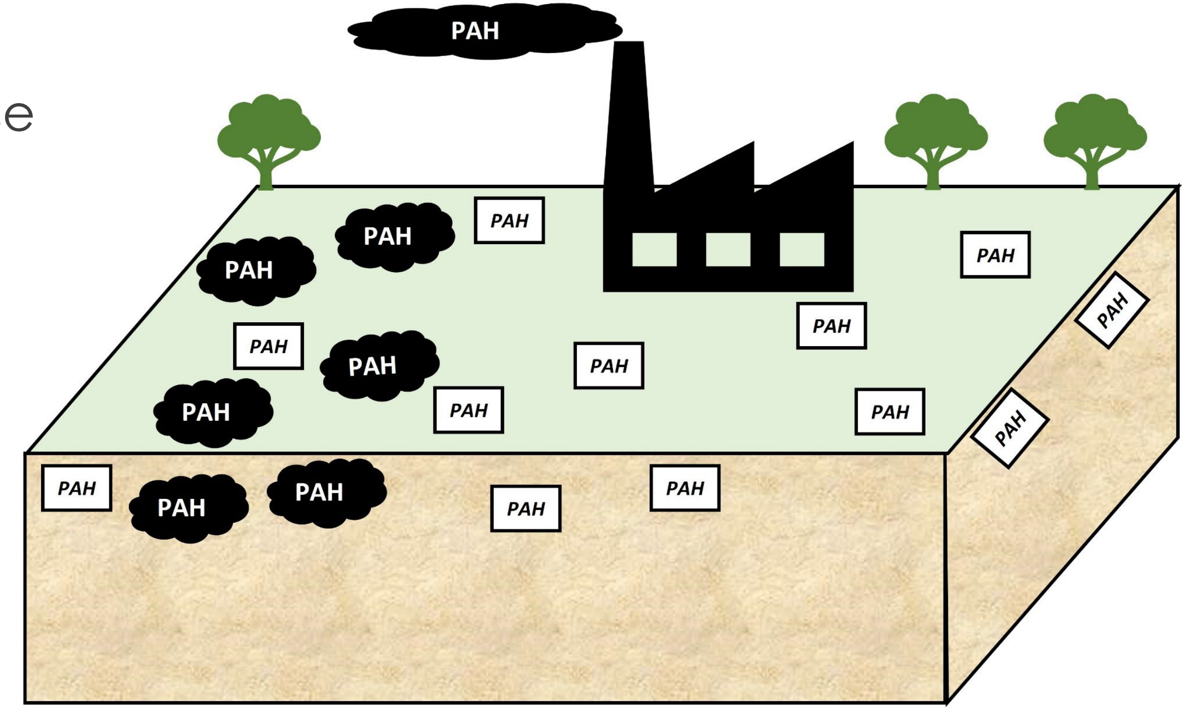
Source: Stout, Uhler, and Emsbo-Mattingly 2004

Figure 7-1. PAH histograms for materials that can contribute to anthropogenic ambient soil background.

"Combustion-derived particles in soils that are attributable to anthropogenic ambient soil background are dominated by 4- to 6-ring PAHs, which can be readily distinguishable from an impact of petroleum, such as diesel fuel"
(Section 7.2.1.1)

Environmental Forensics: PAHs - Spatial/Temporal Analysis

- Comparison of lateral vertical extent
- Identify hot spots/sources compared to diffuse background haze
- Consider historical uses of site/ adjacent sites
- Case Study (Section 14.7)



Environmental Forensics: PAHs - Quantitative Source Apportionment/ Principal Component Analysis (PCA)

PCA is the most common quantitative technique

See references for
CMB: (Chemical Mass Balance)
PMF: (Positive Matrix Factorization)

- "PCA is a mathematical method that transforms a large number of possibly correlated variables into a smaller number of uncorrelated variables called 'principal components.' The principal components are ranked by the amount of variance in the data that they explain. Factor score plots (next slide) are visual projections of the PCA. Factor scores that plot close to one another share similar chemical compositions. Factor scores that plot far apart have different chemical compositions"
  - *Chapter 7.4.3*

Environmental Forensics: PAHs - Quantitative
Source Apportionment/ Principal Component Analysis

Graph of factor scores for ~350 sediment samples (left)

PAH patterns shown on right (parent PAHs only)
- LMW PAHs in gray
- HMW PAHs in black

A = moderately weathered creosote
B = more heavily weathered creosote
C= combustion-sourced urban background

PCA plot shows most samples as mixtures of weathered creosote (B) and urban anthropogenic background (C)

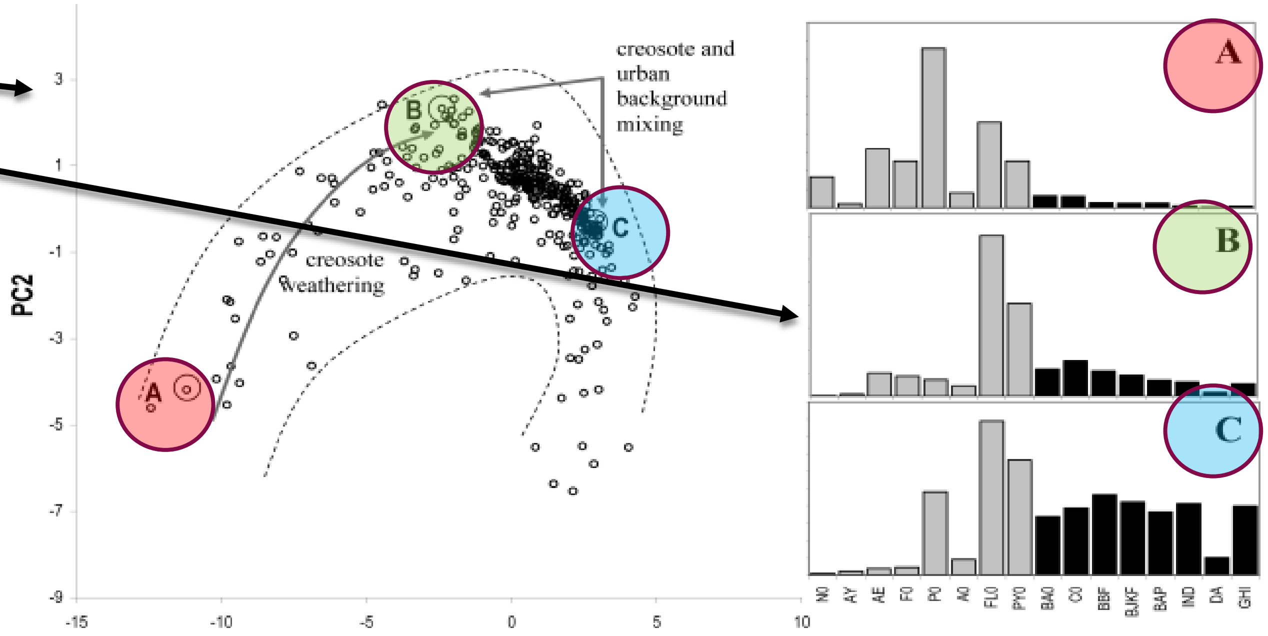


Figure 7-2. Principal component factor score plot.

Source: Reprinted with permission from (Stout and Graan 2010)[364]. Copyright 2010, American Chemical Society.

Poll Question

Compared to a *petrogenic* signature, a *pyrogenic* PAH signature is typically characterized by which of the following?

a) Relatively higher concentrations of high molecular weight PAHs (4+ rings)

b) Relatively lower concentrations of more alkylated (C2,C3, C4) homolog groups

c) Higher anthracene/(anthracene+ phenanthrene) ratios

d) All of the above

https://www.publicdomainpictures.net/en/view-image.php?image=212244&picture=dry-agricultural-brown-soil

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