White Paper:
Important Considerations in the Derivation of Representative Background Concentrations for the Evaluation of Sediment Sites

Sediment Management Work Group (SMWG)

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Executive Summary

While there are some existing federal guidance documents that focus on deriving and applying background concentrations for contaminated upland sites, there is an absence of federal guidance related to deriving and applying background concentrations for contaminated sediment sites. This has resulted in significant variability, uncertainty, and disagreement regarding how representative background concentrations of chemicals of concern should be derived for sediment sites. This document discusses important considerations in the derivation of representative background concentrations of chemicals of concern to be used in the evaluation of sediment sites. Representative background concentrations are critical for putting risk into context, developing a cost-effective and technically feasible remedial approach, understanding the potential for recontamination, and ensuring long-term remedy success.

In order to identify common ground regarding appropriate technical approaches for deriving and applying background concentrations for contaminated sediment sites, a workshop was convened in November 2016. This workshop was hosted by the Sediment Management Work Group (SMWG), and included experts representing the U.S. Environmental Protection Agency (USEPA), other federal agencies, state government regulators, industry, private consulting firms, and academia. The goal of this workshop was to develop key considerations for deriving and applying representative background concentrations at contaminated sediment sites.

This document provides a compilation of technical considerations and methodologies that focuses on four key considerations in the process to derive representative background concentrations, as discussed at the workshop, as follows:

- A thorough understanding of a site is critical to the selection of the background reference areas from which representative background concentrations can be derived. A conceptual site model aids in understanding a site, and highlights important physical, chemical, and biological characteristics that should also be present at the background reference areas. This is discussed in more detail in **Section 2.0**.
- A primary objective of determining representative background concentrations should be to take into account existing levels of substances not contributed by the site, and to adequately account for chemical input that is expected to continue migrating onto the site during and after the completion of the remedy. Potential contributions to background chemical concentrations include non-site-related anthropogenic sources and contributions from watershed-based land use. These types of contributions are discussed in detail in **Sections 2.1 to 2.6**, as are sediment physical properties, hydrodynamic and sediment profile conditions, and geochemistry.
- Data collected to establish representative background concentrations and to compare these to site concentrations should be evaluated using a recognized statistical approach, by a statistician experienced in comparing site and background populations. The two most common statistical approaches used are point-by-point comparisons and background-site population comparisons. Outlier data points should not be removed as part of this statistical evaluation simply because they represent

the highest or lowest concentrations, unless there is a sound technical and statistical basis to do so, because doing so compromises the statistical approach underlying the analysis. Outlier data are often just a manifestation of random variability inherent to the environment. This is discussed in more detail in **Sections 3.0 to 3.5**.

- Geochemical evaluation of trace metals is an additional tool for deriving appropriate background concentrations for contaminated sediment sites. This technique is particularly useful and effective when it is not possible to identify background reference areas. It is typically used in conjunction with standard statistical evaluation. This is discussed in more detail in **Section 3.6**.

This document provides information to support the derivation of technically defensible representative background concentrations, including sites where background concentrations are greater than risk-based cleanup levels. The recommendations contained in this document are offered to help inform, improve, and increase the consistency of sediment site remedy decision-making. Such an approach is supported by existing federal guidance and by scientific and statistical principles underlying site remediation, as discussed in more detail in **Section 1.0** and **Section 4.0**.

Acknowledgement:

The authors would like to thank each of the participants in the Background Workshop conducted on November 15 and 16, 2016, for the contributions of time and ideas that they and their respective organizations made to this effort. Their willingness to share and openly discuss ideas and broadly ranging perspectives were critical to the development of this document. The contents of this document represent the consensus of most of the participants and should not be construed as representing the individual views of all attendees.

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List of Acronyms and Abbreviations

Acronym/ Abbreviation	Definition
APHA	American Public Health Association
BTV	Background threshold value
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CSM	Conceptual site model
CSO	Combined sewer overflow
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
POC	Point of compliance
TOC	Total organic carbon
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

1.0 Introduction

The U.S. Environmental Protection Agency (USEPA) has recognized for more than 25 years that establishing a reliable representation of background is a critical issue at Superfund sites across the country (USEPA 1989a). This document has been prepared to detail the results of a workshop that was held to outline key considerations in the development of representative background concentrations (refer to Section 1.1) at sediment sites. Clear direction is needed because technically defensible, representative background concentrations are critical for putting risk into context; developing an appropriate, cost-effective, and technically feasible remedial approach; understanding the potential for recontamination; and ensuring long-term remedy success.

Once established, representative background concentrations may be applied as cleanup goals at sediment sites where these derived background concentrations are greater than risk-based cleanup levels. USEPA guidance appropriately notes: “The reasons for this approach include cost-effectiveness, technical practicability, and the potential for recontamination of remediated areas by surrounding areas with elevated background concentrations” (USEPA 2002). USEPA’s approach, highlights the importance of deriving representative background concentrations that represent actual background. In some cases, derived representative background concentrations become *de facto* cleanup goals, thereby influencing the scope and scale of the remedy.

1.1 DEFINITIONS

The following USEPA-provided definitions are used in this document:

- **Background.** Substances or locations that are not influenced by the releases from a site and are usually described as naturally occurring or anthropogenic (USEPA 1989a, USEPA 2002).
    - **Natural background.** Naturally occurring substances present in the environment in forms that have not been influenced by human activity (USEPA 2002).
    - **Anthropogenic background.** Natural and human-made substances present in the environment as a result of human activities, not specifically related to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) release in question (USEPA 2002).
- **Background reference areas.** The areas where background samples for chemical concentrations are collected for comparison with samples collected on-site. The reference areas should have similar physical, chemical, geological, and biological characteristics as the site being investigated, but should not have been affected by activities on the site (USEPA 2002). Although in many cases the background reference areas are situated off-site, non-impacted on-site areas may also be suitable as background reference areas (USEPA 2002). Consistent with USEPA guidance, the background reference areas should include anthropogenic inputs unrelated to the site that are reflective of the larger region.

- **Reference area.** A reference area for ecological risk assessments is intended to "mirror the physical, climatic, chemical, and biological aspects of the Superfund Site" (USEPA 1994a). For clarity, this document discusses background reference areas exclusively. [1]
- **Conceptual site model.** A representation of the environmental system and the physical, chemical, and biological processes that determine the transport of contaminants from sources to receptors. Essential elements of a CSM generally include information about contaminant sources, transport pathways, exposure pathways, and receptors. A good CSM can be a valuable tool in evaluating the potential effectiveness of remedial alternatives (USEPA 2005).
- **Outliers.** Measurements that are extremely large or small relative to the rest of the data and, therefore, are suspected of misrepresenting the population from which they were collected.
    - **False outliers.** Measurements that are very large or small relative to the rest of the data, but represent true extreme values of a distribution and indicate more variability in the population than was expected (USEPA 2006).
    - **True outliers.** Measurements that are very large or small relative to the rest of the data, but are a result of transcription errors, data-coding errors, or measurement system problems (USEPA 2006).

Additionally, the term representative background concentration(s) is used frequently throughout this document. **Representative background concentration**, for the purposes of this document, is defined as a chemical concentration that is inclusive of naturally occurring sources and anthropogenic sources not related to a CERCLA release. It is derived from sampling within representative background reference areas that may be located on-site and/or off-site, but are not affected by a site release or site activities. For man-made chemicals, the anthropogenic background concentration and the representative background concentrations are equivalent. For naturally occurring chemicals (e.g., metals), representative background concentrations are equivalent to the sum of the anthropogenic and natural background concentrations.

1.2 OBJECTIVES FOR DETERMINING REPRESENTATIVE BACKGROUND CONCENTRATIONS AND REMEDIATION DECISION-MAKING

At many sediment sites, multiple sources may contribute to the nature and extent of contamination. The largest contribution of contamination at Superfund sites is typically attributed to site releases. However, some contaminants can also result from natural and off-site sources.

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[1] In background reference areas, sediment samples are taken for determination of chemical concentrations only. Of note, when ecological samples are taken from reference areas, sediment samples for measurements of chemical concentrations are usually taken at the same time. When chemical concentration data are available from reference areas and background reference areas, these data are usually pooled into a background dataset to calculate representative background concentrations.

The off-site contamination not associated with site releases is considered a component of representative background concentrations and will continue to be a source of contamination to the site, unless all transport pathways are controlled. A primary objective of determining representative background concentrations is to account for any background chemical input (both natural and anthropogenic) that is expected to continue migrating onto the site. It is recognized that one of the guiding principles for management of contaminated sediment sites is that sources should be controlled to the greatest extent feasible prior to initiating remediation at the subject site. According to USEPA, "Generally, significant continuing upland sources...should be controlled to the greatest extent possible before sediment cleanup" (USEPA 2005). However, it is rarely feasible to control all background sources.

When representative background concentrations accurately reflect ongoing chemical inputs to a site from all sources, this results in defensible representative background concentrations for use in the remedial investigation and remedy selection processes. In addition to informing or establishing cleanup levels, representative background concentrations can assist in:

- Determining a site boundary
- Determining chemicals of concern
- Establishing a realistic long-term monitoring plan, or optimizing existing long-term monitoring plans
- Assessing remedy success

In the absence of representative background concentrations for remediation decision-making, risk-based cleanup levels may be used inappropriately at sites where representative background concentrations are actually greater than risk-based concentrations. Alternatively, if the representative background concentration has been erroneously calculated (e.g., by the inappropriate exclusion of some outlier data points [false outliers]; refer to Section 1.1), inappropriately low cleanup goals could be used in the remedy selection process. Inevitably, in both cases, these sites will eventually return to background conditions after remediation has been completed, so the remedy would be considered a failure if it did not meet cleanup goals over the short- or long-term. This has been demonstrated on a number of sediment sites throughout the United States, under both federal and state lead (Nadeau *et al*. 2015). Moreover, attempting to cleanup to concentrations less than actual background is not sustainable over the long-term, can lead to unnecessary additional ecological disruption of sites, and can require considerable site remediation expenditures that serve no environmental or public health purpose. The considerations discussed in this document are intended to help promote a scientifically sound approach for establishing representative background concentrations, leading to decision-making that avoids costly perceived remedy failures due to recontamination.

1.3 CURRENT REGULATIONS AND GUIDANCE

At the federal level, background is discussed in a number of USEPA documents, but technical guidance describing protocols to derive representative background concentrations at sediment sites (as opposed to soil and groundwater at upland sites) has not been issued. This document has been formulated in the absence of existing USEPA-issued guidance on the derivation of representative background concentrations for contaminated sediment sites.

There are a number of relevant documents with information on the derivation of background concentrations for upland sites, including risk assessment and soil screening guidance (USEPA 1989a, USEPA 1989b, USEPA 1991, USEPA 1994a, USEPA 1994b, USEPA 1996, USEPA 1997, USEPA 2001, USEPA 2003, USEPA 2009), determination of background concentrations of inorganics in soils and sediments at a hazardous waste site (Breckenridge and Crockett 1995), and guidance concerning the characterization of background chemicals in soil at Superfund sites (USEPA 2001).

Further, USEPA issued a guidance document in 2002 entitled, "Role of Background in the CERCLA Cleanup Program"; this document seeks to clarify the "preferred approach for the consideration of background constituent concentrations of hazardous pollutants, and contaminants in certain steps of the remedy selection process, such as risk assessment and risk management" (USEPA 2002). That document is intended to serve as national policy and is the most current federal guidance on deriving and applying background at upland sites; it also finalizes the discussion of sampling and statistical analysis of representative background concentrations at soil sites. The 2002 USEPA guidance does not address sediment sites[2], but considerations for sediment site characterization, as well as developing appropriate cleanup goals, are discussed in USEPA guidance from 2005 concerning remediation of contaminated sediment sites (USEPA 2005). However, the 2005 guidance does not provide a detailed discussion describing the derivation of representative background concentrations.

In addition to the federal guidance, some states have also issued guidance related to the derivation of representative background and/or the use of background; this document focuses on representative background as it applies to federally regulated sites. State guidance is typically similar to federal guidance, but may use different terminology, or may vary in other ways, such as specific statistical procedures recommended for the screening of background data, characterization of background distributions, and calculation of background threshold values (BTV).

Finally, in order to determine representative background concentrations, it is typically necessary to identify background reference areas. A separate, but related, concept that is not addressed here is the use of reference areas in the evaluation of potential ecological risk. This involves identifying one or more suitable reference areas to facilitate sampling for the comparison of toxicological responses and, frequently, resident biological communities (e.g., benthic macroinvertebrates). Note that there are additional documents relevant to the ecological risk evaluation process (for example, USEPA 1997 and 1999a), and again, the terminology may be slightly different.

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[2] The document indicates that "guidance may be updated in the future to address non-soil media. Non-soil media are dynamic and influenced by upstream or upgradient sources. Such media—air, groundwater, surface water, and sediments—typically require additional analyses of release and transport, involve more complex spatial and temporal sampling strategies, and require different ways of combining and analyzing data."

2.0 Elements of a Conceptual Site Model

Representative background concentrations are typically derived from data collected from background reference areas. Selection of appropriate background reference areas depends on a thorough understanding of the site. As provided in the definition in Section 1.1, background reference areas should have key similarities to the site, reflecting similar physical, chemical, geological, and biological conditions; and importantly, should not be influenced by site releases. In addition, background reference areas should have similar land use to the subject site (e.g., if the subject site is in an industrial area, the background reference areas should not be located in watersheds characterized by residential or rural land uses). Ultimately, background reference areas selected for derivation of representative background concentrations should be as similar to the site as possible, while recognizing there will always be differences between the two.

A CSM is typically developed with the objective of obtaining and presenting a detailed understanding of a site. A CSM is "a representation of the environmental system and the physical, chemical, and biological processes that determine the transport of contaminants from sources to receptors" (USEPA 2005). The CSM should provide a robust understanding of the physical characteristics of the site, as well as the sources of contamination, potentially contaminated media, chemical transport pathways, and exposure pathways applicable for ecological and human receptors.[3] While the CSM is an important tool for selecting background reference areas, it also provides additional clarity and steering for proponents, consultants, and the community, and can highlight options for risk reduction.

Figure 1 presents a simplified CSM for a sediment site, focusing on the anthropogenic inputs and natural characteristics outlined in this section. Importantly, Figure 1 does not depict complex interactions, such as the cycling of chemicals of concern within the environmental system, which can be important at some sites. Additionally, Figure 1 and Section 2.0 are not inclusive of all possible chemical fate/transport and exposure pathways that may be relevant to the derivation of representative background concentrations at different sites (e.g., groundwater-surface water interactions, spills).

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[3] The typical elements of a CSM for sediment are provided in more detail in USEPA's "Contaminated Sediment Remediation Guidance for Hazardous Waste Sites," (USEPA 2005), which also includes a discussion of CSMs and their value or applicability at sediment sites.

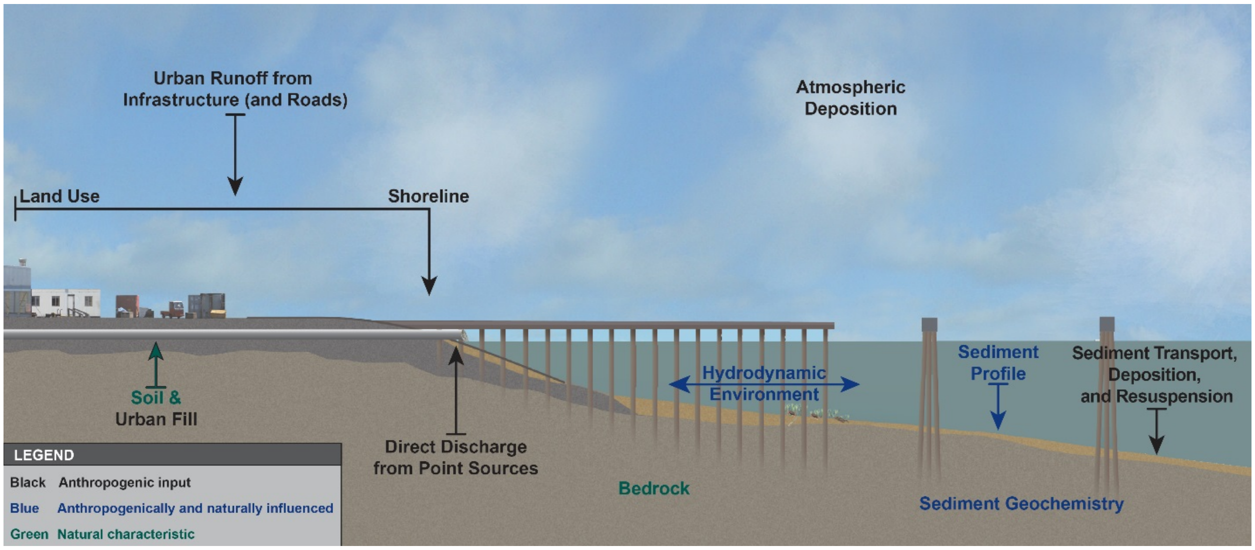

Figure 1. Key Considerations in Conceptual Site Model Development

Ultimately, background reference areas selected for derivation of representative background concentrations should be as similar to the site as possible, except for site-related releases. Therefore, developing a robust CSM will help to ensure that the selected background reference areas are similar to the site and will inherently provide an increased understanding of the factors that may contribute to representative background concentrations at the site. Factors that typically contribute to representative background concentrations (and chemical concentrations on a site, as would likely be shown through the CSM) are detailed in this section, and these factors should be considered when developing the study design for representative background determination.

Sections 2.1 through 2.6 discuss some of the key complexities that are encountered during the CSM development process at sediment sites, and the discussion has been developed for use by a broad audience. Some of the more specific technical considerations, such as evaluation of total organic content and grain size and their specific relationship to organic compounds and data treatment, are not discussed specifically within the following sections. However, the overarching principle is that a robust CSM assists in selection of representative background areas, and these background areas need to reflect the site as closely as possible, with the exception of site-related inputs.

2.1 LAND USE WITHIN A WATERSHED

Several studies, detailed in these subsections, have demonstrated that the degree of urbanization, intensity of land use, and land cover patterns adjacent to a site (or background reference areas) are correlated with chemical concentrations. Generally, a practitioner should recognize that contaminant concentrations tend to increase as the degree of urbanization increases (Moran *et al.* 2012). The degree of urbanization positively correlates to the level of chemical input that can be expected to migrate onto the site before, during, and after the completion of the remedy; so this should be considered in selecting background reference areas and determining representative background concentrations.

2.1.1 Degree of Urbanization

Contamination associated with urbanization moves through the environment via a variety of transport pathways, including surface water transport, urban runoff, bank erosion, and sediment resuspension, among others.

The USGS has evaluated chemical concentrations in watersheds across different degrees of urbanization, in order to better understand the correlation between urban land use and chemical concentrations. These studies have shown that environmental media in more urbanized areas contain elevated concentrations of chemicals compared to less urban areas (Nowell *et al*. 2013, Kemble *et al*. 2013). These studies concluded that concentrations of a wide range of contaminants, including polycyclic aromatic hydrocarbons (PAHs), PCBs, organochlorine pesticides, and metals, were "significantly related to urbanization across the study areas" (Nowell *et al*. 2013).

Consequently, historical and current land use within a watershed has a direct and potentially major influence on anthropogenic background conditions (chemical concentrations). The type and intensity of land use surrounding selected background reference areas should be as similar as possible to that observed at the site, to account for chemical input that is associated with urbanization. This practice will ensure that anthropogenic background concentrations reflect the level of contamination that is generally associated with land use in the vicinity of the site, absent contributions from the site itself. This practice will help facilitate the derivation of representative background concentrations for determining achievable cleanup goals.

2.1.2 Shoreline Conditions

Shoreline condition should be evaluated as part of CSM development (USEPA 2005) when screening and selecting background reference areas. Waterfront development, particularly for industrial purposes, typically includes hardened shorelines such as sheetpile walls, bulkheads, or riprap slopes. Hardened shorelines protect against erosion, but may be susceptible to sediment contaminant migration through sheetpile seams and holes in older steel, due to corrosion or accidental puncture. Unprotected shorelines are more susceptible to erosion from upland runoff, tidal action, and storm surge, releasing soils that may be impacted by site-related activities to the water body.

A number of examples of recontamination in Superfund sites due to contaminated soil erosion (e.g., slumping under docks and scouring after high flow storm events) are described by the Association of State and Territorial Solid Waste Management Officials in *Sediment Remedy Effectiveness and Recontamination: Selected Case Studies* (ASTSWMO 2013). Case studies described include the Torch Lake/Quincy Smelter Site in Michigan and the Denny Way Combined Sewer Overflow (CSO) Site in Washington, where continuing shoreline erosion has negatively impacted the remedies.

Alternatively, natural shorelines may indicate lower levels of land use intensity and could result in a source of less impacted eroding material entering the water column. Potential migration of impacted bank soil into adjacent sediments should be considered, because this migration could impact chemical concentrations in adjacent sediments and downstream.

Finally, floodplains and marshes within sites (or near the site), especially when tidally influenced, are particularly challenging. These features can cover a large surface area, usually have complex patterns of erosion and deposition, and the location of the shoreline is constantly changing. As such, inputs from these areas are often critical components in developing a robust CSM for the site.

2.2 WATERSHED INPUTS

Sediment sites are predominantly affected by historical chemical contributions and point-source releases. These sites are often located within urban areas, with multiple potential sources of additional and on-going chemical inputs from point and non-point sources that are unrelated to the site. Sources of contamination that are not site-related, but are from within the watershed, both historical and current, may include many of the same chemicals being studied at the subject sediment site, making it difficult to discern between site-related releases and inputs from background sources.

For example, almost half of the largest sediment sites have PCBs as a major contaminant, and approximately a quarter or more are contaminated with metals and PAHs from legacy or point-source releases (USEPA 2005). These contaminants are also ubiquitous in the urban environment and are transported through urban runoff, atmospheric deposition, and direct discharges from outfalls (municipal and/or industrial). Consequently, it is critical to recognize that these ongoing sources will continue to contribute contaminant concentrations to background reference areas and the site. Thus, these sources should be included in determining representative background concentrations for these background reference areas.

2.2.1 Urban Runoff

Urban runoff is non-point source pollution defined as “stormwater from city streets and adjacent domestic or commercial properties that carries pollutants of various kinds into the sewer systems and receiving waters” (USEPA 2010). Urban runoff is considered to be a significant contributor of contamination to watersheds and sediments, and contains many chemicals most commonly found at sediment sites (PCBs, PAHs, and metals), as noted in Section 2.2 (USEPA 1995a).

Urban runoff also contains chemicals that are commonly found in urban infrastructure, including asphalt roads, pavement sealants, building materials, roofing materials, and galvanized fences. For example, a recent study by the USGS and the Milwaukee Metropolitan Sewage District stated that “coal-tar pavement sealant was indicated as the primary source of PAHs in a majority of streambed sediment samples, contributing an estimated 77 percent of total PAHs to samples, on average” (Baldwin *et al*. 2016). Releases to the environment are also attributable to motor vehicle use; wear on automotive parts (e.g., tires, brake pads), and vehicle emissions (Chalmers *et al*. 2007, Gallagher *et al*. 2014, Turner and Hallett 2012). Other sources of different chemicals, such as home pesticide application and improper waste disposal, also contribute to chemical concentrations in urban runoff.

Therefore, contributions and chemical loading from urban runoff to a site should also be included in the development of representative background concentrations. Chemical inputs from urban runoff to a site and background reference areas should be as similar as possible in order to obtain representative background concentrations for use at the site.

2.2.2 Direct Discharges

In general, direct discharges are associated with industrial facilities, or municipally owned systems that discharge wastewater and/or stormwater to water bodies through permitted (or unpermitted) conveyance systems, via discharge points such as outfalls and CSOs. Chemical loading from wastewater and/or stormwater discharge is managed by the National Pollutant Discharge Elimination System (NPDES) program under the Clean Water Act, which may set limits for chemical concentrations for discharges from these conveyance systems, but does not completely eliminate chemical loading from the discharge. Additionally, the regulatory programs may not measure or exercise authority over chemicals associated with sediment sites, such as PCBs.

In 2006, a Phthalates Work Group (Work Group) was formed by the USEPA and state and local agencies to address recontamination from phthalates observed in the Thea Foss Waterway located within the Commencement Bay Superfund Site in Tacoma, Washington. A key conclusion identified by the Work Group is that “rapid accumulation of phthalates in sediments (after cleanup) is associated with urban stormwater outfalls” (Work Group 2007). In particular, the head of the Thea Foss Waterway has two 96-inch-diameter stormwater pipes that continuously discharge untreated and treated industrial stormwater, in addition to untreated residential stormwater. These outfalls were determined to be a main source of phthalate input, and the resulting recontamination to the Thea Foss Waterway, particularly in the vicinity of the outfalls (ASTSWMO 2013).

Chemical loading to a site from direct discharges should be accounted for in representative background concentrations. “In some cases, as part of a response to address CERCLA releases of hazardous substances, pollutants, and contaminants, USEPA may also address some of the background contamination that is present on a site due to area-wide contamination” (USEPA 2002). As much as practical, direct discharges affecting background reference areas should be as closely matched as possible to the direct discharges affecting a site. Municipalities overseeing wastewater treatment plant and CSO discharges within a waterbody undergoing sediment cleanup may have data on chemical concentrations in the treatment plant and CSO discharges, which can also be useful in the derivation of representative background concentrations.

2.2.3 Sediment Transport

Sediment sites are dynamic in nature, as they are consistently receiving suspended sediments from off-site areas. Those off-site areas contain background concentrations of contaminants from anthropogenic sources, and may also contain concentrations of naturally occurring chemicals similar to the chemicals of concern for the site. At the Lower Duwamish Waterway Superfund site, sediment transport modeling performed as part of the Remedial Investigation/Feasibility Study indicated that "approximately 99 percent of the total external sediment particle load to the Lower Duwamish Waterway comes from the Green River, upstream of the Lower Duwamish Waterway" (Windward 2010).

An analysis of suspended sediments collected upstream of the Lower Duwamish Waterway site performed by the Washington State Department of Ecology indicated that this loading could potentially be a post-remedy source of recontamination to sediments (Ecology 2009), because the upstream sediment contains chemicals (such as PCBs) that are found at high concentrations throughout the downstream site. A dredge and backfill early action remedy was conducted along the Lower Duwamish Waterway between 2013 and 2015. Within months of completing the remedy, high levels of PCBs were measured in material deposited on the clean sediment surface, with concentrations much greater than what was predicted to occur. Similar post-remedial recontamination was also observed at locations where other early actions were performed on the Duwamish (AMEC Foster Wheeler 2017).

Background reference areas in non-tidal riverine systems are frequently located immediately upstream of the site. In tidally influenced sites, the situation is considerably more complex. At tidally influenced sites, sediment transport into the site may result from upstream sources and may also involve contributions from receiving bodies downstream of the site as sediments are transported on incoming tides. Therefore, within tidal systems it is extremely important to have a strong understanding of hydrodynamics and sediment transport processes. If downstream sediments contain equal or greater concentrations of contaminants than are found at the site, these downstream sediments can be a continuing source of contaminant input to the site and should be considered in developing representative background concentrations.

Because sediment resuspension is a transport pathway for contamination, it is important to acknowledge that representative background levels of contamination will inevitably move into a site through this natural process. It is also important to understand the diversity of depositional environments and the many varying factors such as current directions, tidal pumping, and constant or episodic sediment transport processes. Consideration should be given to multiple potentially significant factors influencing sediment transport at coastal/tidal sites, including the effects of flood events and storm surges. Among these, downstream flows intersect with the tide to create a salt wedge and an estuarine turbidity maximum where dissolved materials flocculate and deposit. This effect, combined with suspended particulate material, creates a locally elevated area of turbidity that moves through the estuary and contributes to sediment transport and deposition. Finally, in some riverine or estuarine systems, the current can reverse direction and head upriver, under certain circumstances.

2.2.4 Atmospheric Deposition

Atmospheric deposition from industrial and urban areas, and areas near major transportation corridors, is a recognized pathway of contamination, particularly for those contaminants ubiquitously found in the environment; these include metals, PAHs, PCBs, and pesticides, as discussed in Section 2.2 (Larson *et al*. 1997, ESA 2000, Landis and Keeler, 2002, Rolfhus *et al*. 2003, Kuang *et al*. 2003, USGS 2005, Urbaniak 2007, Brandenberger *et al*. 2010, Zhang *et al*. 2013, Amodio *et al*. 2014). The impact of atmospheric deposition can be challenging to ascertain. Types and volumes of pollutants deposited from the atmosphere will vary depending on atmospheric conditions (e.g., wind speed, temperature, and rainfall) and particle characteristics (size and shape). The influence of these factors on the resulting contaminant deposition rate may vary (Amodio *et al*. 2014).

Winds can carry chemicals through the air from great distances, further confounding the identification and control of non-point sources of contamination (Cohen *et al*. 1997). At sites with relatively uniform sources of atmospheric deposition (e.g., transportation corridors and urbanized, non-industrial areas), typical concentrations and mass loading effects are usually established through a literature review. Additionally, sites in industrial areas with contributions of airborne chemicals may warrant further consideration of site-specific variations (e.g., physical and chemical characteristics of specific industrial emissions, localized wind patterns) that influence deposition patterns, which may not be readily apparent during a literature review.

In Washington State, studies of air deposition and resulting mass flux loading have generally concluded that air deposition is a small but potentially significant source of certain persistent chemicals, and may account for up to 5 percent of the measured concentration of any particular chemical in sediment that is well outside of the influence of urbanized areas (Brandenberger *et al.* 2010). Similar studies of atmospheric deposition in the Great Lakes region have concluded that atmospheric deposition is a significant source of mercury and some other trace metals to Lake Michigan and Lake Superior (Landis and Keeler 2002, Rolfhus *et al.* 2003). Studies of zinc loading to the Santa Monica Bay determined that atmospheric deposition was responsible for 62 percent of the measured zinc concentration in sediments (ESA 2000). The Delaware River Basin Commission found that "air concentrations of PCBs in the region currently are two orders of magnitude above the concentration required to achieve equilibrium and halt contributions of PCBs from the air to the water" (Fikslin and Suk 2003). Substantial additional literature is available documenting the contributions of air deposition to elevated chemical concentrations in surface sediment. The contribution of chemicals from this pathway should be recognized both at a site, and at its background reference areas; in fact, background reference areas should reflect atmospheric deposition conditions observed at the site.

2.3 SOURCE CONTROL

Source control is generally defined as efforts to eliminate or reduce, to the extent practicable, the release of chemicals from point and non-point sources to a water body (USEPA 2005). Source control measures vary, depending on the transport pathway. For example, reducing contamination from urban runoff typically requires different measures than those used to reduce contamination from direct discharges, although the efforts may be coordinated.

Source control should be fully complete, or at least substantially completed, before remediation of a sediment site begins. If source control has not been completed or is not feasible, then it is critical that the potential inputs from uncontrolled ongoing sources be included in the determination of representative background concentrations, because these inputs would continue to affect the site after remediation and that recontamination of the completed remedy would occur. For example, at a riverine site there may be substantial ongoing CSO contributions upstream of the site boundary, or from within the site itself. If the municipality responsible for the CSOs is not able to implement source control prior to site remediation, the CSO input must be included and represented in the derivation of representative background concentrations, as the input from these point sources will continue into the future, after completion of the remedy.

In general, it is important to recognize that, while source control is key, in many sites it may be impossible to eliminate source contributions altogether. This is particularly the case at urbanized and/or tidally influenced sites. The inability to eliminate ongoing source contributions makes it all the more critical to take ongoing sources into account when setting representative background concentrations for the site.

2.4 SEDIMENT PHYSICAL PROPERTIES

The physical properties of sediment strongly influence the distribution of naturally occurring and anthropogenic background chemicals in the environment. Sediment consists of organic material, inorganic material, and pore water. The relative abundance of these components varies vertically and horizontally within a sediment body, resulting in variable distribution of chemicals at a sediment site. Metals concentrations, in particular, can be heavily influenced by natural processes. Since representative background includes natural sources (as well as anthropogenic sources), a discussion related to contributions of natural background is included within this document.

The organic fraction has an important effect on the concentration of chemicals, because of its high capacity for sorption of some contaminants. The water fraction fills pore space within the sediment, allows for the transport of dissolved chemicals, and is subject to geochemical conditions that strongly influence the transport and sorption of metals (refer to Section 2.6). The inorganic fraction typically makes up the largest portion of sediment mass; the relative fractions of sand, silt, and clay determine the sediment texture.

To accurately quantify sediment characteristics, geotechnical testing and general chemistry analyses are generally recommended, these should be conducted according to ASTM International geotechnical testing standards and USEPA analytical methods. The sediment type (ASTM 2009), particle size (ASTM 2017a, 2017b), density (ASTM 2017c), and moisture content (ASTM 2010) should be the focus of geotechnical tests. The general chemistry analyses that are recommended include sediment pH (USEPA 2000), oxidation-reduction conditions (redox potential; APHA 2011), and total organic carbon (TOC) content (USEPA 1999b).

Sediment texture has a substantial effect on the distribution of chemicals of concern in sediment. Several grain size classifications are available for soil classification, and the Unified Soil Classification System (USCS; ASTM 2011) is most commonly used to classify sediments. Fine-grained sediments, particularly those with a high percentage of clay-sized particles and organic content (as measured by TOC) have greater surface area, so they typically have greater sorption capacity for some contaminants than medium and coarse-grained sediments. Silts typically have moderate sorption capacity, while sands and gravels have lower sorption capacity.

In addition to sediment texture, sorption capacity of some fine-grained sediment is enhanced by surface charge. For example, clays and organic colloids tend to be highly charged relative to their surface areas. Clay minerals are typically negatively charged under normal pH conditions, so they attract positively charged trace metals ions for sorption. This results in clay-rich, fine-grained sediments that have greater trace and reference metal concentrations (refer to Section 2.6). In addition, metal concentrations (in particular) tend to be inversely proportional to grain size.

Given the ability of sediment physical properties to influence the distribution of chemicals in the environment, this is an important consideration in developing a CSM to support representative background determination.

2.5 HYDRODYNAMIC ENVIRONMENT AND SEDIMENT PROFILE

Sediment characteristics that strongly influence the distribution of both naturally occurring and anthropogenic background chemicals are determined chiefly by the physical configuration and hydrodynamic characteristics of the depositional environment. In general, coarse-grained sediments such as sands are deposited in relatively high-energy environments (such as beaches and river channels), while fine sediments settle out only when they reach lower energy areas (such as offshore, lakes, and more quiescent areas of rivers and streams). As described in Section 2.4, fine sediments typically have a greater sorption capacity for contaminants than coarse-grained sediments, so representative background concentrations tend to be greater in more quiescent sediment environments, where the percentage of fine sediments is greater.

The vertical profile of sediment may vary significantly in composition, texture, chemical, and biological characteristics. Changes in the hydrodynamic environment and sediment sources can result in distinct layering. Change in land use over time, such as increasing urbanization, may produce layers with different compositions, texture, and concentrations of anthropogenic background chemicals. Natural or artificial changes to vegetation within a watershed may alter the concentration of organic carbon in sediment layers. All of these factors can influence the distribution of chemicals at a site and within its background reference areas.

The rates of sediment deposition, erosion and removal, and mixing vary widely among aquatic environments and should also be assessed as part of the CSM, as these factors affect chemical distribution in sediments. Pore space and volume of the water within sediments is decreased by compaction as sediments are buried. During this process, chemicals present in sediments may be vertically redistributed by mixing of surface and deeper sediments. Sediment mixing may also occur through bioturbation. Bioturbation may increase pore space, the volume of the water fraction, and organic content, and affect the partitioning of chemicals between aqueous and solid phases.

Age dating and chemical analysis of sediment core samples may indicate chemical concentrations that are associated with sediment layers deposited prior to site-related activities, which may be helpful in estimating representative background concentration ranges. The age of sediment layers and accumulation rates may be estimated by various methods, including radioisotopic decay measurements (USGS 1998).

2.6 GEOCHEMISTRY

It is important to identify the geochemical processes controlling element concentrations in sediment samples. Sediment geochemistry should be characterized by properly qualified geochemists in support of background analysis (e.g., to determine which samples to retain in the background dataset) and should be considered during subsequent comparisons of site versus background datasets. This is also important because metal concentrations (either naturally occurring, or from an anthropogenic source other than a release at a site) commonly exceed risk-based screening criteria. Geochemical processes relevant to background data evaluation include association of elements with minerals, sorption of elements on mineral surfaces, water chemistry, and water-mineral interactions. These topics are summarized in this section. Geochemical methods used for evaluating representative background metal concentrations in sediment are discussed further in Section 3.6.

Chemical properties of sediment particles and the surrounding aqueous phase strongly influence the distribution of metals, and for this reason are useful to measure and include in geochemical assessment of site data. Key properties include metal solubility, pH of the aqueous phase (including the overlying water column and pore water), redox potential of the aqueous phase, metal affinity for organic carbon, TOC concentrations, and reactions of metals with sulfide.

Metals concentrations are controlled by dissolution/precipitation reactions and adsorption/desorption (“sorption”) reactions. Highly soluble metals can remain mobile in the aqueous phase and can be dissolved from the sediment, while low solubility metals can precipitate and accumulate in sediments. The solubility of a metal is highly dependent on characteristics of the aqueous phase including pH, redox potential, and ionic strength. While elements differ in their response to changing pH, acidic conditions tend to dissolve and mobilize some metals, while basic pH conditions can precipitate other metals (resulting in greater concentrations in sediment). The pH also controls the net surface charge of particles, which is an important factor in determining sorption of metals on mineral surfaces. This is important due to the presence of clay minerals and metal oxides that have strong affinities to absorb specific trace metals.

Oxidizing conditions cause many metal ions (e.g., iron and manganese) to precipitate as oxides. Reducing conditions, such as in anoxic sediments, tend to keep specific elements in solution and mobile. In addition to naturally reducing conditions associated with peat or other organic materials in wetlands or similar environments, releases of organic contaminants can stimulate microbial activity, resulting in local reducing conditions and the mobilization of select metals.

Reducing conditions can cause the reductive dissolution of iron and manganese oxides, which may mobilize adsorbed trace elements. Reducing conditions may also directly reduce arsenic, selenium, antimony, molybdenum, and vanadium to more mobile valence states. Sulfate-reducing conditions in sediment can cause specific metals (e.g., arsenic, mercury, copper, lead, and zinc) to precipitate as (or with) insoluble sulfide phases. Sulfide ions, produced from the reduction of sulfate associated with the breakdown of organic compounds and as measured by acid-volatile sulfide, are usually associated with higher metals concentrations in sediment.

As noted previously, sediments with greater TOC concentrations typically have greater concentrations of specific trace elements (e.g., mercury, copper, tin, and uranium), because the organic particles have a greater sorptive capacity for these elements. However, greater TOC concentrations may be associated with reducing conditions, so the metals associated with the TOC may be less bioavailable.

The complexity of contaminant interactions, as overviewed in this section, may hinder the ability to identify the background reference areas with the same sediment geochemistry. For that reason, and the other reasons discussed throughout this document, it may be appropriate to identify and utilize multiple background reference areas in order to define a range of reference conditions.

3.0 Considerations in Data Review and Evaluation for the Determination of Background

Determination of background conditions at a sediment site almost always requires additional sampling and/or data analyses. To ensure the reliability of these evaluations, appropriate procedures should be considered during each phase of the investigation. Topics that require special attention include those related to the practical aspects of sampling design, selecting the representative background reference areas, using existing site data, choosing appropriate statistical methods for comparison, addressing perceived outliers, and geochemical analysis of sample data. These topics are discussed further in this section.

3.1 STUDY DESIGN CONSIDERATIONS

In general, unless existing contemporaneous data are adequate for extracting site-specific background data (USDON 2003; Singh *et al*. 2014), additional sampling focused on the determination of representative background concentrations is necessary. This process is often initiated by identifying suitable background reference areas. All samples collected within the background reference areas should be considered representative of background. Typical components of a sampling design, including the selected type of samples, sampling depth, and sampling methodology for the background reference areas, should match those used during site data collection. The number and location of background samples can be determined based on a number of different statistical approaches. One example is the United States Department of Energy's Visual Sample Plan (VSP Development Team 2017).

Agency agreement on the scope and scale of the sampling effort to determine representative background concentrations is important and should be captured in a site's Data Quality Objectives, using USEPA's Data Quality Assessment approach (USEPA 2006).

3.2 SELECTION OF REPRESENTATIVE BACKGROUND REFERENCE AREAS

One of the critical steps in a background analysis is the selection of representative background reference areas. As discussed in Sections 2.0 and 3.0, representative background reference areas are areas that have "the same physical, chemical, geological, and biological characteristics as the site being investigated, but [have] not been affected by activities at the site," and should be informed by the CSM (USEPA 2002). Further, "the ideal background reference area would have the same distribution of concentrations of the chemicals of concern as those which would be expected on the site if the site had never been impacted" (USEPA 2002). In addition, background reference areas need to include sources of contaminants that reflect the land use in the vicinity of the site, except for the inputs from releases or activities at the site. Unfortunately, selection of such an analogous area is complicated, due to the fact that sediment background often represents mixtures of naturally occurring and anthropogenic influences. In some cases, these mixtures yield geographically distinct background populations (e.g., background reference sub-areas with varying degrees of anthropogenic influences in different parts of the background reference areas). Under such situations, the part(s) of the targeted background reference areas (or sub-areas) that are most analogous to the site should be selected as the background reference areas. Selection of analogous background reference sub-areas is often supported by multiple lines of evidence, including degrees of urbanization, presence or absence of combined sewer outfalls, prevailing sediment TOC content, and grain sizes. Use of this selection methodology should result in a representative background dataset.

3.3 USE OF EXISTING SITE DATA

In many instances, site data include samples that are free of site influences. Particularly within a larger site dataset, there will be samples not affected by site releases that will be reflective of representative background conditions. In these cases, statistical methods, such as probability plot analyses, are recommended for extracting site-specific background datasets from existing site datasets (USDON 2003, Singh *et al*. 2014). This approach involves preparing iterative probability plots to determine break points, indicating a separation between the data points with site release impacts, and the data points free of site release influence that are suitable for use in deriving representative background concentrations. This procedure is especially useful for extracting representative background concentrations from large site datasets (Geiselbrecht *et al.* 2015).

The extraction of representative background concentrations from site data not only maximizes the utility of existing data, but also avoids the often complex task of selecting separate background reference areas that adequately represent the site. Even when data from separate off-site background reference areas are available, an extracted site-specific background dataset provides an additional line of evidence for determining representative background concentrations. Therefore, an analysis of existing site data is always recommended.

3.4 STATISTICAL COMPARISONS

Due to the different types of contamination (e.g., localized versus widespread), USEPA guidance recommends the use of simultaneous tests for a valid and complete comparison of background and site distributions (USEPA 2006). There are generally two statistical approaches for comparing site and background populations: (1) point-by-point comparisons, and (2) background-site population comparisons.

The point-by-point comparison approach is based on comparing individual site measurements to a given BTV, either to delineate the extent of impact or to identify localized (or “hot spot”) contamination. A BTV is a specific value intended to define an upper limit to background concentrations for a given site. Common candidates for BTV include the upper tolerance limit (UTL; typically 95 percent confidence with 95 percent coverage), the upper prediction limit (UPL; typically 95 percent confidence), as well as the upper simultaneous limit (USL; typically 95 percent confidence; USEPA 2005). Regardless of the chosen BTV, point-by-point comparisons are prone to produce excessive false-positive errors. That is, as the number of comparisons increases, the chances of incorrectly detecting exceedances greater than BTV approaches 100 percent, even when the site data are derived from the background population (Gibbons 1994). In other words, the odds are very high (approaching 100 percent) that the analysis will report exceedances of background when the results do not truly exceed background. In fact, the Department of the Navy recommends against point-by-point comparisons, except when coupled with reverification sampling (USDON 2003).

The background-site population comparison approach, involving background reference areas versus site population comparisons, compares site population distribution to those of the background population distribution using specific statistical hypothesis tests. Some of these tests, such as the parametric t-test and the non-parametric Mann-Whitney U test are geared toward the comparison of central tendencies of two populations, to identify widespread contamination. Other tests focus on the comparison of the upper tails of the two populations to identify localized contaminations. In many instances, both widespread contamination and localized contamination should be tested concurrently. Selection of the appropriate test is contingent on the specific conditions presented in Figure 2. Typical conditions include the target statistics of interest, and the type of the distributions displayed by the investigated datasets, as well as their variance equivalency. These tests are designed to maintain the false negative error rates at the user-specified levels, often set at 1, 5, or 10 percent. In practice, non-parametric tests are often preferred because they do not require any specific distributional assumption about the investigated site and background data. Compared to point-by-point comparison, background-site population comparisons are less prone to excessive false-positive errors.

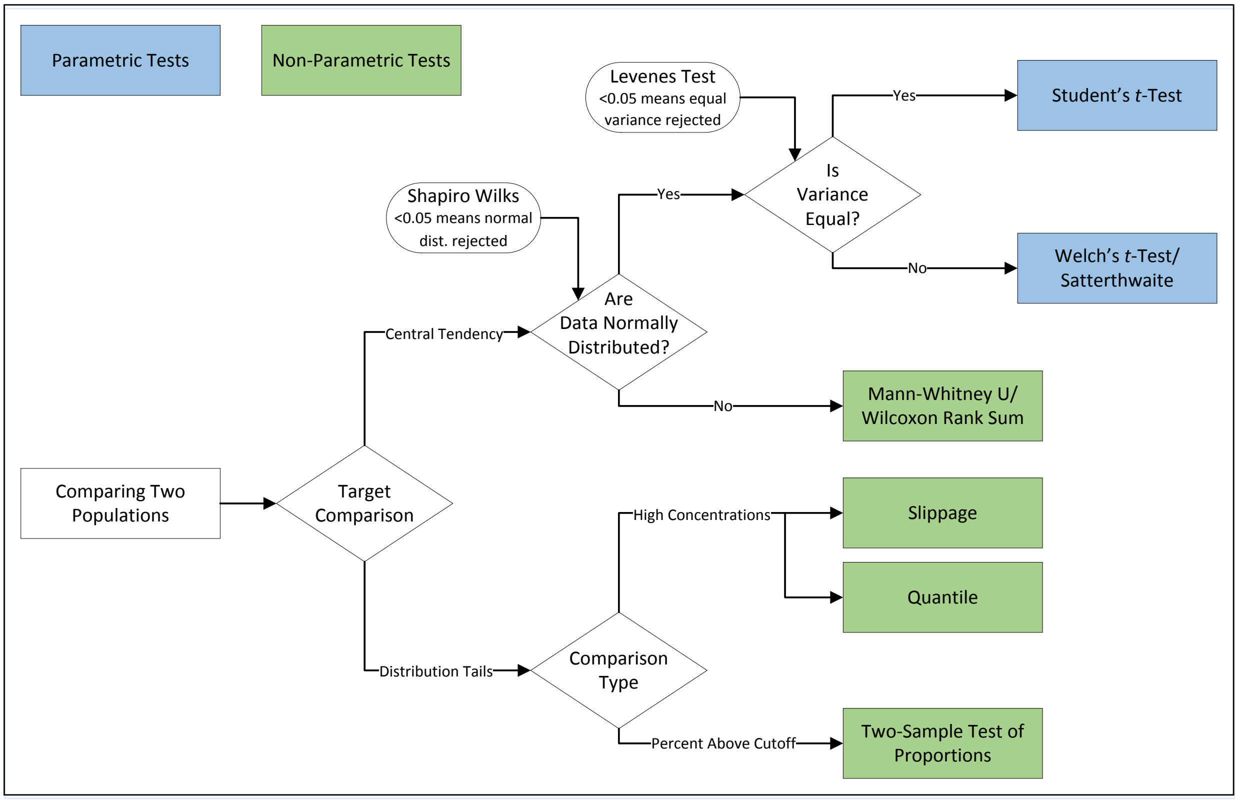

Figure 2. Statistical Tests for Comparison of Two Populations (adapted from USDON 2003)

3.5 OUTLIER EVALUATION

Some background measurements may be perceived as outliers, which are measurements that are disproportionately large or small relative to the rest of the data, so they are suspected of misrepresenting the population from which they were collected (USEPA 2006). Outliers can be attributed to two broad categories of causes: (1) outliers may represent very high or low values from the investigated population that have occurred by chance, or (2) outliers may be the results of errors such as faulty sample collection, laboratory equipment failure, and improper data entry (USEPA 2002 and 2006, Grubbs 1969).

There are well established procedures in statistics to identify true outliers, including visual inspection of graphs using particular techniques, such as probability and box-and-whisker plot, as well as statistical tests, such as Rosner's test and Dixon's test (USEPA 2002 and 2006). The treatment of confirmed outliers, however, requires a thorough evaluation of the causes of such measurements to ensure that purported outliers are not improperly excluded, thereby skewing the statistical analysis. Grubbs' *Procedures for Detecting Outlying Observations in Samples* (Grubbs 1969) states:

> *"An outlying observation, or 'outlier,' is one that appears to deviate markedly from other members of the sample in which it occurs. In this connection, the following two alternatives are of interest:*
>
> 1. *An outlying observation may be merely an extreme manifestation of the random variability inherent in the data. If this is true, the values should be retained and processed in the same manner as the other observations in the sample.*
> 2. *On the other hand, an outlying observation may be the result of gross deviation from prescribed experimental procedure or an error in calculating or recording the numerical value. In such cases, it may be desirable to institute an investigation to ascertain the reason for the aberrant value. The observation may even eventually be rejected as a result of the investigation, though not necessarily so. At any rate, in subsequent data analysis the outlier or outliers will be recognized as probably being from a different population than that of the sample values."*

USEPA itself has recognized the importance of properly evaluating apparent outliers and of not excluding data points simply based on their magnitude. USEPA's *Data Quality Assessment: Statistical Methods for Practitioners* divides (USEPA 2006) outliers into two groups: (1) "true outliers" resulting from transcription errors, data-coding errors, or measurement system problems such as instrument breakdown; and (2) "false outliers" representing true extreme values of a distribution (for instance, hot spots) and indicating more variability in the population than expected. This guidance states that "failure to remove true outliers or the removal of false outliers both lead to a distortion of estimates of population parameters."

In the data review, it is imperative that all sample data, including false outliers, are retained and are not arbitrarily removed. A proper statistical outlier evaluation will at least include the following steps, as discussed in USEPA's 2002 guidance:

- A careful investigation or review should be conducted for each statistical outlier, with scientific reasoning to ascertain the cause of the aberrant value (Grubbs 1969). If there is any error in collecting, transporting, or analyzing the sample, or transcribing the data, then the error should be corrected.
- If the error cannot be corrected, the associated true statistical outliers should be eliminated from the background dataset.[4]
- If no error can be identified or confirmed, false outliers should not be arbitrarily eliminated.

Thus, an outlier should not be eliminated from the background dataset, just because it is the greatest or lowest value in the dataset, or based on the perception that the outlying value is too high or too low to fit into the background dataset. In this case, the outliers "may be merely an extreme manifestation of the random variability inherent in the data [and] the values should be retained and processed in the same manner as the other observations in the sample" (Grubbs 1969). True outliers should be deleted from datasets, and false outliers should be retained. In cases where the nature of the outliers is either unknown or disputed, all statistical analyses should be conducted with both the full and truncated datasets to evaluate the effect of maintaining or eliminating the disputed outliers (USEPA 2002 and 2006). In cases involving actual or potential true outliers, their removal is required before a valid BTV can be calculated. In these cases, a statistically rigorous method must be used for outlier identification and removal.

As noted by USEPA, it is critical that the considerations outlined in this section are followed during the statistical analyses of the background data. Exercising caution not to improperly exclude "false" outliers, that accurately represent conditions at the background reference areas, will ensure technically defensible derivation of representative background concentrations, and will also avoid mistakes in the statistical approach when relying on a preconceived notion that outliers "distort statistics if used in any calculations" (USEPA 2002). Finally, once derived, these representative background concentrations should remain fixed for the duration of the remedial investigation and remedial response. Otherwise, the lack of certainty for stakeholders would be an impediment to the implementation of any remedy.

3.6 GEOCHEMICAL EVALUATION OF METALS CONCENTRATIONS

Geochemical evaluation is a tool with which to evaluate elemental (i.e., metals) concentrations in a given dataset, which may include exceedances of representative background concentrations. Consideration of geochemistry in the evaluation of trace metals concentrations in sediments does not require background reference area data for comparison, so, advantageously, it can be

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[4] "Data points that are flagged as outliers should be eliminated from the dataset if field or laboratory records indicate that the sample location was not a reasonable reference area, or if there was a problem in collecting or analyzing the sample" (USEPA 2002).

used when it is not otherwise possible to identify background reference areas. However, geochemical evaluation is more convincing when data from the background reference areas are available for inclusion in the evaluation.

Geochemical evaluation can be used to determine if trace metal concentration values identified as outliers by statistical methods are actually the result of a release from the site, or if the outlier is simply a manifestation of the normal geochemical variability in the site dataset. When properly performed, geochemical evaluation provides mechanistic explanations for elevated concentrations (Thorbjornsen and Myers 2007). It is important to keep in mind that geochemical evaluation is not a simple graphical technique; all potential geochemical mechanisms, field observations, and available data need to be considered when examining element concentrations.

Background data can be evaluated by using the ratios of specific element pairs that are based on the known geochemical behavior of trace elements and their association with specific sediment minerals. The USEPA's Target Analyte List of 23 metals includes all of the common trace elements of interest, as well as the major elements that are used as reference elements.

Scatter plots may be prepared in which the concentration of a trace element of interest is plotted on the y-axis, and the concentration of a reference element, which represents the mineral (or organic compound) to which the trace element is adsorbed, is plotted on the x-axis. For further analysis, a ratio plot may also be prepared; like the scatter plot, the concentration of the trace element of interest is plotted on the y-axis, but the corresponding elemental ratio (the trace element concentration divided by the reference element concentration) is plotted on the x-axis. If a metal is found at an elevated concentration and that sample's elemental ratio lies outside the range of background elemental ratios, then that sample should be examined further. For example, the elevated ratio might reflect anthropogenic input of the trace element from the site, or it may indicate that the trace element concentration of that sample is controlled by another geochemical process, such as reducing conditions or trace metal precipitation in the sediment. If the sample lies within the range of background elemental ratios, then it is considered representative of background conditions.

The selection of a reference element for the scatter or ratio plot should be based on a careful comparison of the reference element and the trace element of interest, as well as consideration of site-specific geochemical processes. The following paragraphs provide a general overview of a few relevant elemental associations, but the reader is urged to consult the literature for additional information.[5]

- Clay minerals in the pH range of 6 to 8 have a strongly net negative surface charge, and attract positively charged trace metal ions, so that these trace metals adsorb to clay mineral surfaces. Aluminum is a primary component of all clay minerals, and detected aluminum concentrations in sediment serve as proxy indicators of the relative amounts of clay minerals (Thorbjornsen and Myers 2007). In addition, aluminum concentrations are generally not influenced by chemical releases and the element is not redox-active. For these reasons, the concentrations of positively

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[5] Suggested literature is provided in Section 5.0.

charged trace metals (such as copper, lead, nickel, and zinc) commonly covary with aluminum concentrations in uncontaminated sediment samples.

- Iron oxides (including hydroxides, oxyhydroxides, hydrous oxides, and amorphous oxides) typically have a net positive surface charge in the pH range of 6 to 8. Detected iron concentrations serve as proxy indicators of the relative amounts of iron oxide minerals in sediment samples from oxic environments (Thorbjornsen and Myers 2007). Due to their net positive surface charge, they have an affinity for adsorption of negatively charged oxyanions (including arsenic, antimony, selenium, and vanadium), so that the concentrations of these trace metals commonly covary with iron concentration in uncontaminated samples from oxic sediments.
- Because metal species may be positively, neutrally, or negatively charged, other associations occur outside of these generalizations. Reference elements other than iron and aluminum (most typically manganese, which serves as a proxy indicator for manganese oxide minerals, in oxic sediments) are also used in geochemical evaluations. Grain size and TOC content are additional reference parameters that can be used to evaluate trace metal concentrations. For example, due to the affinity mercury has to adsorb on organic matter, covariance of mercury versus TOC concentrations may be observed in the absence of site-related mercury contamination.

Although quantitative statistical techniques are commonly applied to identify outliers or to develop pass-fail criteria for the presence of contamination, they are not recommended for geochemical evaluations that employ scatter plots or ratio plots, for many scientific reasons. For example, each trace element has varying degrees of correlation with the major element(s) with which it is associated; some trace elements have strong affinities for a particular mineral, while other elements will partition themselves among several minerals. Correlation coefficients, confidence limits, and prediction limits are highly influenced in a non-linear manner by outliers, as well as by the analytical uncertainty associated with estimated concentrations less than the reporting limit. Evaluation of a set of geochemical data can be quite complex, as the effects of redox, pH, and other processes should be considered. Trace-versus-major-element correlations are usually not linear and often possess some degree of curvature; this also translates to a higher range of elemental ratios and greater spread of the samples along the x-axis of a ratio plot.

Geochemical evaluation is an important line of evidence when evaluating background data and is commonly performed in conjunction with statistical evaluation of the dataset (refer to Section 3.4). A properly performed geochemical evaluation examines the interrelationships between elements, in the context of all available data, for the purpose of identifying the processes controlling the observed concentrations. Scatter plots and ratio plots, coupled with knowledge of the geochemical behavior of elements in the site-specific environment, may indicate that elevated concentrations, which would otherwise fail statistical outlier tests, have a natural and/or anthropogenic source that is not related to a site release. If the trace-versus-reference-element ratio lies within the ratio range of the representative background samples, then site-related contamination is not indicated.

4.0 Conclusions and Recommendations

Derivation of representative background concentrations is critical to the development of successful remedies for sediment sites. This document highlights concepts, data and considerations that are necessary for deriving representative background concentrations (including both anthropogenic and natural concentrations) to achieve a more complete understanding of historical and on-going sources to the site. In the absence of detailed guidance, these considerations may be overlooked or discounted when calculating representative background concentrations at sediment sites.

CSMs are critical tools for characterizing the complexity of sources to a site, migration pathways, receptors, and exposure pathways, and they inform the appropriate selection of background reference areas. The CSM developed for a site should include these key considerations (as outlined in this document):

- Anthropogenic inputs to the site, such as land use, urban runoff, direct discharge, sediment transport, atmospheric deposition, and source control.
- Natural characteristics of a site, such as sediment physical properties, hydrodynamic environment, sediment profile, and geochemistry.

Similarities between the site and the background reference areas are important, because they influence the transport and fate of contamination. Anthropogenic sources that cannot be controlled contribute on-going contamination and should be fully considered and incorporated into the CSM, as they represent anthropogenic background chemical concentrations that will persist on-site during and after any remedy. It may not be feasible to control all off-site sources of anthropogenic background prior to remediation, which should inform potential cleanup goals.

After selecting representative background reference areas and completing a targeted sampling program that uses sampling methods matching those used during site data collection, the data should be closely evaluated. The focus of the data evaluation should be on comparing site data with background data, using appropriate statistical approaches (along with geochemical evaluation for trace metals) to derive technically defensible representative background concentrations. During the data evaluation, it is imperative that false outliers are retained and are not arbitrarily removed, because natural variability occurs in a dataset. A statistically appropriate outlier evaluation should be performed on the background dataset, and the evaluation should include the key steps outlined in Section 3.5. Of critical importance, only true outliers should be removed from datasets, and false outliers should not be arbitrarily eliminated.

Representative background concentrations should remain fixed for the duration of the remedial investigation and remedial response. Otherwise, the lack of certainty for stakeholders would be an impediment to the implementation of any remedy. Collectively, the considerations and approaches outlined in this document should increase the ability to derive technically defensible representative background concentrations. These recommendations are offered to help inform, improve, and increase the consistency of sediment site remedy decision-making.

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