Evaluating Metals in Groundwater at DWQ Permitted Facilities: A Technical Assistance Document for DWQ Staff

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Contents

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Metals[1] are a common component of wastes disposed at DWQ-permitted facilities[2], including coal ash sites. They also are naturally occurring in soil and groundwater. Because metals occur naturally, their presence in compliance wells is not, by itself, proof of site-related contamination. Site managers must distinguish the difference between ambient, background[3] metals and site-related metals and determine a representative background concentration (also known as "reference background") for individual metals of concern. To do this, a site manager must understand how metals behave in the environment and, in some cases, apply statistical analyses to the groundwater dataset. How metals are retained and mobilized in the environment may influence a number of permitting decisions such as the selection of well locations and depths, well construction and development methods, sampling and laboratory methods, and background determinations. Effective permit writing and enforcement depends on a basic knowledge of these issues.

This document is intended for Division of Water Quality (DWQ) engineers, scientists, and technical specialists who must evaluate metals concentrations at coal ash sites and other permitted facilities. It is designed to provide a basic understanding of (a) metals retention and mobility, (b) the collection of defensible groundwater compliance data, and (c) statistical methods useful for groundwater datasets. This document is not meant to be an exhaustive, step-by-step "how to" manual or policy document, in part because the unique nature of each site precludes such a uniform approach. Rather, it is intended to present key issues that a site manager should consider when evaluating metals, determining background concentrations, and evaluating statistical tests to determine permit compliance. For staff needing additional information on a given topic, key references are provided throughout. The contents of this document do not supersede existing policy, regulations, or guidance by DWQ or the North Carolina Department of Environment and Natural Resources (DENR).

The document is divided into three chapters, plus two appendices:

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[1] For purposes of this document, the term "metals" is used as a general expression to include metals, non-metals, and metalloids at DWQ permitted facilities.

[2] In this document, the term "permitted facility" is used interchangeably with "site-related", "on-site", "application site", "waste site", and "release site".

[3] Note that historic releases (industrial, agricultural, atmospheric, and others) may affect background concentrations in some areas and should be understood prior to making final background determinations. Absent historic releases, background concentrations are synonymous with pristine, naturally occurring concentrations.

Chapter I - “Understanding the Behavior of Metals in Soil and Groundwater”, describes the factors that control the retention and mobility of metals, nonmetals, and metalloids. It describes the important differences between cations (metals) and anions (non-metals), and focuses on those elements commonly encountered at coal ash sites and other DWQ permitted facilities.

Chapter 2 – “Collecting Valid Groundwater Compliance Data”, highlights the issues that a site manager must consider to ensure the collection of valid, defensible groundwater compliance and background data.

Chapter 3 – “Applying Statistical Methods to Groundwater Data”, describes basic concepts to consider when working with background data and planning statistical tests. It also describes techniques for handling data outliers, non-detects, off-scale values, and provides practical information on background soil and stream sediment data. Finally, it discusses the selection, assumptions, and use of statistical procedures and tests commonly recommended by EPA and others to evaluate groundwater compliance data.

Appendix A provides a list of recommended references for typical ranges of background inorganics concentrations observed in different media and settings.

Appendix B provides a list of recommended references related to metals in coal and fly ash and their leaching properties.

Chapter 1 – Understanding the Behavior of Metals in Soil and Groundwater

Understanding how metals behave and are retained and mobilized in the environment is necessary to effectively write and enforce DWQ permits. The retention and mobilization of metals may influence a number of permitting decisions such as the selection of well locations and depths, well construction and development methods, sampling and laboratory methods, background determinations, and statistical test approaches. This section introduces the basics of metals behavior in the environment.

Inorganic constituents fall into one of three categories - metals, non-metals, and metalloids. **Metals** are lustrous elements that readily conduct heat and electricity and occur in the environment as positively charged ions (cations). Cations include aluminum (Al), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), potassium (K), silver (Ag), sodium (Na), thallium (Tl), and zinc (Zn). **Non-metals** occur as negatively charged ions (anions) and include chloride (Cl), fluoride (F), nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), sulfate (SO_4), and others. **Metalloids** share properties of metals and non-metals, and include arsenic (As), boron (B), selenium (Se), and antimony (Sb). Metalloids may occur in the environment as either cations or anions, depending on the metalloid in question and prevailing geochemical conditions. Typical levels of inorganics in groundwaters, soils, and sediments are provided in Appendix A.

Common inorganics:

Metals (cations): aluminum (Al), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), potassium (K), silver (Ag), sodium (Na), thallium (Tl), and zinc (Zn)

Metalloids: antimony (Sb), arsenic (As), boron (B), and selenium (Se)

Non-metals (anions): chloride (Cl), fluoride (F), nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), sulfate (SO_4), and others

The total mass of metals is permanently removed from a site by plant uptake, sediment erosion, aeolian (dust) transport, volatilization (a potentially important mechanism for Hg and, in some cases, Se, and As), and (or) leaching/transport in groundwater. The remainder is retained, either permanently or temporarily, in the soil environment.

Inorganics occur in one of several compartments (Shuman, 1991):

1. dissolved in groundwater (sometimes referred to as the “soil solution”),
2. occupying “specific adsorption sites” on inorganic soil constituents,
3. occupying “surface exchange sites”[4] on inorganic soil constituents,
4. complexed with soil organic or inorganic matter that may be soluble or insoluble,
5. precipitated as independent solids that may be pure or mixed,
6. present in and as the ambient structure of primary and (or) secondary minerals that comprise the aquifer substrate (soil, rock) itself.

Compartments 1 and 3 represent mobile or potentially mobile metals. Compartments 1 through 5 are associated with anthropogenic, permit-related metals. All 6 compartments may be associated with ambient, naturally-occurring background metals.

When in soil solution, metals exist as either free ions, soluble complexes with organic or inorganic ligands[5], or associated with mobile inorganic and organic colloids[6]. Together, all of these contributions make up the total concentration of the metal dissolved in water; this amount is the value typically reported by the laboratory as occurring in water.

Although metals may be mobilized, their natural tendency in the environment is to be retained within the soil/rock matrix. The two primary mechanisms that immobilize metals and prevent their movement in groundwater are <u>sorption</u> and <u>precipitation</u>. Sorption is defined as the retention of metal ions at the interface between soil and water. Sorption differs from precipitation in that the metal does not form a new three dimensional solid phase but is instead bound to surfaces of certain existing host materials. A precipitated metal, on the other hand, occurs as a newly formed solid phase material.

Sorption can be either of two types: specific (inner) adsorption and exchange site (outer) sorption. Specific adsorption is characterized by strong bonding within the inner matrices of a soil surface. The adsorbed metals are tightly bound to specific adsorption sites and are relatively immobile and generally not affected by the input of other ions that may compete for, and release ions from, those same specific adsorption sites. Typically, only after the specific adsorption sites become filled does another mechanism - exchange site sorption - predominate.

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[4] Surface exchange sites are relatively weak and reversible binding mechanisms that are characterized by electrostatic attractions between an inorganic and an oppositely charged host soil constituent.

[5] Ligands are molecules that bind to a central metal ion and serve as potential hosts for metals. Common inorganic ligands include SO_4, Cl, OH, PO_4, NO_3, and CO_3. Organic ligands include soluble constituents of fulvic acids in, for example, sewage sludges (these fulvic acids are not to be confused with humic acids which tend to immobilize metals).

[6] Colloids are substances with diameters of 0.01 to 10.0 µm. Dissolved particles in general are defined as substances that will pass a 0.45 µm filter. Colloids are highly mobile in groundwater and can easily complex with metals. For this reason, a metal complexed to a colloid tends to be mobile.

Exchange site sorption is a weaker (reversible) type of sorption that occurs due to electrostatic attraction between an inorganic and its oppositely charged host. The sorption sites are termed "exchange" sites because the introduction of new ions into solution, in sufficient concentration, causes the substitution or exchange with the bound ions at these sites. In negatively charged soils, cations are replaced by other cations that compete for those negatively charged sorption sites. In positively charged soils, anions are replaced by other competing anions. This retention and release mechanism is also referred to as the "common ion effect" and is the principal behind ion-exchange/water softener potable water filtration systems.

Whether or not exchange site sorption occurs depends largely on the surfaces available for sorption. Some of the most sorptive host surfaces are clay minerals (aluminum silicates) and hydrous oxides of Fe, Mn, and Al. Hydrous oxides[7] are common components of soils formed by the weathering of primary or secondary silicate minerals. Other sorptive surfaces include carbonates and organic matter (living organisms, soluble acids, proteins, and other biochemicals, and insoluble humic substances produced through microbial activity).

Whether or not sorption occurs also depends on the geochemical conditions (mainly soil pH and oxidation-reduction (redox) potential[8] (ORP)) at the site. At high soil pH, the host mineral's exchange sites are mostly negatively charged (due to fewer H+ ions) and thus naturally attract and retain the positively charged cations. At low soil pH, the host mineral's exchange sites are mostly positively charged (due to greater H+ ions) and naturally attract and retain negatively charged anions.

> As long as exchange sites are available, *trace metal* cations tend to be preferentially sorbed before the *major* cations (Na, Ca, Mg, and K). Because trace metals tend to be more toxic than the major cations, this effect is beneficial. However, this has implications for sites with metals contamination because one commonly used management practice is to neutralize acidic soils

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[7] Iron hydroxides are noted for the reddish pigmentation they impart to soils and for their ability to readily retain trace elements such as Cu, Pb, V, Zn, Co, Cr, and Ni and anions such as PO_4. Iron hydroxides also form complexes with organic materials as exemplified in the red filamentous material that lines many sewer pipes.

[8] The redox potential of a soil system is the measure of its ability to donate or accept electrons as part of electrochemical reactions that change the form of the metal. Metals which gain electrons are being reduced, and those which lose electrons are being oxidized. The redox potential indicates whether metals are in an oxidized or reduced state. Metals and other ions that make up the mineral structure of soils and oxides (hydrous oxides) behave very differently depending on whether they are in an oxidized or reduced environment and whether they are positively charged cations or negatively charged anions.

The redox potential of a system is measured using various indicators such as DO and ORP. A DO below about 1 mg/L, and a raw ORP in the low tens or below (including negative values), are commonly observed ranges for systems in an anaerobic, reduced state. In this case oxygen is being consumed faster than it is entering the system. Water logged soils and those with oxygen consuming chemical compounds (microbial degradation of chemical compounds is a principal cause of oxygen consumption) are commonly in a reduced state.

> by adding calcium (lime) to raise the pH to 7 or above; the added calcium ions often are so numerous that they out-compete the trace metals for the limited exchange sites. This can increase the mobility of the once-bound (and more toxic) trace metals.

In general, oxidizing conditions favor retention of cations in soils, while reducing conditions increase mobility. The reverse is true for anions. In oxidized conditions (defined in most cases as DO above ~ 1 mg/L and raw ORP above ~ 30 to 40 mV) (and in alkaline soils), the particularly sorptive hydrous oxides of Fe, Mn, or Al tend to be very *in*soluble (that is, stable) which allows the oxides to maintain their ability to act as a binding agent. In reduced conditions (defined in most cases as DO below ~ 1 mg/L and raw ORP below ~ 30 to 40 mV and including negative values) (and acidic soils), the hydrous oxides tend to dissolve into solution along with the metals they previously bound.

Being a relatively weak retention mechanism, exchange site sorption can be rapid and reversible if geochemical conditions (pH and redox) change. Redox conditions can change at a site in response to the addition of wastes, microbial activity[9], and other factors, and this may change the electrostatic charge (oxidation state or species) of some inorganics. This change in "state" may affect the toxicity[10] of the inorganic and its potential for sorption.

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[9] Unlike many organic contaminants, metals are not removed from a system by microbial degradation to innocuous compounds. Instead, some metals in the presence of changing geochemical conditions (pH and redox, for example) may be transformed to a different oxidation state (species). For example, one species of iron can be changed to another species of iron, as when soluble Fe^{2+} ferrous iron is transformed to insoluble Fe^{3+} ferric iron in the presence of aerobic, oxidizing conditions. When a metal changes oxidation state, its tendency to be retained or mobilized also changes (for example, ferrous iron is mobile, while ferric iron is immobile).

Microbial activity may be monitored indirectly by measuring the redox in soil and groundwater, pH, temperature, DO, ORP, electron acceptor/donor concentrations (that is, the concentration of individual metal species associated with the microbial activity), and concentration of breakdown products that occur as a result of the microbial activity (such as carbon dioxide).

Microbial activity follows a predictable pattern, depending in large part on the redox conditions and electron acceptors (elements such as DO, Fe, Mn, and others) prevalent within the system. Microbial degradation at a site tends to occur in the following order: first, oxygen within the system is consumed (DO is moderate, ORP is high, and aerobic conditions prevail); next, nitrogen (NO^-_3) is consumed (also referred to as "reduced")(DO is moderate to very low, ORP is moderate, denitrification prevails, and N_2 gas is produced); next, Mn5+ is consumed/reduced (DO is low to very low, ORP is moderate, and Mn2+ is produced); next, mostly insoluble $Fe^{3+}$is consumed/reduced (DO is very low, ORP is moderate to low, and soluble Fe2+ is produced); next, SO_4 is consumed (DO is very low or absent, ORP is low or negative, and H_2S gas is produced); finally, fermentation occurs whereby carbon is consumed, DO is absent, ORP is negative, and methane gas is produced.

[10] Metals whose mobility and toxicity are strongly affected by a change in oxidation state include Fe, As, Cr, Se, and Hg. For example, in slightly acidic to alkaline systems, Fe^{3+}precipitates to a highly adsorptive solid phase as ferric hydroxide. The subsequent reduction of $Fe^{3+}$to Fe^{2+} results in the dissolution of ferrous iron (Fe^{2+}) to groundwater along with any metals that were previously adsorbed to the ferric hydroxide surfaces. Also, the oxidized form of arsenic – arsenate, As^{5+} - is relatively immobile, but may transform to the more mobile and toxic reduced form – arsenite, As^{3+} - in reducing conditions. Hexavalent chromium (Cr+6) is a relatively toxic

The measure of a soil's ability to retain metals through exchange site sorption is referred to as cation exchange capacity (CEC) or anion exchange capacity (AEC). CEC is a measure of the amount of negatively charged sorption sites available for cation sorption. Soils with larger surface areas (clays) and high pH have a greater CEC, while those with smaller surface areas (sands) have a lower CEC. AEC is a measure of the amount of positively charged sorption sites available for anion sorption. Soils with low pH have a greater AEC. Sorption studies help determine these and other measures, including equilibrium distribution coefficients used to estimate metal mobility in numerical transport models.[11]

Most metal data that DWQ receives from contractors show only the total concentration of individual metals. That is, the form (oxidation state or species) that the individual metals take is not provided. To learn more about the specific species of metals present and their potential mobility, alternate digestion methods may be used (Page and others, 1982; USEPA, 1986). Metal species determinations may also be made using models such as the popular PHREEQC (Parkhurst and Appelo, 1999), which is designed to evaluate, in part, geochemical reactions along a flowpath.

The binding of metals to organic matter, a type of complexing, is another common retention mechanism. In this case, an insoluble organic ligand (the host to which metals may complex) first adsorbs to a soil surface after which the metal complexes with the sorbed ligand. However, complexing with organic matter may not fully retain metals in some situations. For example, because organic matter generally decreases with depth, the sorptive capacity of the subsurface may be limited vertically. Moreover, if a metal complexes with *soluble* organic and inorganic ligands[12], metal mobility can actually be increased.[13] Therefore, soils with high organic content and elevated soil pH may actually mobilize metals due to complex formation. Complexing is controlled by the type and amount of metals and ligands present, soil surface properties, and soil pH and redox.

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and soluble anion, while trivalent chromium (Cr^{3+}) is far less toxic, relatively insoluble, and strongly adsorbs to surfaces. Selenate (Se VI) is more mobile but less toxic than selenite (Se IV).

[11] The equilibrium distribution coefficient (Kd) is the ratio of metal sorbed to metal in solution at equilibrium. Kd is obtained using sorption studies that evaluate a soil or soil constituent's capacity to retain a metal or several metals. These studies also evaluate the effects of changing groundwater conditions (pH, SC, addition of competing cations, addition of organic and inorganic ligands, and others). Desorption studies are used to evaluate the stability of the sorption reactions and estimate the strength of the association of the metal with the soil surface. Kinetic studies are used to estimate the length of time required for sorption or desorption reactions to reach dynamic equilibrium.

[12] Organic ligands include soluble constituents of fulvic acids in sewage sludges for example (these fulvic acids are not to be confused with humic acids which tend to retain metals). Common inorganic ligands include SO_4, Cl, OH, PO_4, NO_3, and CO_3.

[13] Metals that readily form stable complexes with soluble organic matter, such as Cu, Pb, and Hg, are likely to be mobile in soils. Khan et al (1982) showed that metal mobility followed the order (from highest to lowest): Cu > Ni > Pb > Ag > Cd. Other researchers have also shown the increased mobility of Cu, Ni, and Pb in the presence of dissolved organic matter. Metals that do not form highly stable complexes with organic matter, such as Cd and Zn tend not to be as mobile in the presence of dissolved organic matter as those that do form stable complexes.

Another complexing process that can result in the mobility of metals is colloidal transport, also known as facilitated transport. Colloids are micro particles that are very mobile in groundwater and whose surfaces have a high capacity to sorb or complex metals. A colloid is insoluble but remains dispersed in suspension and not easily filtered or settled due to their tiny size. As a result, some studies have documented much higher metal transport in the presence of colloids (21 times greater than the dissolved metal alone, as reported by Puls and others, 1991, in an arsenate study).

Metals are also retained by precipitation. Metals that precipitate from the soil solution form a three dimensional solid phase in soils. This occurs when the precipitating metal is compatible with the host mineral structure and can uniformly replace an element throughout its mineral structure. In systems having relatively low metals concentrations (and therefore excess, unused sorption sites) such as native soils, sorption often dominates precipitation as the primary retention mechanism. However, in systems with high metals concentrations such as contaminant sites, sorption sites may become filled (saturated), and precipitation of metals from groundwater may be the central mechanism that dominates retention.

To summarize, metals are retained by sorption (specific or exchange site) on host materials, complexing with insoluble (as opposed to soluble or colloidal) organic and inorganic constituents, and precipitation. Whether metals are retained or mobilized depends upon the type and quantity of sorptive surfaces present (clay minerals, organics, and Fe, Mn, and Al hydrous oxides are particularly sorptive), soil pH and redox conditions, and the concentration and type of co-mingled competing ions, organic and inorganic ligands, and colloids in the system.

It should be noted that site conditions can and do change over time, and the mobilization and retention of metals is governed by the prevailing, yet dynamic, mix of controls, including adsorption/desorption, oxidation-reduction, precipitation/dissolution, and inorganic and organic soluble and insoluble complexing. Changes in the prevailing mix of these controls may occur over short or long periods as organic compounds degrade or pH or redox changes with natural weathering or human impact. Any change in the balance of the system can change the potential mobility of metals.

Assessing the retention and mobility of individual metals

To evaluate the behavior of an individual inorganic at your permitted site, three questions should be asked:

1) does the inorganic occur as a cation or an anion?
2) what is the pH and redox potential of the soil system?
3) what is the nature of the sorptive surfaces available in the subsurface at the site?

As stated earlier, cations (metals) behave very differently than anions (non-metals). Each is retained under different soil pH and redox conditions. Cations tend to be retained in alkaline, oxidizing conditions, while anions tend to be retained in acidic, reducing conditions.

Know your inorganic: does your element of interest occur as a cation or an anion?

Cations are metals that occur as positively charged ions. These include: Ag, Al, Ba, Be, Ca, Cd, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Tl, and Zn.

Anions are metalloids and non-metals that occur as negatively charged ions. These include: As, Br, Cl, CO3, F, HCO_3, NO_2, NO_3, PO_4, and SO_4.

Some inorganics occur as either cations or anions, depending on oxidation state and geochemical conditions. These include: B, Cr, Sb, and Se.

Cation and anion retention is also controlled by the nature of the sorptive surfaces available within the subsurface at the site, with retention being greater as sorptive host surfaces decrease in size or increase in organic carbon content. Clay minerals, Fe and Mn oxides, organic matter, and calcium carbonate tend to be particularly sorptive host surfaces, as opposed to sands or other large grained inorganic soil particles. Retention-mobility information for specific inorganics is provided in Appendix B.

Cations

In general, cations tend to be mobilized in acidic soils (more H+ ions). The presence of additional H+ ions (low pH) creates additional positively-charged host sites that tend to repel the positively-charged cations and result in their mobility in groundwater. Therefore, alkaline (fewer H+ ions) clayey soils are most effective at retaining positively-charged cations, and acidic sandy soils are least effective. For systems with a pH of about 6 or higher, cations tend to be retained. Retention is first by sorption and, after the available sorption sites are filled, then by precipitation of trace metals and metals complexed with hydroxides, oxides, carbonates, and phosphates. If the pH of the system drops below about 6 or 7 these oxides tend to dissolve and release the sorbed or complexed metal ions into solution. For example, Fe, Mn, Zn, Cu, Co, and B tend to leach in soils with pH below about 6.5 and be retained at pH above about 7. Studies suggest that the relative mobility of various elements through clays follow this order: the mobility of Cr(VI) > Se > As(III) > As(V) > Cd > Zn > Pb > Cu > Cr(III) (Griffin and Shimp, 1978).

In fewer cases, cation mobility actually *increases* at pH > 7.5, as when cations form complexes with soluble organic matter. At high pH, fewer H+ ions are available to out-compete the cations for sorption exchange sites on the (negatively charged) organic matter. As a result, more cations are sorbed to the organic host. If the organic host is soluble, it, along with the cation to which it is sorbed, will tend to be released into groundwater. Moreover, when cations form complexes with negatively charged ligands, the electrostatic charge of the cation shifts from high to lower; this tends to weaken the bonds to soil particles and results in a further increase in mobility. Metals that readily form stable complexes with soluble organic matter, such as Cu, Pb, Hg, and in some cases Ni, often become mobile in organic waste-rich soils. Metals complexed with *insoluble* organic matter however tend to be retained. Khan and others (1982) showed that metal mobility followed the order (from highest to lowest): Cu > Ni > Pb > Ag > Cd, and the high mobility of Cu and Ni was attributed to their tendency to complex with soluble soil organic matter.

Poorly sorbing soils tend to be medium to large grained, with a moderate to high porosity, low capillary action, and a low cation exchange capacity.

> Because of the high potential for leaching, these soils should be sampled at greater depths in suspected contaminant source areas (such as areas of surface staining) to capture the full vertical extent of contamination.

Strongly sorbing soils tend to be fine grained (fine sands, silt, and especially clays), with a strong capillary action. Clays have a net negative charge and therefore a high cation exchange capacity, and tend to bind cation metals such as Cr(VI), Cd(II), and Pb(II). If the particle size or organic carbon content of background soils and on-site soils differ significantly, it is usually not appropriate to directly compare metals results from these respective samples.

> These soils should be sampled at the interface between fine-grained and larger-grained materials and where fine sand lenses penetrate clay soils. Clays also may form transport channels in the form of cracks due to shrink/swell and freeze/thaw effects, and therefore should be sampled in these areas and in areas that show signs of oxidation (for example where iron minerals change from a natural blue/gray color to a red/yellow/brownish color). Samples also should be collected from layers with excessive organic carbon such as darker soils, upper soil layers, and peat.

Anions

In general, anions tend to be mobilized in alkaline soils (fewer H+ ions). The presence of fewer H+ ions (high pH) means fewer positively-charged host sites that would otherwise retain the negatively-charged anions and results in their greater mobility in groundwater. Therefore, acidic (more H+ ions) clayey soils (more H+ ions) are most effective at retaining negatively-charged anions, and alkaline sands are least effective. Like cations, anion retention is controlled by pH, redox, oxidation state of the anion of interest, and available sorptive surfaces such as Fe and Mn oxides, edges of clay minerals, carbonates, and insoluble organic matter. Anion adsorptive capacity tends to be small compared with cation adsorptive capacity.

The adsorptive strength of anions onto iron oxides tends to be (from greatest to least): phosphate = silicate = arsenate > bicarbonate/carbonate > selenite > fluoride = selenate > sulfate (Balistrieri and Chao, 1987). The anions phosphate, selenite, and arsenate are adsorbed to oxides and soils through specific adsorption (strong) binding mechanisms and thus have reduced mobilities. The more mobile selenate and hexavalent chromium are only weakly bound to soil surfaces and are easily displaced by other anions. In reduced, acidic soils that are not well aerated, selenium is converted to the elemental form and is retained. Arsenic and selenium commonly occur as oxyanions with concentrations that vary spatially. Commonly occurring forms (species) of molybdenum (Mo), Se, and anions in general are m*obilized* in soils with pH > 7 and are mostly retained in acidic soils.

Observed concentrations of arsenic, chromium, mercury, lead, selenium, and others are dependent upon local geology and geochemistry. Short descriptions of the behavior of these elements are provided below.

Arsenic (As) is a metalloid that occurs in the environment as oxyanions (negatively charged). It is found naturally in some in volcanic rocks, sedimentary rocks, and sulfide-bearing rocks and ores, and is also and anthropogenic contaminant in lead arsenate pesticides, wood preservatives, coal ash, and others. Arsenic is considered to be one of the most toxic and carcinogenic among regulated contaminants, and the 2L standard is 10 µg/L.

Arsenic in the environment tends to occur in one of two oxidation states, either as arsenate As (V) or the more mobile and toxic form, arsenite As (III). The form that it takes depends on geochemical conditions. In oxidizing conditions, As (V) predominates. Because As (V) occurs as a negatively charged ion, it is easily sorbed to low pH (positively charged) soils. However, in reducing or high pH conditions, As (V) tends to change oxidation state (be reduced) to As (III). Because As (III) is un-charged, it tends to be un-attracted to charged soils and is therefore up to ten times more soluble than As (V). As (V) and As (III) may co-occur due to the sometimes slow rates of transformation between oxidation states.

Arsenic is strongly adsorbed by clay surfaces and oxides of iron, aluminum, and manganese in oxidized soils. Iron oxides are mostly clay particle-sized weathering products of other iron-containing minerals present in almost all oxidized soils. As dissolved arsenic contacts the iron oxide, the arsenic is adsorbed. This adsorption continues until the sorption sites are filled.

The adsorption of As (V) by iron oxides is greatest at low pH, while the adsorption of As (III) is greatest at high pH between 8 and 10. In a study by Griffin and Shimp (1978), As (V) sorption onto clay mineral surfaces was greatest at a pH of 5. Adsorption of As (V) by aluminum and iron oxide surfaces was greatest at pH 3-4, with a gradual adsorption decrease with increasing pH. The behavior of As (V) is similar to phosphate due to their chemical similarity and, like phosphate, As (V) readily forms precipitates with iron, aluminum, and calcium. Arsenic sorption also may be affected by the presence of competing anions such as phosphate and, in at least some cases, oxyanions of molybdenum, selenium, and vanadium.

The maximum adsorption of As (III) by iron oxide occurred at pH 7 in a study by Pierce and Moore (1980). Arsenic may also be retained through co-precipitation with metal oxides (especially iron oxides) and by its association with organic carbon.

Arsenic, particularly As (III), is also strongly adsorbed by iron (ferrous) sulfide minerals and may co-precipitate with the iron (ferrous) sulfide in highly reduced conditions and in the presence of dissolved Fe^{2+} and relatively high dissolved sulfur concentrations. However, these precipitated minerals are unstable and readily oxidize in the presence of oxygen, which may release the adsorbed or precipitated arsenic back into solution. Pyrite has a high surface area and can also readily adsorb As (III). Changes in geochemistry (pH and redox for example) can cause changes in (1) arsenic's oxidation state (and its mobility), (2) the solubility of the solid phase mineral containing arsenic, and (or) (3) the solubility of the host material providing sorption sites. As a result, in many systems, arsenic may be alternately retained and mobilized along a given flow path over time. For example, alkaline groundwater may flow through arsenic rich soil and release the previously sorbed arsenic. If that same groundwater later encounters acidic conditions for any reason, the arsenic may be re-sorbed or otherwise precipitate out of solution.

Because water-rock interaction tends to consume H+ ions, the pH of groundwater tends to increase with residence time and distance along a flow path. Iron oxide coatings, a very common sorptive surface for As, can hold large amounts of As (V) in particular, so increases to pH along a flow path can liberate the sorbed As (V) to solution.

In summary, four main mechanisms control arsenic mobility in the environment:

1) “reductive dissolution”, in which arsenic dissolves and becomes mobile under reducing conditions. Here sorbed arsenic is released by the reduction of iron oxides in soils, whereby insoluble Fe^{3+} is reduced through microbial mediation to the soluble Fe^{2+} with the consequent release of As (III) and (or) As (V). Example: Fe(III) oxide–As(V) + e- >> Fe^{2+} + As(V), As(III)s

(2) “oxidative dissolution”, in which arsenic dissolves and becomes mobile under oxidizing conditions. Here sorbed arsenic is released by the oxidation of reduced iron sulfide minerals in soils that are exposed to oxygen, with the consequent release of sulfate and As (III) or As (V). Subsequent sorption of the newly liberated arsenic may again occur to Fe(OH)3. Example: FeS-As(III) + 2 O2 >> Fe^{2+} + SO^{-2}_4 + As(III), As(V)

(3) “surface sorption site exchange”, in which sorbed arsenic is released by the exchange (replacement) of another anion like phosphate or sulfate or carbonate at sorptive surface such as iron oxide or other mineral surface, though only phosphate is competitive with arsenic. Example: Fe oxide–As(V) + phosphate >> Fe oxide– PO_4 + As(V)

(4) “dissolution of arsenic complexes”, in which arsenic becomes sorbed to a cationic ligand that itself is soluble and mobile. Example: Fe oxide–As(V) + oxalate >> Fe^{3+} - oxalate + As(V)

Finally, under conditions favorable to microbial activity (high organic matter, warm and moist conditions, and others), the formation of As III can lead to some amount of slow volatilization of As III arsine and methyl arsines from soils (the organic form tends to be released more readily than the inorganic form). As III can be oxidized to As V, and Mn oxides are the primary electron acceptor in this oxidation.

Chromium (Cr) occurs in the environment as a metal (cation) or, when combined with oxygen, as an anion. Although it may be found naturally in certain rocks (often in conjunction with ores containing other elements), it is usually associated with the production or use of metal alloys, protective coatings on metals, magnetic tapes, pigments, wood preservatives, and other chemicals. Short and long term health effects are associated with elevated levels of Cd, and the current 2L groundwater standard is 10 µg /L.

As a cation, Cr exists in two possible oxidation states: trivalent chromium (Cr III) and the more toxic and highly mobile, hexavalent chromium (Cr VI). As an anion, chromium (Cr VI) combines with oxides to form chromate and dichromate. The anion forms of Cr (VI) - chromate and dichromate – are those commonly found in soils.

In acidic settings, the positively charged iron and aluminum oxides and hydroxides coating soil particles tend to adsorb the anionic Cr (VI). However, the adsorbed Cr (VI) tends to be easily desorbed with the influx of inorganic carbon and competing anions such as phosphate and sulfate (the presence of the anions chloride and nitrate tend to have little effect on rates of chromium adsorption). Cr (VI) tends to be immobilized by clay soils containing iron and manganese oxides, and kaolinite sorption of Cr (VI) may be increased by sulfate. Precipitates of Cr (V)I are uncommon in soils with a pH of 1-9.

In alkaline soils, Cr (VI) can be highly mobile (Korte and others, 1976). In this study, soil pH was a key control, while soil properties, cation exchange capacity, surface area, and percent clay had no significant influence on Cr (VI) mobility.

Cr (III) may complex with soluble organic ligands which will increase its mobility. This complexing also may facilitate the oxidation of Cr (III) to the more mobile and toxic Cr (VI). Cr (III) can also be oxidized in some soil conditions; oxidized manganese, which serves as an electron acceptor, is an important factor in this reaction.

Cr (III) forms hydroxyl complexes in natural water, is readily adsorbed by soils, and tends to precipitate between pH 4.5-5.5. Cr (VI) can be reduced to Cr (III) at a slow rate (sometimes requiring years) under normal soil pH and redox conditions, with soil organic matter acting as the electron donor in the reaction. The rate of this reaction is more rapid with decreasing soil pH. In surface soils, organic matter is the principal electron donor for the reduction reaction, but in subsurface soils where organic matter occurs in low concentration, Fe II containing minerals reduce Cr (VI) if the soil pH is below 5.

Iron (Fe) occurs in the environment as a cation (metal) and may take one of two common forms: insoluble ferric iron (Fe^{3+}) or soluble ferrous iron (Fe^{2+}). Iron is very common in rocks found across NC and is considered a nuisance contaminant due to aesthetic issues (taste, odor, and staining) rather than health effects. The current 2L groundwater standard for Fe is 300 µg/L.

The most common source of iron in groundwater is from weathering of iron bearing mineral oxides and rocks. Anthropogenic sources include sewage and landfill leachate, acid mine drainage, and industrial effluent. Like sulfide, iron is often associated with coal seams as ferrous sulfide. In some cases, these anthropogenic sources may change the geochemistry (for example lower the pH or decrease the dissolved oxygen (DO) content) of a groundwater system and thereby liberate otherwise insoluble forms of naturally occurring iron to the groundwater.

Iron is unstable in the environment and readily changes oxidation state and degree of solubility as geochemical conditions change. In oxic settings, insoluble ferric iron Fe^{3+} is retained as iron oxide coating on soils, weathered rocks, and bedrock fractures. If the pH becomes low for any reason or the setting becomes anoxic (reduced redox conditions), the otherwise insoluble ferric iron is reduced to the soluble ferrous iron Fe^{2+} and readily dissolves into groundwater. For example, high concentrations of ferrous dissolved iron can occur in areas where ferric oxyhydroxides are being reduced. Because deeper wells tend to be less oxygenated than shallow wells, dissolved iron concentrations may in many cases (though not all) be higher in deeper rather than shallow wells. Similarly, sorbed iron (Fe^{3+}) may be released in groundwater as Fe^{2+} in soggy, waterlogged wetland areas characterized by low DO.

High dissolved iron can also occur in areas where ferrous sulfides are being oxidized; in this case, the sulfur is acted upon first and altered to sulfate, thereby releasing the ferrous iron.

Ferric iron often forms complexes with anions such as hydroxide (OH-), chloride, fluoride, sulfate, and phosphate. Iron, when it occurs as a component of hydrous oxides, is also an important *host* surface for the sorption of other metals.

Ferrous and ferric iron can also combine and complex with various organic substances, including organic acids and tannins, a condition that is more common in shallow wells or wells affected by surface water.

Because of its instability, dissolved iron concentrations in a well vary with well depth, location, and local geology. Iron concentrations also may fluctuate over time in wells affected by changes in DO, such as those that are influenced by rapid recharge or surfaces water interactions.

Iron concentrations may vary widely in wells across a given facility, and care should be taken to understand the geochemical conditions (DO and pH, in particular) occurring in the well at the time of sampling and how these conditions compare to other facility wells. In many cases, high iron levels in only a portion of facility wells that are screened across a similar groundwater horizon may indicate that a contamination release may be directly (iron source) or indirectly (altered geochemistry that has released iron to groundwater) affecting groundwater at the site.

Manganese (Mn) occurs in the environment as a cation (metal) and may take one of three common forms: Mn^{2+}, Mn^{3+}, or Mn^{4+}. Manganese in the environment behaves very similarly to iron. For example, insoluble manganese oxides become dissolved in groundwater to the soluble form of manganese (Mn^{2+}) under low pH and (or) reducing conditions. However, the soluble form of manganese is often considerably more stable than its counterpart ferrous iron in oxic groundwater. Moreover, high iron and manganese may co-occur, but this is not always the case. Nevertheless, in general, the factors associated with iron – discussed above - are similar to those of manganese. The current 2L groundwater standard for Mn is 50 µg/L.

Lead (Pb) occurs in the environment as a cation (metal). Although it may be found naturally in certain rocks, it is usually associated with the lead acid batteries, alloys, building materials, radiation shields, and others. Lead is highly toxic, and the current 2L groundwater standard is 15 µg/L.

Lead readily reacts with clays, phosphates, sulfates, carbonates, hydroxides, and organic matter and is less soluble than other metals. At $pH > 6$, lead adsorbs on clay surfaces or forms lead carbonate. However, lead has a strong affinity for organic ligands, and the formation of these complexes may greatly increase the mobility of Pb in soil. Although leaded gasoline is no longer used, Pb in soils may be recalcitrant and somewhat elevated in the top few inches of soil along highways; care should be taken when sampling in these settings.

Mercury (Hg) occurs in the environment as a cation (metal). Although it may be found naturally in certain rocks, it is usually associated with the production or use of dental amalgam, thermometers, vapor lamps, preservatives, and other chemicals. Mercury is highly toxic, and the 2L groundwater standard is 1 µg/L.

Mercury is retained by adsorption, precipitation, and volatilization. As with other cations, retention increases with increasing pH. Mercury occurs as three oxidation states in soils: elemental mercury (Hg), mercurous ions (Hg I), and mercuric ions (Hg II). The species that occurs depends upon the soil pH and redox potential. Hg I and Hg II are adsorbed by clay minerals, oxides, and organic matter. Retention of Hg I and Hg II also occurs through the formation of precipitates. Hg II will form complexes with soluble organic matter, chlorides, and hydroxides that contribute to its mobility.

Under mildly reducing conditions, organic and inorganic complexes of mercury can be degraded to the elemental form of mercury (Hg) which can be converted to the volatile methyl or ethyl mercury by biotic and abiotic processes. Methyl and ethyl mercury are toxic, volatile, and soluble. In one study, volatilization increased with decreasing cation exchange capacity of the soil (Rogers, 1979).

Hg I may precipitate with chloride, phosphate, carbonate, and hydroxide, but at typical soil concentrations, only phosphate precipitate is stable. Hg II may precipitate, in alkaline soils, with carbonate and hydroxide to form a stable solid phase; and in acidic soils with high Cl, $HgCl_2$ is formed.

Selenium (Se) occurs in the environment as an anion (non-metal). Selenium is found in sulfide ores such as pyrite (FeS_2) where it replaces the sulfur. It is used in glass making, pigments, photo cells, and others. Selenium is toxic at elevated concentrations, and the current 2L groundwater standard is 20 µg/L.

Selenium exists in the soil environment in four oxidation states: selenide, elemental selenium, selenite, and selenate. The oxidation state and mobility is controlled by soil pH, redox, and soil composition. Similar to other anions, selenium is more mobile at higher pHs. Mobility is also favored in oxidized conditions and in conditions of high Se or other anions (like phosphate) that can displace and de-sorb some of the previously retained Se. As the concentration increases, the limited number of strong specific adsorption sites becomes saturated and the lower binding energy exchange sites are utilized resulting in less retention.

Selenate is the predominant form in calcareous soils, and selenite is the predominant form in acidic soil. Selenite binds to iron oxides; this retention increases with decreasing pH. Maximum retention of selenite on clay minerals seems to occur at pH in the range of 2-3, and the sorption decreased at pH 4-9. Studies of competitive adsorption showed that selenite adsorption decreased significantly in the presence of phosphate and organic acids but not in the presence of sulfate or chloride. Using iron oxide, adsorption strength has been shown to be: phosphate = silicate = arsenate > bicarbonate carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate.

Selenate is the dominate species in alkaline conditions. Unlike selenite, selenate is highly mobile in most soils. Selenate is adsorbed to clays, Fe and Mn oxides, and organic matter. Organic forms of selenium, due to biomethylation, include volatile methyl selenides.

Zinc (Zn) occurs in the environment as a cation (metal). Zinc occurs naturally in certain rocks (with other ores such as Cu and Pb) and is associated with the production and use of alloys, anti-corrosion agents, batteries, supplements, shampoos, luminescent paints, electrical contacts and conductors, alloys, disinfectants, microbiocides, and other commercial and industrial applications. The current 2L groundwater standard for Zn is 1 mg/L.

Zinc is readily adsorbed by clay minerals, carbonates, and hydrous oxides (particularly Fe and Mn oxides). As with other cations, Zn adsorption increases with pH; Zn hydrolyzes at pH > 7.7 and strongly adsorbs to soil surfaces in these conditions. In polluted soils, the greatest percentage of total Zn may be adsorption to Fe and Mn oxides. Precipitation generally is not a major mechanism of retention of Zn in soils because of the high solubility of Zn compounds. Roadside soils can contain elevated Zn from tire debris, so care should be taken when sampling in these settings.

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[14] Breckenridge and Crockett (1995) describe methods by which soil and sediment background levels are determined; provide published ranges of ambient metals concentrations; provide sources (for example, sewage sludges, nitrogen fertilizers, manure, pesticides, etc) and corresponding concentration ranges of metals in soils; describe sampling strategies for different metals and geologic settings; and describe various statistical tests needed for appropriate interpretation of background soils data. Their report focuses on metals contamination in soil, the science behind their mobility, and statistics needed for site evaluation.

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Chapter 2 – Collecting Valid Groundwater Compliance Data

Determining "reference background" (background) is an important part of DWQ's permit review and compliance process. Reference background is the officially accepted value of a given inorganic that represents ambient background conditions. In some cases, concentrations at the compliance boundary are compared to the reference background to determine permit compliance.

Ambient metals concentrations are controlled by parent geology[16] and may vary spatially across a site and from one facility to another. As such, "normal" concentration ranges for a given metal may vary considerably from site to site[17]. While published background ranges are useful for general comparisons (see references listed in Appendix A), the only sure way to determine background levels is to collect samples. Moreover, to be of value, background data must be technically defensible and appropriate for use in permit decisions.

In many cases reference background will be relatively easy to establish. However, at some sites the determination of background may be more difficult. These may include larger, more complex sites, or sites where background concentrations are nearly the same as compliance boundary concentrations, NC groundwater quality (2L) standards, or permit limits. They may also include sites where the local geology contains the same inorganic constituents as the permitted wastes. To withstand technical scrutiny, it is critical that background data be collected in a scientifically defensible manner.

This section addresses the collection of defensible groundwater compliance and background data. It is designed as a checklist to help ensure that key issues are considered, from planning to collecting and assessing data. This information does not supersede existing guidance, policy, or regulation, and is not intended to cover every issue that a site manager may encounter.

Determining the quality and amount of data that will be needed for the site in question. This determination should be based on the physical complexity of the site, the spatial extent and complexity of the waste disposal practices, and the degree of controversy that the site is expected to elicit. For example, are background concentrations expected to be similar to 2L standards, similar to on-site concentrations at the compliance boundary, or otherwise controversial? Will the site be used as a precedent for similar sites in the state? Will statistical proof be required to justify a non-compliance

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[16] Background metals concentrations may be influenced not only by parent geology but also by historic contaminant releases in the area. These contaminants may include metals from wet and dry atmospheric deposition (including vehicle emissions) and from historic land uses like industrial activities, mining, land-filling, crop and animal production, and sewage sludge application.

[17] For example, Se concentration in non-seleniferous soils in the U.S. range from 0.1 to 2 mg/kg, but in seleniferous soils range from 1 to 80 mg/kg with highs up to 1200 mg/kg (McNeal and Balistrier, 1989).

determination? Is site geology expected to vary horizontally or vertically across the site? Are off-site wastes likely to migrate to and contaminate background or compliance boundary wells? Have hydrogeologic anomalies been identified? Have wastes been disposed across particularly large or undocumented areas? Answering yes to any of these questions may mean that greater numbers and types of compliance and background samples are needed. At a minimum, collected data should measure maximum concentrations of permitted waste constituents that exist at the compliance boundary and at ambient background locations, along with any spatial or temporal trends. Moreover, sample numbers and locations should align with statistical data needs as outlined in Chapter 3.

Selecting well locations and screen depths needed to build a defensible dataset. The site manager must determine the maximum contaminant concentrations at the compliance boundary (along with any spatial or temporal trends) as well as reference background. A valid background sample reflects ambient groundwater from conditions geologically similar to those on site. Therefore, background data should be collected from a hydraulically upgradient location (outside the influence of site wastes) in immediate proximity to the site and within the same groundwater horizon (depth/zone) as samples collected from compliance boundary wells. The number of background wells and samples will be driven in part by any statistical monitoring and (or) compliance strategies (see Chapter 3), as applicable.

Because dissolved contaminants move in the direction of groundwater flow, the site manager must have an accurate and thorough understanding of horizontal and vertical flow gradients[18] across the site. While flow gradients are easily determined at some sites, at others they are more complex due to one or more complicating factors[19]. It is the responsibility of the site manager to identify and evaluate any factor(s) that may complicate otherwise predictable groundwater flow patterns or cause the mis-placement of monitor wells or screened intervals. Each of the following should be considered for the site in question.

a) Has a conceptual hydrologic model of the site been formulated? Such a "model" represents the current hydrogeologic understanding of the site and includes simplified assumptions about site geology, recharge and discharge, groundwater flow paths, and contaminant sources and receptors. It is the starting point for any groundwater investigation or monitoring plan and should be improved and built upon as new information is available. Much can be known about a site prior to collecting any "hard" data (see LeGrand, 2004, for example), and this knowledge (and the conceptual model itself) should be refined and updated as data are collected. All other

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[18] Groundwater movement is from higher to lower hydraulic heads, and follows Darcy's law where $Q = kA (h_1-h_2)/L$. (Q = flow rate, k = hydraulic conductivity, h = potentiometric head, L = distance between points 1 and 2, and $(h_1-h_2)/L$ = hydraulic gradient.)

[19] Factors that may create complex or unpredictable flow patterns include seasonal or storm induced rainfall variations, physical characteristics of the site such as land cover, geomorphic or abrupt topographic changes, pumping affects, geologic anomalies, and others.

investigative questions (including items b. through o. below) are intended to improve the conceptual model (understanding) of the site.

b) Are horizontal hydraulic head gradients adequately understood? Horizontal hydraulic head gradients typically are determined by measuring a minimum of three monitor wells synoptically. All measured wells must be screened across similar depths within the same portion of the groundwater system (saprolite, transition zone, or bedrock). In particularly flat areas with uncertain recharge and discharge characteristics, additional wells/water levels may be needed to adequately assess flow directions across the site.

c) Are vertical hydraulic head gradients adequately understood? Vertical hydraulic head gradients typically are determined by measuring a minimum of two nested monitor wells synoptically. Each well should be screened across different portions or depths of the groundwater system. The vertical head gradients are used to identify or confirm areas of groundwater recharge (downward gradients) and discharge (upward gradients) and to ensure proper sampling depths. Dissolved contaminants can move downward into the fractured bedrock flow system and re-emerge in downgradient bedrock supply wells, shallower wells, and (or) discharge areas. For this reason, sampling of bedrock and (or) nested wells often is needed to determine potential concentrations along deeper flowpaths. Depending on the size, topographic setting, and proximity to surface waters, some facilities may require more than one set of nested wells to evaluate vertical groundwater movement in different parts of the site and to ensure that contaminants are not missed at the compliance boundary due to underflow of the sampled interval.

d) Do seasonal variations in rainfall and evapotranspiration rates substantially change groundwater flow patterns? How about high intensity storm events?

e) Is the site covered by large impervious areas, and if so, do these affect the direction of groundwater flow? Large impervious areas may affect the distribution of local recharge and thus the “shape” of the water table and resulting groundwater flow directions.

f) Have nearby pumping wells (within a radius of about 300 to 500 feet) affected hydraulic gradients at the site and, if so, do these affects change with season or over time?

g) Do confined, artesian, perched, or other anomalous conditions affect the movement of groundwater beneath the site?

h) Does geology (particularly the lithologic composition) vary spatially or with depth across the site? And do naturally occurring dissolved metals concentrations vary spatially or with depth across the site?

i) To what extent does anisotropy (elongated or otherwise irregular plumes) in the shallow subsurface (regolith, for example) and deeper flow system affect groundwater flow directions and contaminant movement?

j) Do geologic discontinuities such as prominent fractures, faults, lineaments, weathered igneous intrusions, quartz veins, contacts between different rock types or flow zones (transition zone or uneven weathering, for example) or other preferential groundwater flow paths (artificial conduits, others) affect the direction and rate of groundwater flow and contaminant transport?

k) Does geomorphic setting affect the direction and rate of ground water flow and contaminant transport?

l) Do nearby supply wells affect contaminant movement in the area of the facility. If supply wells are nearby (within a radius of about 500 to 1,500 feet) and operational, it should be determined whether these affect drawdown in the monitor wells which could, in turn, affect contaminant flow paths near the well. A level logger-type transducer may be placed in the site monitor well for several days during dry conditions (to avoid storm-related fluctuations) to evaluate potential supply well interference.

m) Are there groundwater users or surface discharge areas such as streams and springs downgradient and in proximity to the site? In most cases these should be identified, mapped, and considered to be potential receptors.

n) Does proximity to surface water (streams, lakes, ponds, or lagoons) affect the movement of groundwater contaminants? Are vertical hydraulic gradients in the vicinity of the surface water feature understood and do they fluctuate with season, drought, or storm event? It is important to determine whether nearby surface waters are receiving or contributing to groundwater flow and whether this may change in space or time.

o) Does proximity to surface water (streams, lakes, ponds, or lagoons) affect the ability to measure groundwater quality? That is, does the location of the feature affect the optimal placement of monitor wells and the ability to measure groundwater at the compliance boundary?

p) Does the substrate at the groundwater-surface interface (organic soils, rock, sand, silt, clay) affect the potential for contaminants to degrade? Does this substrate affect contaminant transport into or out of the surface water feature?

q) Does near-stream topography or geology (structural features, transition-zone exposure / thickness, bedrock fractures, or others) affect groundwater-surface water interactions and (or) contaminant transport?

r) What effect does a riparian buffer, if present, have on the contaminant transport and attenuation?

s) Do surface water features occur within or directly adjacent to the facility? If a groundwater discharge feature such as a stream or river cuts through a permitted site, care must be taken to ensure that groundwater contaminants are not discharging to the feature and leaving the site by surface flow. If these features are located at or just inside the compliance boundary, contaminant transport modeling may be required to augment samples collected from sub-optimally placed wells. In either case, stream sampling should be conducted at the point where the stream outfalls the facility.

t) For sites with 2L violations at the compliance boundary, has the volume of groundwater flow and mass transport of contaminants from the site been estimated or modeled? Can stream monitoring of conductivity, temperature, and other techniques be used to determine groundwater flow and contaminant transport from the site? Groundwater discharge to surface water may, in some cases, result in significant attenuation of contaminant concentrations by the process of dilution.

u) If applicable, has groundwater investigation, groundwater modeling (flow and contaminant transport), and (or) compliance evaluation been conducted appropriately and in accordance with DWQ policy?[20]

Policy regarding hydrogeologic investigation and reporting may be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=8d7532b6-c7ac-4ba6-8fb4-9f6a66799b52&groupId=38364

Policy regarding groundwater modeling may be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=06a29223-336a-40e4-93ff-41f95e6017ba&groupId=38364

Policy regarding groundwater compliance evaluation of long-term permitted facilities with no prior groundwater monitoring requirements may be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=30b6c9bb-2a82-449b-8288-c4e999093f94&groupId=38364

Assessing the extent and appropriateness of existing background data

a) Do background data exist at the site, and do they represent true background conditions?

b) Do county or regional water quality background data exist, and are these data applicable to conditions found at the site?

c) Are background wells upgradient of suspected contaminant sources?

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[20] All DWQ policies are subject to change. Additional information regarding policy and revisions may be found at http://portal.ncdenr.org/web/wq/.

d) Are background wells located in a comparable geologic setting as compliance wells?

e) Are background wells screened across similar groundwater horizons (for example, saprolite, transition zone at top of bedrock, or particular fracture zone) and (or) depths as compliance wells?

f) Are background wells measuring groundwater that has been impacted by historic releases un-related to the current permit?

g) Are additional background wells needed, and is it known whether background conditions vary spatially? This is particularly important at larger sites, sites underlain by heterogeneous rock types, and when pooling background data for use in statistical comparison tests. Having data from more than one background well can help determine whether or not background concentrations vary spatially.

Assessing the type, extent, and behavior of site wastes

a) What inorganic constituents are likely to occur in the site wastes? Are these expected to occur in the local geology?

b) Are waste locations known or unknown (buried material, pipeline leaks, spills, basin overflow, and others), and are they localized or dispersed across large areas?

c) Which inorganic constituents are likely to be mobilized and transported most easily? Which are likely to be unstable (that is, able to be retained and re-mobilized quickly and easily based on changing geochemical conditions)? Do any of the inorganics of concern commonly have more than one oxidation state (if so, these may need to be speciated during sampling)?

Ensuring that groundwater samples are representative of formation water and are unaffected by materials introduced during well construction or by water from overlying or underlying intervals. <u>Turbidity must be absolutely minimized</u> by proper well design, installation, development, and sampling technique. This is especially important for the collection and analysis of metals since, according to DWQ policy – metals samples must be collected *unfiltered* and are therefore susceptible to sorption on suspended materials.

a) Were careful attempts made to minimize formation disturbance during well drilling and construction?

b) Did the selection and placement of sand filter pack material, bentonite plug, and grout strictly follow all requirements stated in the approved sampling and analysis plans?

c) Was each well thoroughly and properly developed? Well development should strictly follow the requirements stated in the approved sampling and analysis plans, and detailed well development field notes (technique, who, how long, approximate volume removed, etc) should be provided for each well. The need for thorough and complete well development cannot be overemphasized. The goal is to remove turbidity introduced by well cuttings and drill fluids and ensure a proper connection to the screened formation water.

d) Did turbidity compromise the quality of any water sample? Metals may sorb to suspended particles and be digested and included in the laboratory sample as part of sample preparation protocols. The suspended metals would thus be added to the dissolved metals, even though the suspended metals generally would not be transported readily in moving groundwater[21] (and may not be representative of the formation water itself). Importantly, this can affect data consistency and comparability within and between wells. Samples collected under even partially turbid conditions can vary from sample event to sample event as the amount of turbidity changes. Because the official policy of DWQ is to collect unfiltered (rather than filtered) samples at permitted sites it is critical that sample waters be free of turbidity. The DWQ policy on metals collection and analysis using Method 3030C was revised on January 7, 2011 and may be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=2fcae529-e6fc-46a6-aa29-514e7ed57259&groupId=38364

e) Was low flow sampling used? A common method for minimizing or eliminating turbidity from a groundwater sample is low flow sample purging. This technique should be considered when collecting well samples, and the following link provides details about its use. http://www.epa.gov/tio/tsp/download/welldevelp.pdf

f) Were sample methods and purge conditions[22] similar across all sampling events? It is important to use the same sampling and digestion methods and recreate similar purge conditions (purge rate, purge time, and drawdown) at a given well for each sample event in order to maximize consistency and comparability among all sampling events. Sampling a well at different purge rates may result in varying turbidity levels which may, in turn, cause varying water quality results.

g) Were turbidity and total suspended solids collected, analyzed, and reported for permitted wells? Although these parameters may or may not be required by permit conditions, they are often helpful in evaluating turbidity differences between wells. This information often is valuable when determining whether background concentrations vary spatially.

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[21] A possible exception to this is a metal sorbed to a colloid (not dissolved, but small enough to be mobile in groundwater) that can be transported in moving groundwater.

[22] DWQ policy on well purge volumes may be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=df3d7e5c-21c9-4b7d-9175-5464c7e4096f&groupId=38364

Reviewing all current and historic data for appropriateness, including well and screen placement, sample procedures, laboratory protocols, and others.

a) Are wells properly sited to measure any known changes in geology across the site? At some sites, dissolved inorganic concentrations may vary by geologic unit and depth.

b) Have all inorganics of concern been sampled?

c) Is it necessary to determine the oxidation state (species) of individual metals to better understand the retention and mobility dynamics at the site? Special field and (or) lab techniques are needed to speciate individual metals.

d) Are detection levels low enough to be useful?

e) Are soil data consistently presented on the same basis (either wet or dry weight)?

f) Were field meters calibrated properly for all sampling events? Outliers or drift, particularly among pH data, can occur from faulty or uncalibrated field meters and result in incorrect data and temporal trends that are statistically invalid.

g) Were samples collected and handled properly and consistently for all wells and sampling events? (Different collection methods, sampling purge times and drawdowns, holding times, preservatives, sample temperatures, and others can affect results.)

h) Were water samples collected during relatively similar hydrologic conditions from sample event to sample event? This is typically needed to maximize consistency and comparability among all sampling events. For example, a contaminant flush may occur immediately following a heavy rainfall, and inorganic concentrations may be higher at this time than a sample collected during an extended dry period.

i) Were turbidity levels during sample collection consistent for all wells and sampling events? If not, did turbidity appear to affect metals concentrations? Turbidity can introduce excess suspended metals into the samples and result in elevated, inconsistent, and incomparable metals results.

j) Were samples analyzed properly and consistently for all wells and sampling events? Different sample preparation and digestion methods, lab methods and instruments, detection limits, and calibrations may affect results and comparability.

k) Were analytical interferences or dilution effects measured for any metals? The Laboratory uses data qualifiers (for example, J = estimated; Q = holding time exceeded; etc) to report any interference or other quality control issue. These qualifiers highlight data that may be affected, either positively or negatively, and they should be reviewed carefully.

l) Were quality control samples collected and reported for each sampling event, and have these data been reviewed? These include duplicates, equipment blanks, and others. Collection of equipment blanks, for example, can help rule out equipment-related or cross-well contamination, an issue especially important when low concentrations of metals are observed in wells otherwise thought to be uncontaminated.

m) Were data transcribed and computed properly, including dilution factors, statistical computations, etc?

Interpreting results

a) Were elevated metals concentrations detected in background wells? If so, do they reflect natural conditions? Do they reflect contamination from permitted activities? Do they reflect historic releases unrelated to the current permit (for example, elevated arsenic in soil may be due to the use of legacy pesticides on historic farmland, and elevated lead in soil may be from auto emissions)? Are the wells positioned properly? Do background concentrations vary spatially or temporally?

b) Are the metals detected in background wells the same as those in the permitted waste leachate and do they occur in similar ratios? If yes, this may indicate that the background well is impacted by site waste. If a background well is not representative of true background conditions, it should be replaced.

c) Were elevated metals concentrations detected in compliance boundary wells? If so, do they reflect natural conditions? Do they reflect contamination from permitted activities? Do they reflect historic releases unrelated to the current permit? If the wells or screen depths were positioned differently, would higher concentrations be likely?

d) Were elevated metals concentrations detected in soil samples? If so, what is their suspected source?

e) Are there known or suspected preferential groundwater flow paths that affect where contaminants are likely to be observed or not observed, and if so, were elevated concentrations observed in these areas?

f) Do background constituent concentrations vary significantly from concentrations in compliance wells? Are the differences due to local or systemic geologic or geochemical differences (background wells in one formation and on-site wells in another, for example)?

g) Do constituent concentrations vary spatially or temporally in background wells? In compliance wells? If so, are these differences due to storm-induced, seasonal, or long term hydrologic trends at the site? Are these differences due to corresponding differences in geochemical conditions? Because pH, redox, DO, specific conductance (SC), total dissolved solids, and major ions are commonly related, often they can be used to understand contaminant occurrence at a site.

h) Are subsurface physical properties that control retention and mobility of individual contaminants adequately understood? Are these properties similar (and thus comparable) at background and on-site areas? Particle type and size, organic content, parent geology, degree of weathering, subsurface structural discontinuities, and others have a significant effect on metals retention and mobility. For optimal comparability, the aquifer materials associated with compliance and background wells should have similar sorptive surfaces (type, particle size, organic content, and Fe, Mn, or Al hydroxide content, CEC, and AEC).

i) Are the geochemical conditions that control retention and mobility of individual contaminants adequately understood? For example, are the soil pH and redox known? Are these properties similar (and thus comparable) at background and on-site areas? (pH, redox, and others have a significant effect on metals retention and mobility.) For example, a background well with reducing conditions may be expected to have higher dissolved metal (cation) concentrations than a background well with oxidizing conditions.

j) Is microbial degradation occurring at the site and to what extent and, if so, are oxidation states (and mobility and toxicity characteristics) changing for individual metals of concern? Are data adequate to evaluate these conditions? Is it necessary to determine the oxidation state (species) of individual metals to better understand the retention and mobility dynamics at the site?

k) Are background wells screened at the same depth interval as that of the compliance wells? This is typically needed to ensure that water level and water quality data are being evaluated from similar and comparable hydrogeologic horizons.

l) Have changes in the groundwater system caused water quality changes to groups of background wells or groups of compliance wells? For example, do time series water quality data show parallel and simultaneous spikes or dips within *all* background wells or within *all* compliance wells that were analyzed at about the same time? Is this due to changes in hydrology (rainfall patterns), sample collection, or sample analysis?

m) Are metals concentrations likely to move off site under existing or possible future site conditions (for example, changing geochemistry, groundwater pumping, or additional releases)?

n) Are the quality and documentation of the data acceptable? Do the data allow valid statistical conclusions to be drawn? For example, the use of different values for non-detects with different detection limits can result in changes to background prediction (and reference background) limits.

o) If statistics were used (see Chapter 3), was a correct assumption made concerning the underlying data distribution (normal, lognormal, etc)? Was an appropriate test selected and were its underlying assumptions followed? Were the data used in the test of adequate quality? Was the test computed and interpreted correctly? Were false positive error rates and power appropriately balanced? Is there confidence that the final interpretation is not a false positive or false negative result and is that confidence level clearly documented?

Identifying potential artifacts or issues that could skew findings

a) Were observed metals a result of drilling fluids or grout? Samples collected soon after well installation may have turbidity issues related to drill cuttings and insufficient development. Metals sorbed to these suspended materials may cause metals concentrations to appear high.

b) Has turbidity or sedimentation increased over time in any of the sampled wells and, if so, was the increase associated with an increase in metals concentrations? Was increased turbidity associated with hydrologic changes (storm events, for example), improper well construction, or inadequate well development?

c) Have well casings or other plumbing materials released metals to the groundwater sample?

d) Was the sample purge rate and drawdown about the same across sample events? During low flow sampling, differing purge rates may draw water from different depths of the groundwater system.

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Chapter 3 – Applying Statistical Methods to Groundwater Data

Permit decisions must be based on the proper interpretation of scientifically defensible groundwater compliance and background data. Data interpretation may range from simple, descriptive statistics (median, mean, standard deviation, 25th and 75th percentiles, etc) to correlations to formal statistical comparison tests that help determine, for example, whether contaminant 2L exceedances are due to natural background or site conditions. Applying statistics to groundwater compliance data requires that certain assumptions and procedures be followed and that appropriate test(s) be used. The purpose of this section is to (1) review key statistical concepts and their relationship to groundwater compliance data, (2) discuss some of the statistical procedures and tests commonly used for background and compliance determinations, and (3) provide recommended references that describe the selection and use of statistical tests for groundwater compliance data.

Because of the variety and complexity of site conditions, groundwater contaminant mixtures, and statistical approaches, a step by step "how to" guide to statistical testing and background determination is beyond the scope of this document. Instead, the report provides a practical overview of the issues that must be understood and addressed when conducting any statistical analysis of facility groundwater data and points the reader to key references on the subject. It is meant to be a starting point to orient the site manager to the issues involved in statistical analysis of groundwater compliance data. The site manager is strongly encouraged to consult the recommended (or similar) references including EPA (2009), and when in doubt, to seek out the expertise of qualified individuals with a background and experience in groundwater statistics.

Key Statistical Concepts and Their Relationship to Groundwater Compliance Data

The use of statistics is essentially an exercise in formally describing, correlating (that is, observing relationships among), and comparing data. Descriptive statistics are used to understand a dataset in terms of its central tendency (mean and median, for example), spread (standard deviation and percentiles, for example), and skewness. Correlative statistics are used to determine relationships among data and often include correlation analyses and linear regressions. Comparison statistics evaluate potential differences between two or more groups of data (typically during detection monitoring) or between a dataset and a fixed value (typically during compliance or corrective action monitoring). For the site manager analyzing groundwater constituent data, comparison tests typically will be: (1) between wells or groups of wells that measure different settings (compliance boundary wells versus background wells) (inter-well comparisons); (2) within a single well that measures changes in water quality in time (intra-well comparisons); (or) (3) between a 2L standard (or, occasionally, another permit limit or background) and water quality data from a compliance boundary well.

Exploratory data analysis and graphical displays Usually the first step a site manager will take in an evaluation of groundwater compliance data is to table and describe the data. This is done (for each contaminant of concern) with summary statistics, such as mean, median, geometric mean, maximum, standard deviation, and 25th and 75th percentiles. This is typically followed by an assessment of any spatial or temporal trends (concentration versus distance, location, or time) or other data correlations (Pearson Product Moment Correlation for normally distributed data or Spearman Rank Order Correlation for non-normally distributed data). This initial assessment of the dataset is often referred to as "exploratory data analysis" in which the site manager begins to understand the dataset, potential patterns, outliers, 2L exceedances, and how presumed background data compare to compliance data. Central to this "exploration" is the graphical presentation of the data using displays such as box plots, scatterplots, histograms, and others (Helsel and Hirsch, 2002). These displays are critical to providing insight into the dataset and help to illustrate key concepts and findings when presenting the results to others. Graphical displays often help the analyst avoid misinterpretations of results (for example, two datasets can have very different scatterplots but identical correlation coefficients).

Statistical comparison test concepts and assumptions Once the data have been initially explored and graphed, more robust comparison testing may be appropriate to discern statistically significant differences between various groups of data and to establish background for constituents of concern. For example, background data (from one or more wells) may be compared to compliance data, different compliance wells may be compared to one another, or compliance wells may be compared to a fixed 2L standard. In these comparisons, means, medians, and (or) variances (obtained from all sample events and wells in the group) are statistically tested and compared.

The central objective in formal statistical testing is to identify contamination that is real (site related) and reject contamination that is not real (not site related). Using statistical terms, tests must minimize the likelihood of false negative errors (and thereby increase the power of the test) while minimizing the likelihood of false positive errors. These concepts, as well as other basic statistical concepts (hypothesis testing, normality, independence, and others) form the foundation for statistical testing of groundwater compliance data and are introduced below.

Statistical test design A formal statistical test approach must be designed for a facility based on several factors including size and complexity, number and configuration of wells, site hydrology, and constituents being sampled.. The approach should also be based on the statistical characteristics of the sampled constituents, including presense or absence of spatial variability, proportion of non-detects and outliers, type of data distribution (normal, log-normal, non-normal). The design will also be based on the tolerance for false positive and false negative errors.

Finally, the monitoring status (detection versus compliance versus corrective action monitoring) will affect the design and the way the selected tests are carried out. Detection monitoring is the first stage of groundwater monitoring and typically involves the testing of compliance data against a standard and background. In this case background is assessed and established to ensure that ambient conditions are not elevated and resulting in elevated compliance testing. A choice must be made whether separate upgradient wells or past intrawell data provide the most representative and appropriate background data. Compliance and corrective action monitoring are required once exceedance of groundwater standards have been demonstrated. In this case, compliance data typically are tested against a fixed standard or other agreed upon level to evaluate the success of the selected corrective action. Often tests against a fixed standard use a lower confidence limit which is established based on whether the fixed standard limit represents an average concentration, an absolute maximum/ceiling/or upper percentile, or whether the compliance data demonstrate a trend over time. Any approach taken must be carefully developed, documented, referenced, and vetted.

Hypothesis testing Formal statistical comparisons are made using a concept known as "hypothesis testing". Hypothesis testing is a fundamental tenet of statistical theory in which two sets of data are compared according to a "null hypothesis". An example of a null hypothesis is, *there is no difference between the mean contaminant concentration at the compliance boundary well and the background well*. The "alternate hypothesis" would be: *the mean concentration for the compliance well is different from that of the background well.* The tests are conducted at pre-selected probability and confidence intervals to determine whether the null hypothesis holds true at the selected confidence level. For the site manager, if it is shown for example that the mean contaminant concentration at a compliance well is statistically different than the mean at the background well(s), the site may have a contamination issue and be non-compliant. Hypothesis testing is used to make that comparison and helps the analyst minimize errors about contamination presence or absence by specifying confidence levels.

Test power, false positive errors, and false negative errors The *power* of a test refers to its ability to correctly indicate contamination when it is present. Power is directly related to the probability of false positive and false negative errors, and these error levels are established when constructing the statistical test approach for a facility. Indicating that contamination is present when it is not is referred to as a *false positive* (Type I) error. Failing to detect contamination that is actually present is referred to as a *false negative* (Type II) error. These errors are mathematically related so that increasing one automatically decreases the other. Both error types must be minimized and balanced to produce a sound and reasonable overall approach[23].

The selected statistical test approach must also avoid what is referred to as "the multiple comparisons problem" in which the likelihood of a false positive error compounds as additional tests are run. As EPA (2009) states, "if enough tests are run, at least one test is likely to indicate contamination when none exists". To avoid this issue several strategies may be considered[24]: (1) the number of tests can be decreased (for example, in some cases the number of constituents of concern to be formally tested may be reduced to those most that are most critical); (2) the individual test false positive rate can

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[23] For certain tests (including the case where an individual compliance well is compared to a background well), EPA (2009) attempts to balance these errors by recommending that the probability of a single test resulting in a false positive Type I error should be *at least* 1 in 100 (1%), thereby ensuring that the test power remains reasonably high.

[24] These approaches, described in EPA (2009), may or may not be appropriate depending on the overall statistical strategy for the facility.

be lowered; (3) the type of test[25] can be changed, and (or) (4) the background sample size can be increased.

Sample size and frequency The size of a dataset may affect the test selection, false positive and negative error rates, and results. In many cases, a minimum of 8 to 10 independent background observations are recommended before running most statistical tests but this recommendation must be balanced with other competing factors (see EPA, 2009). When a larger statistical dataset is needed for more robust statistical comparison testing, it is preferred that more than one background well be installed and sampled. This approach may be appropriate for particularly large sites or sites at which the background metals determination is in question for some reason.

In many cases and for various reasons, a single background well is all that may be available at a facility. However, a single well is statistically limiting and may not adequately represent the spatial and (or) depth variability of groundwater quality data within the groundwater system in the vicinity of a site. These limitations may be important, especially for larger sites like some of the coal ash facilities, for example. Further, a single well cannot generate a large enough statistical dataset very quickly since samples collected too frequently (including duplicates) are not temporally independent and thus fail an assumption upon which many statistical tests are based. Because of the cost of well installation and sampling, the numbers and screened intervals of wells should be weighed carefully and take into account the size and complexity of the site, extent of existing data, and whether or not background concentrations are in question and formal statistical comparison testing may be required.

In some cases, the size of a background sample set can be increased by pooling[26] various background wells that (1) are screened across similar depths (shallow regolith, transition zone, or bedrock), (2) have similar geochemical signatures (confirm this using Piper and Stiff diagrams and other graphical methods), and (3) have approximately the same underlying population means and variances for the constituent of concern. Because of potential confounding variables, special care must be taken when pooling data (see EPA, 2009).

It is recommended that background data be periodically reviewed and possibly expanded to ensure that they still reflect natural conditions and are up to date. This may be done for example at a 5 year or other agreed upon permit review interval. The data should be tested for spatial or temporal trends and outliers, any of which would compromise data analysis and interpretation of site conditions. Expanding

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[25] Various tests may be used to help balance Type I and Type II errors including are control charts, tolerance intervals, and prediction limits. While a minimum false positive rate may not be specified for these types of methods, their use, along with "re-testing" procedures, can help meet the goal of Type I and II error rates and balance.

[26] Background may be derived from upgradient background wells and augmented by data from "clean" compliance wells, as long as the population mean and variance of the group of background wells is not significantly different from that of the group of clean compliance wells. This could be helpful in cases where background data are limited. Future data from each compliance well may then be tested against this combined background.

the background dataset over time as new data are obtained allows more robust and powerful statistical analyses with tighter confidence intervals. Recommended sample requirements, including number, frequency, and replicate usage and limitations, are provided in EPA (2009).

The number of *constituents* formally tested also should be considered carefully. In many cases, it may not be advisable to test all constituents that are analyzed, due to the “multiple comparisons problem” that can drive up the false positive error rate as the number of individual tests grows. For this reason, if a constituent is not expected to exceed compliance limits or is otherwise of minor concern, in some cases it may be appropriate to omit it from formal testing. Between 10 and 15 formal detection monitoring constituents often are adequate for most site conditions (EPA, 2009).

<u>Statistical test selection</u> Choosing an appropriate statistical approach or test is based on the test objectives, the number of background and compliance wells and sample events, the data distribution (normal or non-normal), and other factors specific to a facility. Often it is the responsibility of the facility operator to propose a statistical approach and demonstrate that it is appropriate for the conditions at the site. Equally important, the operator should show that certain minimum “performance standards” will be met. Performance standards require, for example, (1) matching the test to the type of data distribution (normal versus non-normal), (2) use of adequately low detection limits, (3) proof of absence or corrections for any spatial or temporal trends (including seasonality and others), (4) use of certain agreed upon parameters and procedures if control charts or prediction limits are proposed, and (5) use of agreed upon significance levels that establish the probability of false positive and negative errors. In short, the proposed sampling design (including sample size, location, and frequency) and statistical tests should be appropriate for the site in question, should adequately minimize the likelihood of incorrect conclusions about the presence or absence of contamination at or beyond the compliance boundary, and should be vetted by the DWQ site manager.

<u>Normality</u> Perhaps the most basic statistical concept and assumption inherent in statistical testing is that the dataset in question follow a normal (Gaussian, parametric, bell-shaped) distribution. Whether or not this assumption is met will affect the choice of statistical test. Parametric data have a symmetrical probability distribution (or shape) whose characteristics can be known and are analyzed using hypothesis testing T-tests and Analysis of Variance (ANOVA) type techniques in which the means of two or more groups are statistically compared. If the dataset does not follow a normal distribution, alternative (often less powerful) tests must be used. Non-parametric data do not belong to any particular probability distribution and are often analyzed using “rank order” statistical techniques in which the population of data values are arranged in order from low to high prior to and as part of the statistical computations. Non parametric tests include for example Wilcoxon, Mann-Whitney, and Kruskal-Wallis tests.

Importantly, many, if not most, groundwater contaminant datasets are *not* normally distributed. Instead, they tend to be positively skewed (long tailed, asymmetrical bell curve) and contain occasional elevated outliers. In some cases, non-normal datasets may be normalized by the use of "transformations"[27] (log transformations are common), and the site manager is encouraged to attempt to normalize the dataset prior to any testing. If the data cannot be normalized, non-parametric statistical test methods may be used. Both graphical (plotting the data's histogram versus a normal probability distribution) and statistical methods (Kolmogorov-Smirnov test, for example) may be used to evaluate whether or not a dataset is normally distributed. For small datasets, parametric tests often are more powerful than non-parametric tests.

Spatial and temporal independence Another key concept and an assumption central to statistical testing is that the data being tested be independent. Independent data are random and not susceptible to trends in space or time. Groundwater contaminant datasets collected at relatively short time or space intervals tend *not* to be independent (that is, samples collected in very close proximity – in time or space – tend to be related, a non-independent condition described as autocorrelation).

Data that are trending upward or downward violate the independence assumption (also known as the "stationarity" assumption for temporal data) since the mean is changing over time. Many factors may contribute to a temporal trend or oscillation, including seasonal fluctuations, storm-induced contamination pulses, plume arrival, turbidity from improper well construction or development, and others. Because many groundwater compliance datasets exhibit trends some will likely fail the independence assumption.

Similarly, data also must demonstrate spatial stationarity. This concept holds that the concentration distribution must be the same for all wells within a given comparison group. That is, every well in that group is represented by the same underlying background population mean and variance. This assumption does not always hold for naturally occurring constituents like many metals.

In cases where data fail the assumption of independence[28], other test methods must be used. For example, non-independent data may, in some cases, be appropriately tested using "intra-well" (within a single well) procedures, whereby background levels for each constituent are established for each

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[27] For datasets that are not normally distributed, transformations may be made to attempt to normalize the data. For example, consider taking the log or reciprocal of all values. There may even be chemical or biological reasons, in addition to statistical reasons, for performing a particular transform. If the data are then shown to be normal (a test known as the Kolmogorov-Smirnoff test is available for determining this), parametric tests may be carried out.

For datasets with few samples (small n), it may be difficult to determine whether the data are normally distributed. In this case, previous data from earlier sampling rounds may be used to augment the dataset. When parametric tests are used on small non-normally distributed datasets, the probability value P may be inaccurate. For datasets with many samples (large n, above perhaps two dozen), even data that are not normally distributed often may be safely analyzed using parametric tests.

[28] Another related consideration is that many, if not most, groundwater compliance data are dependent on uncontrolled variables in which a constituent of concern co-varies with soil pH or redox, sediment grain size, or another constituent. This fact should be considered when choosing a statistical approach and interpreting its results.

compliance well and used for future comparisons. Control chart, tolerance limits, and prediction limits (described later in this section) may be designed for intra-well tests. Another approach is to adjust the dataset to remove trends or other forms of temporal dependence and use the *residuals* remaining after trend removal for formal testing purposes. If non-independent data are tested incorrectly, significant consequences on test results and background determinations may result.

If a background well is found to be potentially contaminated and not reflective of ambient conditions, it may be appropriate to test compliance well data using an intra-well test. A linear trend in a background well may signify the need to use a trend test like linear regression when establishing background; otherwise, the background variance may be overestimated and biased on the high side leading to higher than expected background and an increased likelihood of false negative errors. Importantly, each constituent should stand alone and be evaluated individually when choosing an appropriate test and determining whether that constituent's data are spatially and temporally independent.

Non-detects Censored data above or below a reporting/detection limit are another characteristic of many groundwater compliance datasets, particularly for trace metals, and must be considered when choosing an appropriate statistical test. Often, a given trace metal will be "below detect" (also referred to as below the practical quantitation limit, identified with a "U" qualifier) for most wells and most sample events. Censored data tend to result in non-normal data distributions and may be analyzed using special tests or test adaptations (EPA, 2009).

Non-detect values may distort statistical test results and must be handled carefully. If more than half of background values are below the detection limit (DL) and the values below the DL are assumed to be normally distributed, one may alternate "0" and the DL which will result in a net value of half the DL with a variance. Or, if the values below the DL are assumed *not* to be normally distributed, the technique described in EPA, 1989 may be used. If the values below the DL are assumed to be lognormal, other techniques may be appropriate. Additional guidance is provided in EPA (2004).

Outliers Outliers are values that fall outside an expected range and are common among groundwater datasets (Helsel and Hirsch, 2002; Gibbons and Coleman, 2001). Outliers may be caused by recording errors, lab errors, incorrectly calibrated field meters, cross-contamination and decontamination issues, variable sample water turbidity over time or space, and (or) temporary localized hot spots not representative of site wide conditions. Several tests exist to identify outliers, and a good reference on the subject is *Outliers in Statistical Data* by Barnett and Lewis (1994). Outliers should be identified and corrected (or removed from the dataset) only if the basis for the error or discrepancy is positively identified. Otherwise, it is recommended that outliers generally *not* be removed (EPA, 2009, Helsel and Hirsch, 2002) from the dataset. If an outlier is discovered, an option is to take an additional (substitute) sample or use a previously collected "provisional" sample and repeat the statistical test. However, including data outliers in statistical tests may distort the statistical results and conclusions, so great care should be taken when determining whether to keep or remove these data.

A special case of outliers (and in some cases non-detects) are values that are “off scale” (that is, too high or too low to measure for whatever reason, including dilution effects, values below practical quantitation limits, and others) but still valid. Data containing off-scale values generally are considered to be non-normally distributed since all the values are not known and accounted for. As a result, generally, these datasets should be compared using non-parametric test methods whereby a value that was too low to measure is assigned an arbitrary low value and a value that was too high to measure is assigned an arbitrary high value; the non-parametric (rank order) testing can then be carried out as normal. Since this type of test accounts only for the *relative ranks* of the values, it does not matter that all numeric values are not known precisely.

<u>Inter-well versus intra-well testing</u> Inter-well tests are “well to well” comparison tests in which one well or a group of wells is compared to another. Intra-well tests are “within-well” comparison tests in which data from a single well are tested. Choosing which approach to use will depend in large part on whether natural background conditions vary spatially across the site for the constituent of concern. If spatially varying, often an intrawell test is the preferred choice. Choosing whether to use inter-well or intra-well statistics to determine an appropriate background should be made for each individual metal constituent, based on the spatial and temporal variability of that constituent alone.

Some constituents tend to behave in certain ways in natural background that will drive the approach used to test them. Major ions, pH, TDS, specific conductance, and Ba are almost always detectable, tend to have a normal within-well distribution, often have occasional within-well variability (except for seasonal or annual trends in some cases, which should be checked), have frequent well-to-well variability, and often are tested using an intrawell approach. Aluminum, Fe, and Mn have moderate to high detection frequencies, tend to have a log- or non-normal within-well distribution, have relatively frequent within-well variability, have occasional well-to-well variability, and often are tested using intrawell or interwell approaches. The trace metals Be, Cd, Cu, Hg, Pb, Ni, Ag, Tl, V, and Zn, as well as Sb and Cr (occurring as either a cation or anion), tend to have low detection frequencies, have a log- or non-normal within-well distribution, have relatively frequent within-well variability, and are often tested using interwell approaches (or, if never detected, these constituents are sometimes omitted from formal testing to improve the site-wide test power). Arsenic (anion) and selenium (occurring as either a cation or anion) tend to have mixed detection frequencies from zero to high, have a normal, log- or non-normal within-well distribution, have a moderate frequency of within-well variability, have a moderate frequency of well-to-well variability, and often are tested using intrawell or interwell approaches. The tendencies described above hold generally but are site specific and should be assessed at each facility.

Turbidity, changes in geochemistry, and plumes of contamination may affect the data distributions and should be monitored accordingly. Cation-anion balances, along with other tests and methods, may also be used to evaluate the data distribution for constituents of concern. Whether or not a well or a constituent is formally used and tested, in most cases it should continue to be monitored and assessed to provide additional information about groundwater quality at the facility.

Statistical Procedures and Tests Commonly Used for Background and Compliance Determinations

The ability of a statistical procedure to correctly identify contamination that is present and avoid falsely identifying contamination that is not present, depends on the test, choices about error tolerance (significance levels), and the dataset itself. How are the data distributed (normal, log normal, non-normal)? Do spatial or temporal patterns exist that narrow the test choices? Do outliers and (or) non-detects exist? How many wells are being sampled? Of those, how many are background? How often are they being sampled? How many constituents are being formally tested? Do the selected false positive and negative error rates make for a sufficiently powerful test? All of these factors interact to determine the effectiveness of the statistical testing program at the facility. The merits of any proposed statistical approach must, therefore, be evaluated as a whole.

Statistical procedures commonly conducted on normal and non-normal data distributions include the following.

Goal	Normal Data Distribution	Non-normal Data Distribution
Describe one group	mean, standard deviation	median, 25th and 75th percentile
Compare one group to a hypothetical value (e.g. 2L standard)	one sample t test	Wilcoxon test
Compare two unpaired groups	unpaired t test	Mann-Whitney test
Compare two paired groups	paired t test	Wilcoxon test
Compare three or more unmatched groups	One-way ANOVA	Kruskal-Wallis test
Compare three or more matched groups	repeated measures ANOVA	Friedman test
Quantify association between two variables	Pearson correlation	Spearman correlation
Predict value from another measured variable	linear regression	nonparametric regression
Predict value from several measured variables	multiple linear regression	not applicable

General statistical approaches commonly recognized (EPA, 2009) include: (1) parametric analysis of variance (ANOVA) test followed by multiple comparison procedures to identify statistically significant evidence of contamination, (2) non-parametric ANOVA test based on ranks (Kruskal-Wallis, for example), followed by multiple comparison procedures to identify statistically significant evidence of contamination, (3) prediction limit procedure in which a prediction interval (interval of upper limit) is established for each constituent based on the distribution of background data, and each constituent in each compliance well is then compared to the established predicted background limit, (4) control chart procedure that gives control limits for each constituent, (5) single-well comparison to a fixed limit (2L standard), and (or) (6) another method submitted by the permitted facility and agreed upon by DWQ.

Although a simple Student’s t-test may be appropriate for small facilities, larger well networks and constituent lists at larger facilities such as coal ash sites will generally require a multiple comparisons procedure such as the inter-well one-way ANOVA test.

Prediction limits is a comparison procedure that uses existing background data to predict, at a certain probability, the interval into which future compliance observations are expected to fall. If future compliance values fall outside this interval, site related contamination is likely. An advantage of this method is that it is relatively easy to construct, is very flexible, and can accommodate a wide range of multiple comparisons while minimizing false positive and negative error rates. Prediction limits can be based on means, medians, or individual compliance point measurements. Sample re-testing is a common component of the procedure. EPA (2009) describes the procedure and when and how to use it. Key assumptions for prediction limit procedures include the following: background and future measurements must be identically and independently distributed, data do not exhibit temporal trends of any kind, for inter-well tests (upgradient to downgradient comparisons), data are not naturally spatially variable, background data do not include statistical outliers, data are or can be transformed to be normally distributed (for parametric prediction limits), and a minimum of eight background samples are available (more for non-parametric test limits).

Control charts are similar to prediction limits in that they are developed from background data and compared to a sequence of compliance measurements. If any of the values exceeds the control limit there is some probability that the compliance concentrations exceed background. Control charts can be designed as inter- (normally-distributed, parametric) or intra-well (non-normally distributed, non-parametric) tests. Inter-well control charts establish the control limit from an upgradient and potentially other background wells. Intra-well charts use historical measurements from a compliance well as background and are valid only if historical compliance well background began uncontaminated. An advantage of control charts is that the method involves plotting compliance data over time, thereby allowing the site manager to visually discern data patterns. For control chart methods, EPA recommends using the combined Shewhart-CUSUM control chart (see EPA, 2009; Lucas, 1982).

To summarize, key questions that a site manager should ask when conducting statistical analyses of groundwater compliance data include the following:

a) Have the data been tabled (all constituents and sampling dates) in an easy to read format?

b) Have statistical summaries (mean, median, maximum, standard deviation, etc, as applicable) been presented for all constituents of concern?

c) Have the data been initially “explored” for trends, outliers, correlations, etc, as applicable, for all constituents of concern?

d) Have graphical displays been presented that illustrate data distributions, summary statistics, trends, correlations, or other information of relevance, as applicable?

e) Is the value of “reference background” in question for any constituent of concern? If so, are statistical tests needed to establish reference background for any constituent of concern? If statistical testing is warranted, are adequate numbers and locations of background wells currently installed and have these wells been sampled for enough events to statistically establish reference background?

f) Are statistical tests needed to determine whether concentrations, for any constituents of concern, at the compliance boundary are site related and exceed 2L standards? Are concentrations for selected locations (well or group of wells) statistically different than concentrations at other locations (well or group of wells; for example, background wells)?

g) How does the monitoring status (detection versus compliance versus corrective action) affect the chosen statistical approach and testing? Is this described clearly in the submitted documentation?

h) Are the proposed statistical approaches and tests considered to be "standard" approaches (for example, EPA, 2009) and, if not, have alternative strategies been properly referenced and vetted?

i) If statistical testing is proposed, have the data (for each applicable constituent) been tested for normality and shown to be normally distributed or shown to be transformed to a normal distribution? If not, are non-parametric rank order type tests of sufficient power, given the number of samples? Have the data been properly evaluated for outliers, off-scale values, non-detects, and independence?

j) Are sample sizes and sampling frequency adequate for the selected test(s)? Will the background dataset be expanded and, if so, at what interval and in what way? Is re-testing proposed and, if so, under what conditions?

k) Are significance levels and other test parameters appropriate? Are Type I (false positive) and Type II (false negative) error rates balanced appropriately? Is the site wide cumulative false positive error issue properly addressed?

l) Has the overall site wide approach, including individual tests, been clearly and thoroughly presented, documented, and referenced? Has the approach, including individual tests, and documentation been vetted by DWQ?

Soil considerations

For background soil-metals determinations, often it is not feasible or meaningful to establish a single universal background concentration. This is because soils are affected at the local scale by spatial heterogeneities, historical contaminant inputs, and local-scale physical, chemical, and biological processes. Use of background concentration *ranges* may be more practical.

On-site and background soil samples should both be collected from similar soil types since the capacity to retain metals varies significantly with soil properties. A minimum of four samples collected from the same soil type (and, in some cases, depth) is often recommended to establish a background concentration for a given soil type (Michigan, 1991). Four samples help account for inherent variability of ambient metal occurrences and ranges within each soil type. When determining if contaminants have moved downward through a vertical soil profile, samples should be taken at comparable depths or horizons (O, A, B) from similar soil types at both the background and application site. If sampled by horizon, a minimum of four samples from each horizon is generally recommended.

One way to assess whether samples are being collected from similar soil types or not is to ensure that paired samples collected on-site and in background area(s) have similar pH/Eh, salinity, cation exchange capacity, percent organic carbon, particle size and distribution, thickness of soil horizon, and soil type and structure. If this determination is not feasible or the soil profiles do not match, a mean concentration should be determined for the soil type with the lowest adsorption capacity (sands) and for the soil type with the highest adsorption capacity (silts and clays), in both the background and on-site areas. There is a high probability that the site is contaminated if, for samples collected within the high adsorption capacity soils, the mean on-site concentration is above the mean background concentration.

For sites with homogeneous historical use, representative samples may be collected along a consistent sample grid, the intervals of which may be determined using equations that relate the site area to the grid length (Breckenridge and Crockett, 1995). If only some areas of a site are suspected of being contaminated due to historical use, “bias sampling” with a tightened grid in suspect areas may maximize the chance of observing concentrations above background. A very good reference on this subject is ‘Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies’ (EPA 1992b). Bias sampling should account for multiple suspect areas, if applicable, and should focus on locations of staging areas, tanks, piping, spray fields, disposal ponds, and drainage areas.

Determining the depth of sampling should be based on the expected ability of different soil layers to retain (sorb) metals. A field kit may be used to determine whether soil pH is in a range that will retain or mobilize certain metals. For clay and organic soils, sample depth increments of 0.25 to 0.5 feet or by major horizon are reasonable; for silts and loams, 1 to 2.5-foot intervals or by horizons; and for sands, 1 to 5 foot intervals. Depth increments should also consider the amount of suspected contamination released, other soil retention characteristics (organic content, CEC, AEC), and amount of water available to enhance transport (for example, rainfall amounts and potential ponding). Samples collected from different depths can be single or composited, depending on statistical objectives. At locations where soil type is homogeneous, compositing can save costs and often provides a better mean estimate.

Soil properties can be obtained from the local Natural Resource Conservation Service, Soil and Water Conservation Districts, County Extension Agents, or other County staff, US Geological Survey, State Geological Survey, and the Agricultural Stabilization and Conservation Service. Aerial photos used to map soils are also helpful in evaluating past land use, fill areas, locating current or historic stream channels, and determining site factors that could affect the movement of contaminants. Fill areas may be present around sites that would otherwise be inundated with water.

The reference titled “Guidance for Comparing Background and Site Chemical Concentrations in Soil” (Florida Department of Environmental Protection, 2012) presents one approach to evaluating soils at permitted facilities. Additional references and approaches for soil determinations are provided in EPA (1989b) and EPA (2002).

Stream sediment considerations

One valuable source of stream sediment data that has been collected from streams across NC is the report published as part of the National Uranium Resource Evaluation (Reid, 1993). It contains a large number of inorganics in stream sediments, and also includes selected inorganics in groundwater. These data may be helpful in determining background ranges in different regions and settings.

However, because of the potential for severe erosion during flood events, establishing background concentrations in stream sediments must be done with caution. Stream sediment may be moved during storms, so contamination observed in sediments directly downstream of a permitted site may not be attributable to the site in question, particularly after flooding, but may instead be contamination deposited from unrelated upstream sources. For this reason deeper overbank sediment samples, when aggregated, may be a good source for background samples since these settings generally accumulate sediments over time. Care must be taken when collecting and interpreting stream sediment data however, due to potential questions about source origin in these dynamic settings that undergo both deposition and erosion. Understanding a site's effluent, the processes generating the effluent, and historical stream flows and quality can be helpful in determining the source of metal concentrations in stream sediments.

References for Chapter 3

The subject of statistics is vast, and a large number of references are available. However, two references in particular are recommended for the site manager responsible for interpreting groundwater compliance monitoring data at DWQ permitted facilities.

- U.S. Environmental Protection Agency, 2009, EPA Unified Guidance: Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, EPA 530/R-09-007, 888 pages.

  The EPA Unified Guidance: Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities (2009) is a comprehensive, detailed, and widely referenced document that covers the major topics needed to apply statistics to groundwater compliance monitoring data. It is aimed at the "informed groundwater professional with a limited background in statistics". It covers key principals of groundwater statistics, the sampling design and sample sizes, selection of appropriate tests, methods for checking data and running tests, and interpretation of results. It covers the importance of population distributions, normality testing (parametric vs. non-parametric analyses), statistical power, and how to avoid false positive and negative errors (these and other statistical concepts are covered later in this section). It provides an overview of regulatory approaches to using statistics to analyze groundwater compliance data. It describes a variety of commonly used statistical methods for groundwater compliance and background data and describes when and how to use them, from simple box plots and histograms to the t-test, rank sum, ANOVA, and many other robust statistical tests for normal and non-normal data. It also covers data outliers, non-detects, inter-well versus intra-well tests, trend tests, control charts, prediction limits, confidence intervals, compliance tests, and others. Examples are provided throughout.

- Helsel, D.R. and R. M. Hirsch, 2002, Statistical Methods in Water Resources Techniques of Water Resources Investigations, Book 4, Chapter A3, U.S. Geological Survey, 522 pages.

  The Statistical Methods in Water Resources (Helsel and Hirsch, 2002) is recommended for its very clear and concise treatment of statistical techniques commonly used to analyze groundwater data. It was originally written as class notes for a course designed to teach statistical methods to hydrologists. As such, it is a document that explains why a method is appropriate and how to use it. It is considered a very accessible document and provides real world examples on the use of the most common statistical techniques. Chapters include: summarizing data, graphical data analysis, describing uncertainty, hypothesis testing, differences between two independent groups, matched pair tests, comparing several independent groups, correlation, linear regression, trend analysis, methods for data below the reporting limit, presentation graphics, and others.

The site manager may also refer to the ASTM Standard Guide for Developing Appropriate Statistical Approaches for Groundwater Detection Monitoring Programs (2005). This document presents a statistical groundwater monitoring strategy in a handy flow chart form that is designed to simultaneously minimize false negatives (the failure to indicate a 2L exceedance when it is present) and false positives (indicating a 2L exceedance when none is present) at a facility. It assumes a significant amount of prior statistical knowledge and is designed to be a meta-framework for applying a series of statistical methods to arrive at an acceptable monitoring strategy. The methods are applied according to a flow chart decision tree and include tests for normality, prediction limits, confidence limits, trend analyses, control charts, and others. Unlike the EPA (2009) document, it provides very little description about how to apply specific methods but rather is intended to be a meta-framework for working with site data in a consistent and predictable manner. Its effectiveness as a valid approach has not been verified by the authors of this DWQ document and the decision to apply it rests with the site managers of the facility in question. The reference for this approach is: ASTM, 2005, Standard Guide for Developing Appropriate Statistical Approaches for Groundwater Detection Monitoring Programs (D6312-98, 2005).

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[29] Breckenridge and Crockett (1995) describe methods by which soil and sediment background levels are determined; provide published ranges of ambient metals concentrations; provide sources (for example, sewage sludges, nitrogen fertilizers, manure, pesticides, etc) and corresponding concentration ranges of metals in soils; describe sampling strategies for different metals and geologic settings; and describe various statistical tests needed for appropriate interpretation of background soils data. Their report focuses on metals contamination in soil, the science behind their mobility, and statistics needed for site evaluation.

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APPENDIX A – Typical background concentrations in various media and settings

The following references provide information on typical background concentrations of inorganics in different media and settings. Some of these references include handy tables of published values.

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APPENDIX B – Recommended references for constituents in coal and fly ash and their leaching potential

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