

APPENDIX B: Geochemical Normalizers in the Interpretation of Sediment Contaminant Data

Aluminum, iron, TOC, and grain size can be used in particular cases as geochemical normalizers. They will often show strong relationships with site contaminants, and to varying degrees they covary together with sediment texture. In a highly simplified geochemical model, weathering of continental crust results in a two-endmember sediment. The coarse grains (>63 microns) that survive weathering and transport down rivers to coastal depositional areas are predominately the most resistant minerals, such as quartz grains. These large grains have low metals levels in their matrix and relatively low surface areas so little metal is sorbed onto their surfaces. During weathering and transport other minerals are broken down to produce clay and other mineral phases that predominate in the fines fraction (<63 microns). This fines fraction has more metals in mineral matrices, plus a greater relative surface area that sorbs more metals. This fines fraction also contains the majority of TOC, and the organic contaminants that are associated with the TOC. In most cases this fines fraction contains the majority of the metals and organic contaminants sorbed to its surface area that constitute the anthropogenic part of the background, and within its' matrix are the metals that constitute the naturally occurring background. In addition, if there have been site releases that represent additional site sources, these site related metal and organic contaminants will also be sorbed onto the surface area of the sediment (again mainly within the fines fraction). These coarse and fine endmembers are then mixed in varying proportions throughout the depositional areas depending on hydrodynamics to produce the full range of chemistries found around the site. In higher energy nearshore areas (beaches), sandy (coarse) sediments composed mainly of quartz grains are present with relatively low contaminant levels. Moving offshore towards lower energy areas more fines are allowed to settle out and produce the more fines rich sediment that has higher contaminant levels (both metals in the matrices (naturally occurring background) and metal and organic contaminants sorbed onto the surfaces (anthropogenic background)). When geochemical normalization is conducted, it will help differentiate any potential site contaminant releases from background sources (both naturally occurring and anthropogenic). Site samples that plot above a background relationship have an additional source contribution for the contaminant of concern that is not present in background samples, and this additional local source is assumed to indicate a site release. It is these areas with site releases that we want to focus on in the IR program, and produce site exposure and effects risk relationships that focus on site releases and not background chemicals.

In order to use these geochemical normalizations, several assumptions should be checked (Louma, 1990). The first is that there is a significant relationship between the normalizer and the contaminant of concern in reference or background samples. This is done with simple crossplots and checking for high correlation. The normalizer should also be insensitive to anthropogenic inputs and stable (non-reactive) under geochemical conditions found in the sediment. These requirements are not strictly met in every case, so some care and judgment is required for use at individual sites. Aluminum often works well to adjust trace metal chemistries for changes in the naturally occurring metals in the matrix of mineral phases. The trace metal level varies as the mineralogy of the samples varies, but always in constant proportion to the aluminum level. So

normalizing to aluminum “corrects” for changing sample mineralogy and therefore trace metal levels associated with different mineral matrices. In actual practice, however, the trace metals levels that appear on sediment background crossplots are not just from naturally occurring matrix sources, but also sorbed metal from anthropogenic background. In industrial areas, the anthropogenic contribution to trace metals levels may be quite high depending on the metal. This results in portions of the trace metal in the background relationship coming from both naturally occurring and anthropogenic background sources. In addition, many environmental programs use an acid leach rather than total dissolution of all mineral matrices in their sediment chemical preparations, so proportions of naturally occurring and anthropogenic sources may vary depending on preparation technique as well as sample location (so exercise care in combining studies). But as long as samples are treated by the same method (so same amount of matrix is dissolved) and from the same area (so same amount of anthropogenic background sorb onto surfaces), aluminum normalization works well for many trace metals. Aluminum does show very strong relationships for many trace metals. It is naturally present in percent levels in samples so any minor anthropogenic contributions are lost in the noise and can be considered not to affect the relationships. And finally, aluminum is non-reactive in sediment geochemical environments so levels will not change with sediment reactions.

All this being said, aluminum is not universally applicable as a background normalizer. Daskalakis and O’Connor (1995) reviewed NOAA Status and Trends sediment data from around the country and found while aluminum worked well on the east coast, iron and TOC may work better in some cases on the west coast. On the east coast, watersheds tend to drain the coastal plain in front of the Appalachian Mountains, with a relatively constant granitic chemical composition. This results in relatively constant “crustal abundance” ratios (trace metal to aluminum ratios) in sediments from different areas. The geologic history of the west coast results in much more variable chemistries in adjacent (or even the same) watersheds so trace metal to aluminum relationships are also more variable. Iron may therefore work better for metals, and TOC for organics on the west coast. However, even though these normalizers are in percent levels, they may still show significant anthropogenic and sediment reaction contributions and therefore fail in their role as normalizers. Iron is more reactive than aluminum, and it tends to be remobilized under anoxic conditions. Differences in redox state among different sediment areas may therefore lead to confounding factors in relationships. TOC of different types may not carry the same amounts of anthropogenic background, which can also lead to confounding factors in these normalization relationships. Just as one wouldn’t try to use a complicated statistical background method without consulting a statistician, it is advised to consult an experienced geochemist before using these types of geochemical methods to differentiate background. It is therefore advisable to include a geochemist in the discussions so some professional judgement can be used to help decide when these types of geochemical models (these normalization relationships) are appropriate.

In an effort to simplify the various geochemical relationships used to normalize for background contributions, some success has been found in using grain size (Klamer et al, 1990; EPA Region 9,1998) to encompass all these covarying relationships. Since aluminum, iron, TOC,

and grain size all tend to co-vary, the use of a single normalizer can often represent several underlying geochemical relationships. Any single metal or organic contaminant might be better normalized with a different normalizer, but grain size is often a simple compromise that works well enough in many cases. EPA Region 9 (1998) used this approach to develop background (or “ambient”) levels in S.F. Bay. They used the grain size relationship to generate a UCL on the relationship. They recommend point comparisons to this UCL be used to decide if a sample is above ambient levels. Following the reasoning outlined in the background guidance (SWDIV, 1998;1999), it would be anticipated that point comparisons to a UCL might result in a significant number of false positives. Therefore a better approach might be to look at the population of residuals (predicted value from geochemical relationship minus the observed value) at the site and compare to residuals from a reference population. (Note for Discussion: The proposed guidance (6/00) provides a flowchart to guide the use of background techniques. This flowchart splits down two paths, one for a geochemical approach and one for a statistical approach. The last line in this paragraph is suggesting that there may be utility in combining these approaches, but this should have additional discussion before being placed in any suggested guidance.)

Starting with these background geochemical relationships, the simple crossplot normalizations show how geochemistry can differentiate between background and site releases. More involved techniques are also available to fingerprint geochemical signatures. In addition to separating background from site releases, these techniques also show the potential to differentiate different site releases and offer the possibility of fingerprinting non-navy sources. The goal would be to point to different release signatures that indicate non-navy PRPs as the source for some offshore contamination on Navy property. While these exercises might start with simple linear crossplots of contaminants, they usually progress to the use of more involved multivariate techniques such as principle component analysis (PCA). These multivariate techniques are more commonly used with organic contaminants, where compound groups (i.e., PAHs and PCBs) are composed of many similar individual compounds. These more complicated fingerprinting studies fall outside the scope of this discussion but show that these geochemical applications may have many goals in addition to simple background determinations. RPMs should always understand the anticipated goals are for use of any geochemical relationships, and thereby weigh the involved costs with potential benefits to decide how much geochemical analysis is warranted.