Equilibrium Partitioning and Organic Carbon Normalization

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Establishing sediment quality criteria (SQC) requires a determination of the extent of the bioavailability of sediment-associated chemicals. A full discussion of the Equilibrium Partitioning (EqP) approach to developing SQC is presented elsewhere (Di Toro et al., 1991; USEPA, 1993). The main focus of this presentation is field observations of partitioning in sediments. Consider a sediment sample that is segregated into various size classes after collection. The particles in each class were in contact with the pore water. If sorption equilibrium has been attained for each class, then letting $C_s(j)$ be the particle chemical concentration of the jth size class, it is true that

$$C_s(j) = f_{oc}(j)K_{oc}C_d \qquad (1)$$

where $f_{oc}(j)$ is the organic carbon fraction for each size class j, K_{oc} is the partition coefficient for sediment organic carbon, and C_d is the pore water concentration. On an organic carbon-normalized basis, this equation becomes

$$C_{s,oc}(j) = K_{oc}C_d \qquad (2)$$

where $C_{s,oc}(j) = C_s(j)/f_{oc}(j)$. This result indicates that the organic carbon-normalized sediment concentration of a chemical should be equal in each size class because K_{oc} and C_d are the same for each size class. Thus a direct test of the validity of both organic carbon normalization and EqP would be to examine whether $C_{s,oc}(j)$ is constant across size classes in a sediment sample.

Data from three field studies, Prahl (1982), Evans et al. (1990), and Delbeke et al. (1990), can be used to test this prediction. In Prahl's study, sediment cores were collected at three stations near the Washington State coast (Stations 4, 5, and 7). These were sieved into a silt-and-clay-sized fraction (<64 µm) and a sand-sized fraction (>64 µm). This latter fraction was further separated into a low-density fraction (<1.9 g/cm^3) and the remaining higher-density sand-sized particles. The concentrations of 13 individual polycyclic aromatic hydrocarbons (PAHs) were measured in each size fraction.

It is important to realize that these size fractions are not pure clay, silt, or sand, but are natural particles in the size classes denoted by clay, silt, and sand. The organic carbon fractions, shown on Figure 1, range from 0.2 percent for the high-density sand-sized fraction to greater than 30 percent for the low-density fraction. This exceeds two orders of magnitude and essentially spans the range usually found in practice. For example, 90 percent of the estuarine and coastal sediments sampled for the National Status and Trends program exceed 0.2 percent organic carbon (NOAA, 1991).

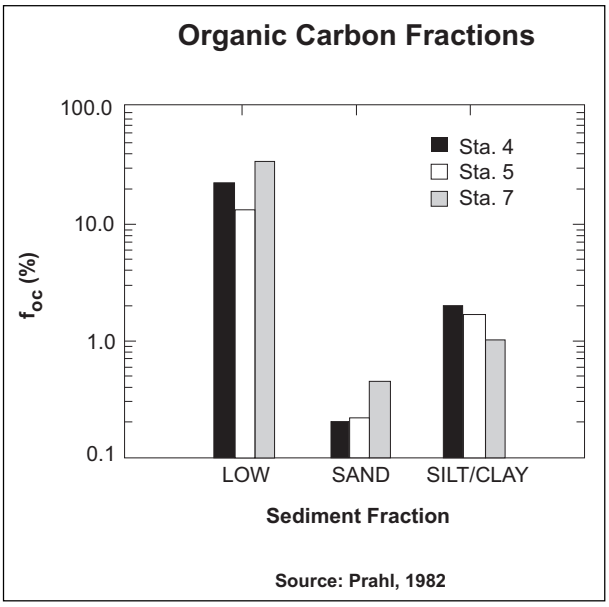

Figure 1. Organic carbon fractions: Sediment fraction.

Figure 2 (top) compares the dry weight-normalized clay/silt-sized fraction sediment PAH concentrations, $C_s(j)$, to the sand-sized high- and low-density PAH concentrations on a dry weight basis. The dry weight-normalized data have distinctly different concentrations—the low-density high-organic carbon fraction is highly enriched, whereas the sand-sized fraction is substantially below the clay/silt fraction concentrations. Figure 2 (bottom) presents the same data but on an organic carbon-normalized basis, $C_{s,oc}(j)$. In contrast to dry weight normalization, the PAH concentrations are essentially

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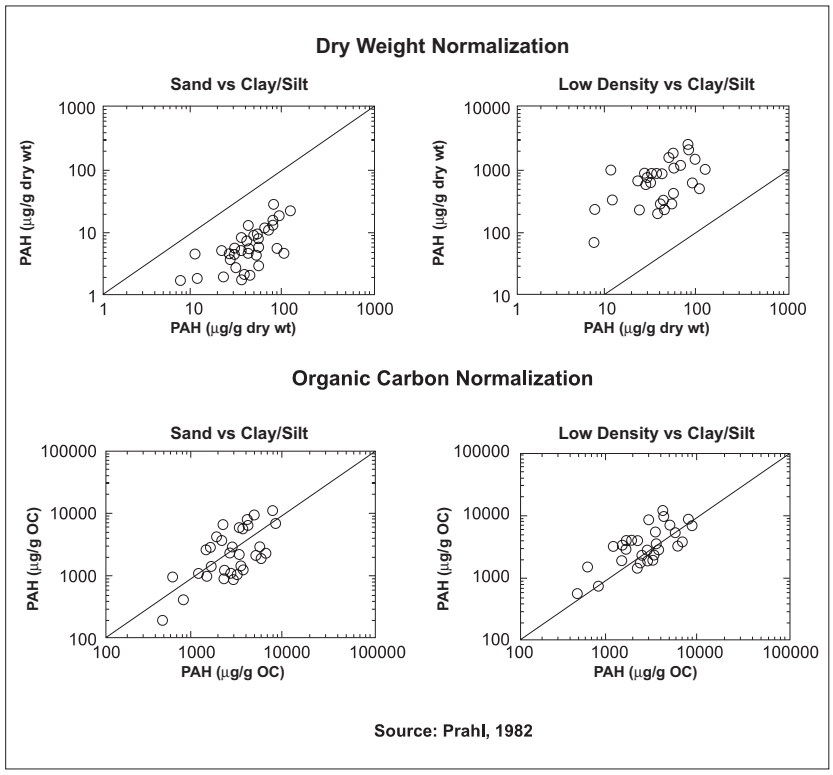

Figure 2. Dry weight normalization and organic carbon normalization.

the same in each size class, as predicted by Equation 2. The lines in Figure 2 represent equality and have been added as a visual aid.

In the field data from Evans et al. (1990), sediments were collected at five sites along the River Derwent, Derbyshire, United Kingdom, and separated into six sediment size classes. The size classes were representative of clay and silt (<63 µm) to coarse sand (1.0 to 2.0 mm). Organic carbon content and total PAH were measured in each sediment size class. Figure 3 presents the size classes and associated organic carbon content. Evans et al. attribute the bimodal distribution of f_{oc} to two types of organic matter. Organic matter in the 1.0 to 2.0 mm size class may be from fragmentary plant material, while the size classes less than 500 µm have organic carbon content that is the result of aging humic material. The organic content in this study ranges from 2.0 to 40 percent.

Figure 4 presents a comparison of PAH concentration for different sediment classes for dry weight normalization and organic carbon normalization. The top left panel compares PAH concentrations on sand (63-500 µm) and clay/silt (<63 µm) on a dry weight basis. The top right panel compares PAH concentrations on coarse sand (0.5-2.0 mm) and clay/silt (<63 µm) on a dry weight basis. The data indicate that the PAH concentration is higher in the coarse sand fraction of sediment. Recall from Figure 3 that the clay/silt and coarse sand fractions contain higher fraction organic carbon content. The bottom panels of Figure 4 present the organic carbon-normalized comparison of PAH concentrations by sediment class. For both panels, the organic carbon-normalized PAH concentrations are similar regardless of the sediment size class as predicted by Equation 2. The lines in Figure 4 represent equality and have been added as a visual aid.

Lastly, Delbeke et al. (1990) collected sediments from seven sites in the Belgian continental shelf and the Scheldt estuary. These sites were analyzed for eight polychlorinated biphenyl (PCB) congeners and organic carbon in the bulk sediment and clay/silt (<63 µm) sediment fraction. In addition, analyses of the samples were done to determine the percent of size fractions ranging from 500 µm to 3 µm that made up the sample. The PCB congeners tested for in this study were IUPAC numbers 28, 52, 101, 118, 153, 138, 170, and 180.

Using concentrations reported for bulk samples, concentrations for clay/silt samples, and percent size fractions of each sample, calculations were done to estimate concentrations on the >63 µm portion of the sample. Similar calculations were done to determine

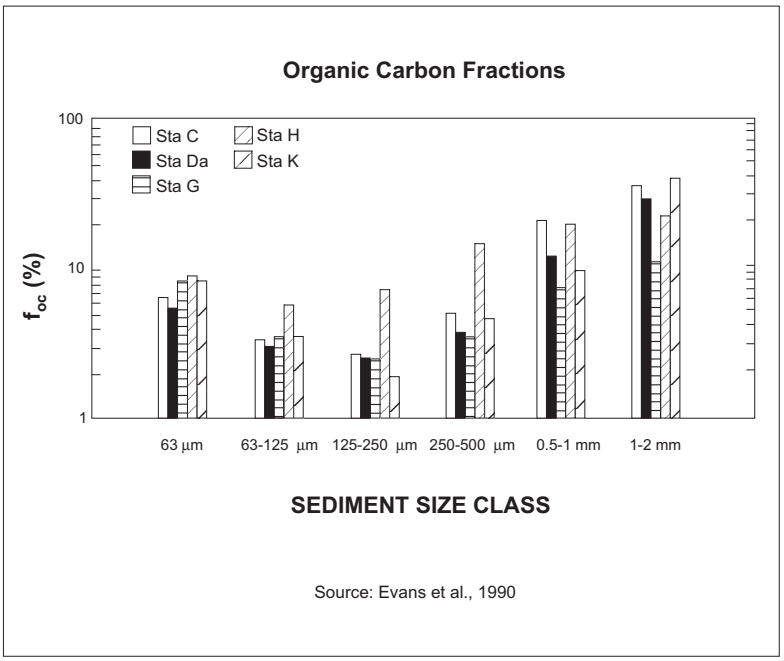

Figure 3. Organ carbon fractions: Sediment size class.

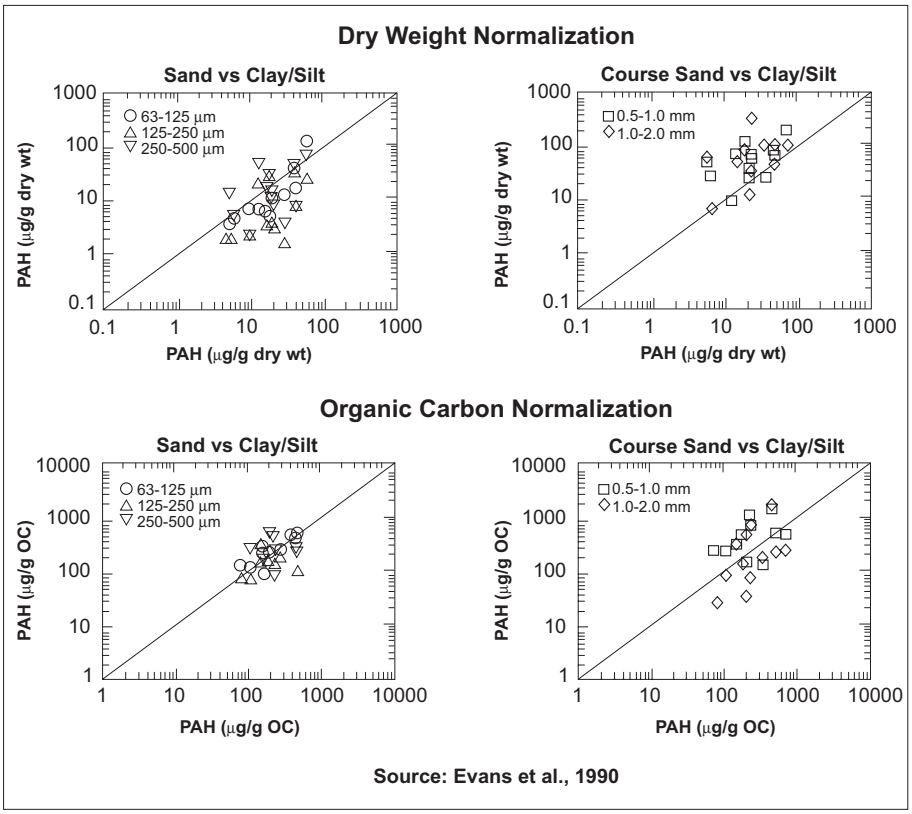

Figure 4. Dry weight normalization and organic carbon normalization.

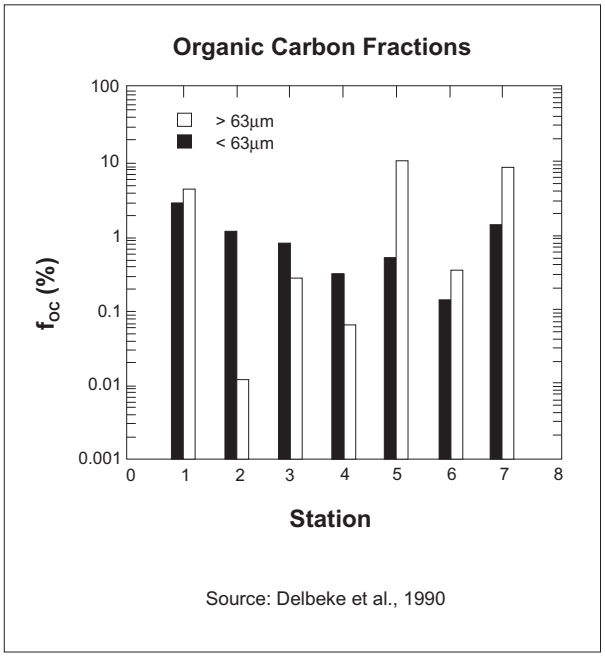

Figure 5. Organic carbon fractions: Station.

organic carbon content on the >63 µm portion of the sample. Organic content varied from 0.01 percent to 10 percent inclusive of both <63 µm and >63 µm portions of the sediment.

Figure 5 presents the percent organic carbon on the <63 µm portion of the sample (black bar) and on the >63 µm portion of the sample (white bar). Comparisons of the PCB congener concentrations on a dry weight basis (top) and on an organic carbon basis (bottom) are shown in Figure 6. Organic carbon content in the >63 µm class size at stations 2 and 4 is 0.01 percent and 0.06 percent, respectively, as indicated in Figure 5. The data for these stations are shown on Figure 6 using filled symbols. Though an f_{oc} >0.2 percent has been presented as the value for which organic carbon normalization applies, normalization at these f_{oc} values seems appropriate for this data set.

The top panel of Figure 6 indicates no evident relationship between PCBs in the <63 µm sample and PCBs in the >63 µm sample on a dry weight basis. When concentrations in either class size are normalized to organic carbon content, the concentrations are similar for both class sizes as shown in the bottom panel. This indicates that PCB concentrations are similar across sediment class sizes, which supports organic carbon normalization. The lines in Figure 6 represent equality and have been added as a visual aid.

The data from Figures 2, 4, and 6 are analyzed to quantify the reduction in variability when the data are carbon-normalized. The variation of the y-axis values from the line of unity presented in Figures 2, 4, and 5 represents the residual difference of the y values from the x values. Coefficients of variation for these residuals are presented in Figure 7 for dry weight- (black bar) and organic carbon-normalized (gray bar) data. The coefficients of variation are reduced significantly. It can be concluded from the data of Prahl (1982), Evans et al. (1990), and Delbeke et al. (1990) that the organic carbon-normalized PAH and PCB concentrations are relatively independent of particle size class and that organic carbon is the predominant controlling factor in determining the partition coefficient of the different sediment size particles in a sediment sample. The organic carbon concentration of the high-density sand-sized fraction in Prahl's data (0.2 to 0.3 percent) suggests that organic carbon normalization is appropriate at these low levels. The data from Evans et al. suggest that EqP can be applied to organic carbon originating from more than one source, that is, fragmentary plant matter and aging humic material.

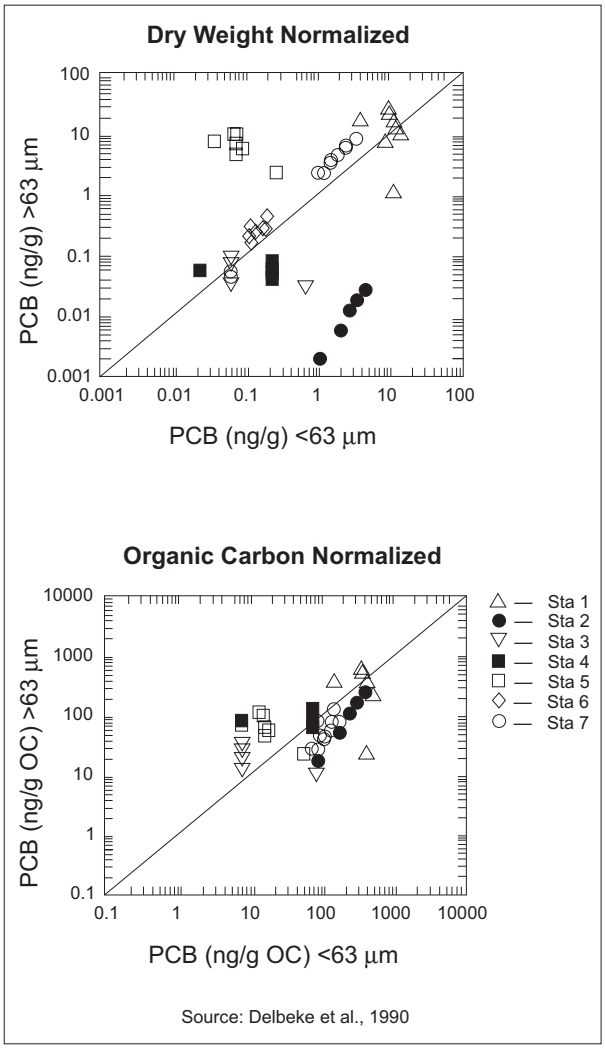

Figure 6. Dry weight normalized and organic carbon normalized.

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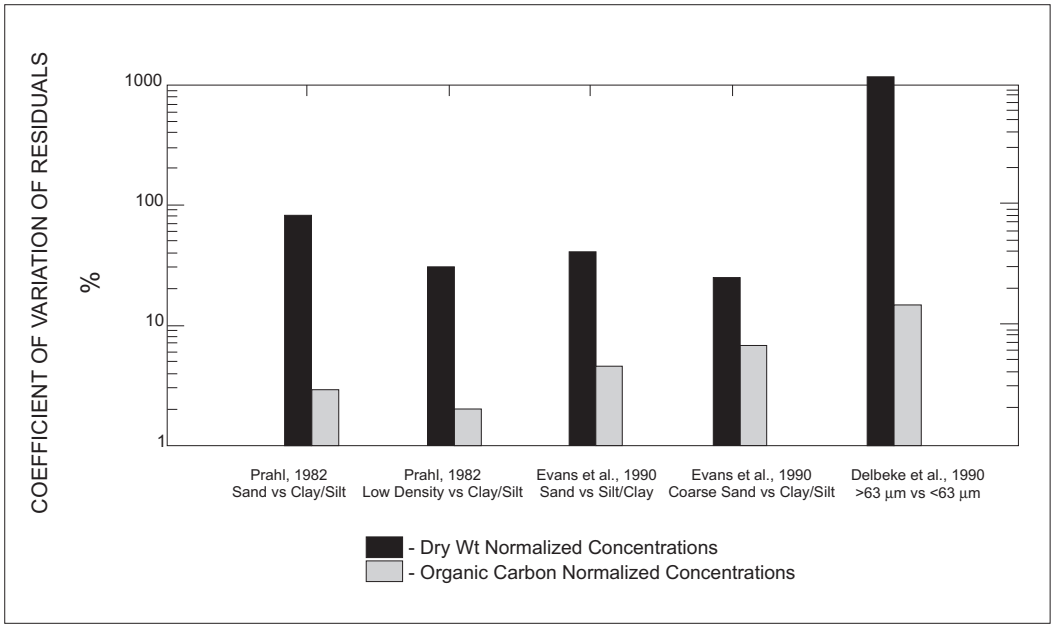

Figure 7. Coefficients of variation.

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