Chapter 3

Development of Sediment Hazard Scores

One major objective of the Point Source Inventory was to develop and employ a screening-level hazard analysis procedure to identify and prioritize watersheds where active point sources may contribute to sediment contamination, and to generate a relative ranking of chemicals and industrial source categories that are potential contributors. To enable screening-level analyses, chemical-specific sediment hazard scores (SHSs) were developed and used to normalize the annual chemical loads (ACLs) in the Point Source Inventory. In the screening-level analysis (described in Section 4), ACLs were multiplied by chemical-specific SHSs to produce hazard-weighted releases (HAZRELs):

$$HAZREL = SHS * ACL \qquad \text{Equation 2}$$

where:

SHS = Sediment hazard score, a product of the FATE and TOX scores as described below, and

ACL = Annual chemical load, the annual release amount (lb/yr) of a specific chemical from individual industrial or municipal treatment facilities.

SHSs are intended to represent both the potential of a particular chemical to accumulate in sediment upon discharge to surface water (independent of the characteristics of the site) and the potential ecological and human health risk posed by the chemical. The SHS is the product of the chemical-specific toxicity (TOX) score and chemical-specific fate (FATE) score. The TOX score is intended to represent the potential for adverse effects to human health and aquatic life from chemicals in sediment. The FATE score is intended to represent the potential for a chemical to partition to and persist in sediment. Four previous works were examined to assist in the development of the screening-level hazard analysis methodology:

- National Sediment Quality Survey (Site Inventory, peer-reviewed, USEPA, 1996b);

- Established methods of determining sediment toxicity (USEPA, 1992b);

- Superfund's Hazard Ranking System, Final Rule (USEPA, 1990a); and

- NOAA's pesticide hazard rating system (Pait et al., 1992).

Calculated SHSs, TOX scores, and FATE scores, along with the information required to calculate them (i.e., sediment chemistry screening values and physical/chemical properties), are presented in Appendix A of this report.

The HAZREL computed for a facility's discharge of a specific chemical is assigned a HAZREL score. The HAZREL score is a unitless index of the magnitude of potential sediment contamination based on chemical/facility-specific releases, physical and chemical properties, and potential environmental risk. The mathematical relationship of HAZREL scores to HAZRELs is given by the following equation:

$$\textit{HAZREL score} = \textit{INT} \; (\log_{10} \; (\textit{HAZREL})) + 1 \qquad \text{Equation 3}$$

Values less than zero or greater than 5 are set to zero and 5, respectively. HAZREL scores indicate the potential contribution to sediment contamination in the absence of any knowledge of historical or nonpoint source inputs and site-specific conditions (e.g., stream velocity, organic carbon content of underlying sediment) affecting chemical fate and intermedia partitioning. HAZREL scores may be used to rank and compare potential sediment contamination sources. Once the HAZREL scores were calculated for each chemical-facility combination, a number of data aggregations were performed to evaluate chemical classes and industrial categories for their relative potential risk of causing sediment contamination, and to identify watersheds where the risk of contamination from active point sources might be the greatest.

Table 3-1 illustrates the assignment of HAZREL scores. In general, the HAZREL score represents the magnitude of the HAZREL (product of SHS times ACL). However, if the HAZREL is less than 1, the release is assigned a HAZREL score of zero. This assumes that these releases are not significant potential contributors to sediment contamination, and is intended to focus attention on larger releases with greater hazard potential. The column headings of Table 3-1 provide chemicals representative of each SHS range as a reference.

Table 3-1. Assignment of HAZREL Score

Annual Chemical Load (lb/yr)	Sediment Hazard Score (TOX Score * FATE Score)					
	0.001 (e.g., phenol)	0.01 (e.g., zinc)	0.1 (e.g., fluorene)	1 (e.g., pyrene)	10 (e.g., mercury)	>100 (e.g., PCBs)
<0.01	0	0	0	0	0	1
0.1	0	0	0	0	1	2
1	0	0	0	1	2	3
10	0	0	1	2	3	4
100	0	1	2	3	4	5
1,000	1	2	3	4	5	
10,000	2	3	4	5		
100,000	3	4	5			

For example, the sediment hazard posed by mercury is approximately 10 times the hazard posed by pyrene. This scoring system allows comparison of annual loads of chemicals that vary in their hazard potential. For example, an annual load of 1,000 pounds of zinc is approximately equivalent to an annual load of 100 pounds of fluorene or 10 pounds of pyrene or 10,000 pounds of phenol: each receives a HAZREL score of 2. These scores can also be summed across aggregate units. For example, 20 facilities each releasing 100 pounds of mercury per year (HAZREL score = 4) in a given watershed would yield a watershed HAZREL score of 80 (20 times 4).

Chemical-Specific Toxicity Score

Sediment contamination is a function of the mixture and concentration of toxic pollutants in the sediment and the physical and chemical characteristics of the site. To assess potential sediment toxicity, sediment chemistry data must be related to adverse biological effects. Numerical effects-based, chemical-specific sediment chemistry screening values have been used to assist analysts and managers in the evaluation of sediment chemistry data and to identify and prioritize problem areas (Di Toro et al., 1991). The TOX score is one component of the SHS. This chemical-specific value was calculated by taking the inverse of the chemical's derived sediment chemistry screening value reported in milligrams per kilogram (mg/kg). Because the inverse of the sediment chemistry screening value is used, the TOX score increases in direct proportion to the toxicity of the chemical.

Several methods are currently available for developing sediment quality screening values (USEPA, 1992b). Most of these methods require information on site-specific conditions (field data) and chemical-specific properties. However, because field data are not available for each point source discharge location, screening values for use in this analysis must be based on empirical methods that make use of available data from a variety of sites, or mechanistic methods where the site-specific components can be reasonably assumed. The NOAA National Status and Trends program's effects range approach and the State of Washington's apparent effect threshold approach use existing sediment chemistry and biological effects data from a variety of sites, and EPA's equilibrium partitioning approach has a site-specific component that can be reasonably assumed. The preferred approach for screening value estimation depends on the properties and expected chemical partitioning associated with the released chemical.

In this study, a combination of the equilibrium partitioning (EqP) approach and biological effects correlation approaches was used to estimate sediment chemistry screening values for the protection of aquatic life. The theoretical bioaccumulation (TBP) approach was used to estimate sediment chemistry screening values for human health assessments. Appendix A contains a listing of all the calculated sediment chemistry screening values for the chemicals of interest contained in the Point Source Inventory.

It is important to note that the certainty with which sediment toxicity can be predicted for each chemical varies significantly based on the quality of the available data and the appropriateness of exposure assumptions. Estimated sediment chemistry screening values are to be used for screening purposes only. Their purpose is to obtain a relative ranking of potential hazard for aquatic bottom sediments from point source pollutant discharges to surface waters. The following limitations of the estimated sediment chemistry screening values should be noted:

- Values may be overprotective or underprotective of actual site-specific sediment because methodological and exposure conditions vary considerably.

- Values are general approximations of concentrations potentially leading to adverse effects because data and assessment methods are continually being compiled and developed.

- Values are based on a composite of several different sediment assessment approaches and a variety of data sources, the application of which EPA has not adopted or endorsed for use outside this and other screening-level analyses.

EPA has proposed sediment quality criteria (SQCs) for five chemicals based on extensive data quality and quantity requirements and methodologies that have gone through extensive peer review. The other estimated sediment chemistry screening values for additional chemicals presented in Appendix A of this report do not represent proposed SQCs. The sediment chemistry screening values were developed or compiled for the evaluation of Site Inventory data. The remainder of this section provides a brief overview of the screening values. The interested reader should consult the Site Inventory report and appendices (USEPA, 1996b) for detailed descriptions and explanations.

Aquatic Life Screening Values

The sediment chemistry screening values used to evaluate potential adverse effects to aquatic life include theoretically and empirically based values. The theoretically based values rely on demonstrated laboratory toxicity and physical/chemical properties of sediment to predict a concentration level that protects the benthic community from chronic adverse reproductive or growth effects. The empirically based, or correlative, threshold values rely on paired field and laboratory data to relate incidence of observed adverse biological effects to the dry-weight sediment concentration of a specific chemical.

The theoretically based screening values, limited to nonionic organic compounds, include the following parameters:

- **Sediment Quality Criteria (SQCs):** EPA (1993a, b, c, d, e) has developed SQCs for five chemicals using the equilibrium partitioning (EqP) approach, which involves predicting a dry-weight sediment concentration that is in equilibrium with a threshold pore water concentration using the chemical-specific organic carbon/water partition coefficient (K_{oc}) and the site-specific organic carbon content. The EqP approach is described in detail in Appendix B of the Site Inventory report. SQCs are based on the highest-quality data available, which have been reviewed extensively.

- **Sediment Quality Advisory Levels (SQALs):** SQALs were also developed using the EqP approach, but the data used to derive the SQALs came from limited sources and have undergone limited peer review.

For purposes of calculating sediment hazard scores for the chemicals with available SQCs and SQALs, a default organic carbon content of 1 percent was used because of lack of site-specific sediment information in PCS and TRI. In practical application, the organic carbon content can vary a great deal, as can important other binding phases at any given site.

The empirically based, correlative approaches used for the Point Source Inventory include the following upper screening values. Each of these parameters has a corresponding lower (more stringent) screening value that was not used in the development of TOX scores and subsequent sediment hazard scores. The primary limitation to use of these values for chemical-specific analyses is the possible effects of other toxic agents that may be present at the field site where biological effects are observed. The correlative approaches tend to result in screening values that are lower than the theoretical SQCs and SQALs, which address the effect caused only by a single contaminant.

- **Effects Range-Median (ERM):** Values above the ERM are defined as being in the "probable-effects range" (Long et al., 1995). The ERM is the 50th percentile of the distribution of measured concentrations associated with an observed adverse effect.

- **Apparent Effects Threshold-High (AETH):** Developed by Barrick et al. (1988), the AET-high or AETH is the highest concentration at which observed adverse effects demonstrated statistically significant differences from reference conditions.

- **Probable Effects Levels (PELs):** Toxic effects were found to occur usually or frequently at concentrations above the PELs (FDEP, 1994).

Human Health Screening Values

To evaluate the potential risk to human consumers of organisms exposed to sediment contaminants, a theoretical bioaccumulation potential (TBP) was calculated. A TBP is an estimate of the equilibrium concentration of a contaminant in fish tissue if the sediment in question were the only source of contamination. At present, a TBP calculation can only be performed for nonpolar organic chemicals based on the concentration of contaminant in the sediment, the organic carbon content of the sediment, the lipid content of the fish, and the relative affinity of the chemical for sediment organic carbon and fish lipid. The relative affinity is a field-measured biota-sediment accumulation factor (BSAF). The TBP calculation and the selection of BSAFs are discussed in detail in Appendices B and C of the Site Inventory report (USEPA, 1996b). Because data on site-specific conditions were not available from the PCS and TRI data sets, average default values for organic carbon content (1 percent) and lipid concentration (3 percent) were used in the TBP calculation in this study.

Human health screening values were derived by using EPA risk levels and solving the TBP equation for sediment concentration. EPA fish tissue risk levels were calculated using a fish consumption rate of 6.5 grams per day and an average adult body weight of 70 kilograms, the same exposure parameters EPA uses to develop human health water quality criteria. Cancer risk levels were calculated using recommended slope factors and a target risk level of 10^{-5}. Noncancer risk levels were calculated using recommended reference doses and a target hazard quotient of 1. Example risk calculations and slope factors and reference doses are presented in the Site Inventory report (USEPA, 1996b).

Chemical-Specific Toxicity Scores

The overall sediment chemistry screening value is the lower of the aquatic life screening value and human health screening value. The aquatic life screening value for a particu-

lar chemical was selected in the following descending order of availability: SQCs, SQALs, ERMs, AETHs, and PELs. This selection hierarchy reflects the EPA preference for screening values that can reliably attribute adverse effects to the chemical of interest, especially for a chemical-specific loading analysis such as this. As previously stated, the inverse of the sediment chemistry screening value serves as the TOX score to produce a positive relationship between screening values and TOX scores. In other words, the more stringent the screening value, the greater the TOX score.

Chemical-Specific Fate Score

The second component of the Sediment Hazard Score (SHS) is the FATE score. The FATE score is the product of the air/water partitioning subfactor (HLC score), sediment adsorption subfactor (KOC score), and biodegradation subfactor (BIODEG score). The potential for a chemical to accumulate in the underlying sediment upon discharge to surface water depends greatly on site-specific characteristics such as sediment organic matter content, temperature, suspended particulate matter, and the lotic or lentic nature of the receiving water body. The physical/chemical properties of the pollutants also affect their transport and persistence in the aquatic environment. The chemicals of interest in the Point Source Inventory differ widely in their physical/chemical properties. Some chemicals are very likely to partition to and to persist in the sediment, some will likely volatilize, and others will rapidly degrade. Therefore, a FATE score with sediment adsorption, air/water partitioning, and aqueous degradation subfactors was used. Three physical/chemical properties for organic sediment contaminants were obtained for the chemicals in the inventory: the sediment adsorption coefficient or K_{oc}, the Henry's Law constant (HLC), and the aerobic aqueous biodegradation half-life.

The two transport subfactors, air-water partitioning and sediment adsorption, are represented by chemical-specific HLC and K_{oc} values, respectively. These subfactors were treated in a manner similar to that used in the pesticide hazard rating system devised by Pait et al. (1992). Individual HLC and K_{oc} values were assigned scores ranging from 0.1 to 1. These values were then multiplied to produce a score that represents the likelihood of transport to the sediment.

The aqueous degradation subfactor is represented by chemical-specific aerobic biodegradation half-lives. Because the sediment hazard score was applied to annual release amounts, the half-life was converted to an annual loss rate constant and multiplied by the transport value (i.e., the product of the two transport subfactor scores) to arrive at the final FATE score.

Air-Water Partitioning Subfactor

The Henry's Law constant (HLC) is the ratio of vapor pressure to solubility and is indicative of the propensity of a chemical to volatilize from surface water (Lyman et al., 1982). The larger the HLC, the more likely the chemical will volatilize. Lyman et al. (1982) state that a chemical with an HLC less than 3×10^{-7} (atm-m^3/mole) is essentially nonvolatile, and a chemical with an HLC greater than 10^{-3} (atm-m^3/mole) will volatilize rapidly from surface water. HLC scores were calculated according to the following steps:

1. All values $> 10^{-3}$ were assigned a score of 0.1.

2. All values $< 3 \times 10^{-7}$ were assigned a score of 1.0.

3. All other values were assigned a score using Equation 4 to evenly distribute scores across the range of values:

$$HLC_{score} = \left[\frac{\log(10^{-3}) - \log(HLC)}{\log(10^{-3}) - \log(3 \times 10^{-7})} * 0.9 \right] + 0.1 \qquad \text{Equation 4}$$

where:

HLC_{score} = air-water partitioning subfactor and

HLC = Henry's Law constant (atm-m^3/mole).

Sediment Adsorption Subfactor

K_{oc} is a chemical-specific adsorption parameter that is largely independent of the properties of soil or sediment and can be used as a relative indicator of adsorption to such media. Although a high K_{oc} value indicates that a chemical is more likely to partition to sediment, it also indicates that a chemical may be less bioavailable. K_{oc} is highly inversely correlated with solubility and fairly well correlated with BSAF.

U.S. EPA (1993b) recommends using the following regression equation to calculate the organic carbon-water partition coefficient (K_{oc}) from the octanol-water partition coefficient (K_{ow}):

$$\log_{10}K_{oc} = 0.00028 + 0.983 * \log_{10}K_{ow} \qquad \text{Equation 5}$$

Where available, K_{oc} values were calculated from the latest EPA-recommended octanol-water coefficient (K_{ow}) (Karickhoff and Long, 1995). Other K_{ow} values used included those derived from the slow-stir flask method, which were selected preferentially over other laboratory values reported in literature (USEPA, 1993f).

KOC scores were calculated according to the following steps:

1. All values $> 10^6$ were assigned a score of 1.0.

2. All values $< 10^2$ were assigned a score of 0.1.

3. All other values were assigned a score using Equation 6 to evenly distribute scores across the range of values:

$$KOC_{score} = \left[\frac{\log(K_{oc}) - \log(10^2)}{\log(10^6) - \log(10^2)} * 0.9 \right] + 0.1 \qquad \text{Equation 6}$$

where:

KOC_{score} = sediment adsorption subfactor and

K_{oc} = organic carbon-water partition coefficient (L/kg).

Aqueous Biodegradation Subfactor

Although many physical and chemical processes can contribute to degradation (e.g., hydrolysis, photolysis, biological degradation), aerobic biodegradation half-life was selected as the sole indicator of environmental persistence of a chemical released to the water column. Ignoring other removal mechanisms is a conservative approach because it can only overestimate rather than underestimate a chemical's persistence potential. Aerobic aqueous biodegradation half-lives are empirically derived time periods when half of a chemical load released to water is degraded by microbial action in the presence of oxygen. Although the degradation products may be equal in toxicity to or even more toxic than the parent, evaluation of chemical metabolites was not considered in the hazard analysis. Aerobic biodegradation half-lives for the current set of potential sediment contaminants range from 4 hours to 16 years.

Half-lives in days were converted to loss rate constants in (years)$^{-1}$ using the following equation:

$$\lambda = \frac{\ln(2) * 365}{t^{\frac{1}{2}}} \qquad \text{Equation 7}$$

where:

λ = loss rate constant (year)$^{-1}$;

$\ln(2)$ = natural log of 2;

$t^{1/2}$ = aqueous aerobic biodegradation half-life (days); and

365 = conversion factor (days per year).

Because other factors, such as deep burial, might become important over time, chemicals with reported half-lives greater than 7 years were assigned a half-life of 7 years. This results in the largest BIODEG score of 10. The BIODEG score was calculated by taking the

inverse of the loss rate constant so that more persistent compounds would have higher values:

$$BIODEG_{score} = \frac{1}{\lambda} \qquad \text{Equation 8}$$

The FATE score was calculated by combining the HLC, KOC, and BIODEG scores according the following formula:

$$FATE_{score} = (BIODEG_{score}) * (HLC_{score}) * (KOC_{score}) \qquad \text{Equation 9}$$

Metals, which will not degrade or volatilize, were assigned a BIODEG score of 10 and an HLC score of 1. The relative partitioning of dissolved metal between the water column and the underlying sediment is a function of site-specific conditions, not inherent properties of the metal. Therefore, metals were assigned a KOC score of 0.5, representing the midpoint of all possible values.

Functions of Sediment Hazard Score Components

The overall general equation for the SHS is:

$$SHS = TOX_{score} * FATE_{score} \qquad \text{Equation 10}$$

where:

TOX_{score} = $(SCV)^{-1}$;

$FATE_{score}$ = $KOC_{score} * HLC_{score} * BIODEG_{score}$;

SHS = sediment hazard score (unitless);

SCV = sediment chemistry screening value (based on screening values in units of mg/kg);

KOC_{score} = sediment adsorption subfactor (unitless);

HLC_{score} = air-water partitioning subfactor (unitless); and

$BIODEG_{score}$ = aqueous biodegradation subfactor (unitless).

The function of the sediment chemistry screening value in the SHS is to increase or decrease the HAZREL relative to the annual chemical load (ACL) based on the toxicity exhibited by the chemical. Ignoring the effects of the FATE score components, a chemical with a sediment chemistry screening value less than 1 mg/kg has an SHS greater than 1 and higher HAZRELs than ACLs. On the other hand, a chemical with a sediment chemistry

screening value greater than 1 mg/kg has an SHS less than 1 and lower HAZRELs than ACLs. The magnitude of the effect on the HAZREL is in direct proportion to the magnitude of the sediment chemistry screening value versus a value of 1 mg/kg. The "standard" of 1 mg/kg is arbitrary and does not have any physical or biochemical significance.

The function of the BIODEG score is to adjust the HAZREL relative to the ACL based on a chemical's persistence in the aquatic environment. Half-life values in days were converted to a loss rate constant in (years)$^{-1}$. The BIODEG score, which is the inverse annual loss rate constant, has the mathematical effect of converting an annual surface water load to a steady-state mass of chemical in the water column. Chemicals with a half-life greater than 253 days (ln(2) * 365 days/yr) have a BIODEG score greater than 1, which increases the HAZREL. This indicates that the steady-state mass is greater than the annual load (i.e., net accumulation). Conversely, chemicals with a half-life less than 253 days have a BIODEG score less than 1, which decreases the HAZREL. This indicates that the steady-state mass is less than the annual load (i.e., net loss). The magnitude of the effect on HAZREL is in direct proportion to the magnitude of the half-life versus a value of 253.

The functions of the KOC score and HLC score are to decrease the HAZREL depending on the chemical's propensity to partition to sediment or volatilize from the water column. If a chemical is hydrophilic and has little propensity to bind to sediment, the HAZREL will decrease by as much as one order of magnitude. Likewise, if a chemical has a strong tendency to volatilize, the HAZREL will also decrease by as much as one order of magnitude. This relatively small adjustment was made because of the many mitigating site-specific factors that affect intermedia partitioning.

The sediment chemistry screening values and ACLs for the chemicals of concern in this analysis vary over more orders of magnitude than do biodegradation half-lives, KOC scores, and HLC scores. Therefore, HAZRELs are primarily driven by ACLs and chemical toxicity.

The sensitivity of the parameters used in SHS calculation, with the exception of K_{oc}, are depicted in Figure 3-1. Note that the x-axis labels represent the factor by which the original values are multiplied (i.e., the effect of doubling a given parameter on the SHS is read from the point labeled "2" on the x-axis). Likewise, the y-axis labels represent the change in SHS values resulting from altering input parameters. For example, if the percent OC is halved ("0.5" on the x-axis), the SHS would be doubled ("2" on the y-axis). The sensitivity of K_{oc} is depicted in Figure 3-2 in three parts: one for the effect based on KOC score (increase in K_{oc} means greater propensity to partition to sediment and higher SHS), one for the effect based on the equilibrium partitioning approach (increase in K_{oc} means less bioavailability and lower SHS), and one for the overall K_{oc} effect.

The overall uncertainty in the SHS precludes their use in analyses that require a high degree of accuracy. However, this level of uncertainty is acceptable for meeting the objective of performing a screening-level hazard analysis.
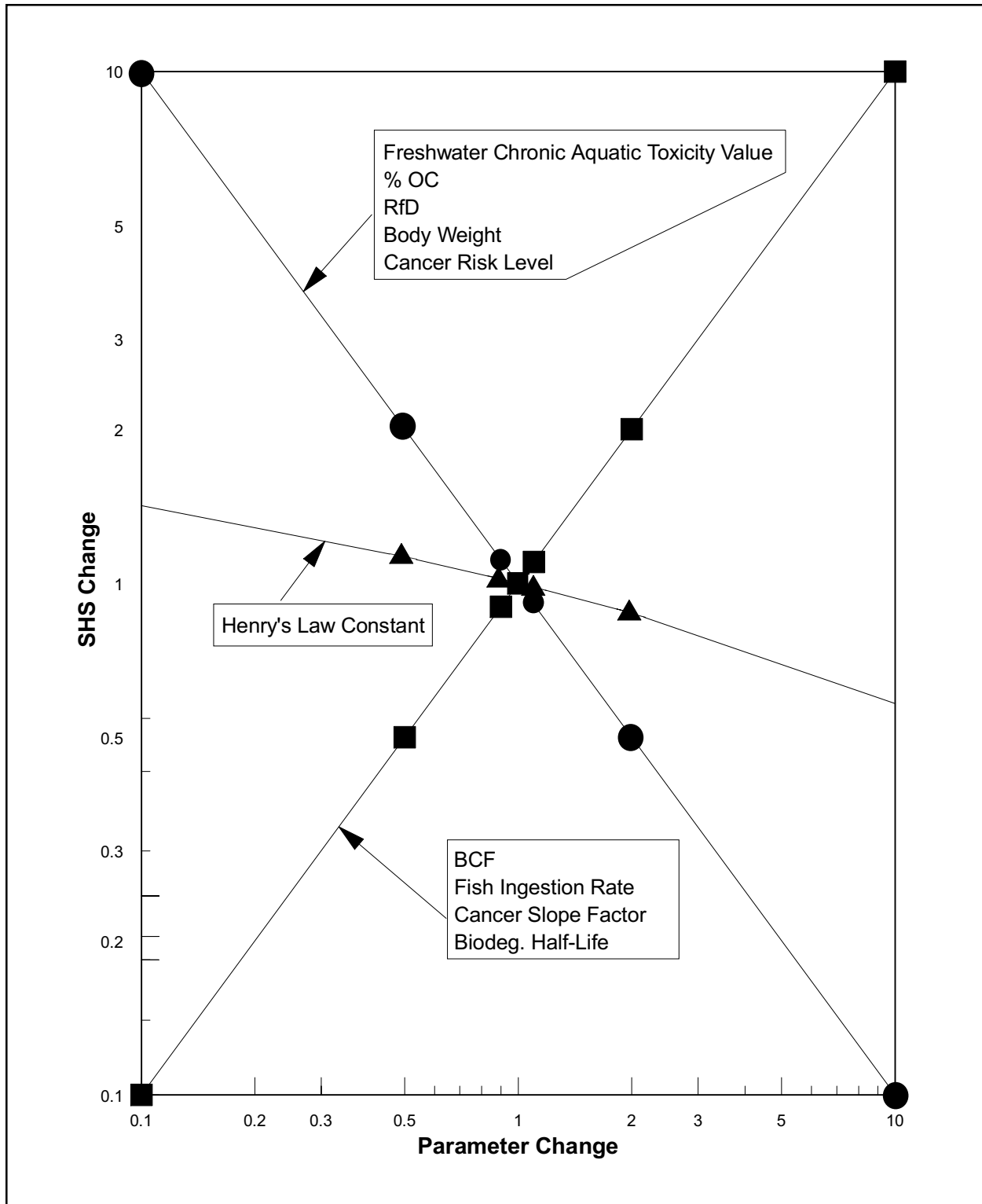
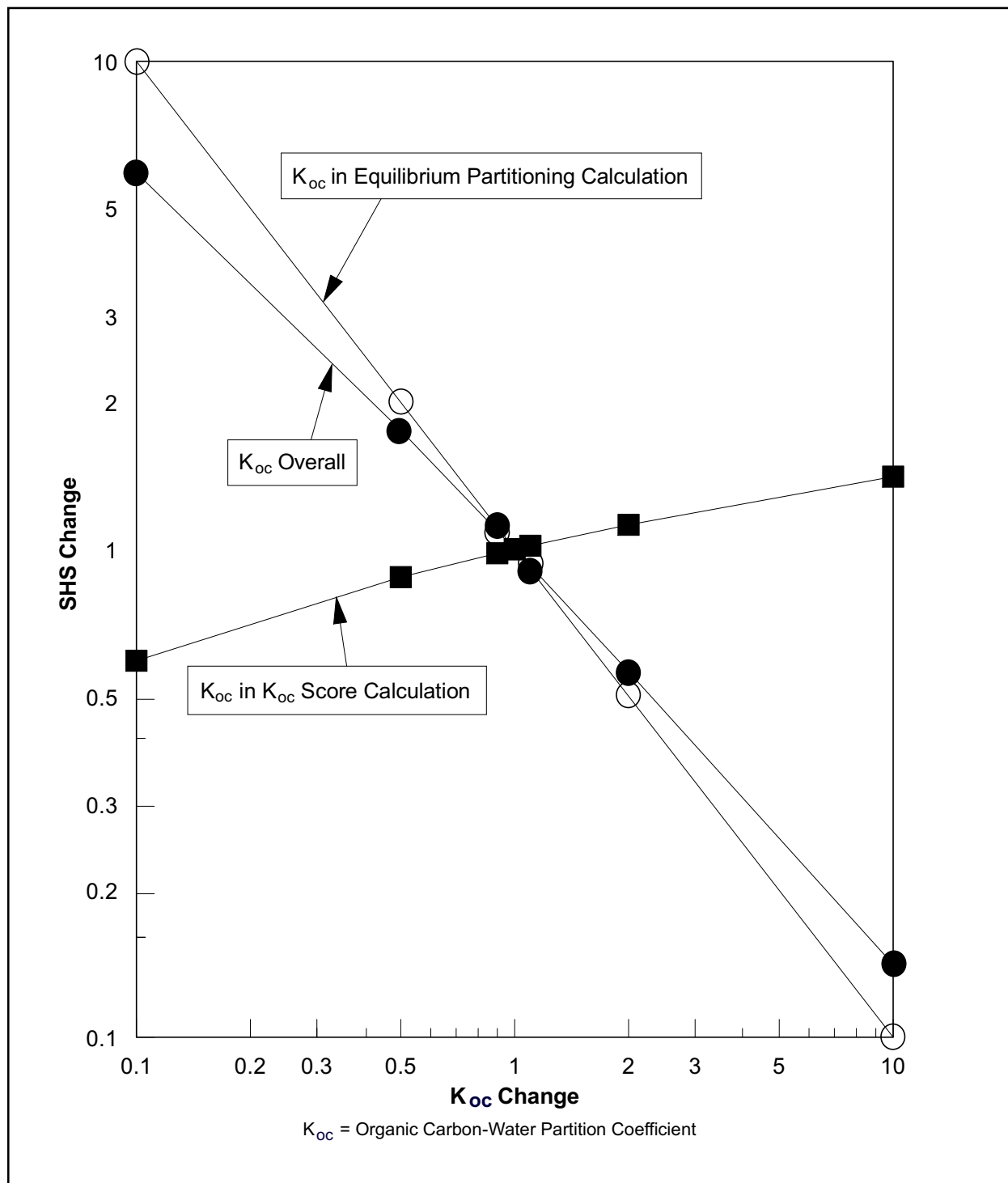**Figure 3-1. Sediment hazard score (SHS)—Parameter sensitivity.**

Figure 3-2. Sediment hazard score (SHS)—K_{oc} sensitivity.