

# Section 5

## Chemical Fate and Transport

An understanding of the fate and transport processes acting on the COPCs in the Calcasieu Estuary is critical when predicting the distribution of the COPCs between different media in the environment (i.e. sediment, water, soil, and air) under various conditions (pH, salinity, etc.). As the conditions change in the environment, the distribution of the COPCs in the media and the form of the COPCs can change (i.e., the oxidation state, molecular configuration, ionic charge, aqueous species), which can affect the mobility and toxicity of the compounds. This section discusses the theoretical aspects of fate and transport processes in the environment, including equations that define and/or control these processes. Section 5.1 provides a general description of the fate and transport processes of concern. Section 5.2 elaborates on the estuarine environment and how conditions can change due to natural cycles (tides and spring run-off), weather patterns (storms), and acts of man (i.e., channel dredging, deforestation, etc.). Described throughout is form and behavior of each of the major types of COPC, including the most important fate and transport processes under various conditions within the estuarine environment.

The fate and transport processes discussed are provided as a basis for understanding the presence of contamination within the estuary. Table 5-1 provides detailed chemical property values (e.g., water solubility, vapor pressure, Henry's Law constant,  $K_{OC}$ , and bioaccumulation factor) for each COPC. These properties and processes will be referred to throughout the data interpretation sections for each AOC (Sections 7 [Bayou d'Inde], 8 [Bayou Verdine], and 9 [Upper Calcasieu] and 10 [Lower Calcasieu]) to describe the distribution of the COPCs between different media.

### 5.1 Fate and Transport Processes

Fate and transport processes determine the phase in which a COPC may exist, and, along with the dynamics of the environment, the mobility and bioavailability of the compound. The most important fate and transport processes depend on the environment (e.g., estuary, river, shallow lake, etc.) and on the chemical-specific properties of the COPC. The major fate and transport processes are:

- Adsorption/Desorption
- Volatilization/Condensation
- Precipitation and co-precipitation
- Degradation/Transformation

These processes will be described in the following sections, along with a summary of the important processes for the major classes of compounds (e.g., metals, PAHs, etc.) of interest in the Calcasieu Estuary.

### 5.1.1 Adsorption/Desorption

One of the key geochemical processes affecting the rate of migration of the COPCs is the adsorption to and desorption from sediments and suspended particulate matter. If the organic chemical is strongly adsorbed to the sediment, the chemical is relatively immobile and will not be leached or transported from the source. If the organic chemical is weakly adsorbed, the chemical can be more readily transported. The degree of adsorption also effects other transformation reactions such as volatilization, hydrolysis, and biodegradation. The rates of such reactions are directly dependent upon the degree of adsorption.

In the following discussions, the word adsorption is used because typically the most important processes causing retention of organic molecules are adsorption processes rather than absorption processes. Some texts have preferred to use the more generic term "sorption" to avoid any mechanistic connotations (Callahan et al. 1979). In selected cases, the word "partitioning" will also be used.

The distribution of chemicals between water and the sediment or suspended particles is often described by the soil/water distribution coefficient,  $K_d$ . The distribution coefficient is a constant, relating the thermodynamic activities of the two phases:

$$K_d = \frac{\alpha S}{\alpha W}$$

Where:

- $\alpha S$  = Activity of the chemical in the sediment (or suspended particles)
- $\alpha W$  = Activity of the chemical in the water (aqueous phase)

Because the activities are equal to the activity coefficients multiplied by the chemical concentrations and the activity coefficients approach unity for environmental concentrations, the distribution coefficient is usually defined as the ratio of concentrations in the solid and water phase (Freeze and Cherry 1979) or as:

$$K_d = \frac{C_s}{C_w} = \frac{\text{mass of solute on the solid phase per unit mass of solid phase}}{\text{concentration of solute in solution}}$$

$C_s$  is usually expressed in terms of milligrams per kilogram (mg/kg) or parts per million (ppm in the solid), and  $C_w$  is expressed in terms of milligrams per liter (mg/L) or ppm in the water, if the density equals one. Therefore, the units on  $K_d$  are:

$$\frac{\text{mg/kg}}{\text{mg/L}} = \frac{\text{L}}{\text{kg}} \text{ or } \frac{\text{mL}}{\text{g}}$$

### 5.1.1.1 Organic Constituents

For organic compounds, the value of  $K_d$  increases with increasing organic carbon content of the sediment. Typically,  $K_d$  values are not available in the literature for all organic carbon contents possible in estuarine sediments. Therefore,  $K_d$  is usually normalized for the amount of organic carbon in the soil, resulting in a new parameter,  $K_{oc}$ , the organic-carbon partition coefficient.

$$K_{oc} = \frac{K_d}{f_{oc}}$$

Where:

$$\begin{aligned} f_{oc} &= \text{The fraction of natural organic carbon in the sediment} \\ &= \% \text{ TOC}/100 \\ &= (\text{mg}/\text{kg TOC})10^6 \end{aligned}$$

This relation implies that adsorption is linearly related to the amount of organic carbon in the sediment. While  $K_d$  may vary greatly in different sediments,  $K_{oc}$  usually does not vary by more than a factor of two to three (Goring 1962).  $K_{oc}$  can also be defined as follows:

$$K_{oc} = \frac{\text{mg of adsorbed chemical}/k \text{ g of organic carbon}}{\text{mg of chemical in solution}/L \text{ of solution}}$$

Historically, reported adsorption results were typically reported on the basis of soil organic matter (rather than soil organic carbon). The ratio of organic matter to organic carbon varies by soil type, but, in most cases, a value of 1.724 is used to convert organic matter to organic carbon. That is,

$$\begin{aligned} K_{oc} &= 1.724 K_{om} \\ \log K_{oc} &= \log 1.724 + \log K_{om} \end{aligned}$$

Studies have shown that the organic matter present in the sediment dominates the adsorption process. However, as the fraction of organic carbon becomes small, adsorption of organic chemicals to inorganic surfaces (mostly clays) also becomes important. The critical level of organic carbon ( $f_{oc}^*$ ) is the concentration below which the inorganic fraction dominates the adsorption process. McCarty et al. (1981) developed the following equation to calculate  $f_{oc}^*$ :

$$f_{oc}^* = \frac{(SA)}{200} \frac{1}{K_{ow}^{0.84}}$$

Where:

SA = Surface area of soil square meters/gram (m<sup>2</sup>/G)  
K<sub>ow</sub> = Octanol-water partition coefficient

When  $f_{oc}$  is higher than  $f_{oc}^*$ , the  $K_{oc}$  value can be estimated from the solubility of the compound in water or the octanol/water partition coefficient ( $K_{ow}$ ). High values of  $K_{ow}$  indicate the compound is hydrophobic and typically partitions out of the water and into the organic phase (in this case octanol). Therefore, by evaluating  $K_{ow}$  and solubility data, the relative importance of adsorption onto organic matter within the sediment for various classes of organic compounds can be determined. Exhibit 5-1 presents examples of typical solubility values and log octanol-water partitioning coefficients.

**Exhibit 5-1 Example Log Octanol-Water Partitioning Coefficients**

Compound Name	Group	Solubility (mg/L)	Log Octanol-Water Partitioning Coefficient (Log K <sub>ow</sub> )
Acetone	VOC	1 x 10 <sup>9</sup>	-2.40
Hexachlorobenzene	SVOC	0.006	5.23
Pyrene	PAH	0.132	4.88
Aroclor 1254	PCB	0.012	6.50
Aldrin	Pesticide	0.0180	5.30
2,3,7,8-TCDD	Dioxin	2.0 x 10 <sup>-4</sup>	6.84

In general, adsorption is most important for the dioxins, pesticides, PCBs, and SVOCs and less so for VOCs. However, other factors can affect the adsorption of organic compounds, including salinity and pH.

Salinity can have an impact on the adsorption of organic chemicals due to a process called salting out. Salting out occurs when water with a high concentration of dissolved ions (i.e., salts) has less water available for dissolving hydrophobic compounds or species. The ions being charged tend to attract the polar water molecules while leaving non-polar organic compounds with less water to dissolve into. Therefore, hydrophobic compounds will have even more tendency to partition to organic matter with the sediment. The process can occur not only with organic compounds, but also with non-charged species such as mercuric chloride (HgCl<sub>2</sub>) and organically complexed or methyl mercury (Turner et al. 2001).

#### 5.1.1.2 Inorganic Constituents

Inorganic constituents adsorb to mineral surfaces and the surfaces of chemical precipitates within sediment. Generally, inorganic adsorption is independent of the amount of organic carbon, with the exception of mercury, cyanide, and copper. Exhibit 5-2 lists the  $K_d$  values for several important inorganic species.

**Exhibit 5-2 Example Partitioning Coefficients for Inorganic Constituents**

Name	Species	Partitioning Coefficient ( $K_d$ ) (for Silt) <sup>1</sup>
Arsenic (V)	$HAsO_4^{2-}$	1.9-18
Cadmium	$Cd^{2+}$	40.4
Cobalt	$Co^{2+}$	1339
Copper	$Cu^{2+}$	1.4-333
Chromium (III)	$Cr^{3+}$	470-150,000
Lead	$Pb^{2+}$	4.5-7640
Mercury (II)	$Hg^{2+}$	5012-1,000,000 <sup>2</sup>
Nickel	$Ni^{2+}$	299
Zinc	$Zn^{2+}$	1339

1. Thibault et al. 1990 except where noted otherwise  
2. Measured in estuaries (Turner et al. 2001).

The  $K_d$  values listed above have some wide ranges of values due to the large number of variables that can affect the measurements. The most important variables include the following:

- pH of the water
- Sediment grain size
- Concentrations of competing ions present
- Ionic strength of the water (salinity)
- Mineralogy and organic carbon content of the sediment

The pH of the water can have an effect on both the speciation of the metals/metalloids and the surface charge of the adsorbing media. At low pH values, the surfaces of most of the important minerals within sediment are positively charged and tend to repel positively charged ions such as metals and attract negatively charged ions such as arsenic. At high pH, the surfaces tend to be negative and attract metals to a greater extent. The speciation of the ions can work against this trend by changing the charge on the ion itself. For instance, at high pH, metals can combine with hydroxide ions in solution, forming an aqueous complex with a neutral or negative charge.

Because adsorption is a surface phenomenon, the smaller the grain size of the adsorbing media the greater the surface area per mass of media and the greater the adsorption. Grain size has been found to be the most important parameter for explaining adsorption in most estuaries (Borrego et al. 2002).

Ions of similar character can compete for adsorption sites on the sediment. For example, sulfate and phosphate can compete for the same sites on a solid and adsorb

to a lesser extent together (in the same solution) than they do when measured separately. Adsorbed ions can be desorbed from the surfaces of soils and sediment when introduced to a solution of different chemistry, especially when the salinity is high. The process is called ion exchange and is very important in estuaries where saltwater and contaminated sediment may combine.

The ionic strength of the water can decrease the concentration of ions actually seen by the surfaces of the adsorbing media, which has the effect of decreasing the  $K_d$ . The process is important in estuaries due to the high ionic strength of saltwater.

The mineralogy of the sediment can influence adsorption of COPC metals or inorganics. For instance, arsenic has a strong affinity for iron-containing minerals while mercury and cyanide are attracted to organic matter.

### 5.1.2 Volatilization/Condensation

Volatilization is the process by which a chemical is transferred from soil or water into the atmosphere. For the discussion of transport in the aquatic environment, COPCs are typically at low concentrations (below saturation) and exist dissolved in the water phase (i.e., no free non-aqueous phase liquids).

The relation between the concentrations in the air and water is described by the following equilibrium:

$$K_H = \frac{1}{H} = \frac{[\text{Conc. in water}] (\text{mg/L})}{[\text{Conc. in air}] (\text{mg/L})}$$

Where H is Henry's Law Constant and typically expressed in units of atmospheres-cubic meters per mole ( $\text{atm}\cdot\text{m}^3/\text{mol}$ ). From the above equations, Henry's Law Constant is the controlling parameter in determining the amount of volatilization. In turn, Henry's Law Constant is related to various factors, the most important of which is vapor pressure expressed in millimeters of mercury (mm Hg). Examples of Henry's Law Constant for selected compounds are provided in Exhibit 5-3. A general guide to evaluate the importance of volatilization is as follows:

	Vapor Pressure (mm Hg)	H ( $\text{atm}\cdot\text{m}^3/\text{mol}$ )
Compound mostly in water	< $10^{-7}$	< $5 \times 10^{-5}$
Compound mostly in air	> $10^{-2}$	> $5 \times 10^{-3}$

The importance of volatilization as a transport mechanism will depend on the depth of the water layer containing the COPC, the degree of turbulence of the water, and the wind velocity just above the air/water interface.

**Exhibit 5-3 Henry's Law Constant for Example Compounds**

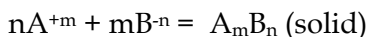
Compound	H (atm-m <sup>3</sup> /mol)	Compound Group
Benzene	5.6 x 10 <sup>-3</sup>	VOC
Vinyl chloride	1.1 x 10 <sup>-2</sup>	VOC
Hexachlorobenzene	6.8 x 10 <sup>-4</sup>	SVOC
Naphthalene	4.60 x 10 <sup>-4</sup>	PAH
Aroclor 1242	1.98 x 10 <sup>-3</sup>	PCB
DDT	1.58 x 10 <sup>-5</sup>	Pesticide
TCDD	1.61 x 10 <sup>-5</sup>	Dioxin

Based on the criteria above, volatilization is only important for the VOCs and some of the SVOCs, PAHs, and PCBs. The molecules with a greater atomic mass tend to be less subject to volatilization than the lighter molecules.

### 5.1.3 Precipitation and Co-precipitation

#### 5.1.3.1 Inorganics and Metals

Precipitation is the process where negatively and positively charged ions in solution combine to form a solid phase compound or mineral. Given the generalized reaction,



precipitation is governed by the following equation:

$$[A^{+m}]^n [B^{-n}]^m = K_{sp}$$

Where:

- [A<sup>+m</sup>] = The concentration of the positively charged ion (cation) in solution
- [B<sup>-n</sup>] = The concentration of the negatively charged ion (anion) in solution
- n = The relative number of cations that form the solid phase
- m = The relative number of anions that form the solid phase
- K<sub>sp</sub> = The solubility product constant

Ion A can represent positively charged ions (cations) such as zinc (Zn<sup>2+</sup>), mercury (Hg<sup>2+</sup>), or copper (Cu<sup>2+</sup>). Ion B represents an anion such as hexavalent chromium (CrO<sub>4</sub><sup>2-</sup>) or arsenic (HAsO<sub>4</sub><sup>2-</sup>). The product of the concentrations of A<sup>+m</sup> and B<sup>-n</sup> in solution cannot exceed the value of K<sub>sp</sub>. If either A<sup>+m</sup> or B<sup>-n</sup> is added to the solution to concentrations that would exceed the K<sub>sp</sub>, a precipitate of A<sub>m</sub>B<sub>n</sub> will form until the solubility product reaches the value of K<sub>sp</sub>. Solid phases or minerals, which are insoluble or have low solubility in water, have a low K<sub>sp</sub> value while very soluble

phases have a high  $K_{sp}$ . Therefore,  $K_{sp}$  values of phases, which contain one or more COPCs, can be used to evaluate precipitation as a potential fate and transport process.

$K_{sp}$  values for some example mineral phases are provided in Exhibit 5-4.

**Exhibit 5-4 Example Log  $K_{sp}$  Values**

Mineral	Formula	Log $K_{sp}$
Iron oxyhydroxide	FeOOH	$10^{-37}$
Birnessite	MnO <sub>2</sub>	$10^{18.1}$
Pyrite	FeS <sub>2</sub>	$10^{-18.5}$
Covellite	CuS	$10^{-23}$
Siderite	FeAsO <sub>4</sub>	$10^{-10.6}$
Mercury(I) hydroxide	Hg <sub>2</sub> (OH) <sub>2</sub>	$10^{5.3}$
Lead chromate	PbCrO <sub>4</sub>	$10^{-13.7}$

While many of the COPC-containing mineral phases listed above have relatively low  $K_{sp}$  values, they typically do not form precipitates due to the comparatively low concentrations of the COPCs present, even in waters that are considered contaminated. Typically, the levels of COPC required to trigger human health or environmental concerns is much less than is required to reach the solubility limit. Therefore, pure-phase minerals rarely control the dissolved concentrations of COPCs. However, precipitation of impure phases is often an important control on COPC concentrations. For example, iron oxyhydroxide, which in the pure phase does not control concentrations of any metals except for iron, can and usually is a very important control on metals such as copper, lead, and zinc when impure.

The process by which metals are precipitated along with iron oxyhydroxide is termed “co-precipitation.” COPC metals can substitute for iron within the structure of the mineral during precipitation, which can be a very important control on the aqueous concentrations of metals in the environment. Precipitation of iron oxyhydroxides can occur as a result of the oxidation of iron, which can be initiated by the turbulent conditions present in the tidal influenced areas of estuaries. Similar effects may be noted in outfall areas if dissolved oxygen is increased by outfall turbulence.

The only pure phases that commonly precipitate metals are the sulfide phases as evidenced by the extremely low  $K_{sp}$  values noted in Exhibit 5-4. Metal sulfides can precipitate under reducing conditions such as exist in the organic mud present in the low energy areas of many estuaries.

## 5.1.4 Degradation/Transformation Processes

### 5.1.4.1 Abiotic Degradation/Transformation

#### 5.1.4.1.1 Oxidation/Reduction

##### *Organic Compounds*

Oxidation is the loss of electrons during a chemical reaction. Typical abiotic oxidation reactions would include treatment processes using chlorine, ozone, or hydrogen peroxide. The result of complete reaction is conversion of the organic molecules to carbon dioxide and water. Such powerful abiotic oxidizing agents do not occur naturally in estuarine environments. Oxidation can occur through either of two major pathways: the polar reaction or free-radical reaction pathways. Typically, free-radical reactions are more common because less activation energy is required. Before an oxidation reaction can occur via the free-radical pathway, a free radical must be formed by the removal of a single electron from a molecule. This can occur through thermal energy, radiant energy, high-energy particles, and other mechanisms. Free-radical concentrations of the single oxygen in natural surface water are approximately  $10^{-12}$  M and results from the photo-disassociation of the water molecule. Once the free radicals are formed, they will react with organic molecules present to form an intermediate organic free radical, which usually reacts further.

Reduction of organic compounds (i.e., the addition of electrons to a molecule) can also transform organic COPCs. For example, chlorinated organic compounds can be transformed into less chlorinated or un-chlorinated compounds by reduction reactions. Typically, the process is biologically mediated.

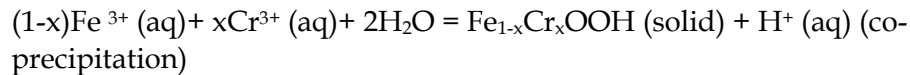
##### *Inorganic Compounds and Metals*

Unlike organic compounds, oxidation or reduction of inorganic compounds and metals cannot change the identity of the COPC. The aqueous species can change, which can have profound effects on the fate and transport properties of the COPC, but not the identity. The important metals and inorganics which undergo oxidation/reduction reactions include iron, manganese, sulfur, chromium, arsenic, and mercury. A roman numeral within parentheses following the name indicates the oxidation state of the metals.

**Iron.** While iron is not typically a COPC, the fate and transport of iron can strongly influence other metals and inorganics due to co-precipitation. The oxidation state of iron is an important parameter for predicting the precipitation of iron oxyhydroxide and the fate and transport of many metals. The formation of iron oxyhydroxide occurs by oxidation of iron (II) to iron (III) (usually by oxygen) followed by a precipitation or co-precipitation reaction as follows:

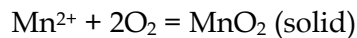


or

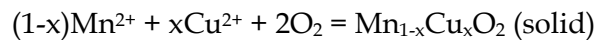


The example shown is for substitution of chromium into iron oxyhydroxide; however, many other metal substitutions can occur simultaneously. Arsenic, which is an anion, can substitute for hydroxide in the phase particularly when arsenic concentrations are high and the pH is low (Whiting 1992).

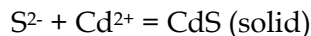
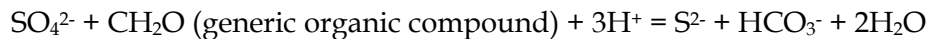
**Manganese.** Manganese, like iron, is mobile in the reduced phase ( $\text{Mn}^{2+}$ ) and relatively immobile in the more oxidized phase ( $\text{Mn}^{4+}$ ). The relevant reaction, which involves both oxidation of manganese and precipitation of manganese dioxide is as follows:



Manganese can also co-precipitate other metals, such as copper and cobalt as follows:



**Sulfur.** Sulfur is more mobile in the oxidized form (sulfate,  $\text{SO}_4^{2-}$ ) than in the reduced form (sulfide,  $\text{S}^{2-}$ ) due to precipitation of metal sulfide phases. The relevant reactions are as follows:



Metals/Metalloids capable of forming sulfide phases include copper, cadmium, iron, lead, nickel, and to a lesser extent arsenic and zinc.

**Chromium.** Chromium exists in two different oxidation states, chromium (III) and chromium (VI). Chromium (III) is much less mobile than chromium (VI) (also called hexavalent chromium) and is the more stable form in nature. Chromium (VI) is typically only encountered when released in this form. Additionally, chromium (VI) is eventually reduced to chromium (III) by fulvic and humic acids within soils or sediments, which is either co-precipitated with iron oxyhydroxide (see equation above) or adsorbed to soil or sediment grains.

**Arsenic.** Arsenic is more mobile in the reduced form (arsenic (III),  $\text{H}_3\text{AsO}_3^0$ ) than in the oxidized form (arsenic (V),  $\text{HAsO}_4^{2-}$ ) because arsenic (III) is uncharged while arsenic (V) is negatively charged. As mentioned previously, arsenic (V) is removed from solution via adsorption and co-precipitation with iron oxyhydroxide to a greater extent than arsenic (III).

**Mercury.** Mercury exists as mercury (I), mercury (II), and metallic mercury. Metallic mercury is much less soluble than the oxidized versions, which are strongly complexed by organics and chloride present in estuaries.

#### *Photolysis*

Photochemical transformation may occur by one of several processes depending upon the chemical structure and substances in the environment. Direct photolysis occurs when the chemical absorbs light and is then transformed from an excited state by rearrangement, dissociation, oxidation, or other mechanisms. The rate of reaction depends upon the sunlight photo flux, the light absorption coefficients of the chemical, and the efficiency of conversion of the absorbed light in the chemical reaction.

Indirect photolysis occurs when substances present in the aquatic environment absorb light to form excited chemical species or free radicals that interact with the COPCs to produce a reaction. Single oxygen and oxy radicals are examples of intermediates that can result in transformations of chemicals. Since these intermediates result from photoreactions of naturally occurring substances and the COPC does not undergo photochemical reaction itself, the reaction should not be referred to as photolysis but rather photo-induced free-radical reactions. An example of a photolysis reaction of hazardous chemicals is the reaction of chlorinated dibenzodioxins with ultraviolet light (UV) to produce two toluene-like molecules that can then be biologically attacked.

#### **5.1.4.2 Biotic Degradation/Transformation**

Removal or transformation of organic chemicals from the subsurface environment can occur through the action of microorganisms that may be attached to the sediment or suspended particles.

Biodegradation of organic chemicals by microorganisms ultimately produces microbial cells, water, and carbon dioxide (i.e., complete "mineralization"). The enzymes produced by the microorganisms are essentially responsible for the degradation of the organic chemicals. Whether or not a chemical is transformed by enzymes depends basically upon the configuration or alignment of the enzyme with the organic chemical during reaction. If an ideal configuration of the enzyme and organic chemicals occur, the reaction will occur. Persistent chemicals have less favorable alignments, and non-reacting or recalcitrant chemicals fail to bond or produce favorable alignments.

Typically, biodegradation rates are found to be proportional to both the substrate, the organic compound providing the energy source, and microbial numbers. However, some organics, termed secondary substrates, do not provide sufficient energy to support growth of the microbial biomass. In this case, a primary substrate must be present. When enzymes, produced for degradation of the primary substrate, can also serve to degrade the secondary substrate, this is termed co-metabolism.

Microbes can facilitate either oxidation or reduction of organics under oxic (aerobic) or anoxic (anaerobic) conditions, respectively. During the oxidation reaction, electrons are donated to an electron acceptor, generally oxygen, which is reduced. Reduction of organics requires the presence of an appropriate electron donor, such as other organics, nitrate, hydrogen, or glucose. Biodegradation can occur when the combined oxidation and reduction half reactions are energetically favorable.

Biodegradation is predicted using degradation kinetics and rate equations that describe the reduction of contaminant with time. Three rate equations that have been developed are the power rate law, the Monod and the Michaelis-Menton equations.

The power rate law, the simplest method, is in the following form:

$$\frac{-dC}{dt} = kC^n$$

Where :

C	=	Substrate concentration
t	=	Time
k	=	The rate constant for chemical disappearance
n	=	0 for zero order reactions and 1 for first order reactions

Concentration and the natural log of the concentration vary linearly with time in zero and first order reactions, respectively. The rate constant is determined by fitting laboratory or field data to the equation. Published rate constants can be used to estimate the relative importance of biodegradation for a given compound or class of compounds in the estuarine environment. Often, the degradation rate is expressed as the half-life of the compound, which is defined as the time required for biotransformation of one half of the initial concentration.

While a discussion of the biotransformation of each of the thousands of organic compounds is beyond the scope of the current discussion, an evaluation of biodegradation trends for organic compounds and groups is appropriate. Dragun (1988) lists the following "rules of thumb" that relate the chemical structure of the organic compounds within a given group to the biodegradation rate:

- Hydroxyl and carboxyl functional groups on benzene rings usually increase biodegradation rates.
- Halogen, nitro, and sulfonate functional groups on benzene rings usually decrease biodegradation rates.
- As the number of chlorine atoms within the molecule increases, the biodegradation rate decreases.

- The presence of hydroxyl, aldehyde, carboxyl, ester, and amide functional groups on organic chemicals usually causes faster biodegradation rates.
- Water-soluble chemicals are usually degraded faster than less soluble chemicals.
- N-alkanes, n-alkylaromatics, and aromatic compounds in the C10 to C22 range are usually readily biodegradable.
- N-alkanes, n-alkylaromatics, and aromatic hydrocarbons in the C5 to C9 range are biodegradable, but in most environments volatilization competes very effectively with biodegradation as a fate process.
- Gaseous n-alkanes (C1-C4) are biodegradable but are usually utilized by a narrow range of specialized hydrocarbon degraders.
- The n-alkanes, n-alkylaromatics, and aromatic hydrocarbons above C22 have very low water solubilities that result in slow rates of microbial degradation.
- Condensed or fused aromatic and cycloparaffinic molecules with four or more rings have very low biodegradation rates.
- Rate of oxidation of straight chain aliphatic hydrocarbons is correlated to chain length; in general, short chains are not as quickly degraded as long chains.
- Unsaturated aliphatic organics have faster biodegradation rates than corresponding saturated aliphatic organics.

A list of half lives for representative compounds and groups is provided in Exhibit 5-5 below.

**Exhibit 5-5 Biotransformation Half-Lives of Organic Compounds and Groups**

Compound or Group	Laboratory Half-Life	Field Determined Half-Life
Benzene group (aromatic VOCs <sup>1</sup> )	1 week	1-2 months
Naphthalene (a PAH <sup>2</sup> )	1 week	1 month
Chlorinated aliphatics (VOCs and SVOCs <sup>3</sup> )	1 month	1 year
Phenanthrene (a PAH)	1 month	Not Available
Benzofluoranthene (a PAH)	3 months	Not Available
Chlorinated pesticides	1 year	Decades
TCDD <sup>4</sup> (a dioxin)	2 years	Decades

1. VOC = volatile organic compound
2. PAH = polynuclear aromatic hydrocarbon
3. SVOC = semi-volatile organic compound
4. TCDD = tetrachlorodibenzo-*p*-dioxin

Under laboratory conditions where the bacteria responsible for biotransformation are carefully cultured and maintained under ideal conditions, the half life of a given compound is dramatically shorter (biotransformation rate is faster) than under field conditions. Note that the degradation of chlorinated pesticides, dioxins, and large molecule PAHs is much slower than for the VOCs, SVOCs, and smaller PAHs.

### 5.1.5 Summary

Exhibit 5-6 summarizes the fate and transport processes and the applicability to COPC groups in the Calcasieu Estuary.

**Exhibit 5-6 Summary of Fate and Transport Process in Relation to COPC Groups**

F & T Process	VOCs	SVOCs	Pesticides	PCBs	Dioxins/ Furans	Metals	Inorganics
Adsorption	Low - Int. <sup>1</sup>	Int.-High <sup>1</sup>	Int.-High <sup>1</sup>	High <sup>1</sup>	High <sup>1</sup>	High <sup>2</sup>	Usually at lower pH
Volatilization	High	Low -Int.	Low	Low-Int.	Low	Hg only	Low
Precipitation	Low <sup>3</sup>	Low <sup>3</sup>	Low <sup>3</sup>	Low <sup>3</sup>	High	Fe, Mn	High
Abiotic Transformation	Low	Low	Low	Low	Low	Oxidation/ Reduction	Oxidation/ Reduction
Biotransformation	High-Int.	High-Int.	Low	Low-High	Low	None	Low

1. Increased in estuaries by "salting-out" effect.
2. An important exception is chromium (VI).
3. Can form non-aqueous phase liquid (NAPL) when salted out.

## 5.2 Fate and Transport in the Estuarine Environment

Conditions in the estuarine environment change due to natural cycles, weather patterns and acts of man. The following sections provide a general description of two fate and transport processes, flushing/physical transport and chemical fate/transformation, in the estuarine environment.

### 5.2.1 Flushing/Physical Transport

Flushing is defined as the average amount of time that freshwater spends in an estuary (Alber and Sheldon 1999). In general, estuaries with a greater input of river flow and smaller volume have short flushing times while estuaries with lower freshwater inflows and greater volumes have long flushing times. Flushing time can be estimated from the salinity of the estuary compared to that of seawater and the total volume of each segment of the estuary as follows (Dyer 1973):

$$t = \text{Freshwater volume/freshwater input}$$

$$= \sum[(S_{sw}-S_i/S_{sw})V_i]/Q$$

Where:

$$t = \text{Flushing time}$$

$S_{sw}$	=	Seawater salinity
$S_i$	=	Salinity of volume segment i
$V_i$	=	Volume of segment i
$Q$	=	Freshwater input

Flushing time can be a reliable predictor of the residence time of a compound in the estuary. In other words, the equation is valid if none of the fate and transport properties described previously are acting on the particular COPC under consideration. The concentration of the compound downstream from a point source (such as an outfall) can be predicted using the following:

$$C_x = (P/Q) f_x$$

Where:

$C_x$	=	Concentration of the COPC at a point x, downstream of the outfall
$P$	=	Rate of supply of the COPC (mass of COPC/time)
$f_x$	=	Fraction of freshwater at point x (calculated from salinity)

The concentration of the COPC downstream of the outfall is directly proportional to the fraction of freshwater (inversely proportional to the fraction of seawater). Upstream (up estuary) of the outfall, the concentration of the COPC does not decrease dramatically as is often the case for point sources discharging to river systems. In estuaries, tidal forces or onshore winds can transport COPCs landward, or upgradient of the outfall. The concentration of the COPC at a point y upgradient of the outfall is given by:

$$C_y = C_0 (S_y/S_0)$$

Where:

$C_y$	=	Concentration of the COPC at point y upstream of the outfall
$C_0$	=	Concentration of the COPC at the outfall
$S_y$	=	Salinity at point y
$S_0$	=	Salinity at the outfall

Upgradient of the outfall, the COPC concentration is directly proportional to the salinity due to the landward flow of higher salinity water caused by tides and onshore winds.

The relationships presented above, while quite useful under the right conditions, are severely limited by the fact that they are only valid for conservative COPCs. For the purpose of this discussion, "conservative" refers to compounds with concentrations that are only affected by dilution processes. Very few COPCs can be considered conservative or are mobile enough to be approximated as a conservative compound.

Instead, most COPCs will be either transformed into another compound or transferred from the water phase to either the solid or gas phase to some extent within an estuary. The extent to which the fate and transport processes will act on a given COPC will depend on the chemical properties discussed above and on the conditions within the water column and sediment of the estuary.

## 5.2.2 Chemical Fate/Transformation

The fate and transport properties discussed above act on most COPCs, such that the flushing equations for conservative species (discussed above) are generally not valid. The degree to which fate and transport processes cause a deviation from the conservative flushing behavior depends on the properties of the COPC (as discussed previously) and on the environmental conditions and processes within the estuary. Numerous investigators have studied non-conservative behavior in estuaries and have identified the key conditions for many different potential contaminants. The most important conditions include:

- Salinity
- Grain size of the sediment
- TOC of the sediment
- Turbidity
- pH and ORP

### 5.2.2.1 Salinity

Salinity is perhaps the most important parameter affecting the fate and transport of both organic compounds and metals within estuaries. Increases in salinity from near zero within a bayou discharge to seawater levels can dramatically shift the equilibrium of the COPCs between the dissolved and particulate phases. In addition, salinity changes can control the sediment load within the water column, resulting in an even more pronounced effect.

#### 5.2.2.1.1 Organics

The salting-out effect is the dominant process controlling hydrophobic organic compounds in the estuarine environment. Means (1995) performed an extensive study of the variation of PAH adsorption with salinity within Lafitte Bayou and Pass Fourchon/Lake Champagne, LA. They reported significant increases in  $K_d$  values with increasing salinity. For example, at a salinity of 9 ppt, they measured a  $K_d$  value of 5,146 liters per kilogram (L/kg) for pyrene while at a salinity of 32 ppt, a  $K_d$  of 9,578 L/kg was obtained. Brunk et al. (1997) found that the phenanthrene  $K_d$  value was 55 percent higher in saltwater than in freshwater. Salting-out affects most organic compounds to some degree but is less significant for charged or polar molecules such as low molecular weight phenols, alcohols, and carboxylic acids.

Brunk et al. (1997) found that salinity increases can result in the precipitation of organic coatings onto the surfaces of suspended particulate matter, increasing the available adsorption sites for hydrophobic organic compounds (thereby increasing effective  $K_d$ ).

Bates et al. (1987) found that the concentrations of aromatic hydrocarbons within Puget Sound were controlled by a rapid vertical flux where contaminated sediments were removed from the water column. While Bates et al. (1987) did not attempt to determine the removal mechanism, it has since been attributed to removal of suspended particulate matter in response to salinity increases (Means 1995).

The combined processes of salting-out COPCs in the aqueous phase, precipitation of organic compounds onto suspended particles, and salinity induced flocculation of suspended particulate matter effectively removes hydrophobic COPCs from the water column.

#### **5.2.2.1.2 Metals**

Salinity can result in the removal of neutral metals species via salting-out (i.e.,  $\text{HgCl}_2^0$ , Turner et al. 2001,) or ionic strength effects for metal ions. Increases in salinity result in an increase in ionic strength, which reduces activity of the species in solution. The result is increased solubility and decreased  $K_d$  values compared to the values obtained for freshwater. Turner et al. (2001) performed modeling to show that formation of  $\text{HgCl}_4^{2-}$  would decrease the mercury  $K_d$ . Depending on the speciation, mobility either decreased (via salting-out of the neutral species) or increased (due to ionic strength effects on mercury ions), resulting from an increase in salinity. Similar trends would occur for other metals.

Seawater ions can also compete with metals for adsorption sites on sediments. Hanor and Chan (1979) (reported in Coffey et al., 1997) found that barium is mobilized within the mixing zone of the Hudson River Estuary due to ion exchange between magnesium from the seawater and adsorbed barium. Investigators have found similar trends for other metals.

Coagulation of suspended sediment has been shown to greatly reduce metals concentrations within the water column. The TSS load within the water column can be an effective means of transporting otherwise immobile compounds.

#### **5.2.2.2 Grain Size**

Grain size is an important parameter for adsorption of inorganic constituents due to the greatly increased surface area per mass of fine-grained sediment compared to coarse sediment. Menon et al. (1998) found that sediment cadmium, copper, lead, and zinc concentrations correlated with sediment surface area within the Hudson River Estuary. Borrego et al. (2002) performed cluster analyses on sediment results from the Odiel Estuary and found that aluminum, iron, phosphorous, copper, lead, and barium cluster together with high contents of silt and clay. The relationship was first

illustrated within estuaries by Gibbs (1977) and has since been used to normalize sediment samples for comparative purposes.

### 5.2.2.3 Sediment TOC

Sediment TOC, as discussed previously, is an important parameter for determining partitioning between organic compounds and sediments. Gunderson et al. (1997) found that within the York Estuary in Virginia, sediment TOC concentrations of only 0.1 percent are required before organic carbon adsorption of chlorinated methoxyphenols predominates ( $foc^* = 0.00001$ ). Brunk et al. (1997) found that adsorption of phenanthrene onto clay minerals is increased due to precipitation of organic coatings onto clay particles. Albanis et al. (1995) found that pesticides were adsorbed by sediments.

### 5.2.2.4 Oxidation/Reduction Potential and pH

Redox potential and pH can be very important within estuaries due to the mixing of seawater and river water and flooding and evaporation cycles within marsh areas. Turbulence, caused by tidal action, can increase the DO levels and, consequently, the redox state within the tidal influenced zones of the estuary.

#### 5.2.2.4.1 Organics

The pH of an estuary is typically higher than that of the river input due to the high alkalinity of seawater. The increase in pH on an organic compound is usually minimal except for compounds with carboxyl or hydroxyl substituents. For example, pentachlorophenol is much more mobile at high pH than at low pH due to the hydroxyl group, which gives the molecule an acid/base character. Gunderson et al. (1997) found that chlorinated methoxyphenols are more soluble and have lower  $K_d$  values at high pH (when the molecule is negatively charged) than at lower pH (when the molecule is neutral and more hydrophobic).

Theoretically, organic compounds can be completely oxidized to carbon dioxide and water within estuaries. However, abiotic oxidation is relatively unimportant except perhaps in the surface water where photo-oxidation may occur. Of much greater importance is the biotransformation of organic compounds within the estuarine environment. The more available oxygen, higher redox conditions within the turbulent tidal areas can result in aerobic biotransformation. The process will be most important for the more soluble and easily degraded compounds such as the aromatic VOCs (i.e., benzene, toluene, phenols, etc.). Other, less mobile and less bioavailable compounds such as the dioxins/furans, SVOCs, pesticides, and large molecule PAH compounds will not biodegrade to any great extent.

Within consistently flooded marshes and other low energy environments, organic matter within fine-grained sediments can produce anoxic conditions, which favor anaerobic biotransformation. Chlorinated organic compounds such as tetrachloroethene can be reduced and sequentially dechlorinated to form cis-1,2 dichloroethene, vinyl chloride, ethene, and ethane.

#### 5.2.2.4.2 Metals

The increased DO and redox can result in the oxidation of ferrous iron and manganese and the resultant removal of metals via co-precipitation. Turner (2000) found that sediments within estuaries have an iron to manganese ratio ranging from <10 to 100, suggesting that iron is removed to a greater extent than manganese within the estuaries. The oxidation kinetics of ferrous iron (iron (II)) are dependent on the dominant iron species in solution. King (1998) found that free ferrous iron ( $\text{Fe}^{2+}$ ) has an oxidation half life of days to weeks while  $\text{Fe}(\text{OH})_2^0$  has a half life of a few seconds. Therefore, an increase in pH can increase the fraction of  $\text{Fe}(\text{OH})_2^0$  and can result in a much faster oxidation rate. The carbonate species  $\text{Fe}(\text{CO}_3)_2^{2-}$  was found to control ferrous iron oxidation rates in seawater due to the high alkalinity and relatively fast oxidation rate of the species. Therefore, when ferrous iron from a river input is mixed with oxygenated, higher pH, higher alkalinity seawater within an estuary, conversion of iron (II) to the much less mobile iron (III) is predicted. Co-precipitation of metals would also likely be the result. Turner (2000) found that sediment concentrations of chromium, copper, lead, and zinc could be correlated with iron concentrations within the Clyde, Dee, Forth, Lohghor, Mersey, and Poole Harbour estuaries in the United Kingdom. Copper from sulfidic sources (i.e., mine drainage) was found to correlate more strongly with iron oxides while copper from industrial sources correlated with anthropogenic organics.

The pH and redox conditions are particularly important within stagnant marshes and salt flats where fine sediments are subjected to repeated flooding and evaporation cycles. When the marshes are flooded, the organics within the marsh sediments can create sulfate-reducing conditions, resulting in the production of sulfide and the precipitation of metal sulfide minerals such as pyrite. However, following evaporation of the stagnant water, the sulfides can become re-oxidized, resulting in acid production and remobilization of metals during heavy rains or spring tides when the areas become flooded. Anisfeld and Benoit (1997) compared two marshes in Connecticut, one with a tide gate, which prevented tidal inflow, and another without a gate. They found that in the more stagnant gated marsh the DO, metals, sulfate, acidity, ammonia, and nitrate levels were much higher than in the more consistently flooded, un-gated marsh. The high nitrate and ammonia levels were attributed to oxidation of nitrogen-containing organic matter within the fine-grained marsh sediments. Borrego et al. (2002) found jarosite ( $\text{HFeSO}_4(\text{OH})$ ) and other hydrated sulfide minerals within the tidal flats above the spring tide line at the Odiel and Tinto estuaries in southwestern Spain. The tidal flats were sterile and contained the highest sediment zinc concentrations anywhere within the estuarine systems. The mineralogy and chemical composition of the sediments in these isolated marsh areas can be very similar to the precipitates found on the surfaces of mine tailings dumps where sulfide minerals oxidize in response to wetting and drying cycles within the piles.

### 5.3 Summary of Fate and Transport Processes

In summary, important fate and transport processes acting on COPCs in Calcasieu Estuary and the environmental factors influencing these processes are as follows:

- Adsorption is one of the most important fate and transport processes in the estuarine environment. It is influenced by salinity, pH, and grain size of the adsorbing sediments. It is a significant process for dioxins, pesticides, PCBs, SVOCs, and some metals.
- Adsorption in the estuarine environment is controlled by processes that affect salinity and pH. Erosion and deposition patterns are related to the energy of the environment.
- Precipitation/co-precipitation is an important removal process for some metals (chromium, copper, lead, and zinc). Co-precipitation tends to be led by the oxidation of iron (II) to iron (III) and is influenced by the presence of iron oxyhydroxides.
- Precipitation is controlled in estuaries by pH, oxidation-reduction potential, and salinity (via salting out). Precipitation of oxides typically occurs in oxygenated, turbulent areas (flood tidal zones) while precipitation of sulfides occurs in anoxic low energy areas, such as marshes.
- Volatilization is important for VOCs. Volatilization is controlled by the turbulence of the water and the wind speed at the surface of the water. Volatilization is greatest in turbulent waters with high wind speeds. High turbulence areas within an estuary occur in the areas influenced by tidal energy while low turbulence areas are in marsh areas and embayments.
- Biotransformation is important for soluble organic compounds and compounds with easily broken bonds, such as aromatic compounds.
- Aerobic biotransformation is important in turbulent oxygenated waters, such as tidal zones, while anaerobic biotransformation is important in low energy marshes and embayments.
- The residence time of a COPC within an estuary depends on the flushing time of the estuary and on the degree of attenuation imparted on the COPC by fate and transport processes.

These processes will be referred to throughout the data interpretation sections for each AOC in Sections 7 through 10.