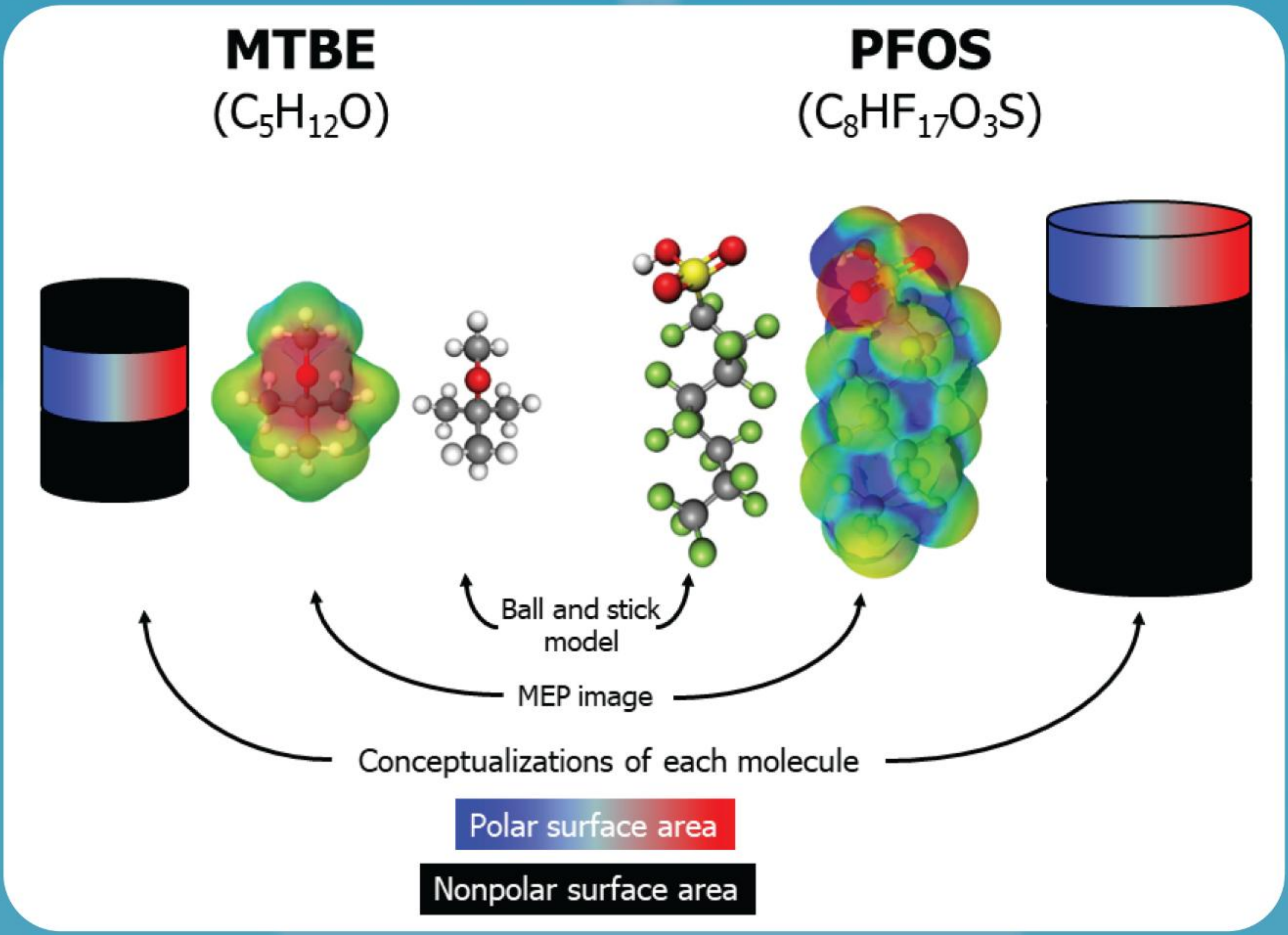

Properties of Organic Contaminants

Douglas M. Mackay, Richelle M. Allen-King, and William G. Rixey

THE GROUNDWATER PROJECT

Properties of Organic Contaminants

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Properties of Organic Contaminants

The Groundwater Project
Guelph, Ontario, Canada
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Dedication

We dedicate this book to students and colleagues who have shared our fascination with fate and transport of organic contaminants in the subsurface. Thankfully there have been many, and we hope this book will sustain many more.

Doug Mackay: Throughout my work, I have had the good fortune to be advised and mentored by the extraordinary John Cherry. I have also been sustained by memories of my brilliant father, my fearless mother, and my brother Randall, a gifted musician. I dedicate this book to them as well as to my partner, Kristina Branch, and to our twins, Alexander and Zoe Mackay, all marvels.

Richelle Allen-King: I dedicate this book to my husband, K. Scott King, who has supported me always. And to the mentors who have guided me along the way.

Bill Rixey: For Mary, Elizabeth, and George.

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The Groundwater Project Foreword

The UN-Water Summit on Groundwater, held from 7 to 8 December 2022, at the UNESCO headquarters in Paris, France, concluded with a call for governments and other stakeholders to scale up their efforts to better manage groundwater. The intent of the call to action was to inform relevant discussions at the UN 2023 Water Conference held from 22 to 24 March 2023 at the UN headquarters in New York City. One of the required actions is *strengthening human and institutional capacity*, for which groundwater education is fundamental.

The 2024 World Water Day theme is *Water for Peace*, which focuses on the critical role water plays in the stability and prosperity of the world. The UN-Water website↗ states that *more than three billion people worldwide depend on water that crosses national borders*. There are 592 transboundary aquifers, yet most do not have an intergovernmental cooperation agreement in place for sharing and managing the aquifer. Moreover, while groundwater plays a key role in global stability and prosperity, it also makes up 99 percent of all liquid freshwater—accordingly, groundwater is at the heart of the freshwater crisis. *Groundwater is an invaluable resource*.

The Groundwater Project (GW-Project), a registered Canadian charity founded in 2018, is committed to advancement of groundwater education as a means to accelerate action related to our essential groundwater resources. We are committed to *making groundwater understandable* and, thus, enable *building the human capacity for sustainable development and management of groundwater.* To that end, the GW-Project creates and publishes high-quality books about *all-things-groundwater*, for all who want to learn about groundwater. Our books are unique. They synthesize knowledge, are rigorously peer reviewed and translated into many languages, and are free of charge. An important tenet of GW-Project books is a strong emphasis on visualization: Clear illustrations stimulate spatial and critical thinking. The GW-Project started publishing books in August 2020; by the end of 2023, we had published 44 original books and 58 translations. The books can be downloaded at gw-project.org↗.

The GW-Project embodies a new type of global educational endeavor made possible by the contributions of a dedicated international group of volunteer professionals from a broad range of disciplines. Academics, practitioners, and retirees contribute by writing and/or reviewing books aimed at diverse levels of readers including children, teenagers, undergraduate and graduate students, professionals in groundwater fields, and the general public. More than 1,000 dedicated volunteers from 70 countries and six continents are involved—and participation is growing. Revised editions of the books are published from time to time. Readers are invited to propose revisions.

We thank our sponsors for their ongoing financial support. Please consider donating to the GW-Project so we can continue to publish books free of charge.

The GW-Project Board of Directors, January 2024

Foreword

Groundwater contamination is an immense global problem, especially complex and challenging. Part of the complexity is the large number and diversity of organic chemicals in this contamination. The organic chemicals listed as potentially harmful to humans range from those of simple to complex molecular structures. Much has been written concerning the occurrence and behavior of organic contaminants in groundwater but some basic knowledge of organic and physical chemistry is required in order to read and understand this literature. This book: *Properties of Organic Chemicals* provides readers with the basic concepts of organic and physical chemistry so they can begin to read the literature about organic contaminants in groundwater in order to address such issues at field sites.

In keeping with the overall aim of Groundwater Project books to foster conceptual thinking expressed in diagrams and sketches, this book includes many superb figures that bring the concepts to life. These figures depict both key chemical processes and the existence of compounds in their different physical states (gases, liquids, and solids), including solutes dissolved in water and attached to solids that make up the host geologic media.

This book is an excellent foundation for reading other Groundwater Project books, such as *Biotic Transformations of Organic Contaminants*↗ about the degradation of common organic contaminants in groundwater, and *Dissolved Organic Carbon in Groundwater Systems*↗ about natural organic matter in groundwater.

The three authors of this book are Douglas Mackay, adjunct professor emeritus at the University of California, Davis; Richelle Allen-King, professor at the University at Buffalo, State University of New York; and William Rixey, associate professor at the University of Houston. They specialize in groundwater contamination, remediation, field and laboratory experimentation, groundwater hydrogeology, chemical engineering, and computer simulation of groundwater transport and fate processes. That experience, coupled with their many years of teaching courses concerning organic contamination of groundwater, contributed to this stellar educational work.

John Cherry, The Groundwater Project Leader
Guelph, Ontario, Canada, April 2024

Preface

The literature of groundwater science is replete with specialized terms and, as interest in groundwater issues becomes ever more multi-disciplinary, the breadth of knowledge required is growing rapidly. This creates a challenge for many readers. In response, we prepared this book as an overview of information and concepts about organic chemicals and contaminants that groundwater scientists and engineers should become familiar with to understand other books published by The Groundwater Project and much of the scientific literature, government reports and guidance, and consultants' reports on groundwater contamination and remediation.

We teach graduate university classes that address the topics covered in this book; consequently, we have written this book much as we would present the material in a class to students with little background in physical or organic chemistry. Accordingly, "we" in this book refers to a group consisting of the authors and our readers to emphasize we are in this pursuit of knowledge together. This collaboration—and that of many other groundwater scientists on various research projects—has improved our collective and individual knowledge of groundwater and fate processes.

We liberally include colorful depictions of molecules for various purposes such as to provoke certain insights and provide visual stimuli. Early drafts of this material were used in some of our classes, all well received by the students.

We anticipate that this book will provide you with foundational knowledge and spark your interest in the fascinating nature and fate of organic chemicals that have become broadly distributed in the environment. Our goal is to lead you and your colleagues to build on this knowledge to improve the management of such chemicals and reduce, or ideally eliminate, the risks they pose.

Acknowledgments

We deeply appreciate the thorough and useful reviews of and contributions to this book by:

- Dr. Jim Spain, Research Professor, University of West Florida, Pensacola, Florida, USA
- Dr. Eileen Poeter, Professor Emeritus, Colorado School of Mines, Golden, Colorado, USA

We appreciate the many and detailed contributions of Joanne Haskins, and we thank Carlos Neto Breda, GW-Project figure creator, Brazil, for assistance with one figure. We are grateful to Amanda Sills and Virginia McGowan of The Groundwater Project for their oversight and copyediting of this book. We thank Eileen Poeter (Colorado School of Mines, Golden, Colorado, USA) for editing and producing this book.

Where figures and tables are derived from another source, that source is acknowledged in the caption. Where no such citation occurs, the figures and tables are original to this book.

1 Organic Chemical Classes and Structures

Are you familiar with the chemical compounds illustrated to the right of the water molecule in Figure 1? If you are seeking insight into groundwater contamination and remediation, perhaps you should be. In Figure 1, the structures of the molecules are indicated by the location of and bonds between atoms, as we discuss subsequently.

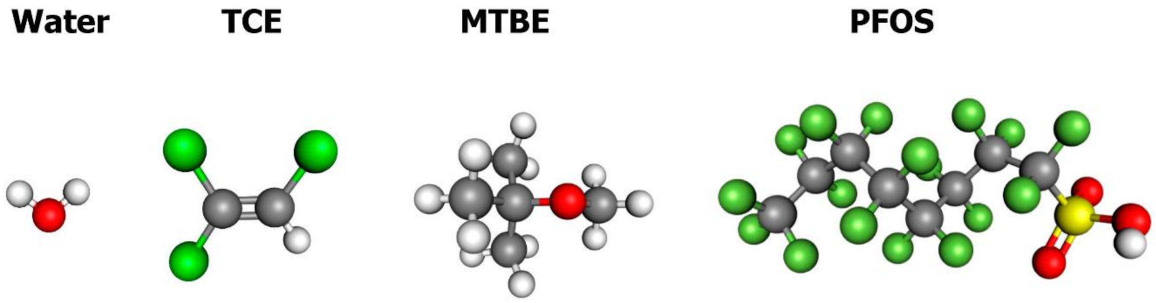


Figure 1 - Water and three of the most frequently detected organic groundwater contaminants. These depictions, and many others in this book, were created using an online molecular modeling site (MolView↗). Throughout this book and in many other references, a black or gray sphere indicates a carbon atom, white is a hydrogen atom, bright red is an oxygen atom, bright green is a chlorine atom (e.g., as in TCE), yellow-green is a fluorine atom (e.g., as in PFOS), and yellow is a sulfur atom, also in PFOS. The bonds are shown as rods between the atoms. TCE and PFOS include double bonds between two carbon atoms in the former and between an oxygen atom and sulfur atom in the latter. The organic contaminants all contain carbon, and all are significantly larger than water.

All of the contaminant molecules in Figure 1 are larger than water. One of the contaminants depicted is a common industrial solvent (TCE, or trichloroethene), one is a former gasoline additive (MTBE, or methyl tert-butyl ether), and one (PFOS, or perfluorooctane sulfonic acid) is a member of a group known as perfluorinated alkylated substances (PFAS), which have been used in a wide variety of industrial process, are present in various commercial products, and have been used in firefighting foams.

All the contaminants in Figure 1 are still detected in groundwater in various parts of the world. Each is considered to present drinking-water risks if they occur above the following levels established or proposed in the US: 5 µg/L (microgram per liter) for TCE, 13 µg/L for MTBE, and 0.00002 µg/L (0.02 parts per trillion) for PFOS. For some perspective, the molecular weight (also called *molecular mass*) of TCE is 138 grams per mole of the compound, where the quantity called a *mole* is 6.02×10^{23} molecules. Therefore, 5 µg/L of TCE is equivalent to 2.2×10^{16} molecules of TCE per liter of water (i.e., $5x10^{-6}$ g divided by 138 g multiplied by $6.02x10^{23}$ molecules).

Even very small masses of these contaminants reaching groundwater can create risks and require management or remediation. How did they and many others get in groundwater, why are they still there, and what can we do about them? This and other GW-Project books explore those challenging questions.

In this book, we present the structures and properties of these and many other organic compounds, including:

- contaminants released by human activities,
- contaminants created by reactions in the subsurface,
- compounds whose presence in groundwater can confirm reactions of contaminants, and
- organic chemicals used to clean up some kinds of organic contamination.

Other GW-Project books provide additional explanations of the prevalence of, environmental transport and transformation of, and methods for removing from the groundwater environment many of the organic compounds discussed in this book.

1.1 FAQs (Frequently Asked Questions)

- *How big are molecules?* Organic molecules vary widely in size, as discussed in Sections 1.2 through 1.7. Water molecules (H_2O) are far smaller than most organic molecules. The size of a water molecule is illustrated in Figure 2. The top part of the figure shows the water molecule shape and indicates that the "diameter" of the V-shaped molecule is approximately 2.8 Å (Ångstroms), or only $2.8\text{x}10^{-10}$ meters. As just one illustration of how tiny a water molecule is, the bottom portion of the figure shows that a drop of pure water (assumed to be 0.05 mL, or about 0.46 cm in diameter) contains a huge number of water molecules.

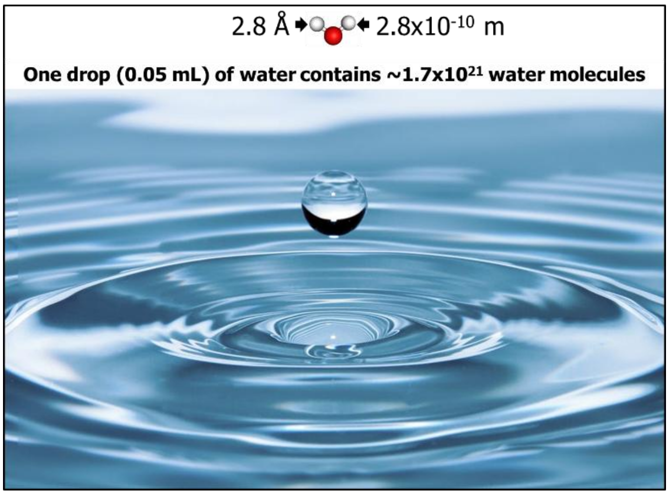


Figure 2 - Illustration of the size of a water molecule.

- *Why are organic chemicals called "organic"?* Organic chemicals are called *organic* for historical reasons. Originally, it was thought they could only be derived from matter produced by living organisms. Although for many years it has been common to synthesize organic chemicals from other organic and/or inorganic chemicals, the organic term is still used.
- *What is unique about organic chemicals?* They all contain carbon (Exercise 1↴)—that is, they are molecules in which carbon is bonded to carbon or other atoms. Figure 3 depicts carbon atoms (dark gray spheres) with bonds (simplified as lines) to other atoms,

showing single, double, and triple bonds. We discuss bonds more thoroughly in other sections of this book (e.g., Sections 1.2, 1.3, and 3).

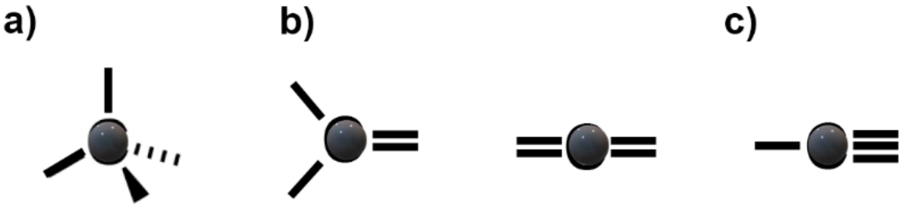


Figure 3 - Bonds to carbon atoms: a) single bonds, b) double bonds, and c) triple bonds.

- *Why are there many more organic chemicals than inorganic chemicals?* Carbon atoms can attach themselves to other carbon atoms in more ways than possible for other elements, starting from simple molecules and including complex organic molecules forming chains, rings, and combinations with side branches and links. Figure 3 shows carbon atoms can form a total of four bonds:
    - four single bonds (in which the straight bonds are in a plane, the dashed bond is behind the plane, and the triangular bond is in front of the plane);
    - two single bonds and one double bond, all in the same plane;
    - two double bonds, also all in the same plane; and
    - one single bond and one triple bond, and also all in the same plane.
- *How can the vast array of organic chemicals be categorized?* Chemists created the structural theory (Benfey, 1958), which addresses the order in which carbon and other atoms are bonded to each other, the nature of the bonds between them, and the shapes and sizes of the resulting molecules. In this section, we use the common names of various structures to highlight some chemicals known to be of importance in studies of groundwater origin, contamination, and remediation.

Many kinds of organic chemicals have been detected in groundwater, either because they have been released by human activities, or arose as byproducts or intermediates of reactions of other chemicals in the subsurface. We need to become familiar with several classes of organic chemicals so we can discuss processes that affect their behavior in the subsurface or during remediation. Millions of organic chemicals have already been created and distributed, and likely more will be created in the future. This book is a basic introduction to the fascinating and diverse universe of organic chemicals rather than a comprehensive overview.

1.2 Organic Chemicals Contain Carbon Atoms Bonded to Other Atoms

Organic chemicals, also called *organic compounds*, are molecules (a group of atoms bonded together) containing carbon atoms connected—via what are termed *covalent bonds*—to other atoms. Each carbon atom can form four covalent bonds, as was shown in

Figure 3, and those bonds can be with carbon and a variety of other atoms, as indicated in Table 1. This can lead to a tremendous variety of compounds, as we will see in this section.

Table 1 - Atoms bonded to a carbon atom in chemicals of frequent interest to groundwater studies. The number of bonds that can be formed is indicated to the left.

Type of bonds	Chemical abbreviation	Chemical names
Only single bonds	H, F, Cl, Br	Hydrogen, fluorine, chlorine, and bromine
Single, double, or triple bonds	C, N, O, P, S	Carbon, nitrogen, oxygen, phosphorous, and sulfur

Covalent refers to bonds that form when two electrons are shared between the bonded atoms; interested readers can explore this in far more detail elsewhere (Schwarzenbach et al., 2016). Table 1 summarizes some of the atoms that bond with carbon, forming one, two, or three covalent bonds depending on the atom involved in the bond. If a carbon atom forms one bond with another atom, then it has three left over for other bonds, and so on.

Chemicals with these bonds are illustrated in various ways in Figure 4. All of these chemicals have been detected in contaminated groundwater. Carbon dioxide and cyanide are not organic chemicals, but carbon dioxide is a compound that arises from degradation of organic chemicals and thus is important in discussions in this and other GW-Project books (e.g., Ferris et al., 2021). Cyanide is included in this table because it is a very toxic contaminant often present along with organic chemicals in groundwater impacted by complex sources such as landfills.

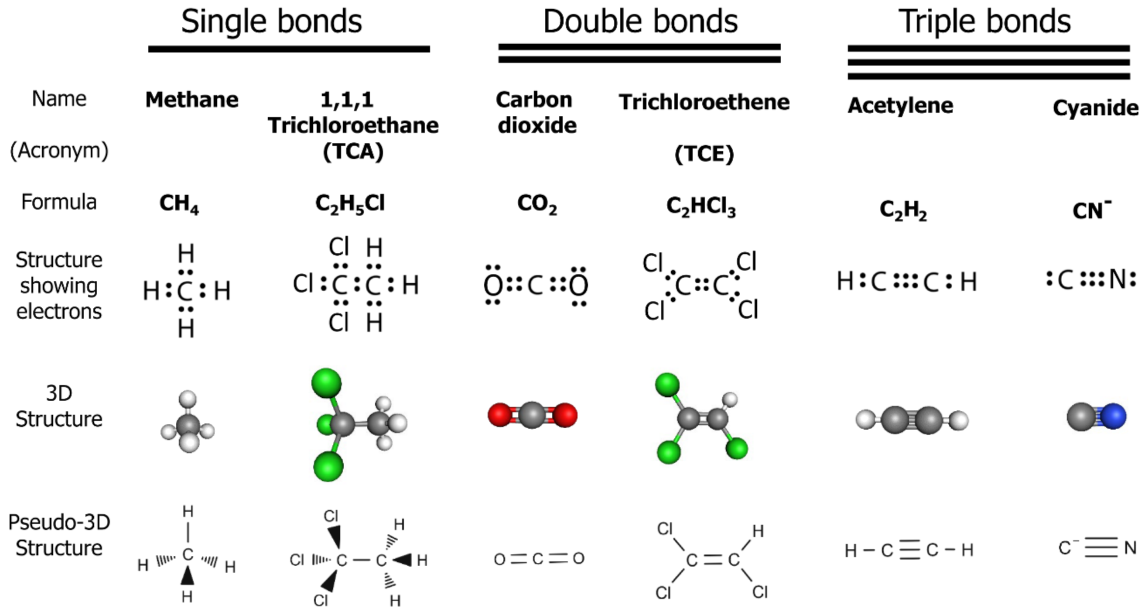


Figure 4 - Examples of chemical formulas and alternative structural representations for selected chemicals. Carbon atoms are dark gray, hydrogen atoms are white, chlorine atoms are bright green, oxygen atoms are red, and nitrogen atoms are blue.

You may need to be familiar with these types of illustrations of structure, as well as the chemical formula. Why? Because you will encounter the formulas and graphical representations in this book, in other references, or in your work. The alternative representations of structure include the following:

- a one-dimensional depiction with dots to show electrons shared by adjacent atoms;
- a three-dimensional (3D) representation in which carbon atoms are usually black or dark gray and other atoms are depicted in various colors (white for hydrogen, red for oxygen, green for chlorine, blue for nitrogen, and so on); and
- a pseudo-three-dimensional representation (more common in the past) in which the 3D structure is implied by heavy triangles and dotted lines to indicate atoms that are in front of or behind the rest.

Figure 4 shows that in 1,1,1-trichloroethane there is only one covalent bond between the carbons (gray) or between the carbons and hydrogen (white) or chlorine (green). Figure 4 also illustrates chemicals with double bonds: carbon dioxide with double bonds between the carbon and both oxygens (red), and trichloroethene with a double bond between its two carbons. Finally, Figure 4 shows two examples of chemicals with triple bonds: acetylene between its carbons, and hydrogen cyanide with triple bonds between the carbon and nitrogen (blue).

Given that double and triple bonds cannot rotate, Figure 4 indicates that simple molecules like CO_2, TCE, acetylene, and hydrogen cyanide are linear or planar. Single C-C bonds can rotate, so the ends of TCA and similar molecules can rotate. This may be important to the fate of such chemicals when they encounter tight spaces such as tiny cracks or pores of molecular dimension (*nano scale*) within grains or rocks present in geologic media (Exercise 2↓).

In the remainder of this book, we explore the range of organic chemicals that can be encountered when studying groundwater issues, and we follow the classifications in common use.

1.3 Hydrocarbons Contain Only Hydrogen and Carbon

Some organic chemicals contain only carbon and hydrogen and thus are called *hydrocarbons* (Exercise 3↓). We have already seen some examples in Figure 1 and Figure 4, but more are shown in Figure 5 to explain other common terms you may encounter. The first structural division of hydrocarbons is between *aromatic* compounds, or those that contain the depicted 6-carbon ring structure, and *aliphatic* compounds, which are the rest. Where did these names come from?

- Fragrant compounds were originally referred to as *aromatic*.
- Fatty compounds were originally termed *aliphatic* (from the Greek word for fat).

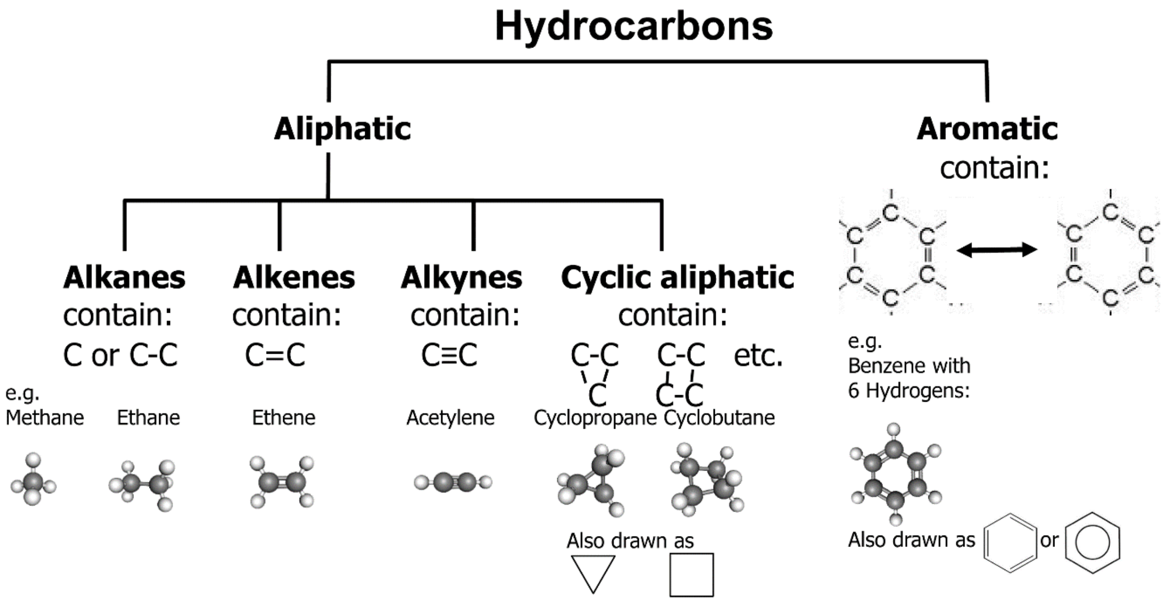


Figure 5 - Nomenclature and structures of classes of hydrocarbons. Carbon atoms are dark gray and hydrogen atoms are white. In “stick” models, which do not show atoms, a carbon atom is at the apex of each angle and H atoms are assumed to be bonded to any available positions on the carbon, to make four bonds total on each carbon (Exercise 4⤵, Exercise 5⤵).

Now the terms aromatic and aliphatic are used as a more general distinction of structure, as shown in Figure 5. Sometimes, for simplicity, the two-dimensional (2D) structures immediately under the titles do not depict the hydrogens connected to carbons, but they are assumed to be there, or sometimes the carbons themselves are assumed but not depicted (e.g., as benzene is depicted at the bottom right). Although not shown in this figure, there are cyclic aliphatics which have double or triple bonds between some of their carbons. The cyclic aliphatic and aromatic rings are relatively rigid but, as discussed in Section 1.7, these basic skeletons can have atoms or groups of atoms other than hydrogen attached to one or more carbon, which themselves can have portions that can rotate.

1.4 Alkanes and Halogenated Alkanes

Figure 6 illustrates several alkanes of different chain lengths (i.e., different numbers of carbons) along with examples of halogenated alkanes of the same chain lengths but with halogens replacing one or more hydrogen. Chlorinated and brominated alkanes are often detected in groundwater (Exercise 6⤵). The numbering in the name indicates the position of the halogens.

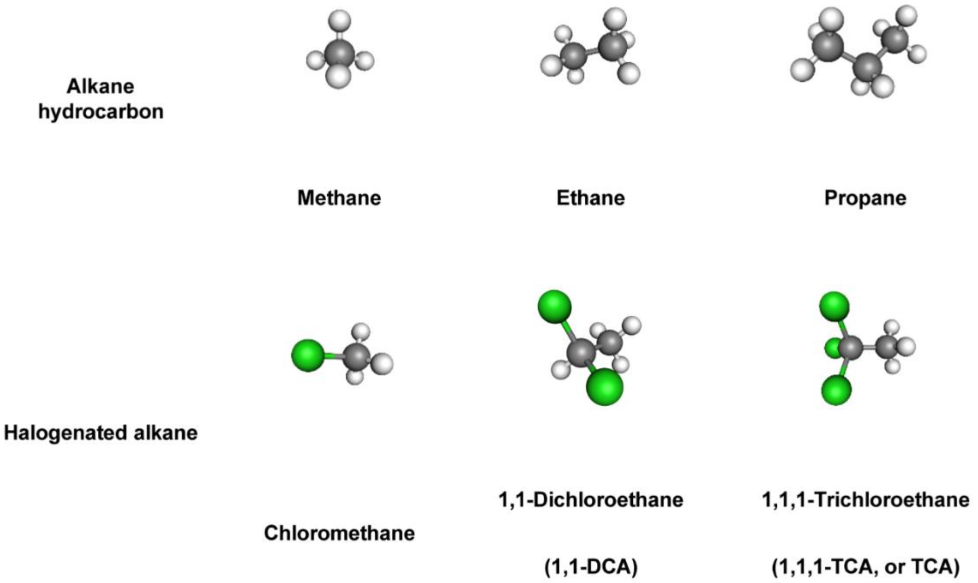


Figure 6 - Examples of 1-3 carbon hydrocarbon and halogenated alkanes. Carbon atoms are dark gray and hydrogen atoms are white. The halogens in this figure are chlorine (bright green). Box 1 shows other examples of halogenated alkanes.

1.5 Alkenes and Halogenated Alkenes

Figure 7 illustrates four alkenes of different chain length (two, three, or five carbons) along with examples of halogenated alkenes with two carbons but with halogens replacing one or more hydrogen. The five-carbon pentene can be in two forms when the double bond is located as shown. These are what are called *geometric isomers* (with the same formula but different geometric confirmation). The double bond cannot rotate. When the parts of the molecule other than single hydrogen are on the same side of the double bond it is called a *cis* isomer. When the parts of the molecule other than single hydrogens are on the opposite sides it is called a *trans* isomer.

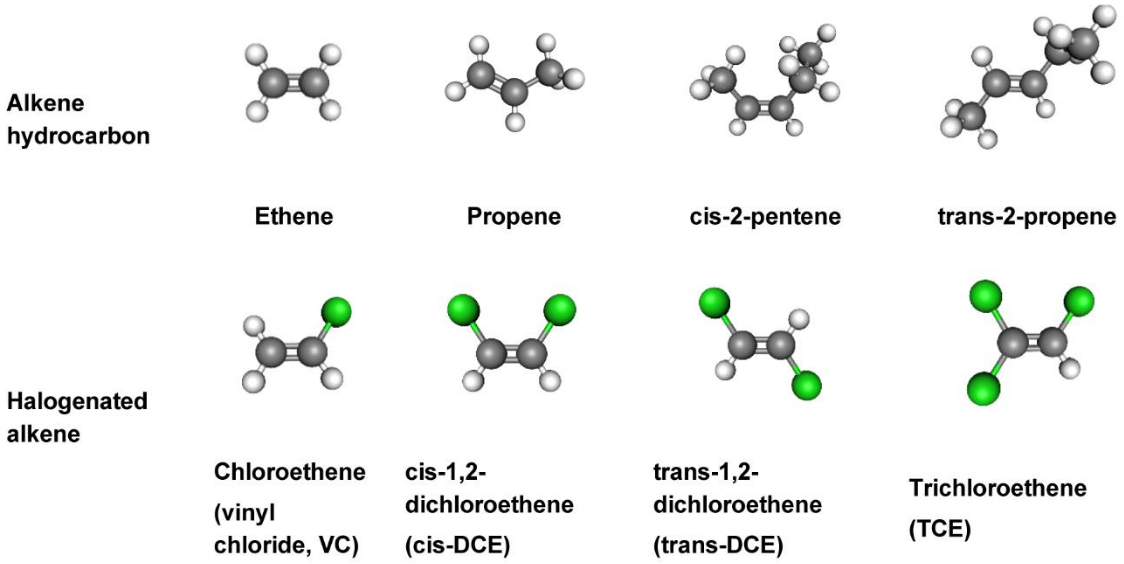


Figure 7 - Examples of 2-5 C alkenes and 2 C halogenated alkenes. Carbon atoms are dark gray, hydrogen atoms are white, and chlorine atoms are bright green.

Figure 7 also illustrates four chlorinated ethenes, all with a two-carbon chain length. Two dichloroethane isomers are shown: *cis* and *trans*. There is another isomer of dichloroethane that can exist but is not shown in Figure 7: 1,1-DCE, with both chlorines on the same carbon. This is an example of a *structural isomer*. Among the most frequently detected organic groundwater contaminants are the chlorinated ethenes—especially vinyl chloride, c-DCE, and TCE—along with tetrachloroethene (with four chlorine atoms and no hydrogens that is not shown in Figure 7).

Why should we care about isomers of chlorinated alkenes? Since analytical methods can often distinguish between the isomers of DCE, the amounts and types can provide important information on contaminant transformation processes occurring in situ. For example, c-DCE can be an indicator of microbiological transformation of TCE (Rittman 2023, Pankow & Cherry, 1996) whereas 1,1-DCE (with two chlorines on one carbon; not shown in Figure 7) can indicate abiotic transformation of 1,1,1-trichloroethane (Vogel & McCarty, 1987).

1.6 Aromatics and Halogenated Aromatics

Figure 8 illustrates two aromatic hydrocarbons—benzene and toluene—along with examples of aromatics with halogens replacing one or more hydrogen. Box 1↴ provides more examples of aromatic hydrocarbons and halogenated aromatics. For the substituted aromatic rings, the positions are numbered; and when the substituents are on adjacent carbons, this is referred to as *ortho* positioning (thus 1,2 dichlorobenzene is sometimes called o-DCB). *Meta* or *para* positioning has the substituents with one or two unsubstituted carbons between them, respectively. So, para positioning would have the two chlorines on opposite sides of the ring.

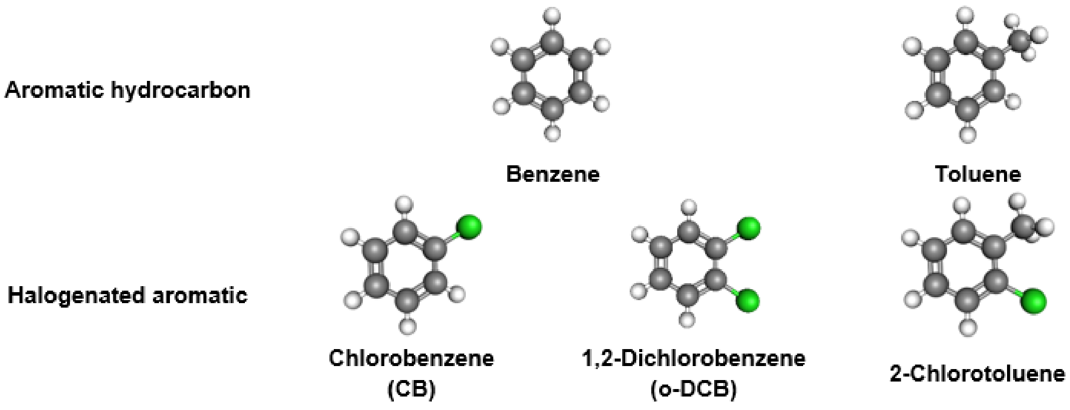


Figure 8 - Examples of single ring aromatic hydrocarbons and halogenated aromatic compounds. Carbon atoms are dark gray, hydrogen atoms are white, and chlorine atoms are bright green.

1.7 Other Important Classes of Organic Compounds

There are many other kinds and structures of organic compounds—far too many to review in detail in this book. Excellent overviews and discussions are available in other references (Schwarzenbach et al., 2017). For our purposes, in Figure 9 we summarize some of the key types of oxygen-containing or nitrogen-containing compounds discussed in this and other GW-Project books as well as in practice. The portion of the molecule that defines its type is noted in parentheses or by a dashed circle on one molecule.

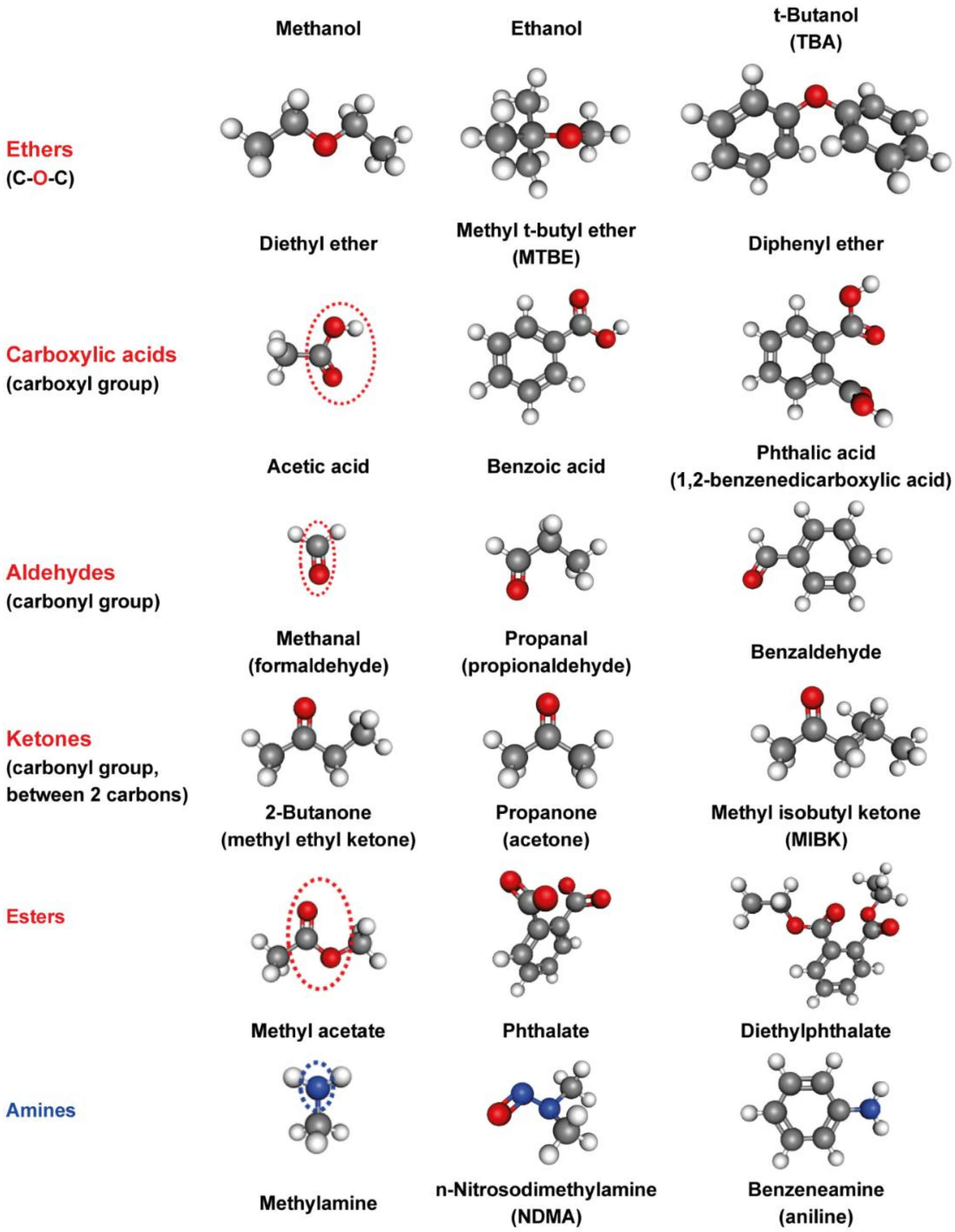


Figure 9 - Examples of several important groups of organic chemicals. Carbon atoms are dark gray, hydrogen atoms are white, oxygen atoms are red, and nitrogen atoms are blue. The portion of the molecule that defines its type is noted in parentheses or by a dashed circle on one molecule (Exercise 7⤵).

Why did we pick these particular chemicals to illustrate in Figure 9? We include simple molecules to point out the substructures that define the type of molecule, and almost all of the compounds illustrated have been found in contaminated groundwater. Ethanol, TBA, and MTBE have been used as gasoline additives, so often are detected near gasoline spills. Others have been used in manufacturing of plastics (e.g., diethyl ether, diphenyl ether, and phthalates) or other industrial processes (e.g., aniline dyes and ketones), and NDMA is an in situ degradation product of some spilled rocket fuels.

Figure 10 illustrates several more groups of organic chemicals encountered in groundwater studies. As shown previously (Figure 7, Figure 8, Figure 9, and Figure 10), these are but a few of the many compounds that fall within each category. Figure 10 does not summarize all groups of problematic contaminants. An important group not presented in Figure 10 includes *nitro* compounds, in which the molecules contain one or more nitro group (-NO_2). Nitro compounds are widely used in explosives (e.g., trinitrotoluene, known as TNT), pesticides (e.g., parathion), and as intermediates in chemical synthesis (e.g., nitrophenols).

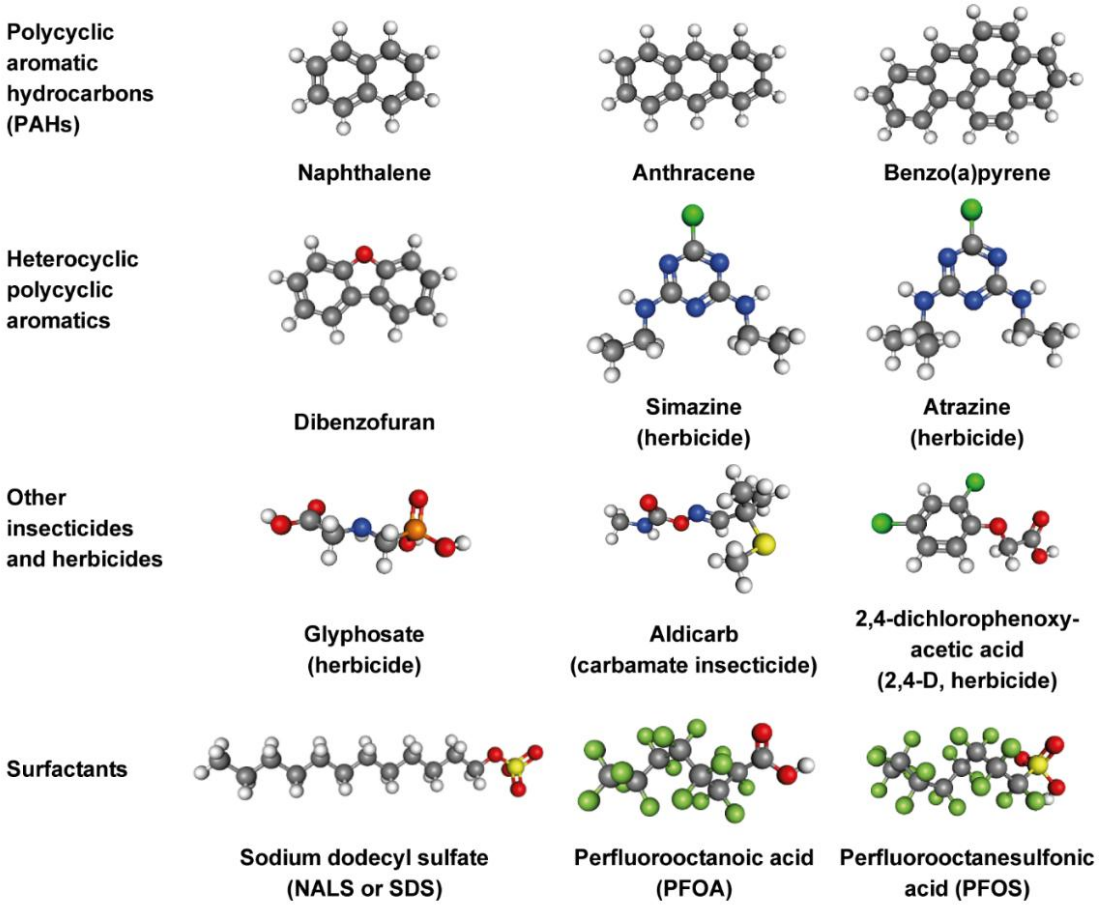


Figure 10 - Examples of complex cyclic aromatic compounds, pesticides, herbicides, and surfactants. Carbon atoms are dark gray, hydrogen atoms are white, oxygen atoms are red, nitrogen atoms are blue, chlorine atoms are bright green, fluorine atoms are yellow-green, sulfur atoms are yellow, and phosphorus atoms are orange.

Pesticides, herbicides, and insecticides are commonly referred to by names that do not necessarily provide much insight into their structure (Barbash & Resek, 1997). One reason is that their formal names are often very long. For example, atrazine is formally named chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, and aldicarb is formally named methyl-2-(methylthio)propanal O(N-methylcarbamoyl)oxime.

Although we have briefly reviewed several kinds of organic compounds, there are many more examples and many more types than we can summarize in this book. We present other examples later in this book, and others are presented in practice, scientific and practical literature, and other books. In subsequent sections we move from our overview of types and structures of organic contaminants to considering the properties of organic compounds. It may not surprise you that organic chemical properties vary widely.

2 Pure Chemical States

2.1 Why Do We Care about Chemical States?

Familiarity with many of the concepts covered in this section is needed to understand the discussions that follow as well as concepts and calculations presented in a wide variety of scientific and practical literature about the transport, fate, monitoring, and remediation of organic contaminants released to the subsurface.

2.2 Solid, Liquid, and Gas Phases

A pure organic chemical may exist as a solid, liquid, and/or gas (Figure 11), depending on temperature and pressure. In Figure 11, very tiny containers are imagined in which the

- molecules of a *gas* fill the container and are in constant motion;
- molecules of a *liquid* are attracted to one another and thus fill only a portion of the container; they are also moving, but not as far as the gas molecules before running into another molecule; and
- molecules of a solid have even stronger attractions to one another than molecules in the liquid, so they create a relatively rigid structure.

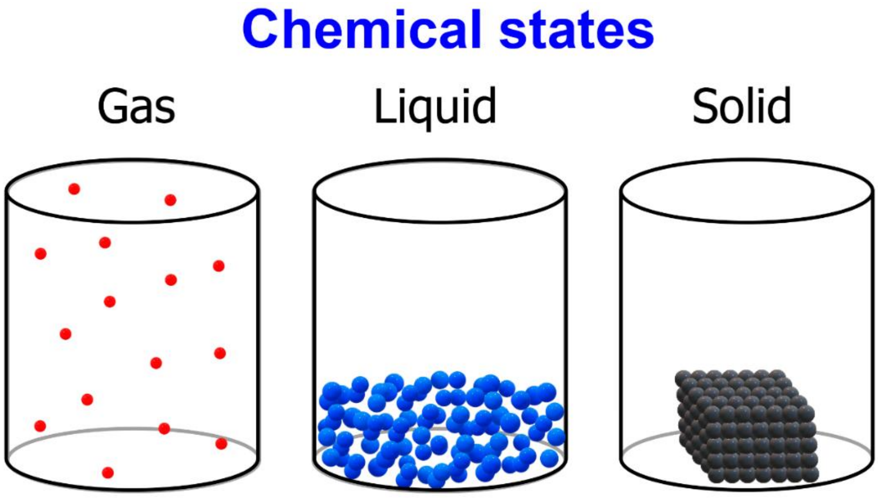


Figure 11 - Chemical states, illustrating conceptual arrangement and mobility of molecules in very tiny containers. In this and the next several figures, we represent molecules as spheres for convenience, ignoring their structures. We will use red to indicate a molecule in a gas phase, blue to indicate a molecule in a liquid, and gray to indicate a molecule in a solid.

In Figure 11 and the next several figures, we represent molecules as spheres for convenience, ignoring the specific structure of the molecules. We use red to indicate a molecule in a gas, blue to indicate a molecule in a liquid, and gray to indicate a molecule in a solid. These colors are used here for molecules to keep this discussion clear and simple; however, their use here should not be confused with how the colors are previously and subsequently used for individual atoms.

Figure 11 is meant only to illustrate the differences between gases, liquids, and solids, and thus does not account for the very important process of vaporization of liquids and solids, which would lead to some of the molecules being present in the space above or around the liquid or solids, which we discuss in Section 6.

2.3 Transitions between Solid, Liquid, and Gas Phases of a Pure Compound

Each chemical compound can exist in each of the phases shown in Figure 11, as observed in nature as steam, water, and ice. When ice is heated, it melts to water; if water is heated further, it vaporizes to steam. You may also know that at ambient temperatures and pressures solid carbon dioxide (so-called *dry ice*) does not melt but sublimes, that is it changes from solid directly to vapor as temperature rises. One or the other is true for all compounds. The transitions between the phases are often depicted in a *phase diagram*, a generalized example of a phase diagram is presented in Figure 12. Phase diagrams are graphs of pressure versus temperature depicting phase transitions as lines for a given chemical compound (a single chemical isolated in a container). The lines divide the graph into regions labeled *Solid*, *Liquid*, and *Gas*; for a temperature and pressure within the solid region, the chemical exists as a solid, and so on. For a point along the line separating the solid and liquid regions (the *fusion line*), the chemical exists as a solid and liquid at equilibrium. Along the *vaporization line*, the chemical exists as a liquid and gas in equilibrium. Finally, along the *sublimation line*, the chemical exists as a solid and gas at equilibrium. The *triple point*, denoted by the filled dot, is the one point at which all three phases coexist in equilibrium. The *critical point*, denoted by the unfilled dot, is the upper limit of the vaporization line; above this point, it is not possible to distinguish between liquid and gas phases.

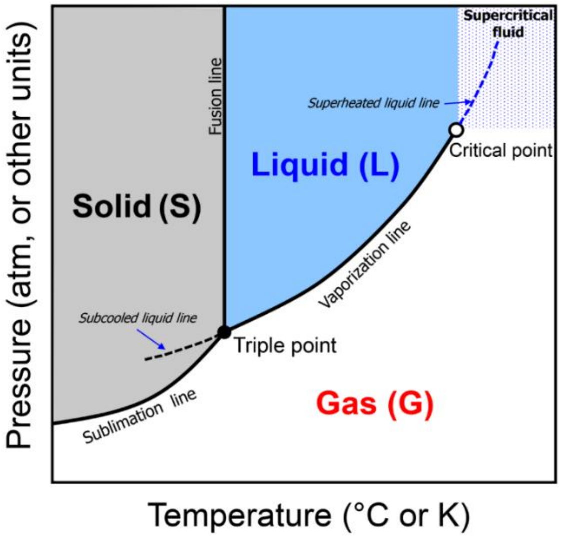


Figure 12 - Generalized phase diagram for one compound in isolation, showing boundaries between phases. The colors are consistent with the phases illustrated in Figure 11.

Why do we need to know these details? It is important for some discussions about calculations you may want to make for mixtures of chemicals. These discussions are presented in Section 7.10. First, let's discuss the generalized phase diagram a bit more.

At the triple point, the slope of the sublimation line is always greater than that of the vaporization line. For reasons discussed elsewhere (Schwarzenbach et al., 2017), a hypothetical liquid state (the subcooled liquid) is assumed to have properties that may be approximated by the extrapolation of the vaporization line below the triple point (the black dashed line in Figure 12). Another hypothetical liquid state (the superheated liquid) is assumed to have properties that may be approximated by the extrapolation of the vaporization line above the critical point (the blue dashed line).

The solid-liquid phase transition line (melting/freezing line) is generally nearly vertical (the fusion line in Figure 12). For most chemicals (and most of the contaminants discussed in this book), the fusion line has a slight positive slope, whereas for a few chemicals (most notably water) it has a slight negative slope. Nevertheless, the melting point of most chemicals is a very weak function of pressure and thus varies little from the melting point (T_m) at one atmosphere pressure.

This slight slope of the fusion line is illustrated in the three frames of Figure 13, which present phase diagrams using linear axis scales (instead of the arbitrary and non-scaled axes in Figure 12) for (a) carbon dioxide, (b) water, and (c) 1,2,4,5-tetrachlorobenzene. These compounds were selected for discussion since, at ambient temperatures and pressures, they are a gas, a liquid, and a solid, respectively. For all three, the melting point is, in fact, a weak function of temperature. The boiling point (T_b), on the other hand, is a strong function of pressure for all three as indicated by the slope of the vaporization line. The critical point for water is off the chart (374 °C, 218 atm). The triple points (the solid black circles) for carbon dioxide and water are at or well below the low end of typical environmental temperature ranges, so we are not concerned about defining their subcooled liquid lines. For 1,2,4,5-hexachlorobenzene, however, the triple point is at 140 °C—well above the typical environmental temperature ranges. Therefore, its subcooled liquid line is important in calculations related to mixtures of 1,2,4,5-tetrachlorobenzene and organic liquids at typical environmental temperatures. For example, as we discuss in Section 6.10, estimating the vapor pressure of 1,2,4,5-hexachlorobenzene in an organic liquid mixture requires use of its subcooled vapor pressure at the relevant temperature (estimated from the subcooled liquid line).

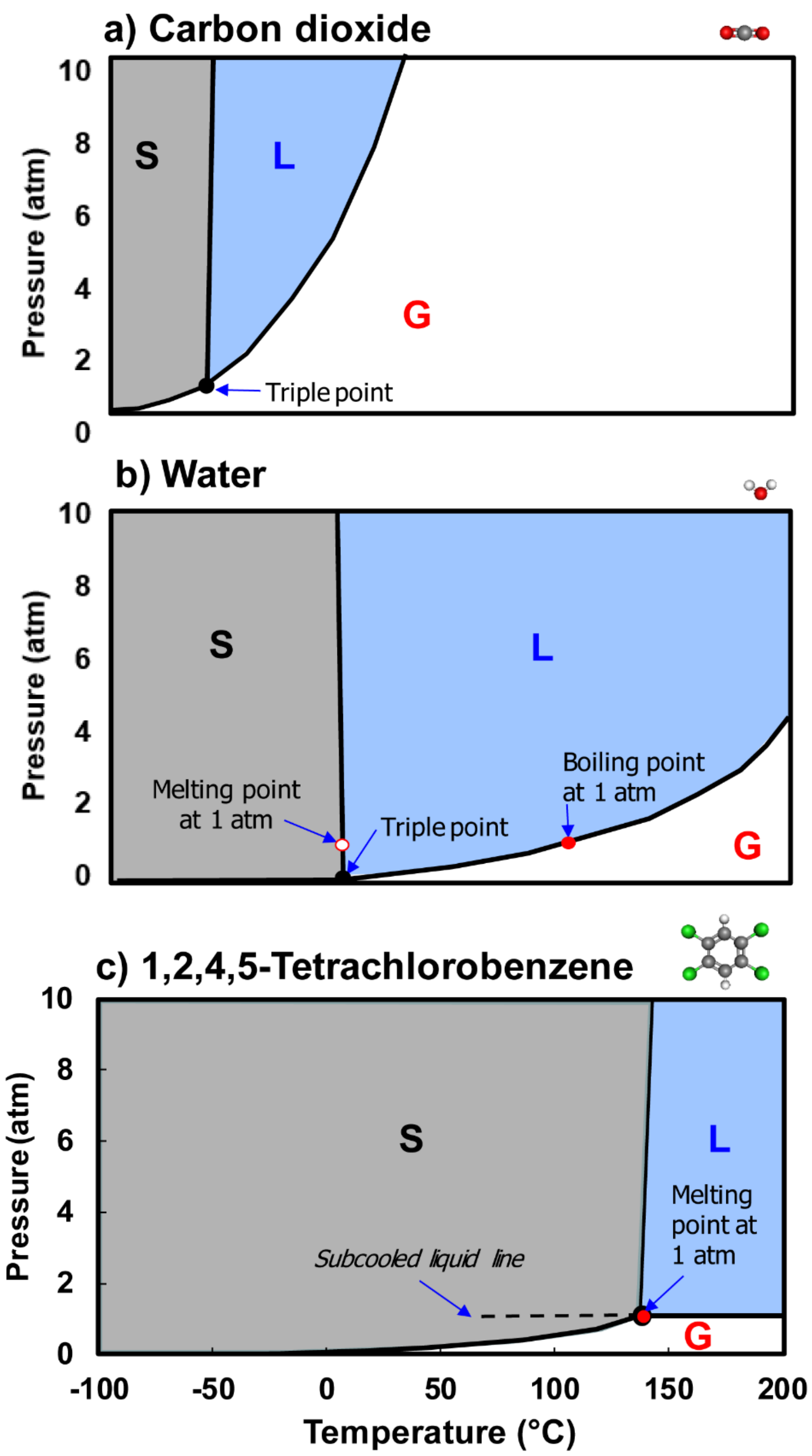


Figure 13 - Phase diagrams for specific compounds with linear scales in ranges near environmental conditions. The boiling point for 1,2,4,5-tetrachlorobenzene is off the scale (244.5 °C at 1 atm).

2.4 Melting and Boiling Points

A wide range of organic compounds are of interest to us and, as presented throughout this section, their properties also vary widely. First, consider melting points and boiling points under ambient sea-level conditions (one atmosphere pressure). Figure

14 illustrates that there is indeed a wide variation in melting and boiling points (MP and BP) overall and within classes of compounds. MP and BP values for specific organic compounds can be found in many online compilations (e.g., https://pubchem.ncbi.nlm.nih.gov↗). Box 1↴ contains a table of such values for examples of each compound class shown in Figure 14 (Exercise 8↴).

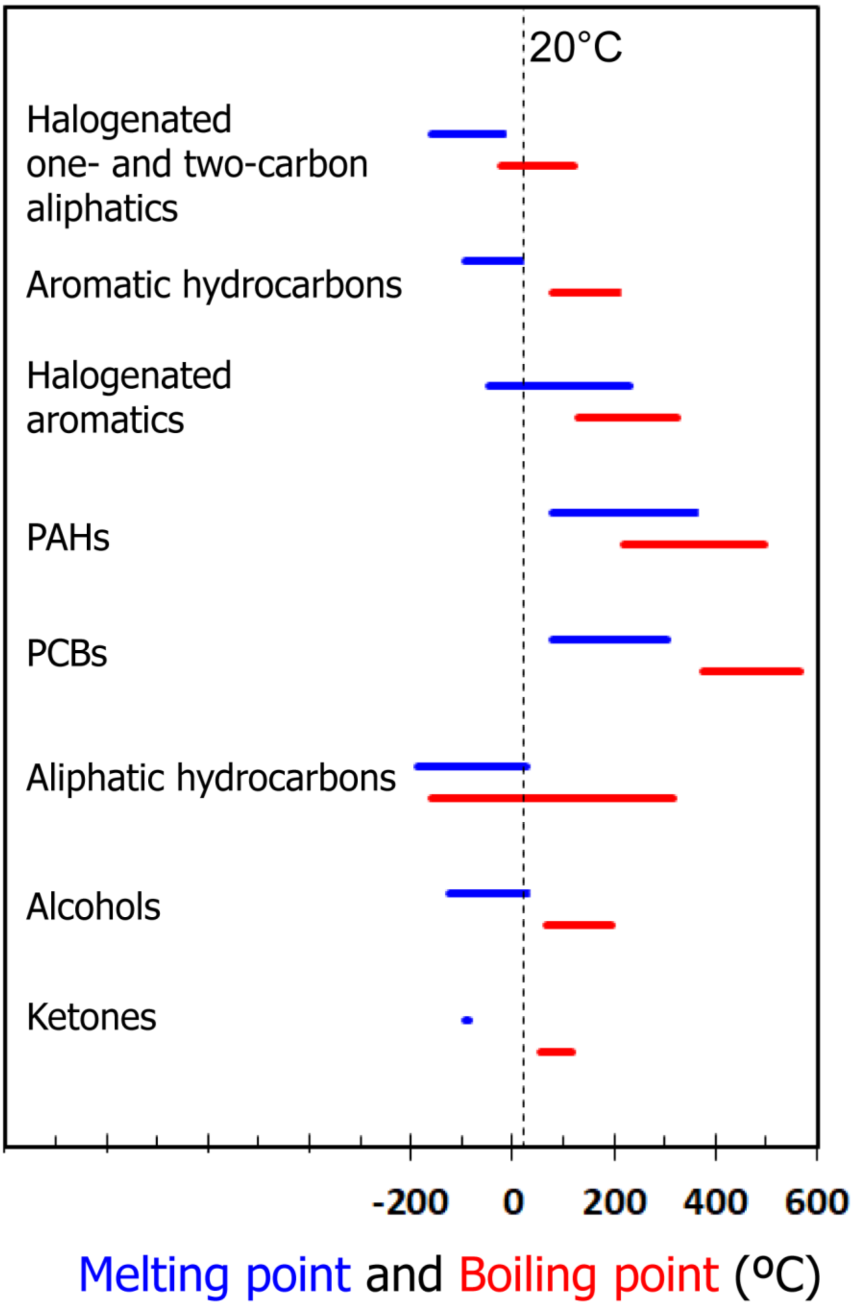


Figure 14 - Range of melting and boiling points for classes of organic chemicals.

Compounds whose melting point is above ambient temperature, assumed to be 20 °C (vertical dashed line in Figure 14), are solids under ambient conditions if pure (not mixed with any other chemicals). This includes:

- many halogenated aromatics (1,4-dichlorobenzene and those with 3 to 6 chlorines),
- all PAHs and PCBs,
- high molecular weight aliphatic hydrocarbons (heptadecane or higher), and
- one alcohol of relevance to our focus (tert-butanol).

Compounds with boiling points below 20 °C at one atmosphere are gases under ambient conditions at that temperature, if pure. These include:

- a few low molecular weight halogenated aliphatics (chloromethane, chloroethane, and chloroethene), and
- several low molecular weight aliphatic hydrocarbons (methane, ethane, propane, and butane).

The rest are liquids under ambient conditions, when pure.

In Section 6.10, we discuss how organic compounds that are solids and liquids, when pure, can be solids or liquids when mixed in different proportions. Lastly, organic compounds that are gases, when pure, can be mixed with organic liquids to yield a liquid mixture; gasoline is such a mixture, as discussed in Section 6.7.

In melting (the transitioning from solid to liquid), enough energy is added to overcome the intermolecular forces that solidify the chemical mass and allow the molecules to move freely about one another. Similarly, in vaporization (the transition from liquid to gas), additional energy has to exceed the remaining intermolecular forces to allow the molecules to separate and subsequently move essentially independently.

Because the melting points and boiling points vary widely among organic compounds, the attractive forces between molecules of a given chemical vary widely. For example, if the intermolecular attractions are strong, then it will take more energy to melt or boil the pure compound. The types and strengths of intermolecular attractive forces are discussed in some detail in Section 3 as preparation for understanding other physical properties of the chemicals that are of importance to us in assessing contaminant transport and fate.

2.5 Densities

The density of a gas, liquid, or solid is the amount of mass per unit volume of the pure compound, often presented in units of g/cm^3. Density is a critical control on the distribution and movement of some organic compounds in the subsurface, as discussed later in this book. Figure 15 shows the range of density of various classes of organic compounds. Values of density for specific compounds are provided in Box 1↴.

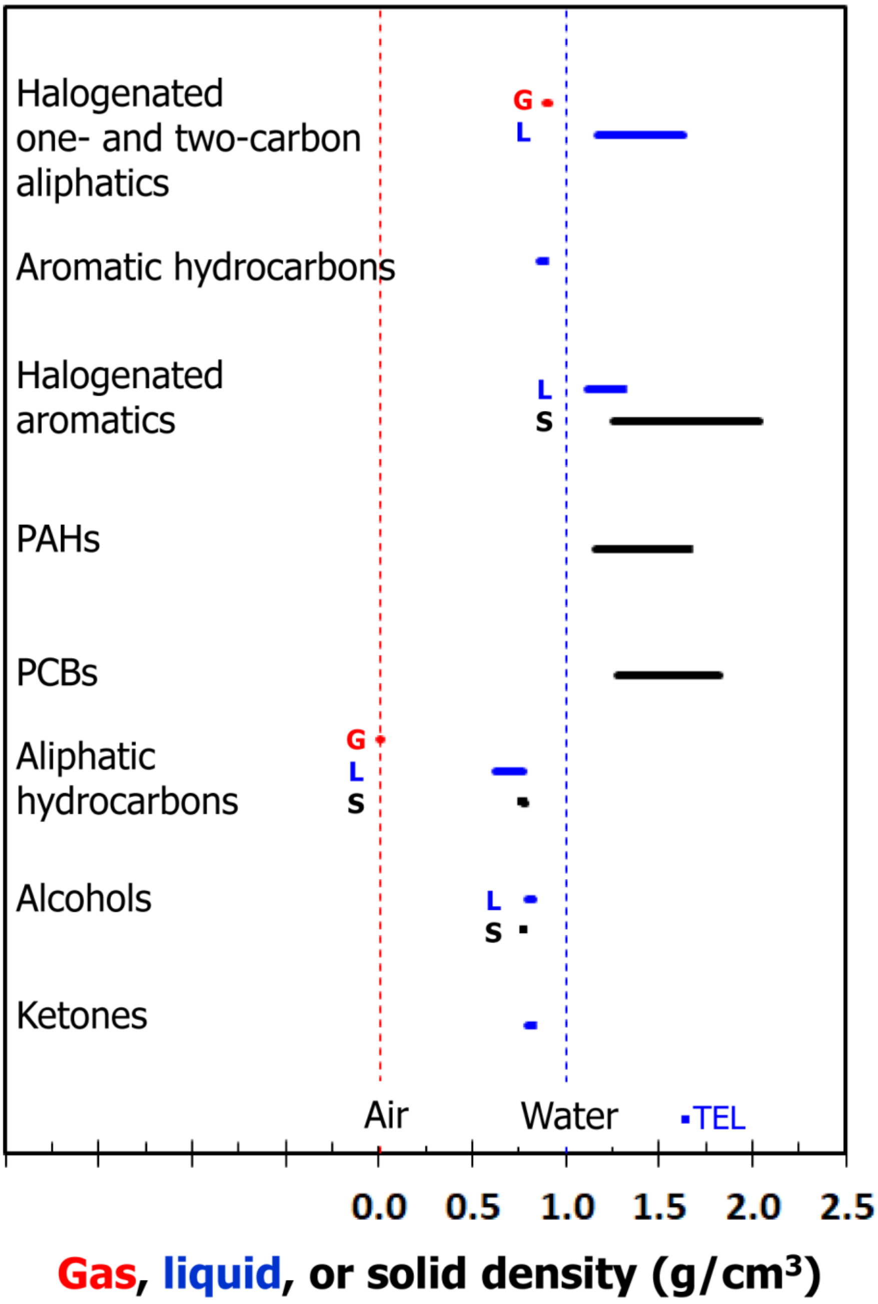


Figure 15 - Range of densities for classes of organic chemicals at 20 °C and 1 atm. As noted with a G, L, or S, some chemical classes contain only liquids, some contain gases and liquids, some contain liquids and solids, and one class contains all three. The vertical red dashed line shows density of dry air, and the vertical blue line shows density of water. TEL signifies tetraethyl lead.

Gases

The following halogenated organic gases are much denser than air:

- chloromethane,
- chloroethane, and
- chloroethene (vinyl chloride).

These aliphatic hydrocarbon gases are similar in density to air:

- methane—slightly less dense, and
- ethane, propane, and butane—slightly more dense.

Liquids and Solids

The following are less dense than water:

- aromatic hydrocarbon liquids,
- aliphatic hydrocarbon liquids and solids,
- alcohol liquids and solids, and
- ketones.

The following are more dense than water:

- halogenated liquids,
- halogenated aromatic liquids and solids,
- PAHs,
- PCBs, and
- tetraethyl lead (TEL) liquid—included here since it was once used as a gasoline additive for automobiles and thus produced in large quantities and may still be in use in some places as an additive for aircraft fuel.

Elsewhere in this and other GW-Project books, we discuss the implications of the density of a gas compared to air and the density of a liquid/solid compared to water. For the organic liquids, we must consider whether they are of low solubility in water and thus form a separate phase when contacted with water or whether they are miscible with water, which means they can be mixed with water in any proportion and thus form a homogenous mixture. To prepare readers for those important discussions, we review what is known about the nature of molecules and the attractive forces between them.

3 Polarity of Bonds and Molecules

3.1 Why Do We Care about Polarity?

The polarity of molecules can impact their environmental behavior in a variety of ways. First, we consider how the molecules of a given compound will interact with each other.

3.2 What Is Polarity?

A covalent bond between two atoms is characterized by the sharing of two electrons between the nuclei of the two atoms. Bonds between atoms are called *polar* if the two nuclei do not share the electrons equally—that is, the two atoms differ in their tendency to attract electrons. A term used to describe the tendency of an atom to attract electrons is *electronegativity*. The atoms composing most of the organic compounds involved in subsurface contamination are listed here in decreasing order of electronegativity (Schwarzenbach et al., 2017).

Electronegativity: $\mathrm{F > O > Cl, N > Br > C, S, I > H, P}$

When two different atoms are bonded covalently, the distribution of the electrons they share (the *electron cloud*) is asymmetric since the electrons are attracted more strongly to the more electronegative atom. This leads to a net negative charge (denoted as $\delta-$) at the end of the bond near the more electronegative atom and a net positive charge (denoted as $\delta+$) at the other end.

Figure 16 illustrates two chlorinated organic compounds: tetrachloromethane (also called carbon tetrachloride) and chloromethane, with strong charge separation along carbon-chlorine bonds (and the resulting bond dipoles drawn as arrows with a cross, pointed at the positive end of the bonds). In addition to the illustrations of the bonds, the figure includes small 3D depictions of the distribution of *electrostatic potential* around the molecules, also called *molecular electrostatic potential*, or MEP (both depictions for each molecule were produced using the online molecular modeling tool MolView↗).

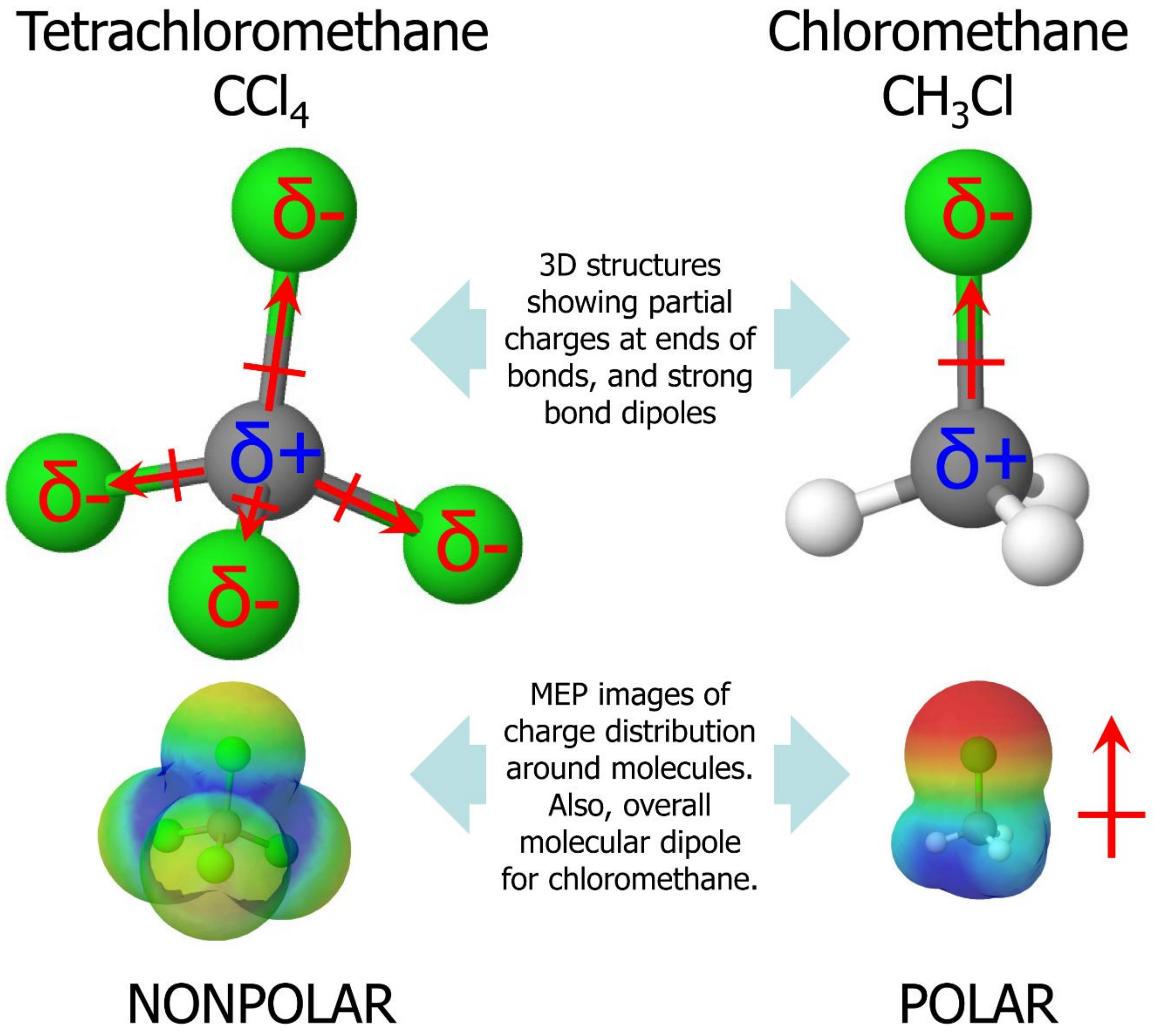


Figure 16 - Polarity of bonds and molecules illustrated for two chlorinated methanes. In the upper ball and stick models, carbon atoms are dark gray, hydrogen atoms are white, and chlorine atoms are bright green. The lower images show molecular electrostatic potential (MEP).

3.3 Polar and Nonpolar Molecules

Figure 16, shows that there are four strong bond dipoles in tetrachloromethane, but they are symmetrically arranged so the electrostatic potential is also symmetrical; molecules like this are called *nonpolar* since their overall molecular dipole (the vector sum of all the bond dipoles) is zero. Chloromethane, which has only one strong bond dipole, as depicted, has a very asymmetric electrostatic potential, with one portion of the molecule with a net positive charge compared to the rest. This leads to an overall molecular dipole as sketched by the red arrow with the cross. Molecules with a molecular dipole are referred to as polar (Exercise 9↴).

The story gets more interesting for more complex molecules. Figure 17 depicts 1,1,1-trichloroethane (also known as TCA), in which one of its carbon atoms is bonded to three weakly electronegative H atoms, whereas the other carbon atom is bonded to three strongly electronegative Cl atoms. This leads to the carbon bonded to the chlorine atoms having a positive charge compared to the carbon bonded to the hydrogens, so there is a significant dipole for this C-C bond. For bonds between atoms of similar electronegativity, the direction and magnitude of the bond dipole is affected by the atoms attached to the atoms at either end of the bond in question.

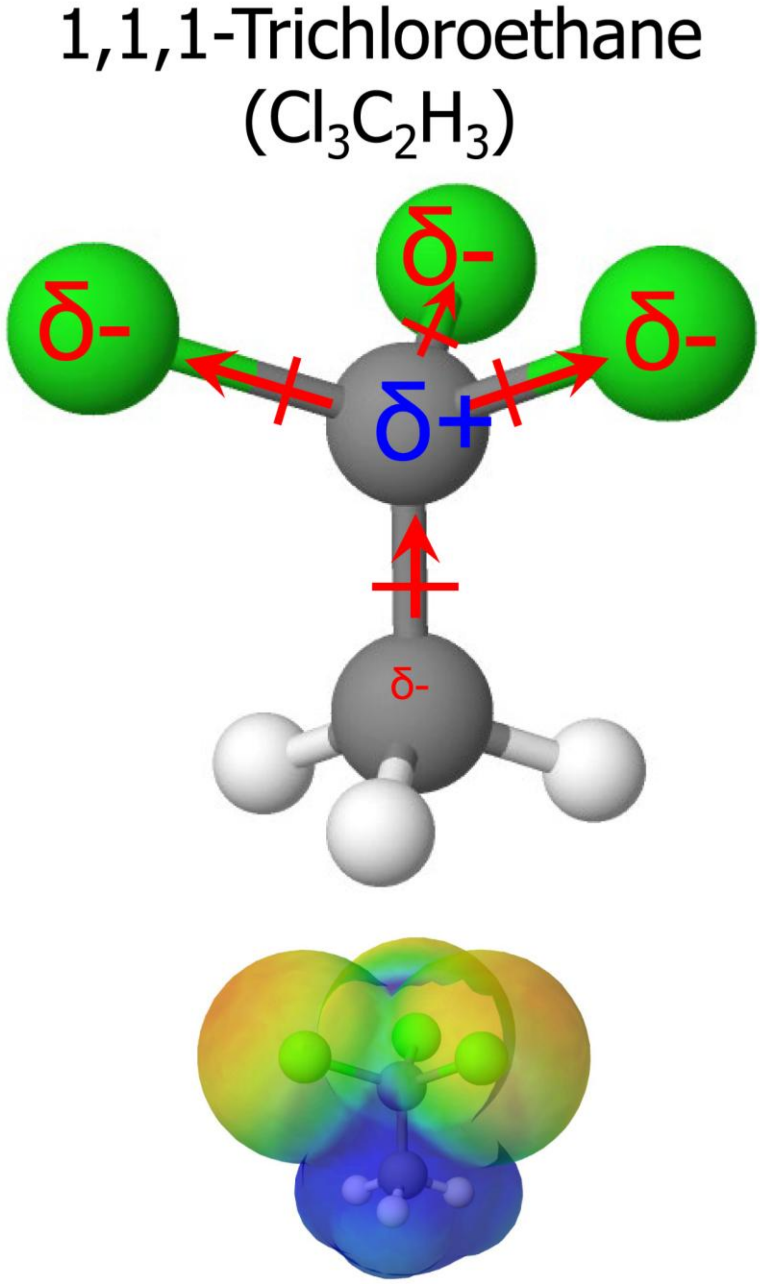


Figure 17 - Structure of 1,1,1-trichloroethane. In ball and stick models, carbon atoms are dark gray, hydrogen atoms are white, and chlorine atoms are bright green. The lower image shows molecular electrostatic potential (MEP).

3.4 Polar and Nonpolar Surface Areas of Molecules

Some larger molecules can be composed of both polar and nonpolar portions, as illustrated in Figure 18, which depicts a long-chain alcohol (octanol) and a surfactant (PFOS). You can see from the figures that the top portion of the molecules are quite polar, while the bottom portions are nonpolar. This dual nature of the molecules is a strong determinant of their behavior in the lab or in the environment.

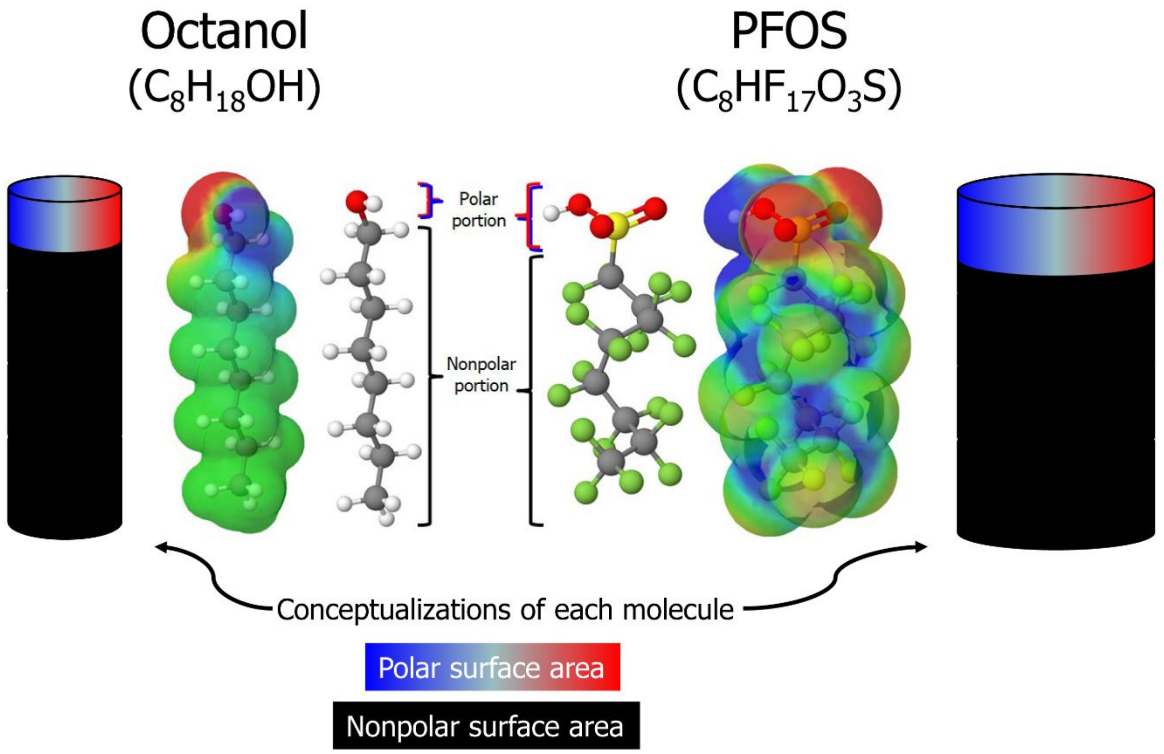


Figure 18 - Structures and conceptualizations of molecules with polar and nonpolar portions. In the ball and stick models, carbon atoms are dark gray, hydrogen atoms are white, oxygen atoms are red, sulfur atoms are yellow, and fluorine atoms are yellow-green. Next to the ball and stick models are images showing molecular electrostatic potential (MEP). The cylinders are conceptualizations of polar and nonpolar portions.

Another way to characterize molecules is to estimate the fraction of their total surface area (TSA) with regard to relative polarity. Thus, each of the molecules in Figure 18 has more nonpolar surface area (NPSA) than polar surface area (PSA), whereas in Figure 16, tetrachloromethane has 100 percent NPSA and chloromethane has nearly equal amounts of polar and nonpolar surface area. The utility of TSA, PSA, and NSA, and how to estimate them, are discussed in detail in the scientific literature (Yalkowsky & Valvani, 1976; Yalkowsky et al., 1979; Yalkowsky & Valvani, 1979; Rao et al., 1985). In this book, we use the concepts only in a general way in our discussions.

Special polar molecules

There are some special cases of molecules with bonds between atoms of significantly different electronegativity. These are the bonds between hydrogen (H) and strongly electronegative atoms such as O, N, and F. In such bonds, the distortion of the electron cloud leaves the hydrogens with a strong positive charge, as illustrated in Figure 19 for water, methanol, and ammonia.

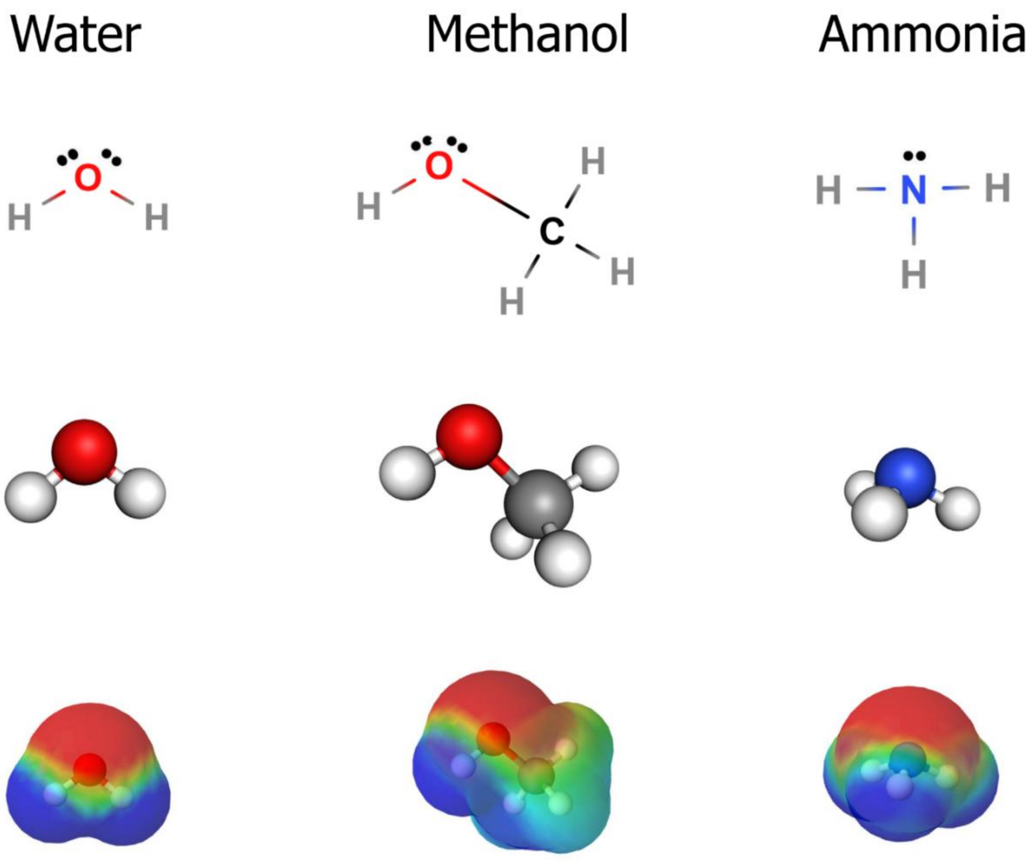


Figure 19 - Bonds with strongly electronegative atoms, using oxygen and nitrogen as examples. In ball and stick models, carbon atoms are dark gray, hydrogen atoms are white, oxygen atoms are red, and nitrogen atoms are blue. Lower images show molecular electrostatic potential (MEP). In such bonds, the distortion of the electron cloud leaves the hydrogens with a strong positive charge.

In water, the strongly electronegative oxygen is bonded to two weakly electronegative hydrogens but also has two pairs of unshared electrons—that is, electrons not shared with other atoms via a bond. The pairs of unshared electrons create dipoles of their own, leading to a strong net molecular dipole, as implied in the MEP illustration for water. The hydrogens possess a strong partial positive charge, while the oxygen possesses a strong partial negative charge. Methanol and ammonia also have unshared electrons and strong molecular dipoles.

3.5 Intermolecular Forces

Why do we care about intermolecular forces?

Many of the processes we will consider are affected by the degree to which molecules are attracted to one another. In general, the degree to which one molecule is attracted to another is controlled by the attractions that occur between its electron-poor and electron-rich parts and those of the other molecule.

Conceptualizations of polar and nonpolar portions of molecules

An organic molecule can be composed of polar and/or nonpolar portions. Figure 20 simplifies the conceptualization and coloring into three general cases:

a) a molecule that is completely nonpolar, that is, lacking in any polar functional groups, and thus 100 percent nonpolar surface area (NPSA); and

b) and c) molecules that contain both nonpolar and polar portions but in varying proportions and/or locations of the polar and nonpolar surface areas (PSA and NPSA).

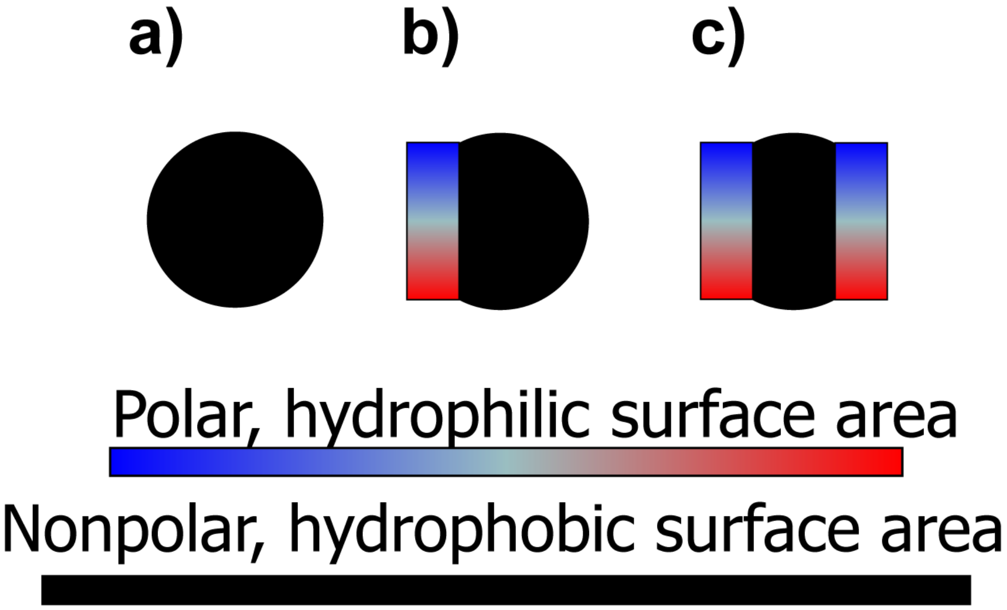


Figure 20 - Simplified conceptualizations of organic molecules for use in later figures: a) a completely nonpolar molecule, and b) and c) molecules containing both nonpolar and polar portions in varying proportions and/or locations of the polar and nonpolar surface areas.

These simple graphical representations will be useful in subsequent discussions of physico-chemical properties of organic molecules. In addition, organic molecules can be conceived of as having surfaces, portions of which are nonpolar and portions of which are polar. As discussed in the literature (Yalkowsky & Valvani, 1976; Rao et al., 1985) some physico-chemical behavior of organic molecules can be predicted based on the amounts of NPSA (sometimes called *hydrocarbonaceous surface area*) and PSA.

The illustrations in Figure 20 depict molecules of roughly the same overall size. This is purely for convenience, since organic molecules can vary widely in size and shape (Figure 16, Figure 17, Figure 18). In short, both the overall size and the relative proportion of the polar and nonpolar surface areas vary widely among organic molecules.

We briefly discuss four types of intermolecular attractions in increasing order of strength. Note that the overall attraction between two molecules may result from one or more of these types of attractions.

Why do we need to know about intermolecular attractions?

We need to know about intermolecular attractions because the environmental fate of compounds is affected by their interactions with other compounds and the mineral and other surfaces they encounter, as discussed in Sections 7 through 12.

van der Waals forces

All molecules are affected by weak attractions to other molecules. These attractions, termed *van der Waals forces*, are caused by short-duration displacements of electrons within a molecular structure that lead to localized electron-rich and electron-poor sections of the structure, and thus transient dipoles. Since similar displacements can occur in all molecules, the fluctuating dipoles in one molecule can induce similar dipoles in an adjacent molecule. This results in weak attractive forces. Although the positions of these weak dipoles shift constantly about each molecular structure, the overall intermolecular attraction can be significant for large molecules with many parts in which dipoles can develop.

Figure 21 is a conceptual illustration of van der Waals interactions for hypothetical nonpolar molecules, drawn as oblongs for clarity of illustration and to remind us that molecules can have various shapes. As the molecules approach each other, transient positive and negative charges may occur on one and induce the reverse in another. Although relatively weak, the van der Waals attractions are extremely important. Such forces control the interactions of molecules of straight-chain petroleum hydrocarbons (such as methane, ethane, butane, propane, and hexane) and other molecules that do not have permanent dipoles. In addition, van der Waals forces maintain the structural integrity of cell walls and control how detergent molecules behave and affect other chemicals in aqueous solution.

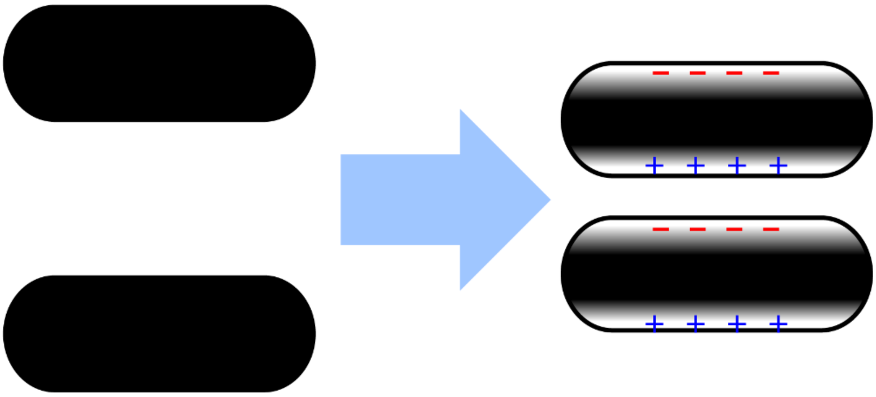


Figure 21 - Illustration of formation of van der Waals forces between two molecules, each depicted as oblong shapes for this figure to allow clear depiction of the transient positive and negative charges.

Dipole-induced dipole attractions

Permanent dipoles within one molecule can induce a temporary redistribution of electrons within a nearby molecule, producing an *induced* dipole therein and an attractive force between the two molecules. This is illustrated in Figure 22 for two hypothetical molecules, where one has a permanent dipole (like chloromethane in Figure 16) and the larger pill-shaped molecule does not. Many compounds of interest to groundwater studies have permanent dipoles whereas others do not, so this kind of interaction can be important in some circumstances. As a different example, in 1,2 dibromoethane, each bromine–carbon bond may be expected to be a reasonably strong dipole. These dipoles may induce electron redistribution in nearby molecules that otherwise have no permanent dipole (such as pentane), leading to a weak and transient attraction between the unlike molecules.

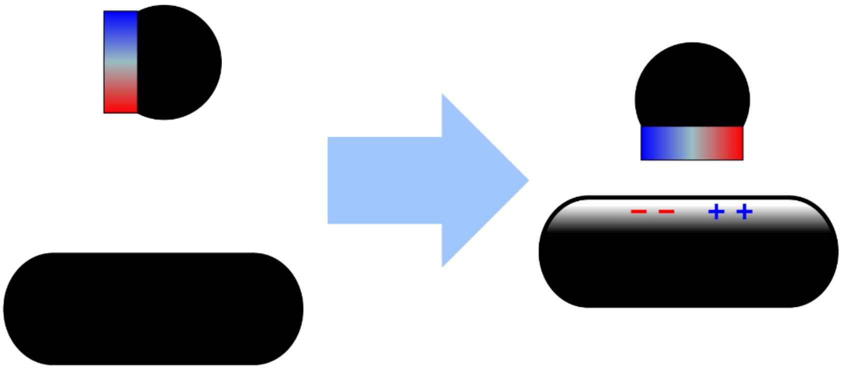


Figure 22 - Illustration of formation of dipole-induced dipole bond between two molecules.

Dipole–dipole attractions

If two molecules both have permanent bond dipoles, the dipoles will be attracted to one another, as illustrated conceptually in Figure 23 for hypothetical molecules with polar ends.

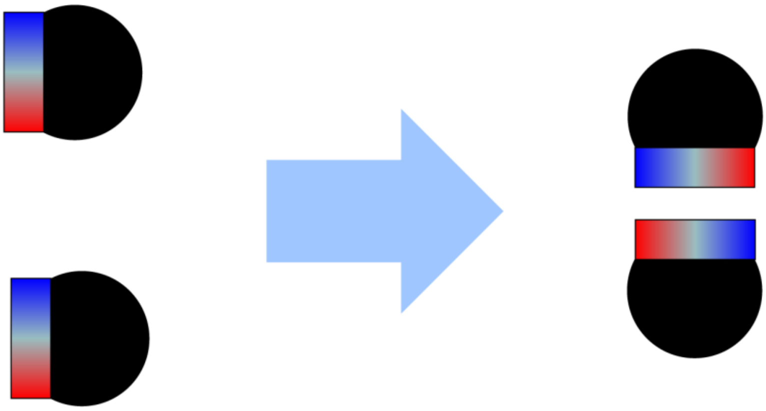


Figure 23 - Illustration of formation of dipole–dipole bond between two molecules, each of which has a permanent bond dipole.

All halogenated organic compounds have permanent bond dipoles of varying strength due to the presence of the strongly electronegative halogen atoms. Thus, dipole–dipole interactions are important in pure liquid or solid phases of any of these compounds or in mixtures of them.

Hydrogen bonds

We have discussed the unusual character of the bonds between hydrogen and the strongly electronegative atoms oxygen, nitrogen, and fluorine. The hydrogens in these bonds possess a permanent partial positive charge, while the oxygen or nitrogen possess a permanent partial negative charge. Molecules possessing one or more of these bonds can form what is called a *hydrogen bond* with each other when a hydrogen of one molecule becomes strongly attracted to an oxygen, nitrogen, or fluorine of the other molecule.

One important example of hydrogen bonding occurs between molecules of water (H-O-H), as illustrated in Figure 24a. Why do we need to know this? Because for compounds to dissolve in water, they need to insert themselves in the water, which involves breaking the strong hydrogen bonds, as we discuss a bit later in this section. It is estimated that the hydrogen bonds between water molecules have an average lifetime of 10^{-11} seconds (https://en.wikipedia.org/wiki/Hydrogen_bond↗), essentially instantly reforming (Exercise 10⤵). Other examples of hydrogen bonding are illustrated in Figure 24b for water-methanol ($H_2O - HOCH_3$) and in Figure 24c for water-methylamine ($H_2O - H_2NCH_3$).

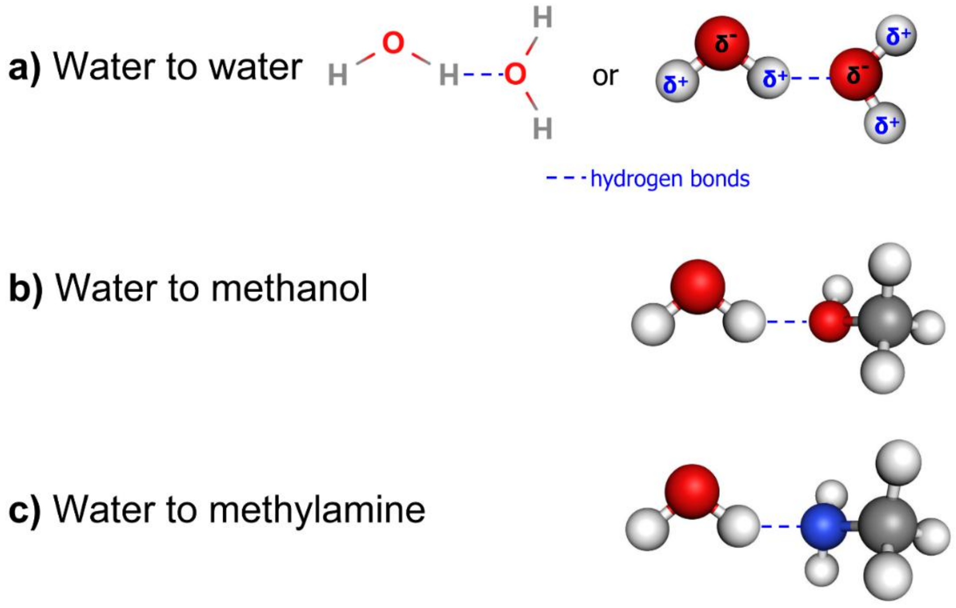


Figure 24 - Hydrogen bonds between molecules: Three examples where oxygen atoms are red, hydrogen are white, nitrogen are blue, and carbon are dark gray.

Other examples of intermolecular hydrogen bonding include water–phenol, water–aniline, and methanol–phenol. Aside from such interactions between molecules, there are many other instances in which hydrogen bonding is important. These include (a) intramolecular attractions, in which one part of a molecule is attracted to another part of the same molecule, which are particularly important in large molecules such as the humic and fulvic acids that exist in most natural waters as discussed by Chappelle (2022); and (b) attractions of molecules to inorganic surfaces, some of which present electronegative oxygens to the adjacent solution.

4 Viscosity

4.1 Why Do We Need to Know about Viscosity?

Viscosity is an important characteristic of water and organic liquids that is addressed in greater detail in literature related to the behavior of liquid organic contaminants in the subsurface. Here we need only a basic understanding of the term.

4.2 What Is Viscosity?

Viscosity, a term applied to fluids, is a measure of the resistance to flow under stress. Figure 25 is an illustration of the familiar macroscopic effects of different viscosities, using water and honey as examples of low- and high-viscosity liquids, with viscosities of ≈ 1 and ≈ 10,000 cP (centipoise, or milliPascal sec) at 20 °C, respectively.

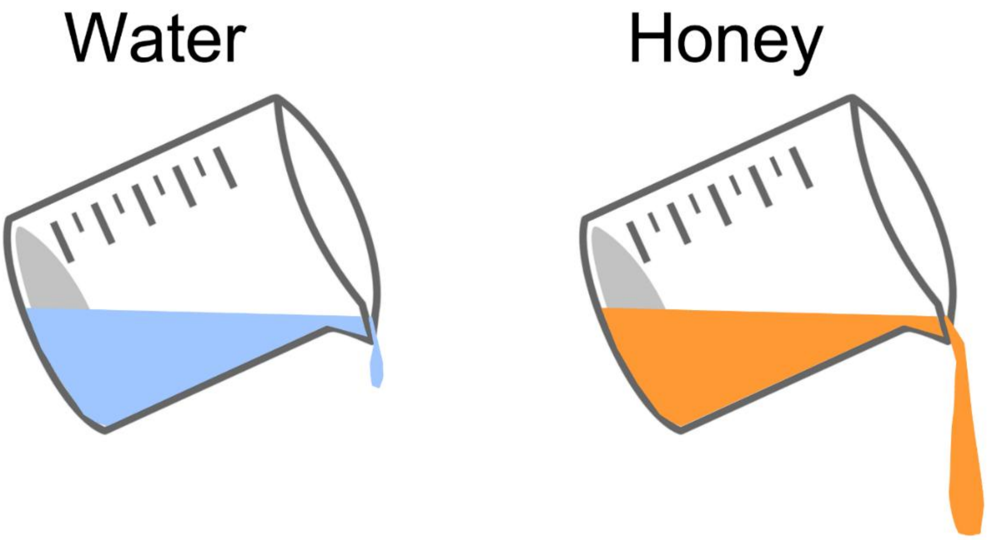


Figure 25 - Illustrations of the macroscopic effects of viscosity, comparing water and honey at the same temperature.

The viscosities of organic liquids at 20 °C range from a bit lower than water (for example, 0.88 cP for methanol) to higher values but still much lower than honey. The viscosity of o-dichlorobenzene—a relatively nonpolar molecule only weakly attracted to others of its kind—is 1.4 cP (at 25 °C), lower than that of o-chlorophenol (4.11 cP at 25 °C) and octanol (7.4 cP at 20 °C). Both o-chlorophenol and octanol molecules are capable of hydrogen bonding with others of their kind.

Molecules in a liquid are much closer together than those in a gas. As a result of this molecular proximity and the range of strengths of intermolecular attractions, the viscosities of liquids are much greater than those of gases. The importance of viscosities to understanding the fate of gases and liquids in the subsurface, along with the impact of temperature on viscosity, are described in other books and literature (including in Newell et al., 1995; Pankow & Cherry, 1996; Kueper et al., 2003; Poling et al., 2001).

5 Surface Tension

5.1 Why Do We Need to Know about Surface Tension?

Surface tension is discussed in greater detail in many other scientific and practical publications. Here we need only a basic understanding of the term.

5.2 What Is Surface Tension?

Surface tension is defined as the force acting on the surface of a liquid, which tends to minimize the area of the surface. Figure 26 illustrates the macroscopic effects of differing surface tensions, and compares equal volumes of three liquids with high, medium, and low surface tension sitting or spreading on the same surface.

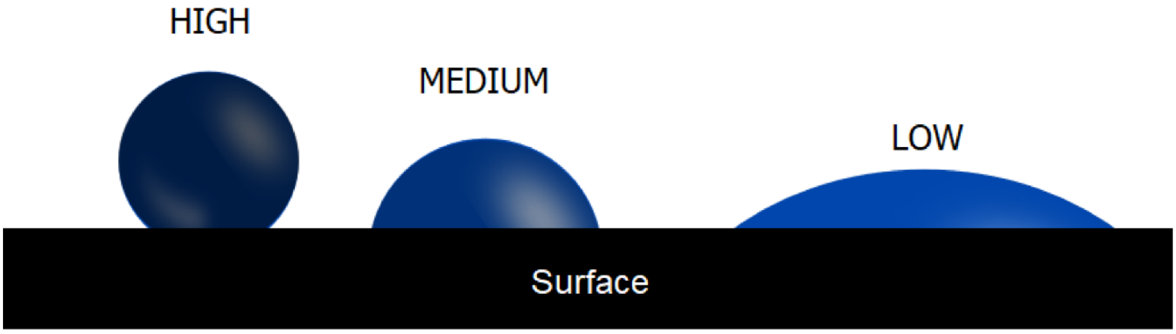


Figure 26 - Illustration of three liquids with different surface tensions on a surface.

Surface tension can be understood by considering that the molecules within the volume of the liquid are surrounded by and thus attracted to like (i.e., similar) molecules, essentially symmetrically. Thus, on average, such molecules do not experience any net force in any direction. On the other hand, a molecule at the surface of the liquid only has like molecules “below” or “behind” it, within the volume of the liquid; thus, it experiences a net attractive force toward the volume of the liquid. Moving a molecule from within the volume of the liquid to the surface of the liquid requires the input of energy and increases the surface area of the liquid. The energy required to cause an increase in surface area is called the *surface tension* of the liquid.

In practical situations, of course, the organic liquid surface is in contact with some other phases such as air, water, and minerals. Because the molecules at the surface of the organic liquid experience some attractive forces to the molecules within the surrounding or adjacent phase, the surface tension depends on the surrounding phase or the nature of the interface. Thus, it is most common to report *interfacial tension*, specifying either organic liquids surrounded by air or organic liquids surrounded by water. This is a fascinating and complex topic that is treated in more detail elsewhere (including Pankow & Cherry, 1996; Kueper et al., 2003).

One consequence of this is that the surface of a liquid in a container is curved. This called a *meniscus* in the lab (illustrated in Figure 27) or *capillarity* in porous media, which is an important phenomenon, as made clear in many other papers and books (such as in Panko & Cherry, 1996; Kueper et al., 2003).

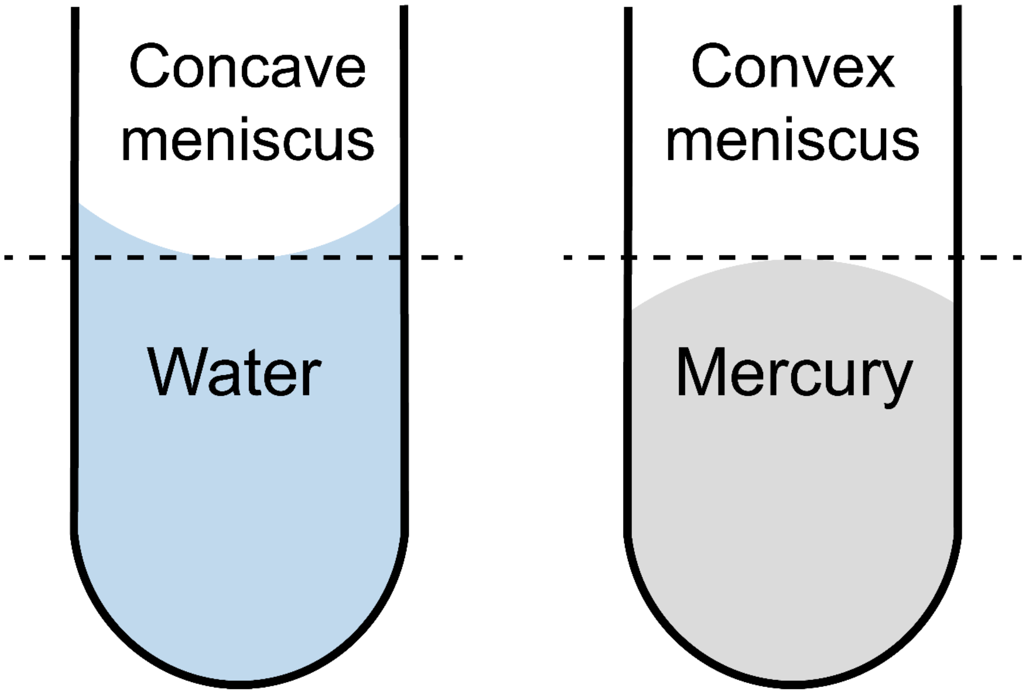


Figure 27 - Consequences of interfacial tension for different liquids in test tubes.

6 Vapor Pressure

6.1 Why Do We Need to Know about Vapor Pressure?

Vapor pressure is an important property of organic chemicals. In addition to controlling the evaporation of solid or liquid chemicals, it is important in understanding the transfer of chemicals from water to vapor phases.

6.2 What Is Vapor Pressure?

The saturated vapor pressure (P^{sat}) often simply called the vapor pressure, is the pressure created by a chemical vapor when it is in equilibrium with its pure condensed phase (liquid or solid) at a given temperature, as illustrated in Figure 28.

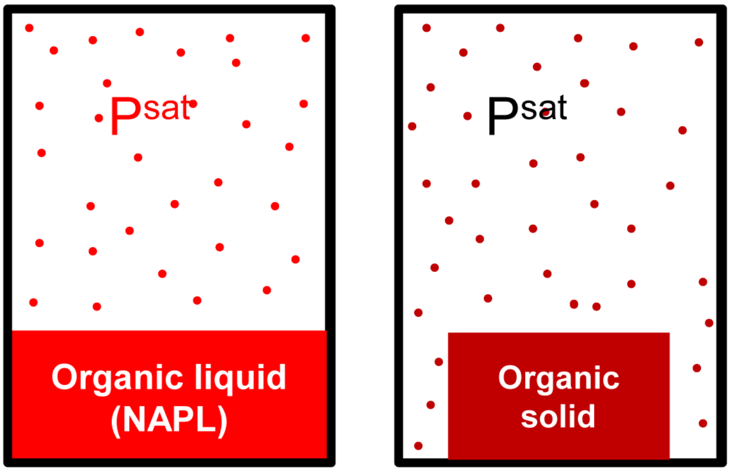


Figure 28 - Conceptualization of vaporization into evacuated container.

If a solid or liquid chemical is placed in an evacuated container, but the solid or liquid does not fill the entire container, some of the molecules in the liquid or solid transfer to the headspace (i.e., evaporate) as illustrated in Figure 28. At some point, assuming excess liquid or solid (condensed) phase remains, the net transfer of molecules to the headspace ceases, as evaporation would be balanced by condensation (transfer of molecules from the vapor to the condensed phase). This establishes equilibrium between the two phases (Exercise 11↴), and the total pressure exerted by the vapor is the saturated vapor pressure at the temperature of the system, which varies among different compounds. In most cases of practical interest, equilibrium is reached rapidly (within minutes).

Figure 29 illustrates the enormous range of vapor pressures exhibited by classes of organic compounds at approximately 25 °C. Values of vapor pressure for specific chemicals and temperatures are available via web searches for individual compounds (for example, https://pubchem.ncbi.nlm.nih.gov↗). For comparison, the vapor pressure of water is 0.03 atm at 25 °C, indicated by the vertical blue dashed line in Figure 29.

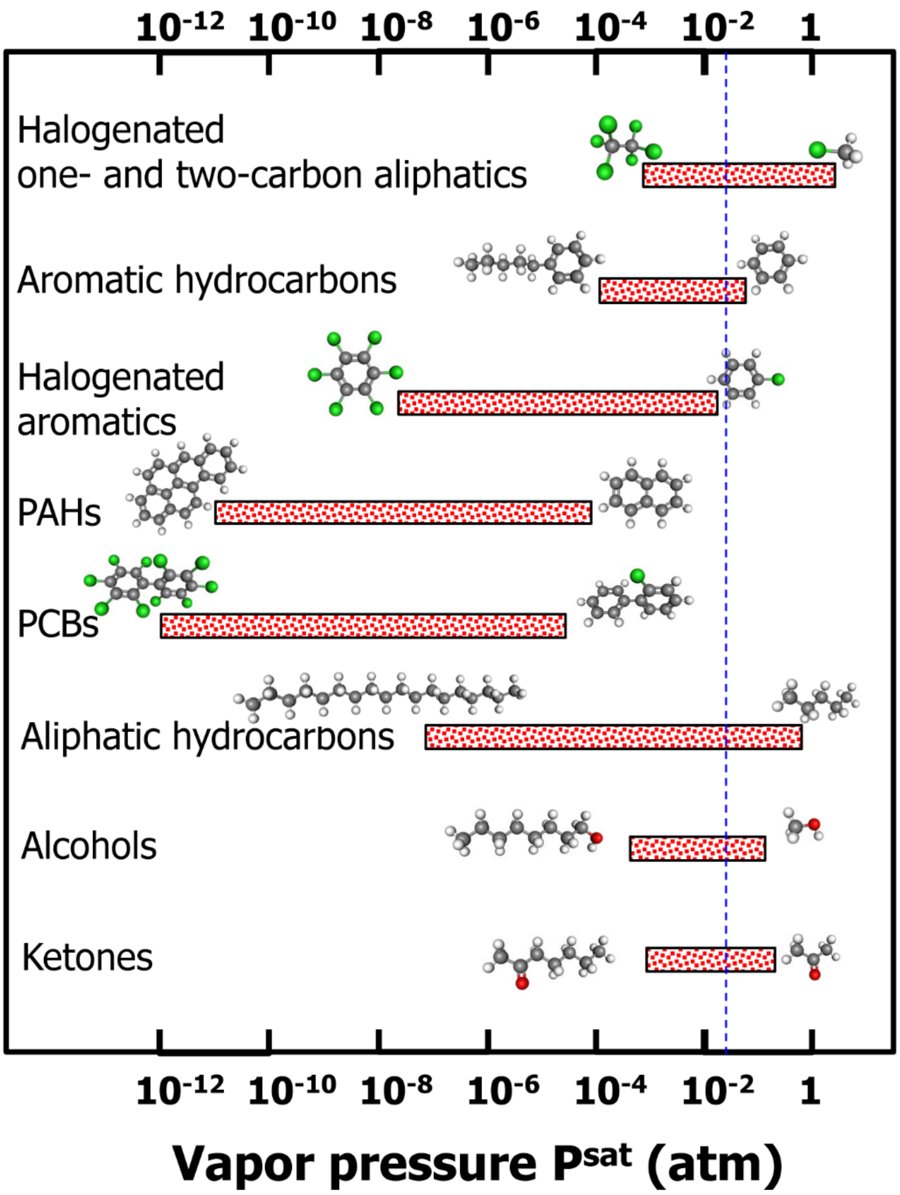


Figure 29 - Vapor pressures for chemical classes at ≈ 25 °C (redrawn, modified, and annotated from Schwarzenbach et al., 1993).

6.3 Units for Vapor Pressure

Vapor pressure is reported in a variety of units. We have used *atmospheres* (atm) in this book. The unit of pressure in the SI system is the *pascal* (Pa), where 1 atm = 101,325 Pa. In other cases, pressure is presented in *mm of mercury* (mmHg), which is nearly identical to another pressure unit called *torr*, where 1 atm = 760 mm Hg = 760 torr.

6.4 Conceptualization for Variation in P^{sat}

Based on the discussion earlier in this section, we ask you to imagine that the vapor pressure of a pure chemical in its condensed phase depends on the degree to which the molecules are attracted to one another.

As illustrated in Figure 30, molecules that are weakly attracted to each other—for example, molecules of nonpolar compounds between which weak van der Waals forces exist—are expected to have higher vapor pressure than compounds whose molecules are more strongly attracted to each other. This is shown in Figure 29 by comparing three similarly sized molecules:

1. chloromethane,
2. the lowest molecular weight halogenated aliphatic compound (whose vapor pressure is significantly higher than methanol), and
3. acetone (the lowest molecular weight ketone).

All three have higher vapor pressure than water, which has very strong intermolecular bonds, as we have discussed.

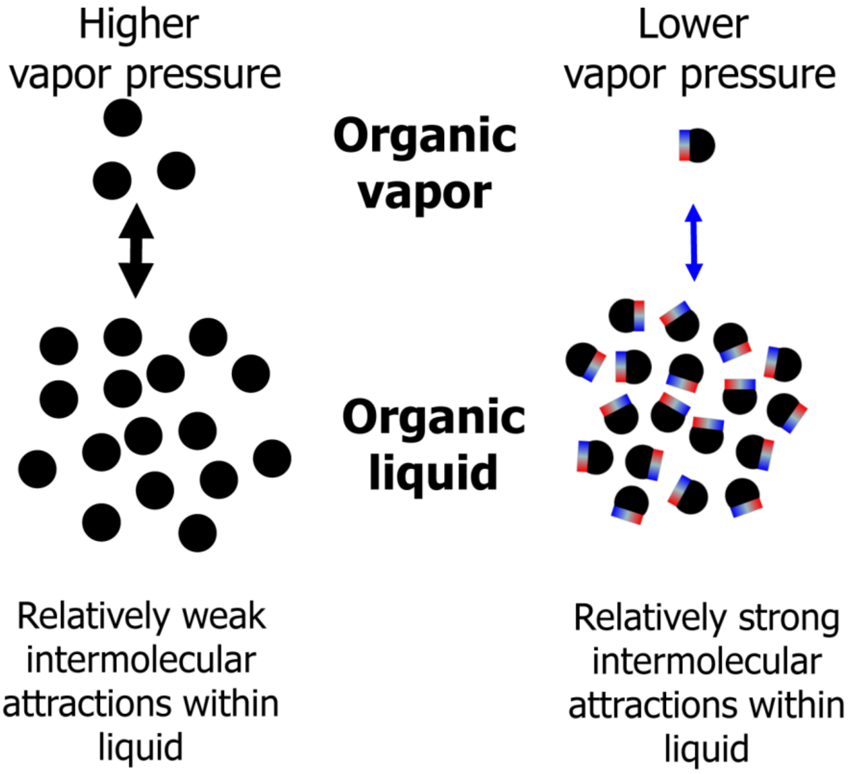


Figure 30 - Conceptualization of the impact of the polarity of similarly sized molecules on vapor pressure.

Large molecules, which can form a number or variety of bonds with other molecules of their kind, have low vapor pressures. Figure 31 presents two examples:

a) the surfactant octoxynol, which has a vapor pressure of 0.001 (10^{-3}) atm; and
b) aldicarb, an insecticide of the carbamate class (Barbash & Resek, 1997), which has a vapor pressure of only 0.00000004 (4×10^{-8}) atm.

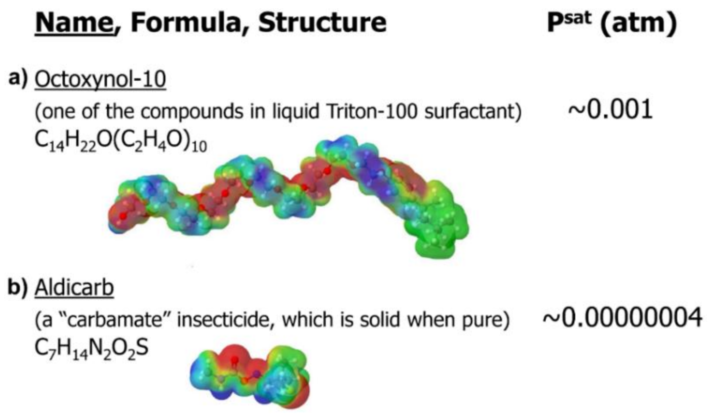
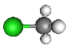
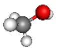
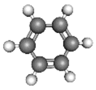
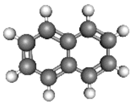


Figure 31 - Examples of two large molecules with low vapor pressures: a) octoxynol-10 and b) aldicarb.

6.5 Conversion of Vapor Pressure to Concentration

In environmental applications, one often encounters references to *vapor concentration*, instead of vapor pressure. Vapor concentration is often reported in units of mass per volume (e.g., g/L, mg/L, µg/L). Box 2↴ illustrates how to convert vapor pressure to vapor concentration in units of mass per volume using the ideal gas law equation ($PV = nRT$). Table 2 depicts several compounds, along with their saturated vapor pressures and corresponding saturated vapor concentrations at 20 °C. Water is included for comparison. The lowest and highest vapor pressures and concentrations in the table are for naphthalene and chloromethane, a solid and gas, respectively, at 20 °C.

Table 2 - Examples of vapor pressure expressed as vapor concentration. Shading indicates gas or condensed phase (white = gas, blue = liquid, gray = solid). MW is an abbreviation for molecular weight.

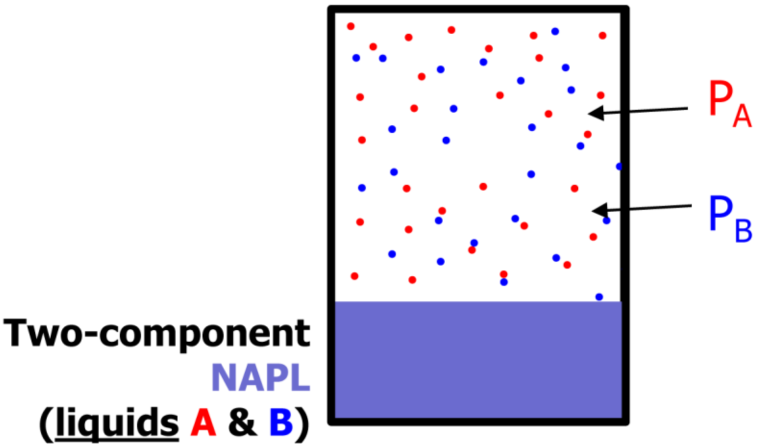
Compound	Formula	Structure	Molecular Weight	Saturated vapor	
				Pressure (atm)	Concentration (g/L)
Water	H_2O		18	0.03	0.02
Chloromethane	CH_3Cl		51	4.99	11
Chloroform	$CHCl_3$		119	0.21	1.0
Methanol	CH_3OH		32	0.13	0.2
Benzene	C_6H_6		78	0.10	0.3
Naphthalene	$C_{10}H_8$		128	0.0001	0.0005

6.6 Vapor Pressure Rises with Temperature

Vapor pressure is a strong function of temperature, as illustrated in Box 3↴ for examples of various classes of organic compounds with water included for comparison. For many organic compounds of interest to us, a 10 °C rise in temperature increases the vapor pressure by a factor of 1.5 to 2 (Exercise 12↴). More detailed discussions of the temperature dependence of vapor pressure are provided elsewhere (e.g., Schwarzenbach et al., 2017). Reference books and websites often contain tabulations of vapor pressure for various temperatures (https://pubchem.ncbi.nlm.nih.gov↗) or tabulations of parameters that can be used to calculate vapor pressures for a temperature of interest (Poling et al., 2001).

6.7 Vapor Pressure for Components in Mixtures of Organic Liquids

Many liquid organic contaminants (NAPLs, or nonaqueous phase liquids) that have been encountered in the subsurface are composed of more than one compound—that is, they are mixtures, also called *multicomponent liquids*. Figure 32 illustrates the simplest case: a two-component NAPL, also called a *binary mixture*.



5

Figure 32 - Illustration of the simplest mixture of organic liquids (binary mixture). Each vapor pressure for liquid A and liquid B is lower than the respective single-component vapor pressure.

Often more complex mixtures are present. For example, fuels (gasoline, kerosene, jet fuel, and so on) are mixtures of hundreds of individual organic compounds, most of which in their pure state are liquids under typical environmental conditions. Another example is waste industrial solvents, which have historically been combined in storage or disposal units, leading to multicomponent organic liquids that have too often escaped into the environment. Furthermore, single-component liquid compounds can become mixed with other single-component liquid compounds after release into the environment, yielding a multicomponent liquid in the subsurface.

It may be important to know when such multicomponent liquids exist in the subsurface, since the behavior of the individual compounds can be markedly different in a mixture than when they are present on their own (not in mixtures). For example, for an organic compound whose condensed phase is liquid, the vapor pressure of that compound in equilibrium with a multicomponent organic liquid (containing that compound and others) is lower than that in equilibrium with its pure liquid phase. In a multicomponent phase (such as mixture of gases or a mixture of liquids) the fraction of each component is called a *mole fraction* when it is expressed as the moles (or molecules) of that component divided by the total number moles (or molecules) of all components (Exercise 13⤵)

For organic liquid compounds and mixtures thereof, the vapor pressure of component *i* (P_i) in equilibrium with a multicomponent liquid can be estimated by Raoult's law, which is described by Equation (1).

$$P_i = \gamma_i x_i \mathrm{P}_i^{\mathrm{sat}} \qquad (1)$$

where:

γ_i = activity coefficient of component *i* in the liquid mixture, 1 for ideal mixtures (dimensionless)

x_i = mole fraction of component *i* in the liquid mixture (dimensionless)

$\mathrm{P}_i^{\mathrm{sat}}$ = saturated vapor pressure of pure component *i* at the system temperature ($MT^{-2}L^{-1}$) often expressed in atmospheres (atm)

In most cases of practical interest, equilibrium would be reached rapidly enough that it can be assumed to exist. The vapor pressure P_i is lower than the saturated vapor pressure since the mole fraction (x_i) of component i has to be less than 1 in the mixture, and the activity coefficient (γ_i, the Greek letter gamma with subscript *i*) is 1 or less. The activity coefficient is a measure of the ideality of the mixture—in simplest terms, the degree to which the components of the vapor and liquid interfere or interact with one another. In an ideal mixture, the activity coefficient equals 1 and the components do not interact and thus behave independently. Schwarzenbach and others (2017) provide a more fundamental discussion of activity coefficients.

6.8 Vapor Pressure for Binary Mixtures of Organic Liquids

Figure 33 illustrates the effect of Raoult's law for two binary mixtures: (a) toluene and benzene and (b) acetone and chloroform. Benzene and toluene are two structurally similar compounds, and it is known that their mixtures exhibit ideal behavior—that is, conform essentially perfectly to Raoult's law as illustrated in Figure 33a. The experimental data (solid lines) are linear, as would be predicted. In other words, the vapor pressure of benzene decreases linearly as the mole fraction of benzene decreases (and thus the mole fraction of toluene increases). At the same time, the vapor pressure of toluene increases. In an equimolar mixture of the two (containing the same number of molecules of each, so the mole fraction of each is 1/2), the vapor pressures of each would be one-half of the pure component saturated vapor pressure. This ideal behavior can be explained in a qualitative way by noting that the intermolecular attractions between the two slightly different molecules are similar to those between molecules of either one (Exercise 14↴).

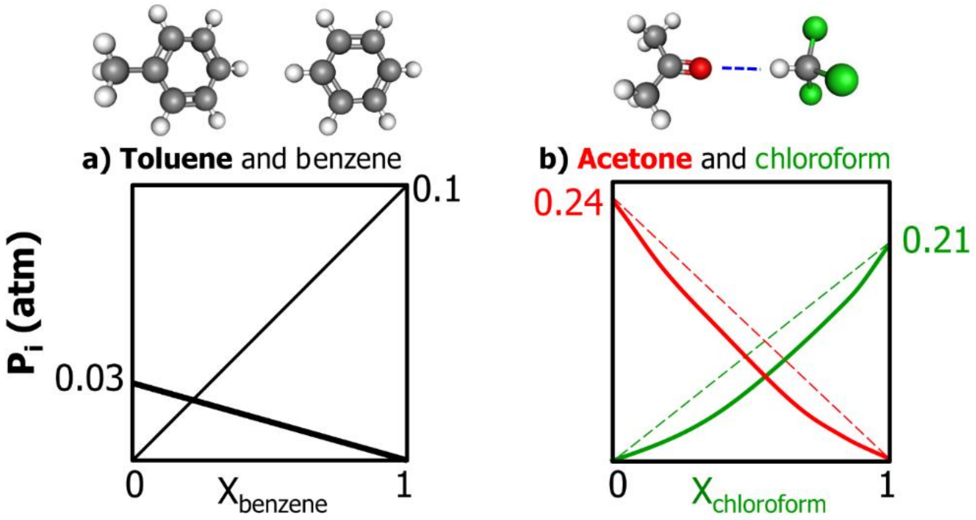


Figure 33 - Vapor pressure versus composition for examples of ideal and nonideal binary mixtures at 20 °C. The x-axis is mole fraction of the subscript species. The blue dashed line illustrates hydrogen bond between case (b) species.

On the other hand, some binary mixtures of dissimilar molecules exhibit nonideal behavior. One such example is illustrated in Figure 33b for a mixture of acetone and chloroform. In this case, the experimental data (solid lines) have negative deviations from the ideal expression of Raoult's law (dashed lines)—that is, the measured vapor pressures of the components are lower than predicted solely based on the mole fractions. This implies the activity coefficients for these compounds in the mixture are less than 1.

This behavior can be understood in a qualitative manner by imagining that a molecule of acetone is more strongly attracted to a molecule of chloroform than it is to another molecule of acetone (and vice versa). The explanation is in part because of hydrogen bonding between the dissimilar molecules (indicated in Figure 33b by the blue dashed line between the red oxygen in acetone and the white hydrogen in chloroform). Thus, each type of molecule is more strongly attracted to the mixed liquid than it is to its own pure liquid; therefore, a smaller fraction of each type of molecule will vaporize from the mixed liquid than from its own pure liquid.

In many cases of practical interest, the nonidealities may be less significant than suggested in Figure 33b. In such cases, we assume ideality (activity coefficients equal to one) for estimating vapor pressures in equilibrium with many multicomponent organic liquids. The assumption is considered justified since the error introduced by the assumption is often much smaller than that introduced by other unknowns (such as analytical precision and fluid flow rate in a porous medium).

However, one notable exception is for mixtures of ethanol and hydrocarbons such as occur in ethanol-blended gasolines (sometimes called *gasohols*). Isooctane is often used as a single compound to represent the average properties of the numerous hydrocarbon components in typical gasoline. Figure 34 is a graph similar to those in Figure 33 but illustrates the strong positive deviations from Raoult's law that occur for mixtures of ethanol and isooctane. Mixtures of other alcohols and hydrocarbons also have positive deviations (Exercise 15↴).

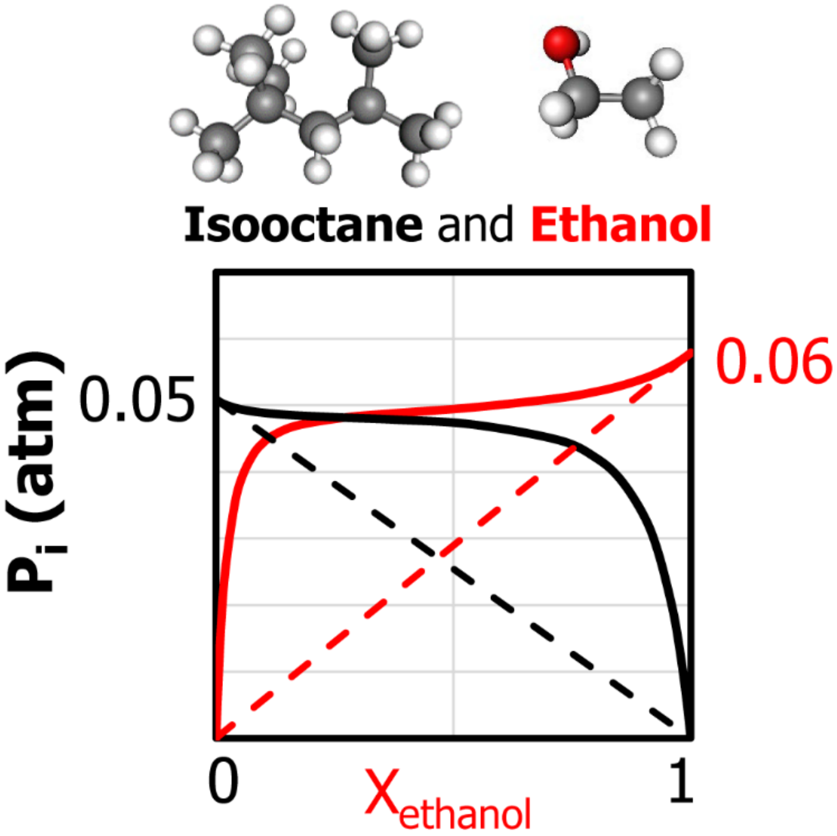


Figure 34 - Vapor pressure versus composition for ethanol-isooctane mixtures. The x-axis is mole fraction of the subscript species (data compiled from the scientific literature on vapor–liquid equilibrium and plotted by W. Rixey, University of Houston, for use in this book).

6.9 Vapor Pressure for Ternary Mixtures of Organic Liquids

Table 3 illustrates the effects on vapor pressures in a *ternary mixture* (three-component mixture) containing benzene, toluene, and trimethylbenzene; this mixture is nearly ideal since the intermolecular attractions between the three different molecules are similar to those between identical molecules. For an equimolar mixture (one in which the mole fraction of each of the three components is 1/3), the vapor pressure of the individual components would be 1/3 of the vapor pressures of the pure chemicals (the saturated vapor pressures). Similarly, the vapor concentrations of the components would be 1/3 of the saturated vapor concentrations (corresponding to the saturated vapor pressure).

Table 3 - Vapor pressure at 25 °C for single components and an equimolar mixture of all three.

Chemical	**Single component**		**Ternary mixture**		
	P_i^{sat} (atm)	Vapor concentration (mg/L)	Mole fraction (-)	P_i (atm)	Vapor concentration (mg/L
Benzene	0.1	324	0.333	0.0333	108
Toluene	0.03	115	0.333	0.0999	38
1,2,4-trimethylbenzene	0.002	10	0.333	0.0007	3

This has important consequences in practice. For example, if you were trying to determine the likelihood of liquid organic chemicals being present in the subsurface environment by monitoring the vapor phase (*soil gas*), measuring a vapor concentration well below the saturated vapor concentration could not be taken as evidence that organic liquids were absent unless you knew without a doubt that only the single component liquid could be present. Similarly, if you were trying to remove organic liquid contaminants from the subsurface by extraction of vapors (also called *soil venting*), you would have to consider that the amount of mass removed per unit volume of extracted vapor could be significantly lower than expected for a single component case if, in fact, the organic liquid was a multicomponent one. These and related issues are discussed in more detail elsewhere (e.g., Rathfelder et al., 1991; Bloes et al., 1992; Pankow & Cherry, 1996).

6.10 Vapor Pressure for Mixtures of Organic Liquids and Organic Solids

One may often encounter organic liquid mixtures containing chemicals that would be liquid if present in their pure form and others that would be solid if present in their pure form. Examples of the latter are 1,2,4,5-tetrachlorobenzene (Figure 13c) in chlorinated solvent mixtures and naphthalene (Table 1) in hydrocarbon fuel mixtures at temperatures below their melting points. Other examples include higher molecular weight polyaromatic hydrocarbons (such as fluorene and anthracene) in coal tar liquids and polychlorinated biphenyls in transformer oils. In these cases, the vapor pressure of the subcooled liquid (Figure 12) needs to be used in Equation (1), since a chemical is in a liquid state when dissolved in a liquid mixture. Subcooled liquid vapor pressure can be estimated from more readily available solid vapor pressures using Equation (2).

$$P_{i,liquid}^{sat} = P_{i,solid}^{sat}\ \exp\left(A\left[\frac{T_m}{T} - 1\right]\right) \tag{2}$$

where:

T_m = melting point of solid chemical (Θ), degrees kelvin (K)

T = temperature of interest (Θ), degrees kelvin (K)

A = coefficient specific to the chemical (dimensionless)

Temperatures in this equation are in degrees above absolute zero, called degrees kelvin and denoted K. The reader is referred to others for a derivation and detailed discussion of this equation and the coefficient A (e.g., Miller et al., 1985; Schwarzenbach et al., 1993; Feenstra & Guiger, 1996). For our purposes, first-approximation calculations made with Equation (2) using a value of 6.8 for the coefficient A are acceptable. A similar equation is discussed in Section 7.10 for determining subcooled liquid solubilities to be used for estimating solubilities of organic solids in mixtures of organic liquids.

7 Aqueous Solubility

7.1 Why Do We Need to Know about Aqueous Solubility (Water Solubility)?

Aqueous solubility is another important organic chemical property. In addition to controlling the dissolution of compounds in water, aqueous solubility is known to be correlated with other important phenomena including partitioning of chemicals from water to air and sorption of chemicals to solid media in the subsurface. We start this section by making an important distinction between organic liquids, such as ethanol that you may know can readily mix with water, and those that we know cannot, such as oil.

7.2 Some Organic Liquids Can Mix with Water and Some Cannot

Completely miscible organic solvents (CMOSs)

These organic liquids can mix with water in all proportions. CMOSs are generally chemicals capable of hydrogen bonding and "fit" easily into the structure of liquid water. Figure 35 depicts three examples of CMOSs and shows the polar nature of the molecules. Other CMOSs not shown in the figure include ethanol and ethylene glycol, both of which are polar (Exercise 16↴).

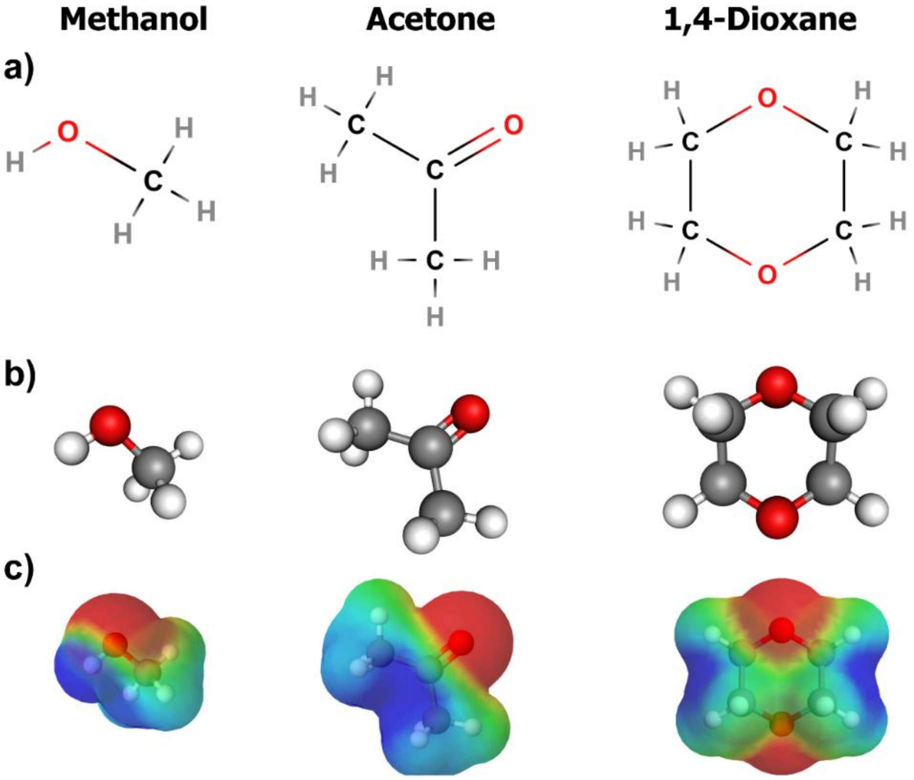


Figure 35 - Examples of completely miscible organic solvents (CMOSs), illustrating the polarity of each. Three depictions of each molecule are shown: a) the typical 2D structure, b) the 3D ball and stick model, and c) the 3D molecular electrostatic potential (MEP).

Partially miscible organic solvents (PMOS)

These organic liquids are not completely miscible with water. *Partially miscible organic solvents* (PMOSs) are only slightly soluble in water, as we discuss in Section 7.4. Examples include:

- chlorinated solvents,
- aromatic hydrocarbons,
- aliphatic hydrocarbons, and
- some halogenated aromatics.

Additional common terms are used for PMOSs. PMOSs are often referred to as *non-aqueous phase liquids* (NAPLs) since if they are added in significant volume to a container of water they will remain in a separate phase, dissolving only slightly—a household example is cooking oil added to a container of water (Exercise 17⤵). Indeed, most of the NAPL contaminants are also often called *hydrophobic organic chemicals* (HOCs) for this reason. HOCs are neutral compounds—that is, they do not contain ionizable functional groups (Exercise 18⤵). Another important subcategory of PMOSs includes compounds that have one or more ionizable functional groups (such as carboxylic acids and anilines), which can strongly affect their solubility. These are called *hydrophobic ionizable organic chemical*s (HIOCs) and are discussed later in this section.

7.3 Aqueous Solubility of Neutral Organics: Single Component Gases, Liquids, and Solids

Figure 36 illustrates aqueous solubility in which we imagine a pure, single-component organic chemical phase placed in contact with pure water in a closed vessel at a temperature and pressure within the narrow ranges of typical environmental significance (near 20 °C and one atmosphere). Distribution of the chemical after equilibrium is reached are illustrated in Figure 36.

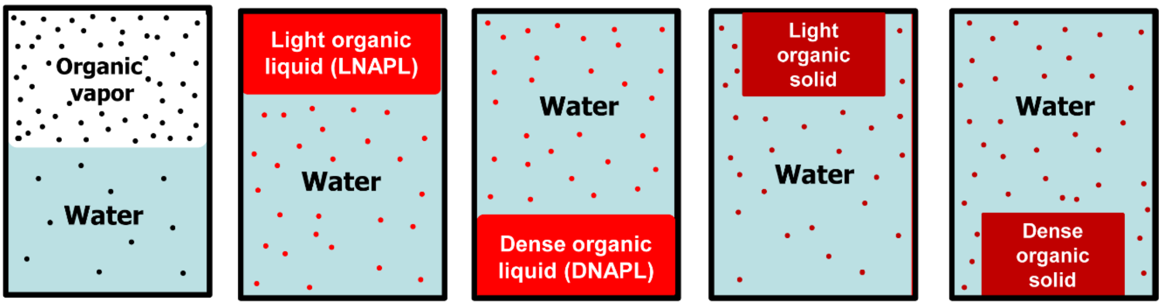


Figure 36 - Conceptualizations of water solubility for organic vapors and partially miscible organic solvents (PMOSs, also called LNAPLs and DNAPLs) and organic solids.

In Figure 36, five cases illustrate (from left to right) the following phases in contact with water:

1. a pure organic vapor, an example of which is chloromethane;
2. a pure organic liquid that is not miscible with water (a PMOS) and is less dense than the water and thus floats upon it (called an LNAPL, or light nonaqueous phase liquid); examples include many aromatic and aliphatic hydrocarbons, such as benzene and octane (Exercise 19⤵);
3. an organic liquid that is not miscible with water (a PMOS) and is more dense than the water and thus sinks to the bottom of the vessel (called a DNAPL, or dense nonaqueous phase liquid)—for example, chlorinated aliphatics such as trichloroethene and chlorinated aromatics such as chlorobenzene;
4. an organic solid that is less dense than the water and thus floats such as heptadecane or heavier alkanes, and tert-butanol (although its melting point is near 25 °C); and
5. an organic solid that is more dense than water and thus sinks—for example, any of the PAHs and PCBs.

In each of these cases, organic chemical mass would be transferred from the organic vapor, liquid, or solid into the water until the aqueous concentration of the organic reached an equilibrium value. Provided excess gas, liquid, or solid organic phase remained after equilibrium was reached, the equilibrium concentration would be the aqueous solubility (water solubility) of the organic chemical for the temperature of the container (Exercise 20⤵).

The same set of phases could exist for situations in which the phases are not composed of a single component but are mixtures of more than one compound. Multicomponent phases are more likely to be encountered in practice, but before we consider the complexities of such situations, we present the single-component case.

7.4 Aqueous Solubilities of Pure Organic Compounds

Aqueous solubilities of pure organic compounds range over more than ten orders of magnitude. This very wide range is illustrated in Figure 37 for the indicated classes of organic compounds at approximately 25 °C. The starred endpoint of the horizontal lines for the alcohols (or ketones) represents the lowest molecular weight, completely miscible, member of those classes. Thus, those points correspond to the moles of methanol (or acetone) per liter of methanol (or acetone). That could be the case immediately after the release of such compounds to the subsurface before the organic liquid and water start dissolving into one another.

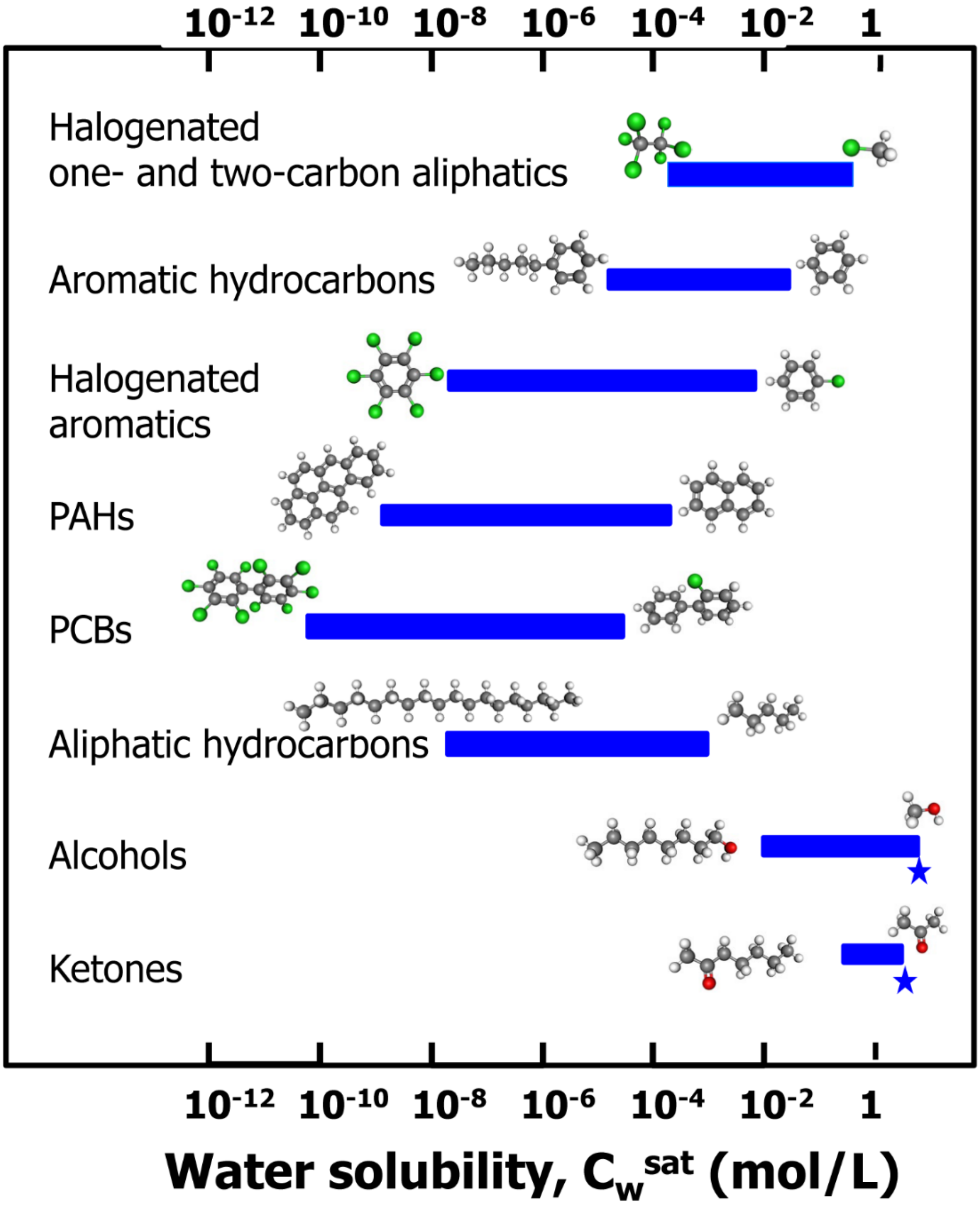


Figure 37 - Water solubility ranges for chemical classes at approximately 25 °C (redrawn, modified, and annotated from Schwarzenbach et al., 1993). The stars indicate CMOSs in which the liquid is 100 percent CMOS (no water).

The aqueous solubility of an organic chemical is often denoted by C_w^{sat}, which may be read as *the saturated water concentration* or *the saturated chemical concentration in water*. We also use that term throughout this book. In other texts, journal articles, and reference books, aqueous solubility may be denoted in other ways—most often simply as S. However, we avoid that since it is ambiguous, does not refer to the medium in which the dissolution takes place, and is identical or similar to other terms commonly used for other parameters in literature related to groundwater contamination and remediation. Aqueous solubilities for specific chemicals are available in reference books (such as Schwarzenbach et al., 2017) and many online sources (including https://pubchem.ncbi.nlm.nih.gov↗).

To provide a physical sense of the incredibly wide range of solubilities, we examine a very-low- and very-high-solubility organic compound. The number of water molecules that would surround each contaminant molecule is calculated for low solubility and high solubility organic compounds as follows:

1. *Low solubility:* PAHs, with solubilities as low as 10^{-8} mol/L. At solubility, in 1 liter of water there would be 10^{-8} moles of PAH and 55.6 moles of water. Another way to express the concentration of PAH is the *mole fraction*, which is the ratio of the number of moles of PAH per liter to the number of moles of water per liter, or $10^{-8}/55.6$. This implies:
    - one high molecular weight PAH/PCB molecule per 5.6 billion water molecules (that is very dilute); yet it also means there are
    - $3\text{x}10^{11}$ molecules of contaminant per drop of water (i.e., 0.05 ml which is $1.7\text{x}10^{21}$ molecules of water) and that is still a lot of contaminant.
2. *High solubility:* Chloroform has a solubility equivalent to a mol fraction of 0.0012. This implies:
    - one chloroform molecule per 832 water molecules, but there is still a lot of water separating the chloroform molecules; and it also means there are
    - $2\text{x}10^{18}$ molecules of contaminant per drop of water (0.05 mL), which is a staggeringly large number of contaminant molecules.

Thus, even for the most soluble of the immiscible organic contaminants there are a lot more water molecules than contaminant molecules in a single-component solution. On the other hand, there are a very large number of molecules of each organic compound in just one drop of water at their solubility limit. However, it is useful to keep in mind that these high solubilities are rarely encountered in field samples of groundwater either because contaminants enter the groundwater from dilute sources, or because contaminated water near pure-component NAPLs in the subsurface mixes with less contaminated water near the NAPLs during the sampling process.

7.5 Conceptualization of Solubilization of Organic Gases, CMOSs, and Organic Liquids

The dissolution of organic chemicals into water is critical to their subsurface fate and environmental impact. It is useful, as shown later in Sections 7.7 and 7.10, to conceptualize the dissolution process as a series of steps as illustrated in Figure 38.

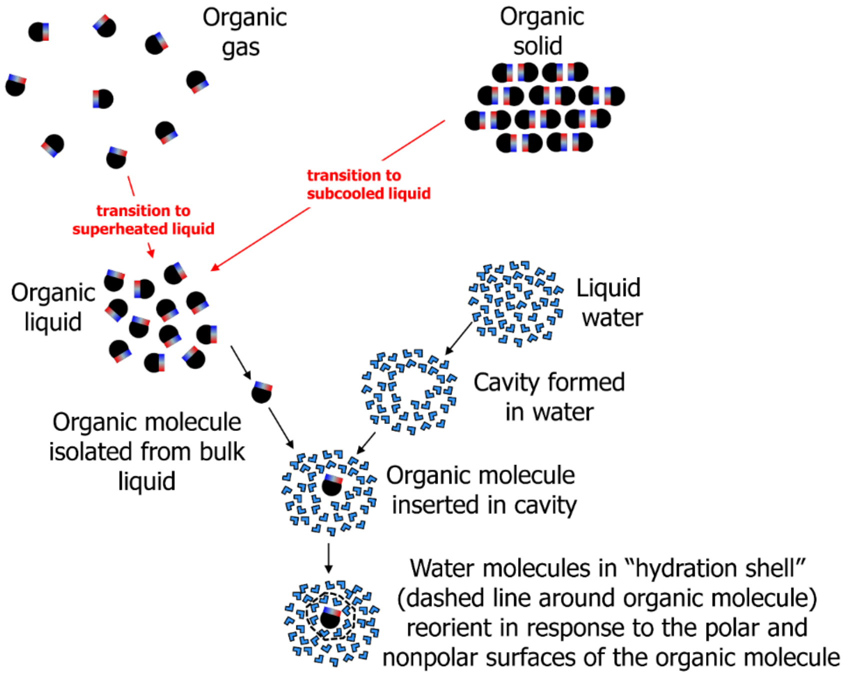


Figure 38 - Conceptualization of the process of dissolution of a pure organic phase (vapor, liquid, or solid) as a series of steps, each of which involves making, breaking, or rearranging intermolecular attractions (redrawn, modified, and annotated from Schwarzenbach et al., 1983).

At typical environmental temperatures and pressures, pure organic compounds may exist either as gases, liquids, or solids, as illustrated in the upper left corner of the figure. Once dissolved in water, however, all types of organic compounds exist in a liquid state. They are free to move about—not as free as they when in a vapor state, but certainly much less constrained than in a solid state.

The first conceptual step in the dissolution of organic vapors or organic solids is their conversion to a superheated or subcooled liquid state, respectively (Figure 12). No such conceptual conversion is required for organic chemicals that are liquids under environmental conditions. There is an energy cost to this conceptual step in either compressing the gas or melting the solid.

The second conceptual step involves two events:

1. an organic molecule is separated from the bulk liquid (or superheated or subcooled liquid), and
2. within the liquid water, water molecules are moved to create a cavity.

The third conceptual step involves the insertion of the organic molecule in the cavity within the liquid water. You can imagine that the size and shape of the cavity that is required depends on the size and shape of the organic molecule and its affinity for water (for example, its ability to form hydrogen bonds).

The fourth conceptual step reorients the water molecules surrounding the cavity in response to the polar and/or nonpolar portions of the organic molecule.

Energy changes are associated with each of these steps, as discussed in more detail by others (such as Schwarzenbach et al., 1993). As we discuss in Section 7.7 and 7.10, this conceptual model of the dissolution process is useful in understanding the effects on dissolving compounds that occur when there are mixtures of organics in contact with water or when the aqueous phase contains significant concentrations of other compounds besides those that are dissolving.

One issue not addressed in these conceptual models of dissolution (Figure 36 and Figure 38) is that the initially pure organic phase will become invaded by water molecules for the same reason that the liquid water becomes invaded by the organic molecules. In other words, water will have a solubility in the organic liquid, just as the organic has a solubility in the water. In many cases, it is acceptable to ignore this. For example, the mole fraction of some common nonpolar organic liquids (hydrocarbons and chlorinated hydrocarbons) remains above 0.99 even when they are fully saturated with water at environmentally relevant temperatures (Schwarzenbach et al., 1993). On the other hand, the mole fractions of relatively polar organic liquids may be much lower when fully saturated with water—for example, about 0.7 for PMOSs such as octanol, pentanol, methyl acetate, and 2-butanone (Schwarzenbach et al., 1993).

7.6 Effect of Solution Conditions on Solubility of Hydrophobic Organic Chemicals (HOCs)

The previous discussion has addressed differences in solubility among or within classes of compounds, considering only the case of the chemicals dissolving in pure water at a given temperature. However, natural water is not pure, varies in pH and temperature, and contains natural inorganic solutes (such as calcium, magnesium, sodium, and carbonate). Natural uncontaminated water also contains organic macromolecules derived from natural organic materials (such as humic and fulvic acids) and microparticles arising from inorganic matter (such as clays and inorganic precipitates). However, we will save consideration of the latter two for later.

There are wide variations in natural geochemical conditions in the subsurface and thus wide variations in the type and amount of natural inorganic and other dissolved constituents that may be present (Poeter et al., 2020; Chapelle, 2022). We need to consider how these conditions might affect the solubility of the organic compound of interest, as well as other processes related to solubility (discussed in Sections 7.7 through 7.10). *This section addresses only neutral compounds, often called HOCs (hydrophobic organic compounds).*

Temperature

Solubility may increase or decrease with temperature in the environmental range of interest, but the effect is slight for contaminants that would be liquid in their pure state. So, in many cases this effect may be minor compared to all the other uncertainties we encounter when making calculations or predictions for chemicals in the subsurface. If the contaminants are gases or solids in their pure state, their solubilities are more sensitive to temperature.

pH

Among uncontaminated and contaminated groundwaters, pH may vary widely. Furthermore, pH may vary temporally at a given site for a variety of reasons. Therefore, it is important to consider the effect that pH may have on the solubility of important classes of organic contaminants. In this section, we focus on HOCs, which are neutral species (uncharged). The effect of pH variation on the solubility of HOCs is generally insignificant. In the context of understanding the subsurface fate of HOCs, the effect of pH variation may safely be ignored since other uncertainties are quite large by comparison.

Dissolved Inorganic Compounds

A common way to express the impact of dissolved inorganic compounds is to consider the aggregate impact of the total dissolved solids (TDS). This is often expressed by calculating or measuring the ionic strength (I) of the solution (Solomon, 2001). Increasing ionic strength decreases the solubility of HOCs, but the effect on HOCs is slight. For example, solubility in seawater may be 50 to 90 percent of that in distilled water (Xie et al., 1997). In practice, the effect of TDS on the solubility of organic contaminants in freshwaters with low TDS is generally assumed to be negligible, or at least very minor compared to other factors.

Dissolved Organic Compounds

This topic covers a broad range of compounds thus is not discussed in a brief paragraph here, rather subsequent sections will cover the following:

- non-natural organic co-solvents and co-solutes,
- non-natural surfactants (e.g., detergents and foaming agents), and
- natural organic macromolecules (also called dissolved organic matter, or DOM).

We first consider the impact of non-natural organics.

7.7 Effects of Organic Co-solvents and/or Co-solutes on Solubility of HOCs

We consider the effect on an HOC of interest when other organic compounds are also dissolved in or mixed with the water. As suggested in Figure 39a, the term *co-solvent* is generally used to describe organic liquids that are completely miscible with water (CMOSs, including those shown). Therefore, co-solvents can be present at high mole fractions in the aqueous solution, likely affecting the way water molecules interact with the molecule of interest (in the dashed oval), as suggested in Figure 39a.

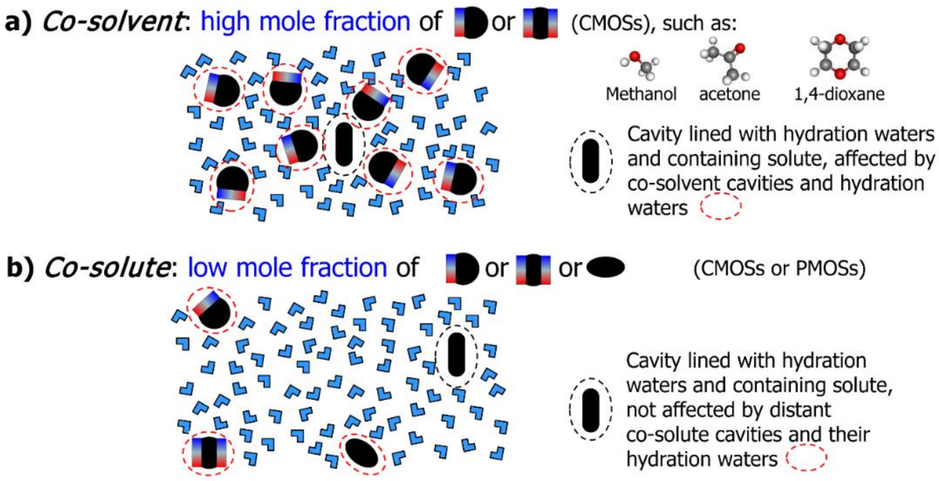


Figure 39 - Conceptualization of a solute (PMOS, solid black object) within its cavity (dashed black oval) in aqueous solutions also containing co-solvents or co-solutes, each within their own cavities (red dashed ovals) (redrawn, modified, and annotated from Schwarzenbach et al., 1993).

Since they affect the structure of the water surrounding the HOC, the presence of high concentrations of co-solvent can profoundly affect an HOC's solubility, as shown in the next section. In Figure 39b, we show the other extreme, co-solutes, in which the other organic molecules are present in low concentrations (or mole fractions) and may not significantly affect the structure of the water interacting with the compound of interest. So, we expect the effect of co-solutes on an HOC's solubility would generally be much less significant than the effect of co-solvents (Exercise 21↴). Co-solutes can be either CMOS molecules or PMOS molecules.

Co-solvents

Figure 40 illustrates the enhancement of solubility of tetrachloroethene (PCE) as a function of volume fraction of solvent in a mixed solvent–water system after equilibrium is reached.

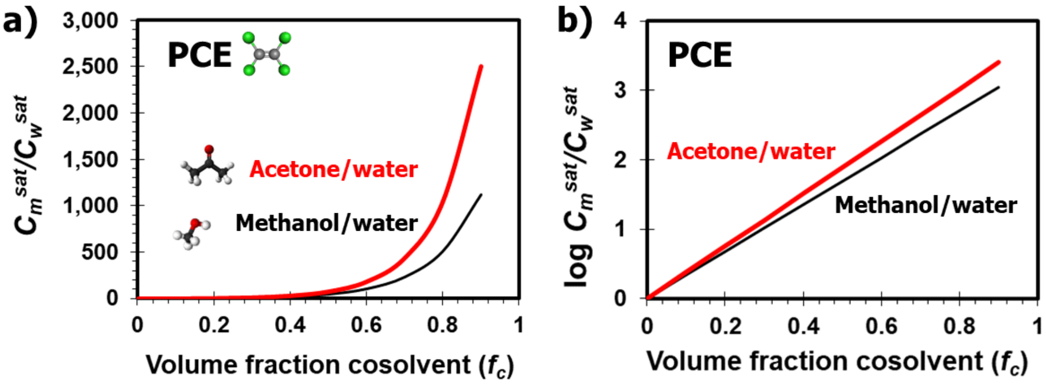


Figure 40 - Effect of co-solvent fraction (acetone or methanol) on solubility of tetrachloroethene (PCE): a) the ratio of solubility in the mixed solvent to solubility in water plotted against volume fraction of the solvent in the solvent–water mixture; b) the log of the solubility ratio plotted against volume fraction of the solvent in the solvent–water mixture (based on theory and parameters presented by Li & Yalkowsky,1998).

In Figure 40a and Figure 40b, the y-axis is the ratio of enhanced solubility in the mixed solvent system (which we call C_m^{sat}, where the subscript "m" refers to the mixture) to the water solubility (C_w^{sat}). The impact of the co-solvent on PCE solubility is strong for either solvent (acetone or methanol); the solubility in the mixed system can rise by a factor of 1,000 or more. Figure 40 also shows that acetone has a greater impact on PCE solubility than does methanol.

Similar graphs can be made for other potential co-solvents (other CMOSs, such as ethanol and 1,4-dioxane). For a given co-solvent, the impact on solubility varies widely among different organic solutes. For example, a 50 percent acetone–water mixture increases the solubility of phenanthrene by a factor of 300, whereas it increases PCE solubility by less than a factor of 80. This difference arises because the co-solvency power of a solvent depends on the properties of the solute being dissolved—notably, its water solubility or its hydrophobicity.

Co-solutes

Studies have shown that what are referred to as *co-solutes* generally have little to no impact on the solubility of other organic compounds.**Figure 41** Figure 41 illustrates two cases: a) a co-solute with minor impact and b) a co-solute with no impact.

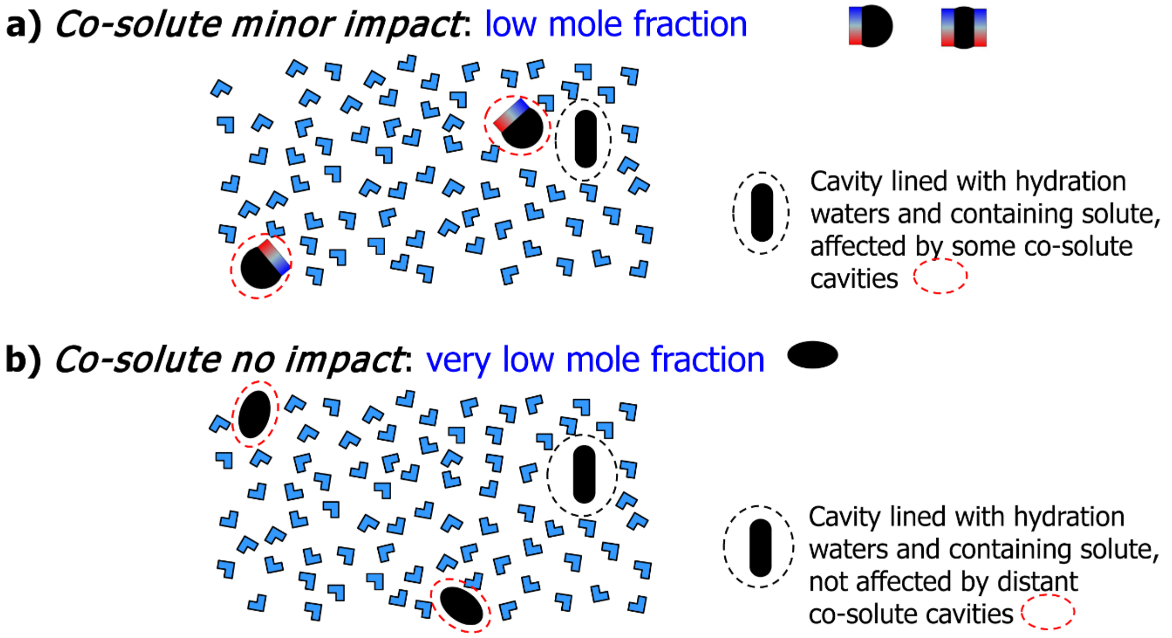


Figure 41 – Illustration of two cases for impact of co-solutes on solubility of organic solutes: a) minor impact of some co-solutes on very hydrophobic organic solutes, and b) negligible or no impact of nonpolar co-solutes on other organic solutes (redrawn, modified, and annotated from Figure 5.8 of Schwarzenbach et al.,1993).

Figure 41a suggests that in some cases co-solutes may affect the solubility of some organics, particularly those with very low solubilities, if they affect some of the water surrounding cavities containing the solute of interest. Based on experimental data, Chiou and others (1982) calculated that, in water saturated with octanol, the solubility of hexachlorobenzene was increased by less than a factor of 2, whereas the solubility of DDT was increased by less than a factor of 3. These experiments were conducted with very high concentrations of octanol, which perhaps would rarely be encountered in practice. Schwarzenbach and others (1993) estimated the octanol volume fraction was only 0.0007 (0.07 percent) in that work.

Figure 41b illustrates that some low-solubility co-solutes have negligible impact on the solubility of other organic solutes since the hydration shells do not overlap with those of the target solutes. For example, Leinonen and Mackay (1973) conducted laboratory experiments showing solubility enhancements of alkanes impacted by other alkanes were less than 4 percent. Such low solubility enhancements are of no concern to practical studies in which other uncertainties are far greater.

In summary, while co-solutes may in some cases have a detectable impact on the solubility of other organic compounds of interest, the impacts are small and correspond to cases that are rarely encountered in practice (Exercise 22↴).

7.8 Aqueous Solubility of Hydrophobic Ionizable Organic Chemicals (HIOCs)

An HIOC contains one or more functional groups that can ionize; the degree of ionization depends on the solution pH and other solution conditions. HIOCs include organic acids, such as chlorophenols, and organic bases, such as amines (Exercise 23↴). As illustrated in Figure 42 for two example HIOCs, organic acids may exist as neutral and anionic species in aqueous solution, while organic bases may exist as neutral and cationic species, the proportion of acid and base change with pH. For both acids and bases, the ionized forms are much more soluble in water (because they are more polar) than the neutral forms. Thus, the overall solubility of organic acids and bases depends strongly on the degree of ionization, which depends strongly on the pH of the solution as illustrated in Figure 42 for the following:

- *an organic acid* with a single ionizable functional group: pentachlorophenol, which loses a proton to form a pentachlorophenolate anion, and
- *an organic base* with a single ionizable functional group: 4-methyl aniline.

A neutral acid is abbreviated HA, while the anion formed by losing the $H^+$is called A^-. A neutral base is abbreviated B, while the cation formed by gaining an H^+ is called BH^+.

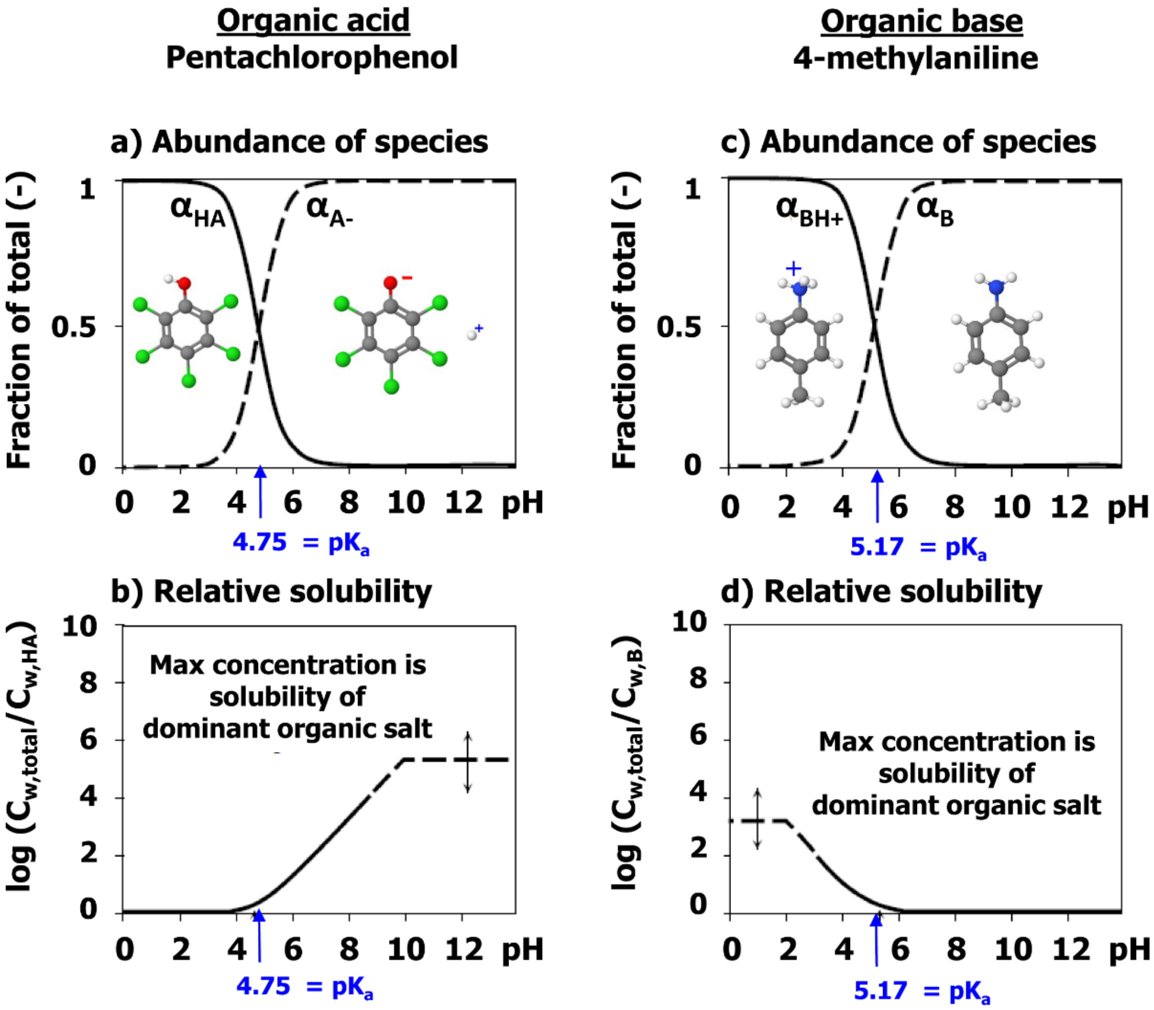


Figure 42 - Species abundance and total solubility versus pH for two examples: an organic acid (pentachlorophenol) and an organic base (4-methyl aniline). Graphs were created by D. Mackay using pK_a and saturation concentrations of the protonated acid ($C_{w,HA}$) and the deprotonated base ($C_{w,B}$). a) and c) are graphs of relative abundance of the neutral and ionized species for pentachlorophenol and 4-methyl aniline; b) and d) are graphs showing that total solubility rises sharply above the pK_a for the acid or below the pK_a for the base (Exercise 24⤵) (Exercise 25⤵). The y-axis in lower graphs is logarithmic.

Figure 42a and Figure 42c present graphs of relative abundance of the neutral and ionized species for pentachlorophenol (an acid) and 4-methyl aniline (a base) at equilibrium. Box 4⤵ presents the equations and assumptions needed to calculate the abundance of the neutral or ionized species as a function of pH. At a pH called the pK_a, there are equal numbers of each. For pH above or below the pK_a by 2 units or more, one species dominates. Tabulated solubilities are for neutral species. The ionized species are much more soluble because they are more polar.

Figure 42b and Figure 42d are graphs showing that total solubility rises sharply above the pK_a for the acid or below the pK_a for the base. The y-axis is the logarithm of the ratio of the total solubility to the solubility of the neutral species. The solubility can rise by orders of magnitude, as shown, but is capped at the solubility defined by the dominant organic salt (a compound composed of the organic ion and an inorganic ion of opposite charge). Since natural waters often contain dissolved calcium (a positively charged ion, called a *cation*), the cap for the illustrated organic acid could be set by the solubility of the calcium salt of pentachlorophenolate.

Similarly, since carbonate is a common inorganic anion in all natural waters, the solubility cap for the base could be set by the solubility of its carbonate salt. Unfortunately, data on solubility of organic acid/base salts are difficult to find (Schwarzenbach et al., 2017), so specific values are not depicted in Figure 42b and Figure 42d. Nevertheless, the bottom line is that it is important to be aware of the following.

- For *organic acids*, the total concentrations in water can greatly exceed the tabulated solubility of the neutral species when the pH is above the pK_a (this could be important for pentachlorophenol since the pH of groundwater is usually greater than 4.75).
- For *organic bases*, the total concentrations in water can greatly exceed the tabulated solubility of the neutral species when the pH is below the pK_a. This may not be too important for the example compound since the pH of groundwater is rarely below 5.2. However, this effect could be important for other compounds.

7.9 Aqueous Solubility for Mixtures of Organic Liquids

Organic chemicals are often released to, and/or present within, the environment as mixtures. Let's consider the simplest case in which the mixture contains chemicals that in their pure state would all be liquids. As in the case of vapor pressure, the aqueous concentration of a given organic chemical in equilibrium with such a multicomponent organic liquid is less than the aqueous solubility of the pure liquid chemical (Figure 43).

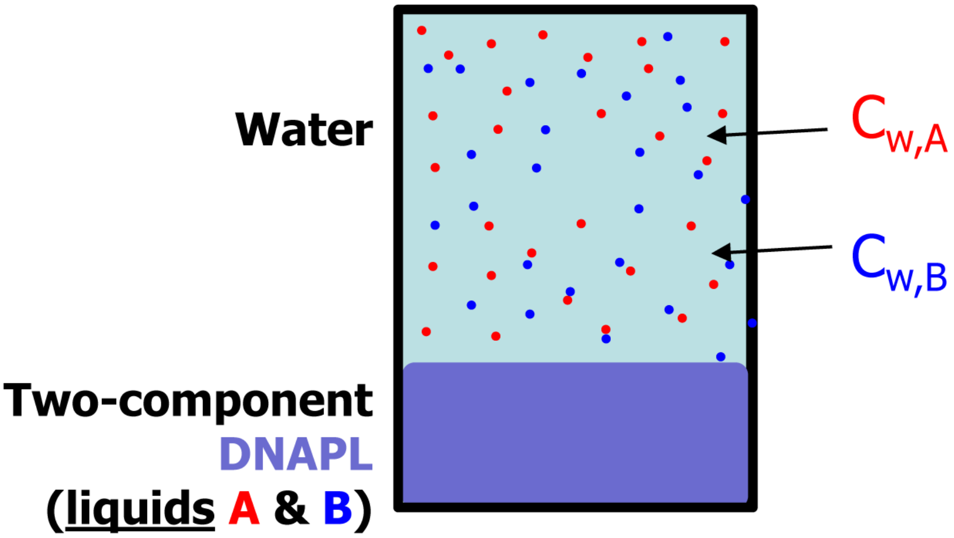


Figure 43 - Illustration of an organic liquid mixture (DNAPL in this case) composed of two compounds, A and B, and equilibrium concentrations in water of the two compounds. Each illustrated concentration is lower than respective single-component solubility.

For many organic liquids and mixtures thereof, the aqueous concentration of component i ($C_{w,i}$) in equilibrium with a multicomponent organic liquid mixture can be estimated by an analog of Raoult's law often called the Effective Solubility Model as shown in Equation (3).

$$C_{w,i} = \gamma_i x_i C_{w,i}^{sat} \tag{3}$$

where:

$C_{w,i}^{sat}$ = aqueous solubility of pure component i at system temperature (ML^{-3}), e.g., mg/L

γ_i = activity coefficient of component i in the liquid mixture (dimensionless), which equals one for ideal mixtures

x_i = mole fraction of component i in the organic liquid mixture of z components = n_i/ntotal = $n_i/(n_1 + n_2 + \ldots + n_i + \ldots n_z)$ (dimensionless)

n_i = the number of molecules of component i divided by the total number of molecules of all components in the mixture (components 1, 2, $i \ldots z$) (dimensionless)

Strictly speaking, this model only applies when the liquid is an ideal mixture. When the mixture is ideal, γ_i equals 1, and the mole fraction of the mixture determines the aqueous concentration of that component in equilibrium with the mixture. A mixture is ideal when the components do not affect each other in aqueous solution. The reader interested in a more detailed discussion of such issues is referred to Schwarzenbach and others (1993).

Figure 44 presents effective solubility data for two different mixtures of organic liquids: Figure 44a, a mixture of 1,1,1-trichloroethane and tetrachloroethene and Figure 44b, a mixture of 2-methylpentane (2-MP) and benzene.

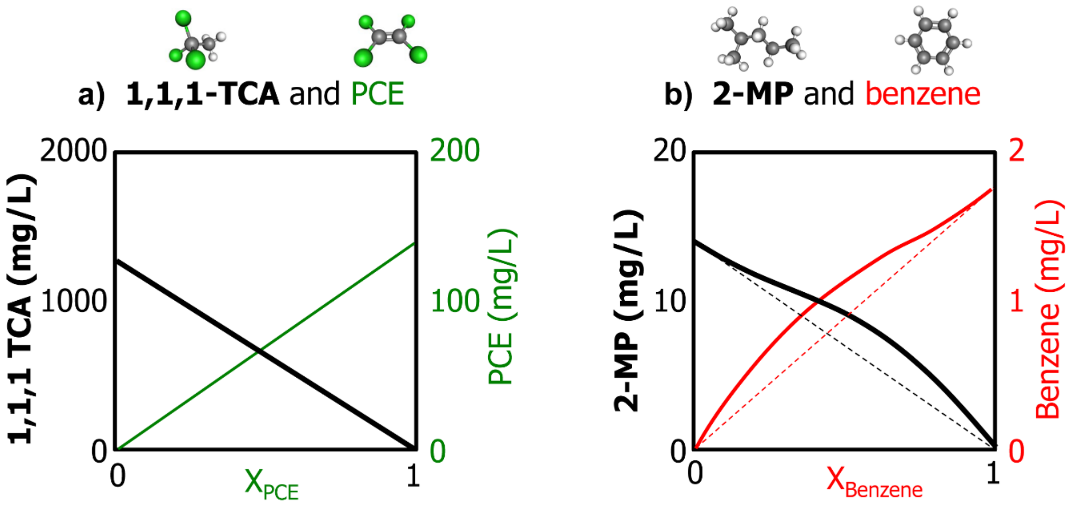


Figure 44 - Effective solubility examples. a) Nearly ideal behavior (redrawn, modified, and annotated from Broholm & Feenstra, 1995), and b) departing slightly from ideality with the dashed lines showing expected behavior of an ideal mixture (redrawn, modified, and annotated from Leinonen & Mackay, 1973).

The dashed lines in the frames represent the expectations for an ideal mixture at equilibrium—that is, the predictions of the Effective Solubility Model with $\gamma_I = 1$. Figure 44a depicts a nearly ideal mixture, with measurements closely conforming to expectations. Broholm and Feenstra (1995) found similar ideality for binary mixtures of chloroform, tetrachloromethane, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. On the other hand, Figure 44b depicts a distinctly nonideal case, with measured values exceeding the calculated effective solubilities over much of the range of conditions. However, the differences between measured values and values predicted assuming ideality are small when compared to the uncertainties in the other parameters we must either measure or estimate to calculate environmental fate of contaminants. The departures from ideality in mixtures of nonpolar/HOC organic liquids are generally assumed to be insignificant and thus are ignored (Exercise 26⤵).

If the NAPL mixture contains a chemical that would also partition into and function as a co-solvent in the aqueous solution, then the situation is more complex than represented in these simple illustrations. One example of this is ethanol in gasoline fuel blends that can partition into water and enhance the aqueous solubility of hydrocarbon components present in the gasoline mixture (Heerman & Powers, 1998).

7.10 Aqueous Solubility for Mixtures of Organic Liquids and Organic Solids

When we encounter organic liquid mixtures containing chemicals that would be solid if present in their pure form, calculation of the effective solubility of the solid chemicals requires an additional step be taken before application of the Effective Solubility Model. As we discussed in Section 6.10, such chemicals are in a liquid state when dissolved in a liquid mixture. Thus, the reference solubility for solid chemicals in this state is the sub-cooled liquid solubility rather than the aqueous solubility of the solid. The former can be estimated from the latter using Equation (4), which is analogous to Equation (2).

$$C_{w,liquid}^{sat} = C_{w,solid}^{sat}\, exp\left(A\left[\frac{T_m}{T} - 1\right]\right) \tag{4}$$

where:

T_m = melting point of solid chemical (Θ), degrees kelvin (K)

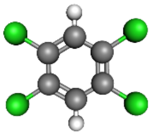
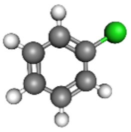
T = temperature of interest (Θ), degrees kelvin (K)

A = coefficient specific to the chemical (dimensionless)

Derivation and detailed discussion of this equation and the coefficient A follow that for Equation (2) (e.g., Miller et al., 1985; Schwarzenbach et al., 1993; Feenstra & Guiger, 1996). First-approximation calculations may be made with Equation (4) using a value of 6.8 for the coefficient A.

As an example, consider Table 4, addressing a mixture of 1,2,4,5-tetrachlorobenzene (1,2,4,5-TetCB; a solid at room temperature) and chlorobenzene (CB; a liquid at room temperature). When mixed in the proportions indicated in the table, the mixture is a liquid (the solid dissolves into the CB). Banerjee (1994) determined that the aqueous solubility of the pure 1,2,4,5-TetCB solid was approximately 2.17x10^{-6} mole/L. He also found that for a mixture with a very low mole fraction of TetCB (e.g., 0.023, as in Table 4), the measured concentration in water was about 28 times higher than the concentration predicted on the basis of the pure TetCB solubility—but only about 1.8 times the value estimated using the subcooled liquid solubility. Why? Using Equation (3), the subcooled liquid solubility is estimated to be about 16 times higher than the solid solubility at 20 °C.

Table 4 - Solubilities of a mixture of two organics, one which is liquid (chlorobenzene, CB) and one that is solid (1,2,4,5-tetrachlorobenzene, TetCB) at the temperature of interest (20 °C).

	1,2,4,5-TetCB	**CB**
		
Melting point (°C)	140	–45.6
Aqueous solubility (20 °C)	2.17x10^{-6} mol/L	470 mg/L
Subcooled liquid solubility (20 °C)	35.1x10^{-6} mol/L	Not applicable
Mole fraction in mixture	0.023	0.977
Measured concentration	1.4.1x10^{-6} mol/L	457 mg/L
Estimated concentration (using pure component solubility)	0.05x10^{-6} mol/L	459
Estimated concentration (using subcooled liquid solubility)	0.8x10^{-6} mol/L	Not applicable

At first this may seem confusing, since it seems to imply that if the mole fraction of the chemical were high enough in the organic liquid mixture, then its concentration in the water contacting the mixture could actually exceed the true solubility of the solid. This, however, cannot occur at equilibrium. If the mole fraction were indeed high enough to create water concentrations exceeding the solid solubility, then solid crystals of the chemical would form in the water. This would buffer the water concentrations at the solid solubility and drain chemical mass from the NAPL, thereby reducing the mole fraction of the chemical.

It is possible that the discrepancy between predicted and measured values of TetCB is due to nonideal behavior in the organic liquid mixture that was not accounted for, or because of uncertainty in the reported solubility of the pure solid, and/or because the value of the A coefficient is higher than assumed. Nevertheless, given the many other uncertainties involved in predictions of subsurface dissolution and transport of contaminants, this sort of discrepancy in aqueous concentration estimation would, in practice, generally be ignored.

8 Air–Water Partitioning

8.1 Why Do We Need to Know about Air–Water Partitioning?

Partitioning of organic chemicals is a process that affects many aspects of the fate of organic contaminants during migration within the subsurface or remediation. It is important to be familiar with what is known about this topic. For example, contaminants dissolved in a shallow groundwater plume could partition to air in the unsaturated zone above the plume, possibly leading to migration of the contaminant in the gas phase toward the surface. Contaminants that partition strongly to air from water can be removed from water by an above-ground remediation approach called air-stripping, in which water is made to contact a constantly replenished flow of air. Also, this partitioning is important when we collect water in an open bottle and seek to keep all the contaminants in the water for later analysis, as is discussed in more detail in Section 8.2. If the bottle is not completely full of water, the air-filled headspace left in the bottles can remove contaminant mass from the water—in some cases, a significant fraction.

8.2 What is Air–Water Partitioning?

Consider a system that has water in contact with air, and an organic compound distributed between the two phases. It has been found that, if time is allowed for the transfers of the compound between phases to reach equilibrium, the abundance of the compound in one phase is proportional to the abundance in the other phase. Figure 45 illustrates this equilibrium partitioning for two compounds with very different air–water partitioning behavior: methyl tert-butyl ether (MTBE), a former gasoline additive, one of the oxygenates; and vinyl chloride (VC), also called chloroethene or CE, a compound most often found in groundwater due to in situ biotransformation of trichloroethene or tetrachloroethene.

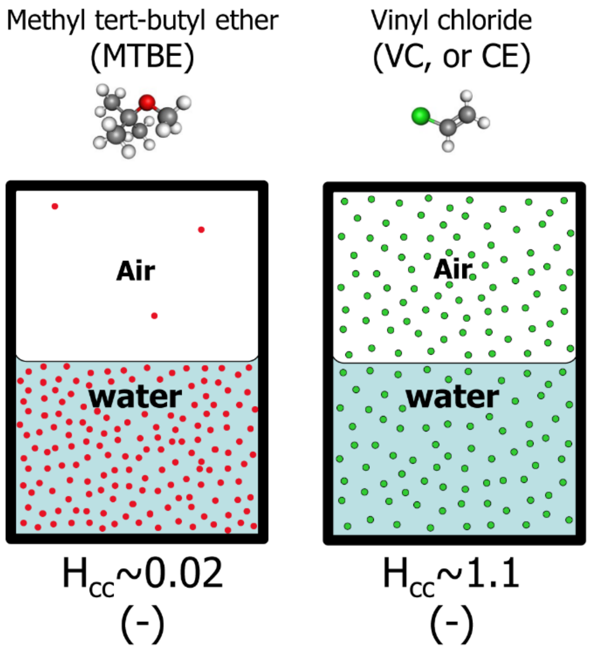


Figure 45 - Air–water partitioning examples. Illustrations of molecular distributions are approximately correct, assuming for the illustration that there are 160 molecules of each compound added to the containers with equal volumes of air and water.

Assuming ideal behavior in both phases, the ratio of concentrations of the compounds (in the same units—e.g., mol/L) in the two phases is equal to what is called a Henry's constant (often expressed as H, and often with subscripts; Exercise 27↴). Equation (5) is one expression of Henry's law.

$$H_{cc} = C_a/C_w \tag{5}$$

where:

H_{cc} = Henry's constant when concentrations in air and water are in same units (dimensionless)

C_a = concentration of the compound in air (ML^{-3}) often expressed in mg/L

C_w = concentration of the compound in water (ML^{-3})

Since the Henry's constant of MTBE and VC are quite different, so is the distribution of the two compounds, as shown in Figure 45. MTBE is quite polar and thus has high aqueous solubility (51,000 mg/L), affinity for water, and does not partition much to air. Vinyl chloride is far less polar and has a lower water solubility (2,700 mg/L), so distributes itself more evenly between the phases.

It is useful to realize that since this partitioning process has been of interest to many disciplines over a long period of time, there are a range of ways to define the law and the terms in it. Why? Because each discipline uses different methods of quantifying abundance including terms such as partial pressure, mole fraction, and concentration. Table 5 summarizes the primary alternatives for defining Henry's law in reference sources for the equation and the units of the corresponding Henry's constant (we use subscripts in Table 5 that you may not find in other sources but allow us to distinguish between the various definitions of Henry's constants when they are discussed in this book). This is important to know, because it is essential to carefully check the units of a Henry's constant you may select from a reference source. There are many sources on the web (https://pubchem.ncbi.nlm.nih.gov↗) and in textbooks.

Table 5 - Alternate expressions of Henry's law for organic chemicals, clarifying units by using examples for two quite different contaminants. *It is essential to know which version you are using or seeking*. In most literature, these subscripts are not used, so you have to figure out which set of units is assumed in whatever source you are reading. For this table, H_{pc} was taken from pubchem.ncbi.nlm.nih.gov/↗, and other versions of the constant were calculated from those.

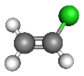
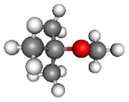
Alternate expressions of Henry's law	**Units of Henry's constant and subscripts used in this book, though likely not in other sources**	**Units for compound abundance in air**	**Units for compound abundance in water**	**Henry's constants for two example compounds (25 °C)**	
				Vinyl chloride (chloroethene)	Methyl t-butyl ether (MTBE)
					
$p = H_{px}\, x$	H_{px} (atm)	Partial pressure (atm)	Mole fraction (dimensionless)	1,539	32.5
$p = H_{pc}\, C_w$	H_{pc} (atm-m^3/mol)	Partial pressure (atm)	Concentration (mol/m^3)	0.028	0.00059
$C_a = H_{cc}\, C_w$	H_{cc} (dimensionless)	Concentration (mol/m^3)	Concentration (mol/m^3)	1.14	0.024
$y = H_{yx}\, x$	H_{yx} (dimensionless)	Mole fraction (dimensionless)	Mole fraction (dimensionless)	1,539	32.5

Table 5 shows why it is essential to carefully to check the units of a Henry's constant. For each tabulated contaminant, the numerical values of Henry's constant vary by more than a factor of 50,000! This is because the units of the constants are different. Additionally, the convention for expressing Henry's constant varies. For atmospheric gases, such as O_2, CO_2, and so on, the convention is to express Henry's constant as the aqueous concentration divided by the partial pressure. In other words, inverted compared to the equation shown in the second row of Table 5 for organic chemicals. So, one must be careful when seeking and selecting a Henry's constant. Also, it is essential to use the correct equation for Henry's law given the selected values of Henry's constants.

In much environmental literature, H_{pc} is a commonly encountered form of Henry's constant, defined as the ratio between pressure and dissolved concentration. One way to estimate Henry's constant is therefore to consider the case where the water and vapor are saturated with the chemical. Assuming that Henry's law applies over the entire range of concentration from 0 to the saturated solubility, H_{pc} would be the ratio of the vapor pressure to the aqueous solubility as shown in Equation (6).

$$H_{pc} = \mathrm{P}^{\mathrm{sat}}/C_w^{sat} \tag{6}$$

Henry's constants vary widely among organic contaminants. Furthermore, for each compound the Henry's constant varies significantly over the environmental temperature range, as shown in Figure 46 for C1 and C2 halogenated alkanes. This aspect of Henry's constant closely follows the temperature dependence of the vapor pressure for most compounds because aqueous solubility is relatively constant with temperature.

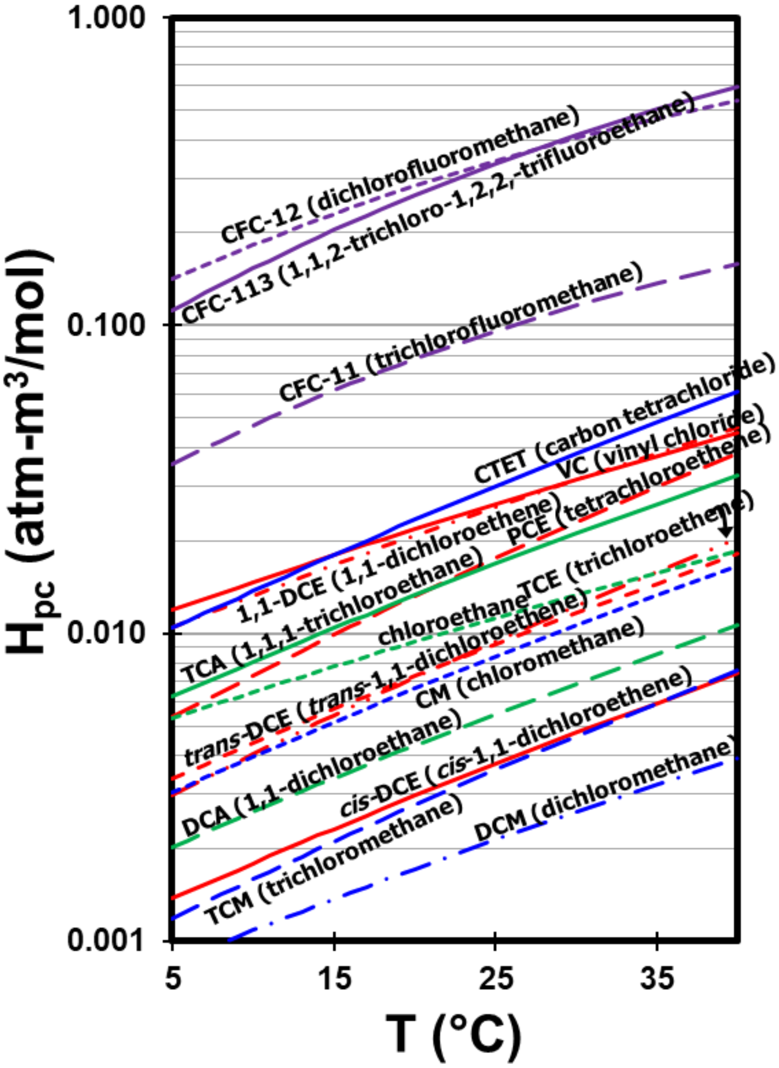


Figure 46 - Examples showing how Henry's constants vary with temperature for C1 and C2 halogenated alkanes. Color legend: CFCs are purple, chloromethanes are blue, chloroethanes are green, chloroethenes are red (coefficients for estimates are from Gossett, 1987; Warner & Weiss,1985; and Bu & Warner,1995).

Figure 46 shows Henry's constants for the C1 and C2 hydrocarbons increase by a factor of approximately 2 (1.5 to 1.8) per 10 °C temperature increase. Temperature dependence of Henry's constant can be estimated for a given chemical as shown in Box 5↴.

Let's consider one practical question that has affected protocols for collecting water samples for later analysis: Does a bubble in a water sample bottle have a large effect on the concentration of volatile chemicals in the water? Figure 47a illustrates the types of glass sample bottles often used to collect water samples for later analysis, which generally range in volume from 20 to 60 mL. The most common sample bottle size in environmental work is 40 mL.

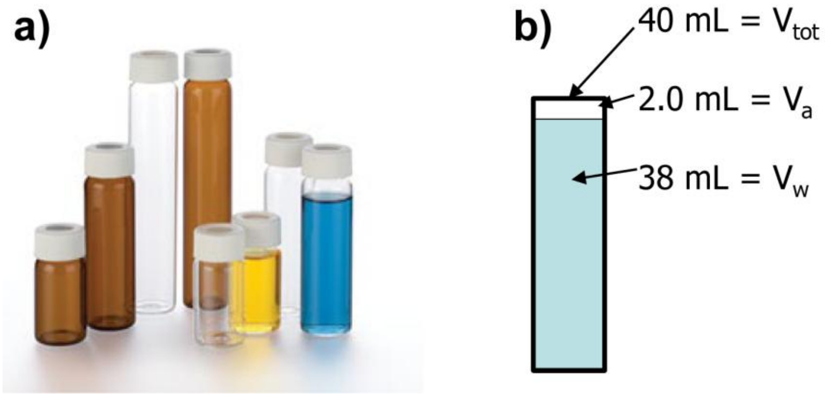


Figure 47 - a) Typical glass sample bottles and b) example for calculation in text, illustrating the interior of a 40-mL bottle, containing 38 mL of water.

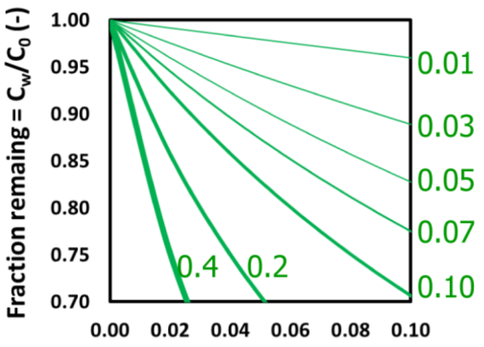
Let's see how important a bubble might be if left in a sample bottle after the bottle is filled, but not quite completely, before being capped. We follow the approach outlined by Pankow (1996) and use Henry's law to make this calculation (details are provided in Box 5). As illustrated in Figure 47b, we assume water containing vinyl chloride (VC, also known as chloroethene) at 1 mg/L is collected in a 40-mL sample bottle at 20 °C, but the sampling team left 2.0 mL headspace (filled with air) when they sealed the bottle. That is a pretty big bubble, even though it is only 5 percent of the sample bottle volume. This error should have easily been noticed and corrected by the sampling team, but let's assume for now that the bubble was as big as illustrated in Figure 47b.

After the sample bottle is sealed and VC partitioning from water to air comes to equilibrium, there will be a lower concentration of VC in the water. However, as calculations presented in Box 5 show, even this fairly big bubble changes the VC water concentration by less than 5 percent at 20 °C.

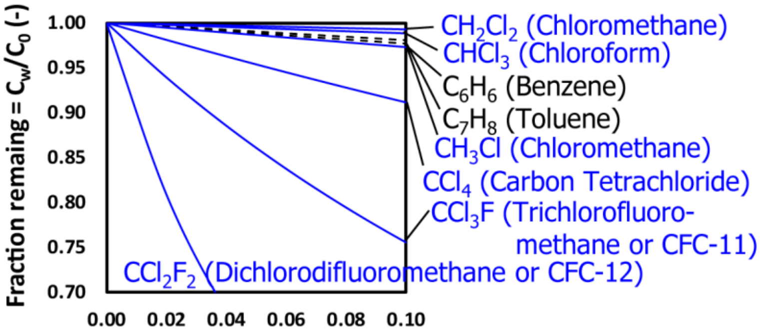
The impact of bubbles on partitioning between the phases can be more or less significant than just discussed, since other compounds have different Henry's constants, as we explore subsequently. In addition, we should note that air bubbles in samples can have other effects. Therefore, although partitioning to the headspace for a particular compound may not have much direct effect on the observed concentration, there are other important reasons to completely fill sample vials to help preserve sample integrity. One example is to avoid aerobic biodegradation (Ferris et al. 2021; Rittman & McCarty, 2001) during sample storage.

Figure 48 presents several graphs to illustrate the fraction of the volatile chemical left in the water (C_w/C_0) as a function of the ratio of bubble volume to water volume. The y-axis in all frames extends from 0.7 to 1.0 while the x-axis extends from 0 to 0.1 (assuming a bubble of 10 percent of the bottle volume would be the largest likely to occur).

a) As function of H_{pc} (atm-m^3/mol)



b) For halomethanes and aromatics



c) For chloroethenes

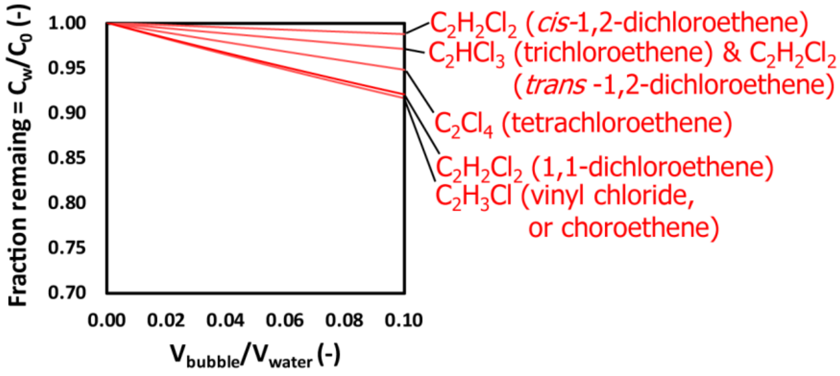


Figure 48 - Fraction of VOC remaining in water caused by leaving a bubble of air in the sample bottle: a) shows the effect on the fraction of a VOC remaining in the water as a function of its Henry's constant; b) illustrates examples for a few specific halomethanes and aromatics, including all the chloromethanes, two chlorofluoromethanes (CFCs), and two aromatic hydrocarbons; and c) illustrates the effect for specific chloroethenes.

These sorts of figures are helpful to identify the chemicals whose water concentrations would be most impacted by incompletely filled sample bottles. The CFCs are most affected and thus are properly collected from groundwater using special methods designed to preserve them in the samples. Vinyl chloride, 1,1-dichloroethene, and carbon tetrachloride are also quite sensitive to this problem.

9 Octanol-Water Partitioning

9.1 Why is Octanol–Water Partitioning Important?

The equilibrium partitioning of an organic chemical between octanol and water is described by the octanol-water partition coefficient (K_{ow}). You may find it interesting that K_{ow} has its roots in aquatic toxicology since octanol was selected as a surrogate for the lipid content in organisms. As a result, there is an extensive database of measured K_{ow} values for many chemicals of environmental concern. Since these values are readily available, other forms of partitioning (such as partitioning of organic compounds from water to the organic content of soil) have been correlated to K_{ow} (Exercise 28↴).

In some cases, it may be far easier to measure or estimate K_{ow} than some other desired parameters. Thus, if the type of parameter we want is reasonably well predicted by K_{ow}, we at least have a good first estimate of the parameter we want for a specific chemical. In Section 12.8 and Box 6 of this book, we discuss parameters that can be estimated from K_{ow}—for example, parameters describing sorption of organic molecules by geologic media.

9.2 What Is Octanol–Water Partitioning?

A laboratory-determined parameter that is often used as a predictor of environmental behavior is the octanol–water partition coefficient, commonly abbreviated as K_{ow}, although some references use other symbols. As illustrated in Figure 49, this parameter describes the partitioning of an organic compound between two specific liquid phases: water and octanol. Experimentally, since the liquids are mixed and then allowed to separate, equilibrium is reached rapidly, and the partition is referred to as linear and reversible. *Rapidly* means equilibrium is reached in the partitioning process in short time frames (for example, minutes). *Linear* means the amount of compound partitioned to the octanol is proportional to the concentration of the compound in solution, and *reversible* means that the compound will partition back into solution to a new equilibrium concentration if the solution concentration decreases for some reason.

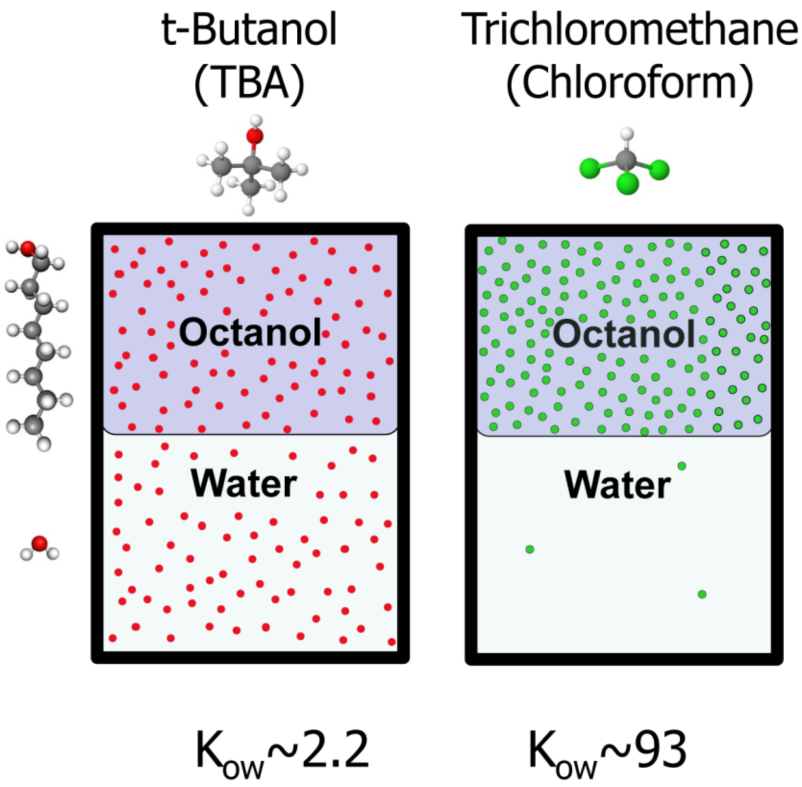


Figure 49 - Partitioning of two organic compounds between water and octanol. Illustration of molecule distributions of TBA and chloroform (molecular structures at top) are approximately correct, assuming for the illustration that the same number of molecules of each compound are added to containers with equal volumes of octanol and water (whose structures are shown to the right). The K_{ow} of each compound is shown at the bottom of the figure.

Figure 49 illustrates partitioning between octanol and water for two quite different compounds: TBA with K_{ow} of about 2.2 and chloroform with K_{ow} about 93. These were selected since it is possible to illustrate their partitioning with some accuracy, as they have the proper ratio of imagined molecules (red dots) in each phase. In the literature, you will often find the base-10 logarithm of K_{ow} (log K_{ow}) listed instead of K_{ow}. For TBA and chloroform, the log K_{ow} is about 0.35 and 1.97, respectively (K_{ow} about 2.2 and 93, respectively). The reason we say "about" is that there is some variation of reported log K_{ow} values in the literature.

Figure 50 illustrates the wide variation of K_{ow} among selected organic compounds. In fact, an even wider range of 10^{-3} to 10^{7} has been estimated when including other compounds than depicted in Figure 50. For example, some compounds of environmental interest, including TBA and other weakly hydrophobic compounds, are off the chart to the right and down.

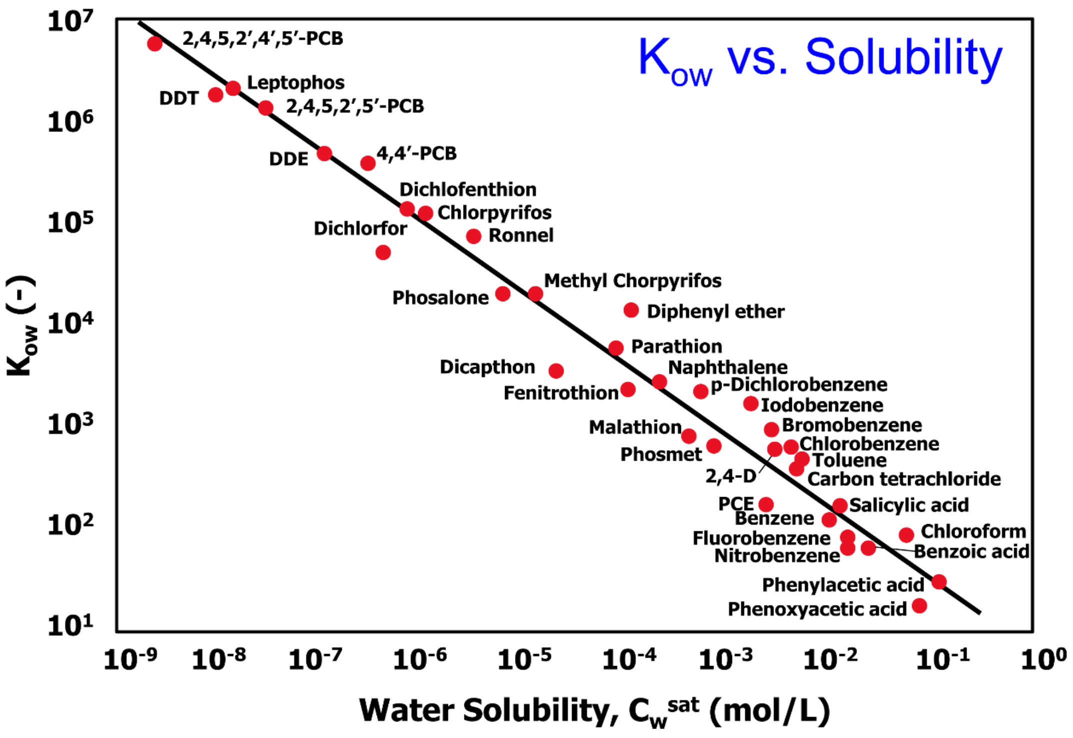


Figure 50 - Graph of octanol–water partition coefficient versus water solubility for a wide range of organic compounds (redrawn, modified, and annotated from the figure in Mackay,1980).

K_{ow} has also been used to define some terms we hear and use a lot:

- *Hydrophilic co*mpounds have K_{ow} less than 10.
- *Hydrophobic* compounds have K_{ow} greater than 10,000 (10^4).

Figure 50 also illustrates how solubility might be predicted from K_{ow} if one knew K_{ow} but not solubility. When might this be the case? One example is for very slightly soluble compounds for which it may be much easier to measure K_{ow} than solubility.

10 Partitioning between Water and Surfactants or Surfactant-Related Phases

10.1 Why Do We Care about Surfactants?

Surfactants have useful properties in manufacturing, cleaning, fire-fighting, and subsurface remediation (for example, surfactant flooding to dissolve and reduce NAPL contamination). Surfactants are groundwater contaminants in their own right, and they can strongly affect the transport and fate of other contaminants. Furthermore, some surfactants have been used to facilitate groundwater remediation. Familiar surfactants are the detergents we use to remove grease from dishes or clothes. Surfactants are also present in some pesticides and in various wastes that may impact groundwater (e.g., municipal wastewater, septic tank effluent, and industrial wastewater). Even if the concentrations are low, some surfactants have proven to be quite resistant to biodegradation. For example, PFOS (*perfluorooctane sulfonic acids*) and PFOA (*perfluorooctanoic acids*) are members of a group called PFASs (*polyfluorinated alkyl substances*) which are often referred to as “forever chemicals,” as discussed by ChemTrust (2019). Since the PFASs are both mobile and a health concern, their entry into groundwater has led to long plumes (contaminated portions of groundwater) that have become new challenges for remediation. Familiarity with surfactants is necessary to understand a lot of research and practical literature.

10.2 What Is a Surfactant?

Surfactant is the common term for a surface-active agent, examples of which are illustrated in Figure 51. As can be seen in the figure, surfactants have polar and nonpolar portions and are thus amphiphilic (Exercise 29⤵), with both water-loving hydrophilic portions and fat-loving lipophilic (also called hydrophobic) portions (Exercise 30⤵). The first four surfactants in Figure 51 are anionic, having a negative charge in solution. CTAB (cetrimonium bromide) is a cationic surfactant, with a positive polar end, and the two Tritons are nonionic, with polarity created by the oxygens. The structures shown in Figure 51 are only one depiction of molecules that are flexible, so they are not necessarily linear in the environment.

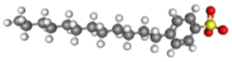
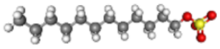
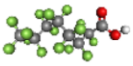
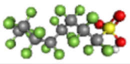
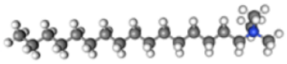
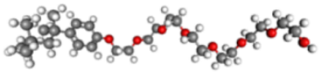
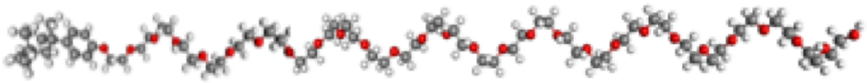
Name **Formula** **Structure**	**MW (g/mol)**	**CMC (mg/L)**
Water H_20 	18	NA
LAS (linear alkyl benzene sulfonate) example: sodium dodecyl benzene sulfonate $C_{18}H_{29}NaO_3S$ (sodium ion not shown in structure below) 	348	510–560
SDS (sodium docdecyl sulfate) $NaC_{12}H_{25}SO_4$ (sodium ion not shown in structure below) 	288	2,100
PFOA (perfluoro-octanoic acid) $C_8HF_{15}O_2$ 	414	1,600–16,000
PFOS (perfluoro-octane sulfonic acid) $C_8HF_{17}O_3S$ 	500	540–4,800
CTAB (cetrimonium bromide) $C_{16}H_{33}N(CH_3)3^+$ (bromide ion not shown in structure below) 	364	361
Triton X114 $C_8H_{17}C_6H_4\,(OCH_2CH_2)_nOH$ (avg n=7.5, depicted n=8) 	536	110
Triton X405 $C_8H_{17}C_6H_4\,(OCH_2CH_2)_nOH$ (avg n=40, depicted n=28) 	1,966	620

Figure 51 - Examples of surfactants. Water is presented in the first row for comparison to seven of many surfactants relevant to studies of groundwater contamination and remediation. The polar ends of the surfactants are to the right. The first four surfactants are anionic, CTAB is cationic, and the Tritons™ (Dow Chemical Company) are nonionic. Tritons vary in chain length, so the number of units (*n*) in a particular molecule varies. In the table, the Triton formulas are general and the average and depicted *n* values are noted. MW is the molecular weight, while CMC stands for critical micelle concentration, as discussed in the text; micelles are depicted conceptually in Figure 52 (values of MW and CMC at 25 °C are taken from Kile & Chiou (1989) for Tritons, SDS, and CTAB; from Interstate Technology Regulatory Council (ITRC) (2023) for PFOA and PFOS; and Zhu (1986) for LAS).

The surfactant molecule is often schematically represented as illustrated in Figure 52, namely a round head (the polar portion) with a hydrophobic tail. While the tail is often drawn as a line, in fact it can take various shapes due to its flexibility; similarly, some surfactants have long flexible polar ends, such as the Tritons. Nevertheless, the simple head-and-tail schematic is commonly used in figures such as Figure 52.

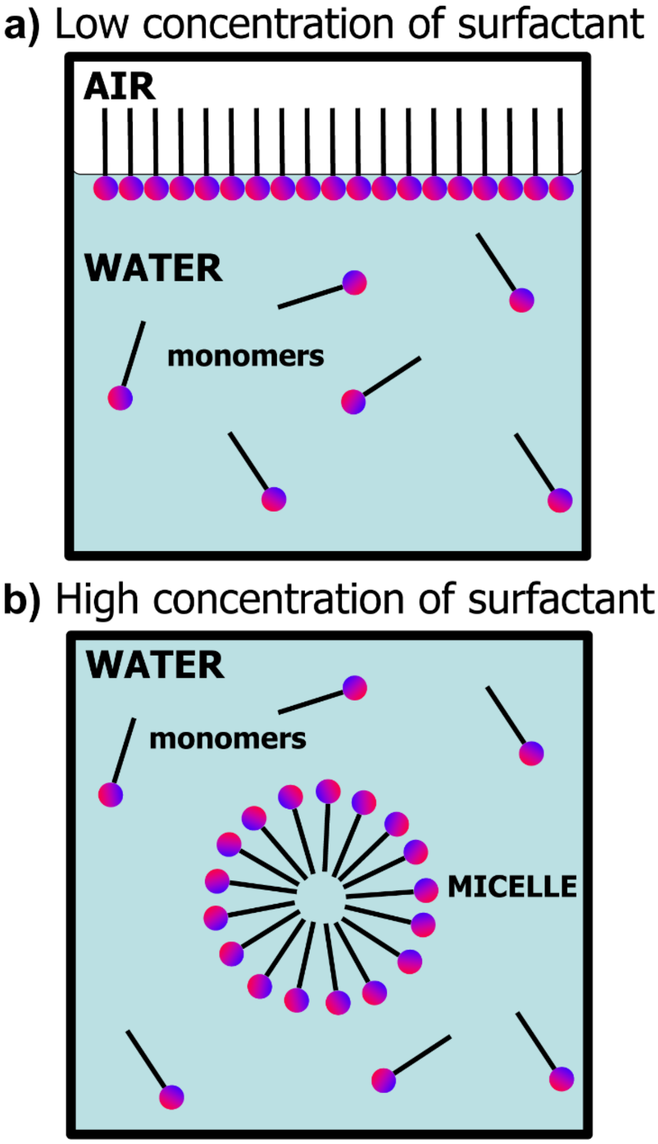


Figure 52 - Illustrations of surfactant molecules (each as a polar ball with black hydrophobic tail) showing when a) at low concentrations, surfactants are present as monomers in solution or at air–water interfaces (or other interfaces not depicted) and b) at higher concentrations (≥ CMC, critical micelle concentration) surfactants are present as self-assembling micelles as well as monomers.

Each surfactant molecule is called a monomer. Figure 52a shows that the hydrophobic portions of the monomers can extend above the air–water surface, which profoundly affects the surface, stabilizes foams, and so on. At low total surfactant concentrations, the monomers are dispersed throughout the water phase as illustrated in Figure 52a. When the total surfactant concentration exceeds what is called the *critical micelle concentration* (CMC), some of the monomers assemble into what are termed *micelles*, as illustrated in Figure 52b. The micelles assemble with the hydrophobic portions in the interior and the hydrophilic portions on the exterior where favorable interactions can occur with adjacent water molecules (Exercise 31⤵). Note that the CMC is specific to each surfactant; in some cases, the CMC spans a concentration range for commercial surfactant mixes that contain a range of surfactant molecular weights (due to different lengths of the hydrophobic portions). This is discussed more in this section.

The size of micelles varies with the type of surfactant and composition of the water. Generally, micelles are thought to be spherical and composed of 20 to 200 monomers. Under some circumstances, micelles in solution may be other shapes (Pennell & Abrioloa, 1998). If water containing surfactants contacts solid surfaces, other assemblages of monomers may form, such as hemi-micelles (forming a portion of a micelle on the surface of the solid), as discussed by others (Schwarzenbach et al., 2017).

Other organic compounds—for example, HOCs and HIOCs—can partition from the water to the surfactant monomers and the micelles. Figure 53 illustrates this partitioning for an HOC. HIOCs can also partition into micelles, but since they have both polar and nonpolar portions, it is believed they prefer to settle closer to the outside of the micelle (in the HOC-unfilled portion of the micelle in the figure), whereas HOCs prefer the more hydrophobic interior.

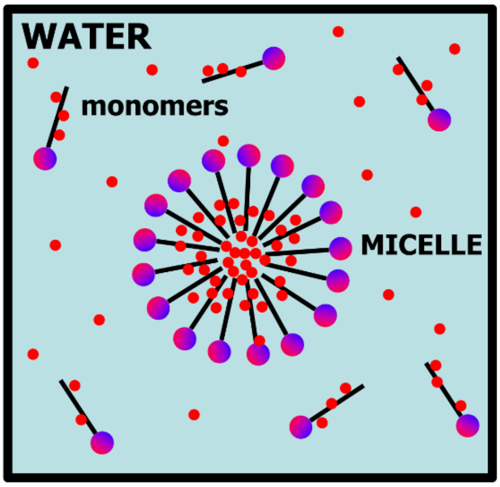


Figure 53 - Illustration of partitioning of hydrophobic organic compound (red dots) to tails of surfactant monomers or interiors of surfactant micelles.

10.3 How Do Surfactants Affect the Solubilization of HOCs?

Figure 54 illustrates solubilization by SDS (Sodium Dodecyl Sulfate) surfactant of the HOCs DDT and 1,2,3 trichlorobenzene (TCB) when the systems reach equilibrium. Both frames are redrawn, modified, and annotated from Kile and Chiou (1989), who conducted lab experiments with water, various surfactants, and various HOCs. They added surfactants and observed the creation of micelles by noting a change in the surface tension of the solution and conducted experiments with various HOCs and increasing concentrations of surfactants.

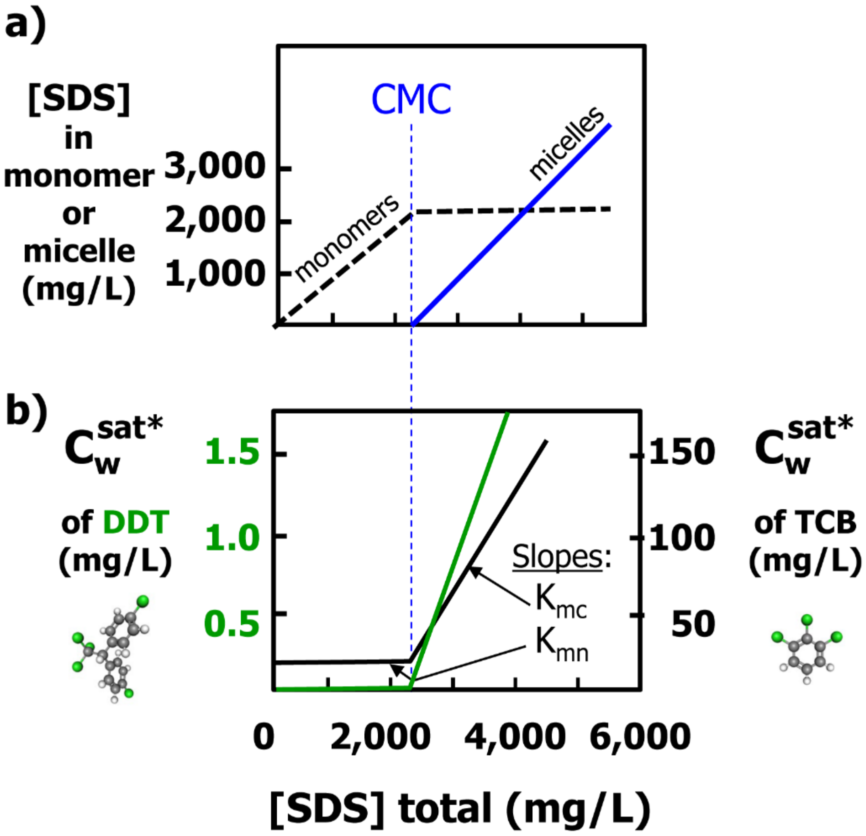


Figure 54 - Illustrations for SDS surfactant (CMC approximately 2,100 mg/L) of a) amounts of monomers and micelles as total SDS concentration rises and b) apparent solubility of DDT and 1,2,3-trichlorobenzene (TCB) as total SDS concentration rises (separate experiments). The slopes are discussed in the accompanying text (redrawn, modified, and annotated from Kile & Chiou, 1989).

Figure 54a shows the concentration of surfactant (abbreviated [SDS], where the brackets indicate concentration) present as monomers or micelles versus the total surfactant concentration. Below the CMC, all of the surfactant is present as monomers. As the total [SDS] rises above the CMC, all of the additional surfactant assembles into micelles, so the concentration of monomers is constant while the concentration of micelles increases.

Figure 54b shows that the apparent solubilities of DDT and TCB stay relatively constant at [SDS] less than the CMC (actually, DDT solubility rises, but it is not discernible on the graph). Above the CMC, the apparent solubilities of DDT and TCB rise sharply and linearly as [SDS] increases. When [SDS] is 1.5 times the CMC, the apparent solubilities of DDT and TCB are over 200 and 4 times their solubilities in the absence of surfactants, respectively (5.5 µg/L and 18 mg/L). This is a huge effect.

The apparent solubility of an HOC impacted by surfactants that behave like SDS is a direct function of the concentrations of monomers and micelles and the degree of partitioning of the HOC to each. The strengths of partitioning to monomers and micelles are the slopes of the lines in Figure 54b. The slopes are called the water–monomer partition coefficient K_{mn} and the water–micelle partition coefficient K_{mc} (Exercise 32↴).

Table 6 compares the two surfactant partition coefficients (to monomers and micelles) to the octanol–water partition coefficient for TCB and DDT. The partition coefficients are presented in log form for brevity.

Table 6 - Partition coefficients for DDT and TCB to octanol and to SDS monomers or micelles (data from Kile & Chiou, 1989).

Compound	**Log K_{ow}**	**Log K_{mn}**	**Log K_{mc}**
TCB	4.1	≈ 0	3.5
DDT	6.4	2.7	5.4

The main points of Table 6 are:

- HOCs partition to SDS micelles almost as strongly as to octanol.
- HOCs partition to SDS monomers much less strongly than to micelles.

For additional perspective, HOCs partition to SDS micelles much more strongly than to natural dissolved organic matter (discussed in Section 11).

So far, we have examined apparent solubility data for only one surfactant (SDS) and two HOCs. However, the K_{mn} and K_{mc} have been shown to depend both on the surfactant and the organic compound whose solubility is in question. There are many references in the scientific literature that explore impacts of SDS and other surfactants on a variety of HOCs (Kile & Chiou, 1989; Pennell & Abriola, 1998). One illustrative example is presented in Figure 55, which shows DDT's apparent solubility for various concentrations of several surfactants.

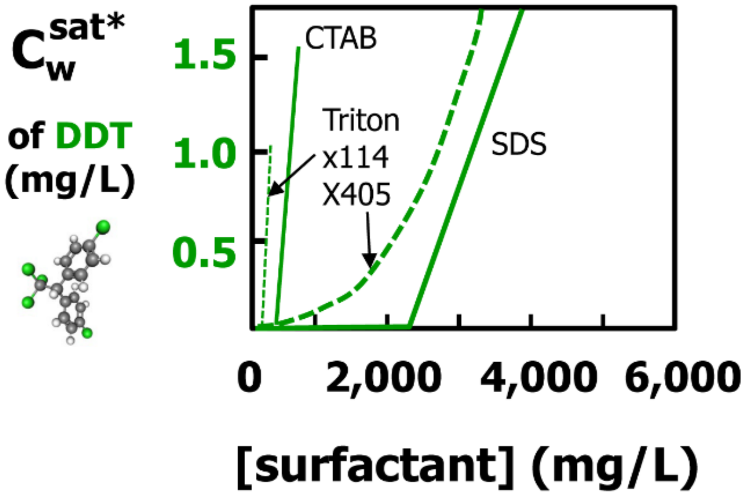


Figure 55 - Apparent solubility of DDT versus total concentration of surfactant for four example surfactants: CTAB, Triton x114, TritonX405, and SDS (redrawn, modified, and annotated from Kile & Chiou, 1989).

Figure 55 shows that CMCs vary widely and the CMC for Triton X405 is not well defined. The reason is that the Triton X405 is a commercial product that is a mixture of surfactant monomers of different chain lengths, each of which would have its own CMC if present as the sole surfactant. Therefore, the impact of the Triton X405 mixture is a combination of the impacts of the individual monomers and the micelles made of them, leading to the curvature shown, which is in contrast to the sharp slope break noted for the other surfactants. Although less clear in the figure, the K_{mc} values also vary among the surfactants.

10.4 More Complex Situations Involving Surfactants

There are often oily (nonaqueous-phase) liquids along with surfactants in wastewaters or other matter (e.g., pesticide formulations) discharged to the subsurface, or surfactants may be discharged into aquifers where other contaminants already reside. Other examples of sites with combinations of oily liquids and surfactants are firefighter training areas or aircraft fires in which jet fuels have been released, either purposefully or after accidents, and then fires extinguished by flooding the area with foams containing PFOS, PFOA, and/or other fluorinated surfactants.

In such cases, surfactants can impact the mixture of oils and water, potentially leading to a variety of colloidal species suspended in either the water or the oily phase, as illustrated in Figure 56. Other compounds—such as contaminants (HOCs, hydrocarbons, pesticides) and chemicals added to enhance remediation—can partition into any or all of those phases, creating a situation far more complex than suggested in Figure 52 through Figure 55. In some cases, emulsions are created and injected on purpose; for example, emulsified vegetable oil has been used to enhance microbial growth in subsurface contaminated zones and thus enhance in situ biodegradation of contaminants (Borden, 2007; Watson et al., 2013; Borden et al., 2013). In other situations, emulsions can contain and distribute contaminants; for example, Tang (1995) discussed a spill to the shallow subsurface of a water-in-oil emulsion created by an enhanced oil recovery technique, in which there was concern about the fate of contaminants such as phenol present in the emulsion.

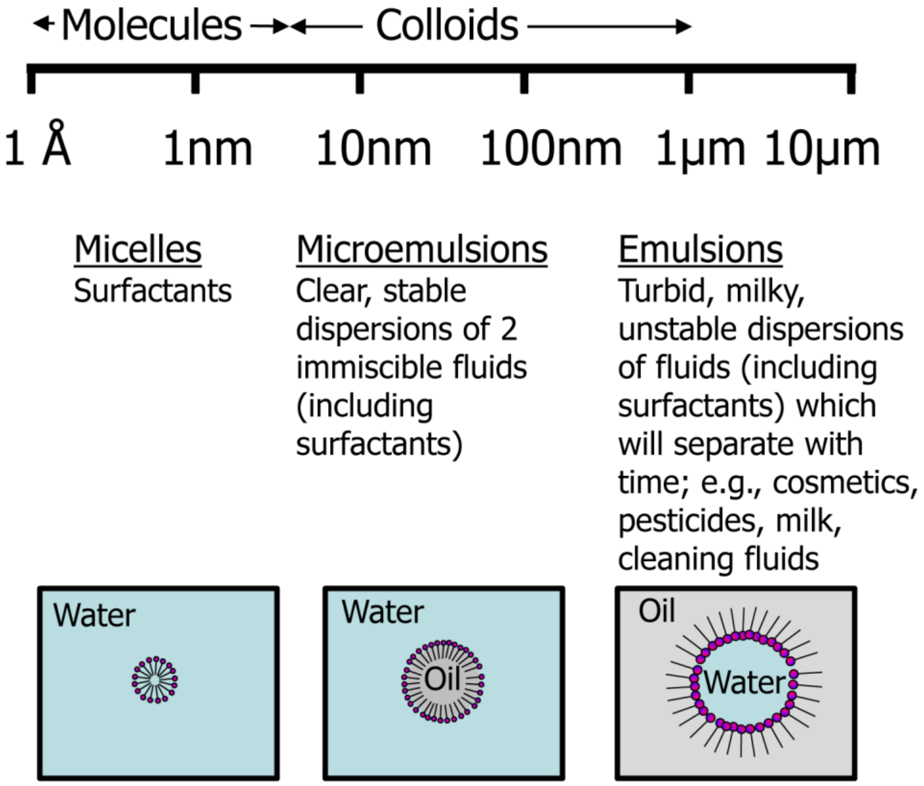


Figure 56 - Illustration of the range of sizes of surfactant related species that can be present in a solution including micelles, microemulsions, and macroemulsions. Although not depicted, even more complex solutions can exist in macroemulsions such as surfactant stabilized water droplets inside larger oil droplets themselves suspended in water by surfactants, or surfactant stabilized oil droplets present inside larger water droplets themselves suspended in oil by surfactants.

11 Partitioning between Dissolved Natural Organic Matter (DOM) and Water

11.1 Why Do We Care about Partitioning of Organic Contaminants from Water to DOM?

In some cases, partitioning of organic contaminants to dissolved organic matter (DOM) can increase the rate of transport of the contaminant by groundwater through a porous medium or alter their rate of abiotic or microbiologically mediated transformations. The extent of the partitioning must be known to identify the cases where such issues might warrant closer attention.

11.2 What Is DOM?

Large molecular weight natural organic matter in groundwater and surface water is often referred to as dissolved organic matter (or DOM), as discussed by Chapelle (2022). The DOM of natural waters generally ranges from 1 to 10 mg/L. The primary natural components of DOM—fulvic and humic acids—arise from decomposition of plant materials such as leaves and roots, or release from older carbonaceous materials associated with sediments (Chapelle, 2022). By convention, humic acids are components of DOM that can be rendered insoluble (precipitated from solution) by lowering the pH to 1, whereas fulvic acids remain in solution at pH 1 (Exercise 33↴).

Figure 57 illustrates generalized structures of fulvic and humic acids. In nature, there is a range of molecular weights and structures of fulvic and humic acids, depending on the environmental setting (Chapelle, 2022). Here, we only note that humic acids in natural waters can have molecular weights above 2,000 g/mol, with some greater than 70,000 g/mol. The latter are better described as colloids than molecules. Fulvic acids in natural waters likely range in molecular weight up to 2,000 g/mol. Figure 57 shows only two of the many and generally more complex structures that have been hypothesized for fulvic and humic acids found in nature. These examples provide a sense of how large and complex these molecules can be.

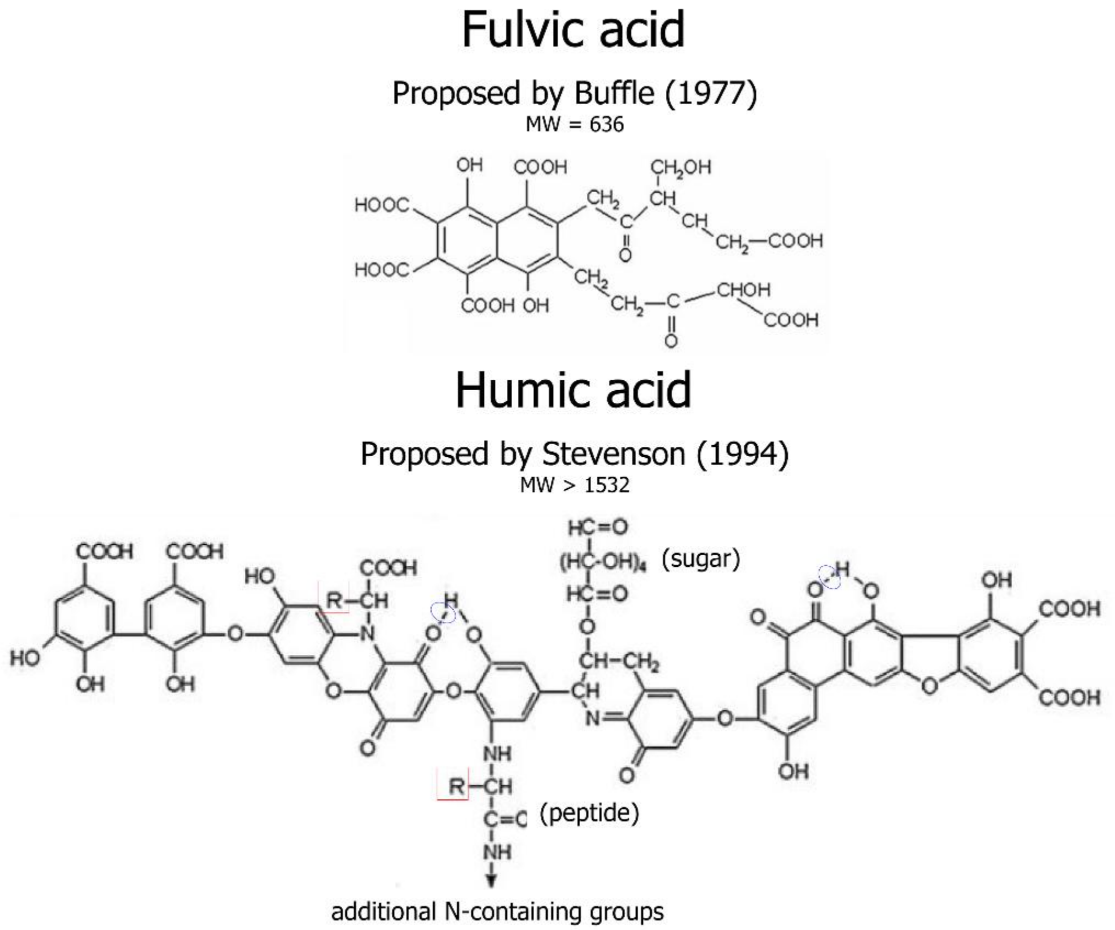


Figure 57 - Proposed structures of fulvic and humic acids. Fulvic and humic acids in nature include many different compounds and structures. These diagrams are suggested as reasonably representative examples. Hydrogen bonds in the humic acid structure are surrounded by blue ovals. R in the humic acid formula refers to any group containing carbon and hydrogen, so the molecular weight of the illustrated example is 1532 plus whatever the formula of a specific R group would imply.

In groundwater, humic and fulvic acids are present in folded or coiled forms dependent on the pH and type and concentrations of inorganic solutes present (Exercise 34↴). Figure 58 presents this concept as a simple graphic.

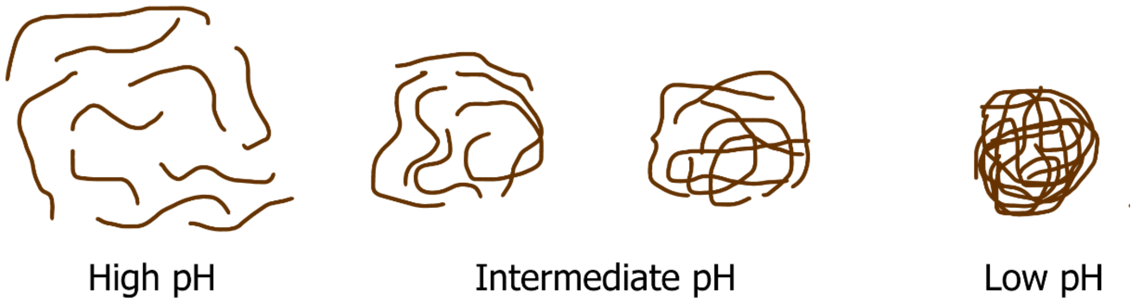


Figure 58 - Changes in conformation and aggregation of low concentrations of humic acids (brown lines) from linear to coiled as solution goes from alkaline (high pH) to acidic (low pH). At high concentrations, both humic and fulvic acids are expected to be coiled at typical intermediate pH values in groundwater (Stevenson, 1982) (redrawn, modified, and annotated from Gomes de Melo et al., 2016).

11.3 How Strong Is Partitioning of Contaminants from Water to DOM?

Contaminant molecules can be attracted to the fulvic and humic acids, which have both polar and nonpolar portions. Therefore, the presence of DOM in water could lead to higher apparent solubility of some HOC compounds because some of the HOC could partition to the hydrophobic portions of DOM, including the interiors of coiled DOM, as shown schematically in Figure 59.

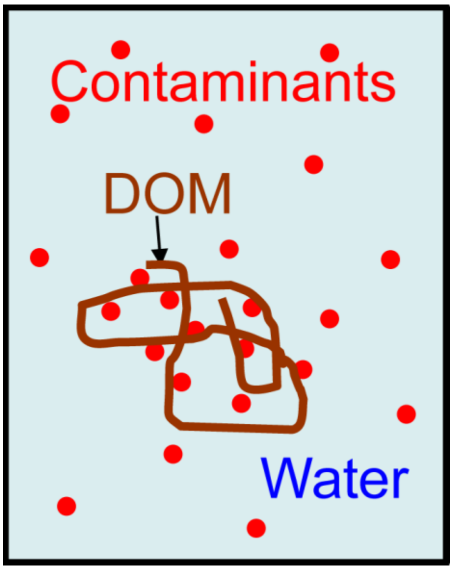


Figure 59 - Illustration of the partitioning known to occur between organic contaminants and fulvic and humic acids (DOM).

Researchers have found that HOCs partition to natural DOM, and that it is a rapid, linear, and reversible process (Chiou et al., 1986). It has also been noted that the partitioning of HOCs to DOM is closely related to the carbon content of the DOM (which presumably is closely related to the hydrophobic surface area of the large molecules). The fraction of the DOM mass that is carbon is referred to as the f_{oc} (fraction of organic carbon). This term is also used to express the carbon content of other materials, including geosorbents, as discussed later in Section 12.8 of this book and elsewhere (e.g., Schwarzenbach et al., 1993; Pankow & Cherry, 1996).

Research by the US Geological Survey and others (e.g., Kile & Chiou, 1986; Chiou et al., 1987) determined for natural DOM that the partition coefficient of HOCs from water to humic acids ($K_{HA,oc}$) is greater than the coefficient to fulvic acids ($K_{FA,oc}$). Note that both partition coefficients are expressed as a function of the f_{oc} of the humic and fulvic acids. The implication is that the impact of DOM on the apparent solubility of an HOC in a particular natural water would depend on both the amount and the composition of the DOM—that is, the amount and composition of the humic and fulvic acids that also vary among natural waters.

It is possible to estimate the increase of apparent solubility of an HOC due to partitioning to a particular DOM using Equation (7).

$$C_{w,i}^{*sat} = C_{w,i}^{sat}\left(1 + f_{oc,DOM}K_{oc,DOM}C_{w,DOM}\right) \tag{7}$$

where:

$C_{w,i}^{sat}$ = solubility in pure water of the HOC at system temperature (ML^{-3}) often expressed in mg_i/L_w (mg of compound i per liter of water)

$f_{oc,DOM}$ = fraction organic carbon of the DOM (dimensionless), $g_{oc,DOM}/g_{DOM}$

$K_{oc,DOM,i}$ = partition coefficient for compound i to carbon fraction of DOM (L^3M^{-1}) often expressed in $L_w/g_{oc,DOM}$

$C_{w,DOM}$ = concentration of DOM in the water (ML^{-3}) often expressed in g_{DOM}/L_w (g of DOM per liter of water)

The enhanced solubility (denoted by the asterisk) of a particular HOC (denoted by subscript i) is equal to the normal water solubility of the HOC at the system temperature multiplied by 1 plus the product of the fraction of organic carbon (f_{oc}) of the particular DOM, the carbon-normalized partition coefficient (K_{ocDOM}) of the particular DOM, and the concentration of DOM in the water ($C_{w,DOM}$). DOM concentration and the carbon-normalized partition coefficient vary among natural waters, but it is reasonable to assume the fraction of organic carbon is about 0.5 for all DOM.

Figure 60 shows the enhancement of solubility of two hydrophobic compounds in the presence of humic acid studied by Chiou and others (1986). The humic acid was extracted from the Suwannee River in Georgia, USA.

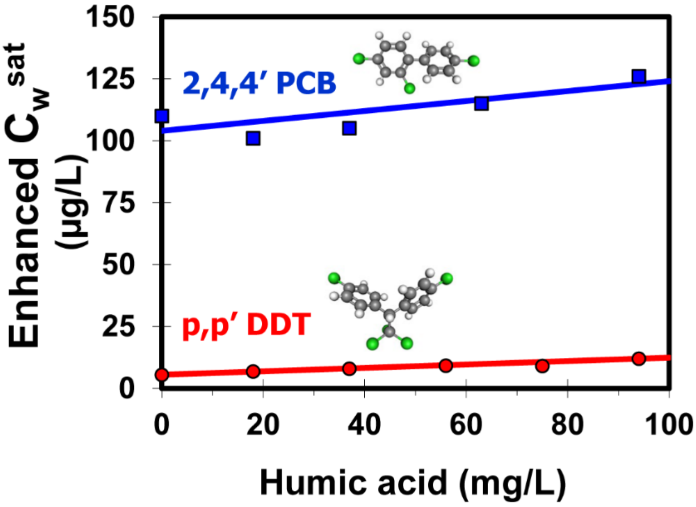


Figure 60 - Enhancement of water solubility of two very hydrophobic organic compounds by DOM, in this case the humic acid was extracted from river water (redrawn, modified, and annotated from Chiou et al., 1986). Note that solubilities are in micrograms per liter.

Table 7 lists the partition coefficient for DDT to the natural DOM (the slope of the red line in Figure 60), along with DDT's octanol–water partition coefficient and partition coefficients to monomers and micelles of SDS (Sodium dodecyl sulfate) surfactant, discussed earlier.

Table 7 - Partition coefficients for DDT to DOM and SDS surfactant monomers and micelles.

Compound	**Log $K_{oc,DOM}$**	**Log K_{ow}**	**Log K_{mn}**	**Log K_{mc}**
DDT	4.4	6.4	2.7	5.4

11.4 Conclusion about Partitioning of Contaminants from Water to DOM

In terms of its enhancement of solubility of DDT, the DOM that Chiou and others (1986) studied is in between monomers and micelles of SDS (Table 7). However, because the DOM concentrations in most fresh natural groundwater are low, the solubility enhancement of contaminants by natural DOM is likely to be quite low in most cases. This means that the facilitation of groundwater transport of organic contaminants may often be relatively insignificant except when the concentration of DOM or the K_{ow} of the contaminant is very high.

12 Sorption: Partitioning between Geosorbents and Water

12.1 Why Do We Care about Partitioning of Contaminants to Geosorbents?

Sorption affects the rate of movement of dissolved contaminants through porous media and sometimes affects the rate of reactions that contaminants undergo. Additionally, sorption complicates efforts to remediate contamination in the subsurface.

It is known that organic chemicals present in soil gas or groundwater may be attracted to geologic media or microparticles within the fluid phase. *Sorption* is the general term for the transfer of chemicals from the fluid phases (aqueous or vapor) to the solid phases, which are themselves sometimes referred to as *geosorbents*.

12.2 What Do We Mean by Geosorbents?

Organic contaminants have been found in all kinds of groundwater environments, so the term *geosorbent* encompasses a wide range of materials, including fractured rock, porous rock, and granular media composed of varying percentages of gravel, sand, silt, and clay. Although the concepts underlying geosorbent attraction to HOCs are the same for all of these, we focus here on granular media.

Even for granular deposits, however, geosorbents can be quite varied. For example, a porous or granular media can include grains that are aggregates of smaller grains of different minerals or rock fragments cemented together. Another type of complexity found in some geosorbents are grains with partial coatings of solid organic matter (SOM), minerals (for example, precipitates, or weathering products), and/or biofilms (layers of microbes attached to the geosorbent). Intragranular and intra-coating porosities can include some porosity that is not accessible to vapors or solutes that can reach the other pores. In some cases, the intraparticle or intra-coating pores may be so small that vapors or solutes can enter or exit them only very slowly.

These and other complexities make it difficult to understand what parts of the geosorbent dominate the overall sorption process for a given type of contaminant, including the sorption strength and the rate of approach to equilibrium. We touch on some of these matters in Section 12.6, but a deeper review is beyond our scope.

We acknowledged some of the complexities that can be encountered in granular geosorbents. However, for clarity in the following discussions, we simplify our conceptual model of a geosorbent particle in a saturated medium to that shown in Figure 60 where we ignore inorganic coatings and intragranular porosity. However, in Box 6⤵, we conclude that microbes are unlikely to be a significant sink for HOCs, allowing further simplification of this conceptual model (Exercise 35⤵). We seek these simplifications so we can clearly define equations often used to describe sorption. But it is important to keep in mind that this conceptual model is idealized.

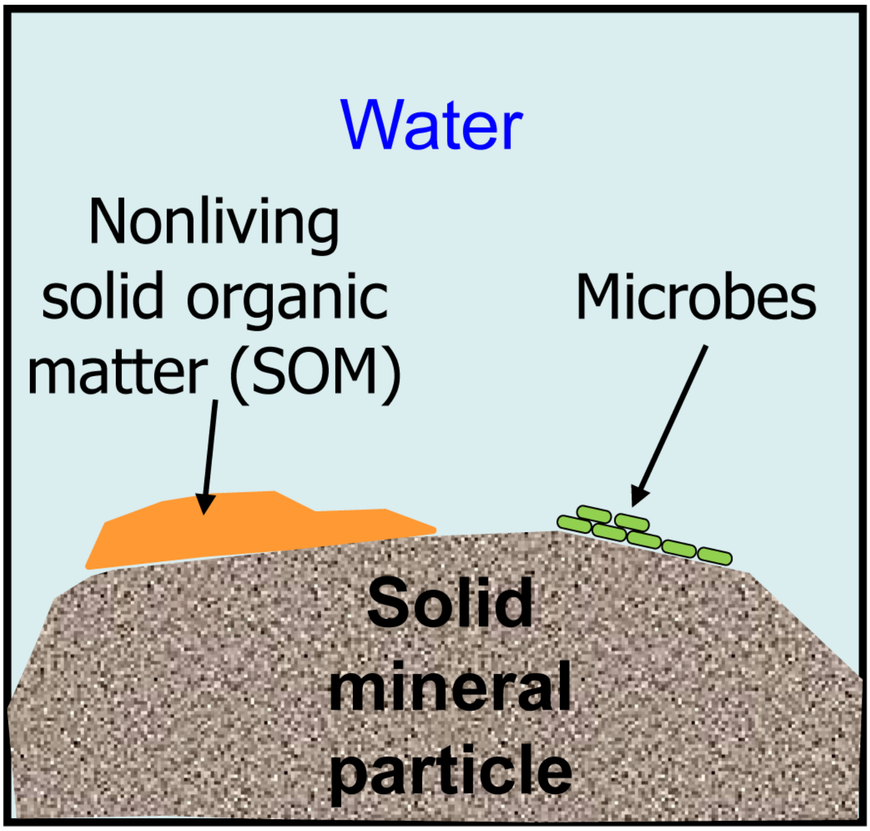


Figure 61 - A tremendously simplified conceptual model for a granular geosorbent in contact with water.

12.3 What Is Sorption?

Sorption can be due to *adsorption* (collection of the chemicals on the surface of the solid phase) or *absorption* (penetration of the chemicals into the interior of the solid phase). Since it is rarely clear whether the chemical transfer to a specific geologic medium is due to adsorption and/or absorption, the more general term *sorption* is typically used.

12.4 Simplest Conceptualization of Sorption and the Sorption Coefficient

Let’s build our understanding of sorption by starting with a further simplification of our conceptual model. Figure 62 presents this simplified conceptual model for sorption of HOCs in a unit volume within a uniform porous medium.

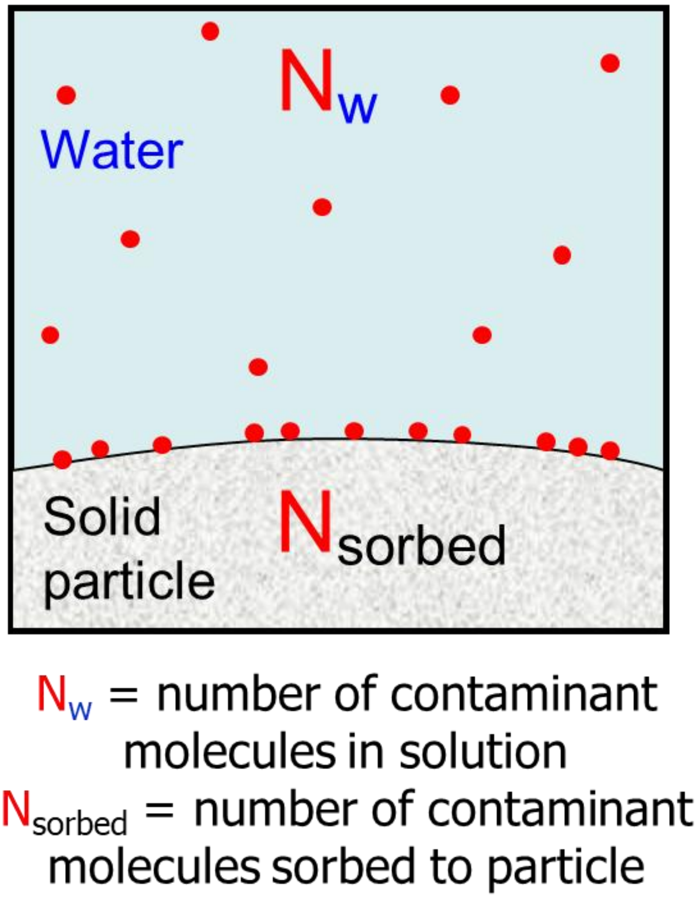


Figure 62 - Conceptualization of sorption of organic molecules by a solid particle within a unit volume of a uniform saturated porous medium. Contaminant molecules are depicted as red dots. The geosorbent is assumed to have a smooth surface with no variation in properties. Two terms are defined: the number of contaminant molecules sorbed and the number of contaminant molecules in solution in the unit volume. This simplification allows us to define a sorption distribution coefficient, as discussed in the text of this section.

In Figure 62 and the discussions that follow, we assume the following.

- The fluid phase is immobile.
- Sorption results in some fraction of the chemical molecules in the unit volume of porous medium being sorbed to the solids.
- Sorption is instantaneous and reversible. This means that sorption is in dynamic equilibrium, with molecules sorbing (moving from fluid to solid) and desorbing (moving from solid to fluid) constantly, but with the fraction of the total that is sorbed remaining constant over time.
- The sorbed fraction does not depend on the total number of molecules in the volume (i.e., does not depend on total or dissolved chemical concentration).

Under these assumptions, sorption is equivalent to a phase partitioning process and an equilibrium partition coefficient can be defined. Using the terms in Figure 62, Equation (8) presents one way to define the sorption partition coefficient.

$$K_{sorption} = \frac{N_{sorb}}{N_w} \tag{8}$$

However, we cannot count molecules directly in either phase. Therefore, the sorption coefficient is commonly expressed as a ratio of the measurable concentration of the compound on the solid (in mass/mass units such as mg compound per kg solid, or μg/g) and the measurable concentration of the compound in the water (in mass/volume units such as mg compound per liter of water, or μg/cm^3). Although many symbols are used for this coefficient in scientific literature, in contaminant hydrogeology the symbol most commonly used for the sorption partition coefficient is K_d (since early terminology referred to it as the distribution coefficient). We use that symbol throughout this book.

Equation (9) shows the relationship of K_d to $K_{sorption}$.

$$K_{sorption} = \frac{\rho_b}{\theta} K_d \tag{9}$$

where:

$K_{sorption}$ = partition coefficient in unit volume of media (dimensionless)

ρ_b = bulk density of the medium, the mass per total volume of medium (ML^{-3}) often expressed in g/cm^3

θ = porosity of the medium, fraction of the total volume that is pores and assumed water-filled in this calculation (dimensionless)

K_d = sorption distribution coefficient (L^{3}M^{-1}) often expressed in cm^3/g or L/kg

As presented in Equation (9), the sorption partition coefficient is most often reported as K_d in units of cm^3/g, or the equivalent units of mL/g or L/kg. Why these units? Because the distribution coefficient is often determined experimentally as the ratio of the sorbed concentration of the compound (μg/g) to the solution concentration of the compound (μg/cm^3). In the sorption literature, you may never encounter the sorption coefficient defined as $K_{sorption}$ as in Equation (8), but you may need to use such a definition when making some types of calculations (Exercise 36↴). One example is in mass balances on the compound in porous media with phases other than water and solid present (for example, if there is also air-filled or NAPL-filled portions of the total porosity). Such a situation is posed in the final exercise at the end of this book (Exercise 37↴).

12.5 The Most Common Conceptual Model for Sorption of HOCs

Research has shown that sorption of HOCs by granular geosorbents is often dominated by partitioning of the HOCs to the solid organic matter (SOM) on the particles, as illustrated in Figure 63. Biofilms that are not involved in transforming the contaminants are generally assumed to be insignificant sorption sites except perhaps under unusual conditions described in Box 6, so are not depicted in Figure 63. Thus, in many cases it is reasonable to assume that most of the porewater is in contact with SOM or minerals. To allow further simplification, the inorganic minerals, which often carry a surface charge and thus are hydrophilic, are generally thought to be far less important than SOM in sorption of HOCs, so we are left with a model in which HOCs partition from water only to SOM, as shown in Figure 63.

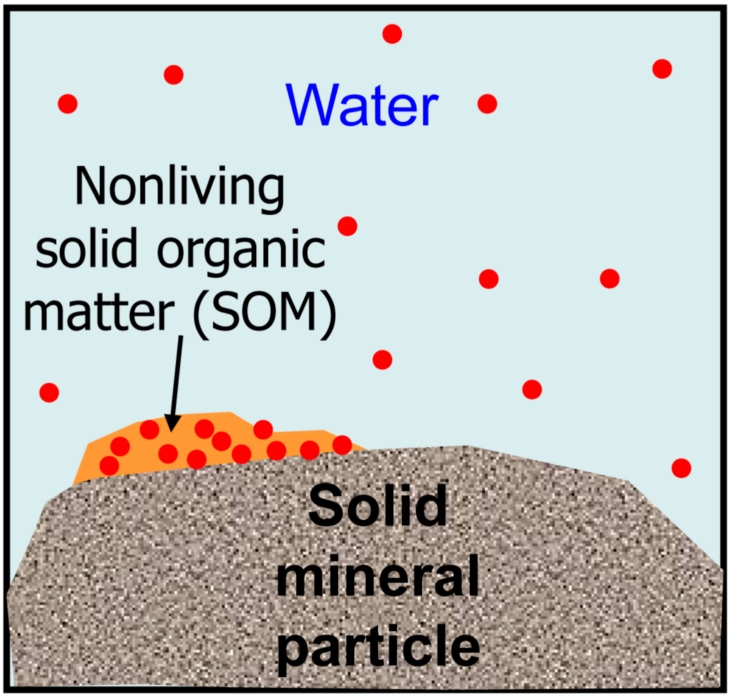


Figure 63 - Most commonly used conceptualization of sorption of HOC molecules by a solid particle within a unit volume of a uniform saturated porous medium. Contaminant molecules are depicted as red dots. As illustrated, partitioning to the solid organic matter (SOM) is thought to dominate sorption in most cases. While there may be some partitioning to the mineral surfaces, it is thought to be minor compared to the partitioning to the SOM.

12.6 What Is Solid Organic Matter?

As generally used, the term *SOM* encompasses all the natural organic matter (NOM) associated with the stationary geologic media—that is, nonliving matter as well as microorganisms and associated extracellular organic material. There are two conceptual extremes for SOM attached to external grain surfaces: patchy “blobs” and thin layers. It is thought that organic contaminant vapors and solutes present in or moving through the voids of a porous medium can interact with the external surfaces of SOM and/or diffuse within the SOM volume and stay therein once equilibrium is achieved.

In many cases, these are fully reversible processes; in other cases, it is thought that certain types of contaminants may become irreversibly bound to the SOM. Even for the reversible case, it is known that SOM may serve as a favorable medium for partitioning of certain types of vapors and solutes, thus giving the grains the capacity to concentrate the contaminants in the SOM. Finally, because SOM includes such a broad range of materials, it may vary appreciably in its origin, abundance, location/geometry, and properties.

There are two types of nonliving SOM in the subsurface:

1. organic matter of biological origin, and
2. carbonaceous matter deposited as the result of biomass fires and other combustion sources.

Organic matter of biological origin

Organic matter of biological origin is composed of residues of surficial biomass. In shallow soils, there may be a considerable amount of organic matter that has been altered only partially by natural microbiological or chemical processes. Consider that the bulk of the starting material, plant biomass, is composed of four main components:

1. cellulose and similar compounds, cellulose being a linear polymer of D-glucose with the empirical formula $(C_6H_{10}O_5)n$;
2. lignin, a high molecular weight and complex polymer derived from phenylpropane monomers;
3. organic-solvent-extractible compounds (extractives) such as waxes, fats, oils, and resins; and
4. inorganic compounds.

Cellulose is relatively hydrophilic and easily degraded by soil microorganisms. Lignin and some of the extractives, on the other hand, are relatively hydrophobic and relatively resistant to microbial attack. As the plant biomass is decomposed in the soil, the cellulose is preferentially removed, creating particles containing primarily lignin and/or extractives. These are subject to further decomposition and yield what is known as soil humus.

Soil humus consists of three components:

- soil humin, which is essentially insoluble in water and thus becomes associated with the geologic media (e.g., gravel, sand, silt, clay);
- soil humic acid, which is somewhat more soluble; and
- soil fulvic acid, which is the most soluble of the three.

These fractions cannot be represented by any specific chemical formula but rather are operationally defined (Chappelle, 2022). As described by Chappelle (2022), humic and fulvic acids may leach from the soil zone and be transported by the water flow into deeper portions of the subsurface. During that transport and as a result of additional chemical and microbiological processes, they may become strongly attached to the mineral surfaces they encounter, largely via interaction of their functional groups with multivalent metals on the surfaces, as well as by hydrogen bonding, and some other processes. Soil humus in the shallow soil horizons and humic and fulvic acids that become attached to minerals in deeper horizons are generally termed *young SOM*, implying that they have not been subjected to other processes that may occur over much longer periods (e.g., geologic time).

Much as for DOM, the configuration of SOM is generally assumed to be an amorphous 3D assembly of various size and types of organic molecules, sometimes called a supramolecular assembly (Schwarzenbach et al., 2017). Like surfactant micelles, SOM will self-assemble so that the more hydrophobic parts are in the interior, with the more hydrophilic parts on surfaces exposed to water. SOM is assumed to allow partitioning of contaminants to both the hydrophobic portions of its water-facing surfaces and its more hydrophobic interior.

Organic carbon from biomass fires and other combustion sources

An important component of the SOM in soils and subsurface geologic media may in some cases be particles of soot or char deposited into the soils as the result of biomass fires over geologic time or, more recently, from human activities such as intentional combustion of crop wastes, wood, oil, and coal or accidents such as oil-field and forest fires. Char particles are created by incomplete combustion of fuel particles at the combustion location and can be of all sizes, of course—but are likely to be crushed or abraded into small particles as they are incorporated into soils over time. Soot particles formed by the vapor-phase condensation of carbon are quite small, with diameters less than a few microns. Soot particles may be transported significant distances via the atmosphere before deposition.

Griffin and Goldberg (1983) analyzed a core sample of Lake Michigan sediment and concluded that the soot and char input to the lake had varied over time; on a dry weight basis, the char/soot content of the sediments rose from about 0.1 percent to 0.6 percent from 1923 to 1978. From various evidence, they concluded that prior to 1900, most soot/char arose from biomass burning. After 1900, they concluded that there was increasing input of char and soot derived from the combustion of coal and, to a lesser extent, oil.

Cornelissen and others (1997) developed a sensitive method for the analysis of very fine soot particles in soils and sediments. They applied it to a profile of sediment samples from a lake; the total organic carbon content of the samples was approximately 10 percent, of which soot accounted for 0.2 to 0.7 percent. Thus, the soot carbon to total organic carbon ratio (SC/OC) was quite low, on the order of 0.05. However, they found that sediments from the harbor in Boston (Massachusetts, USA), with total organic carbon contents of about 4 to 5 percent, had higher SC/OC ratios (on the order of 0.1).

Others are working to evaluate the importance of soot carbon in other geologic media. It is important to note that even if these materials do not represent a large fraction of the total SOM, their properties are likely to make them of special importance to the fate of organic chemicals. Soot and char are the products of incomplete combustion of biomass and are high in carbon content. Such carbonaceous materials are known to be good sorbents for organic chemicals (in fact, activated carbon that is used to remove organic contaminants from water is made from soot and char). Char may possess significant internal microporosity generated during the thermal distillation and restructuring of the carbonaceous mass. The micropores may be poorly interconnected, constricted, or totally blocked to outside access, depending on the conditions encountered by the particles while at elevated temperatures. The process of activation during the production of activated carbons is in part intended to open up this microporosity to allow better access to sorbing chemicals.

Alteration of SOM in the subsurface

The long-term processes that alter biomass and SOM include sedimentation and burial, which can convert the organic matter into a complex material called *kerogen* that is present in sedimentary rocks such as shales. Another important process is *coalification*, in which bulk deposits of biomass are subjected to conditions that create peat, lignite, bituminous coal, anthracite, or graphite (in increasing order of alteration). During the production of kerogens and coals, the organic matter is altered in structure and composition by polymerization and condensation reactions, leading to an increase in the carbon content of the material and a decrease in the content of functionalities—such as hydrogen and oxygen. This is often described as a decrease in the hydrogen/carbon ($\mathrm{H/C}$) and oxygen/carbon ($\mathrm{O/C}$) ratios.

Soot, char, kerogen, and coal are subject to weathering after they escape the conditions under which they were produced (e.g., via geologic cycling by earth movements). In general, the weathering will introduce new polar functionalities, increase the $\mathrm{O/C}$ ratio, and further alter the structure of the organic matter.

SOM is usually quantified by determining geosorbent organic carbon

The term *solid organic matter* (SOM) encompasses an enormous range of materials with a broad diversity of ages and processes by which they were created and altered. Detailed analysis of the components of SOM is rarely conducted, especially in geologic media below the soil horizons where the total SOM content is relatively low. In recent years, it has become common to quantify SOM on the basis of its carbon content—that is, the amount of solid organic carbon (SOC). It is now common to refer to the amount of SOC as the fraction of organic carbon (f_{oc}) that typically has units reported in a percentage as mass of organic carbon per mass of dry soil (g/g).

Organic carbon contents have been measured for a wide variety of geosorbents. Considering only a few representative examples, the fraction of organic carbon ranges from 0.016 percent to 0.011 percent in sands from locations in Ontario, Canada, and in various states in the USA (Ball et al., 1990; Farrell & Reinhard, 1994; Holmen & Gschwend, 1997). Holmen and Gschwend (1997) separated the coatings from the sands and determined that the f_{oc} of the coatings ranged from 0.65 percent to 1.6 percent. The fraction of organic carbon ranges from 0.11 percent to 3.8 percent in silts and clays and silts from locations in Saskatchewan and Ontario in Canada, in California in the US, and in Mexico City (Farrell & Reinhard, 1994; Allen-King et al., 1996).

The organic carbon contents of soils are typically higher than that of the most geologic media collected well below the soil horizons—that is, from aquifers and many aquitards. Note also that the f_{oc} of all of these media greatly exceed the f_{oc} expected from microbial biomass. Thus, it is generally assumed that the f_{oc} of natural media is dominated by nonliving SOM.

Summary regarding the nature of SOM

Although the nature of SOM remains a subject of considerable research, there seems to be an emerging agreement that SOM contains components whose characteristics fall into one of two conceptual extremes:

1) a soft, amorphous, or rubbery fraction, and
2) a hard, glassy, or crystalline component.

There is argument about the definition of these relatively vague terms, but the point is that most researchers agree that components of SOM have a wide range of physical characteristics, especially as they relate to the SOM's ability to interact with organic contaminants. This is discussed in Section 7.5 of this book.

Some researchers conclude that glassy SOM is present as small microcrystalline regions, perhaps on the order of nanometers thick, and generally found within a matrix of rubbery SOM. Thus, the glassy SOM is accessible only by diffusion through the rubbery phase. Others state that the glassy phase may sometimes be in direct contact with the pore fluids. Still others assert that a more realistic model of SOM is that there are bits of high-surface-area carbonaceous material, similar to soot or char, contained within otherwise relatively homogeneous and amorphous polymeric SOM. There is yet another camp that convincingly argues that SOM can undergo structural changes as geochemistry changes and/or chemicals diffuse into it. This camp conceives of the SOM as having internal voids with characteristics and accessibility that change with geochemistry and/or invading chemicals.

With new information continually arising, it is neither possible nor perhaps necessary for our purposes in this book to judge which of the conceptualizations is likely to be most universal. In fact, considering the wide range of origins of SOM and the conditions to which SOM is subjected, it may be most reasonable to assume there is truth to all of the conceptualizations and, perhaps, even more variations and options than currently identified.

12.7 Is Sorption of HOCs Rapid, Linear, and Reversible?

As discussed in Section 11.3, partitioning of HOCs to DOM has been found to be a rapid, linear, and reversible process (Chiou et al., 1986). Recall that *linear* means the amount of compound partitioned to the DOM is proportional to the concentration of the compound in solution and *reversible* means the compound will partition back into solution to a new equilibrium concentration if the solution concentration decreases for some reason.

As discussed earlier, sorption of HOCs from the aqueous phase to the solid phase is thought to be dominated by partitioning to the organic matter content of the geosorbent (SOM). Would we expect partitioning of HOCs to SOM to be rapid, linear, and reversible? The short answer is “sometimes.” The composition of SOM is known to vary among geosorbents, sometimes dominated by a soft fraction similar in some respects to SOM but often containing a glassy fraction that is very different and likely varies among geosorbents. When sorption of HOCs from the aqueous phase occurs only to a soft type of SOM, it may be rapid, linear, and reversible under some circumstances, particularly when the HOCs are not too hydrophobic. But when sorption from the aqueous phase involves a glassy fraction, it may not be rapid, linear, or fully reversible.

Although this may not often be an issue for typical environmental settings, sorption of organic compounds from the vapor phase when water is not present (or at least significantly below its saturation vapor pressure) is often nonlinear even on nonpolar material surfaces. A deeper discussion of these issues is beyond the scope of this book, but it is important to be aware that sorption may not always be linear and reversible.

Despite this fact, it is generally assumed that sorption from the aqueous phase is rapid, linear, and reversible in transport simulations, and the assumption underlies other methods used to estimate sorption, as discussed in Section 12.8.

12.8 Estimating the Sorption Coefficient K_d of an HOC

Many methods have been proposed to estimate sorption of HOCs to geosorbents of various types; a good review is provided by Schwarzenbach and others (2017). The most commonly used approach is to use Equation (10).

$$K_d = f_{oc} K_{oc} \tag{10}$$

where:

K_d = sorption distribution coefficient for the compound (L^3M^{-1}) often expressed in cm^3-water/g-geosorbent

f_{oc} = fraction of organic carbon in geosorbent (MM^{-1}) often expressed in (g-carbon/g-geosorbent)

K_{oc} = sorption distribution coefficient on carbon basis (L^3M^{-1}) often expressed in cm^3-water/g-carbon

This approach is appealing because it allows estimation of the sorption distribution coefficient from a property of the geosorbent (fraction of organic carbon, which can be measured or estimated) and a property of the sorbing contaminant. This assumes that all organic carbon is similar in properties, which we know is not true. However, this approach has gained widespread acceptance because so many K_{oc} values have been measured for a wide variety of contaminants and geosorbents. Furthermore, the measured values have been compared to the compound's octanol–water partition coefficient, and regressions of those data yield equations such as Equation (11) to allow estimation of a compound's log K_{oc} from its log K_{ow}.

$$\log\ K_{oc} = A \log K_{ow} + B \tag{11}$$

where:

A = slope of the regression line

B = y-intercept of the regression line

Discussions of the most appropriate values of A and B for different groups of organic chemicals are available in the literature, but one set of commonly used values are those that were proposed by the EPA (1996), namely $A = 0.7919$ and $B = 0.0784$. This regression may yield an estimate within a factor of ≈ 2 to 3 of the true K_{oc} value for soils and sediments containing dominantly amorphous or modern SOM. Comparisons of many such regressions can be found in Allen-King and others (2002) and in some references cited therein.

12.9 Impact of Sorption on the Distribution of HOCs in Granular Porous Media

Figure 64 was created using Equation 11, and assuming sorption is dominated by soft SOM. Figure 64 shows the fraction of the contaminant mass that is sorbed as a function of the logarithm of the contaminant's K_{ow} for different assumed values for the fraction of organic carbon (f_{oc}) of the geosorbent. Figure 64 shows that 50 percent or more of the contaminant in a unit volume of a granular medium will be sorbed if the contaminant has a log K_{ow} greater than about 2.5 (which is the case for most of the HOCs you will encounter) and the medium has an organic carbon content greater than 0.001 (0.1 percent), which is the case for some silty and clayey media. For geosorbents with glassy fractions in the SOM, the fraction sorbed for a given f_{oc} will be greater.

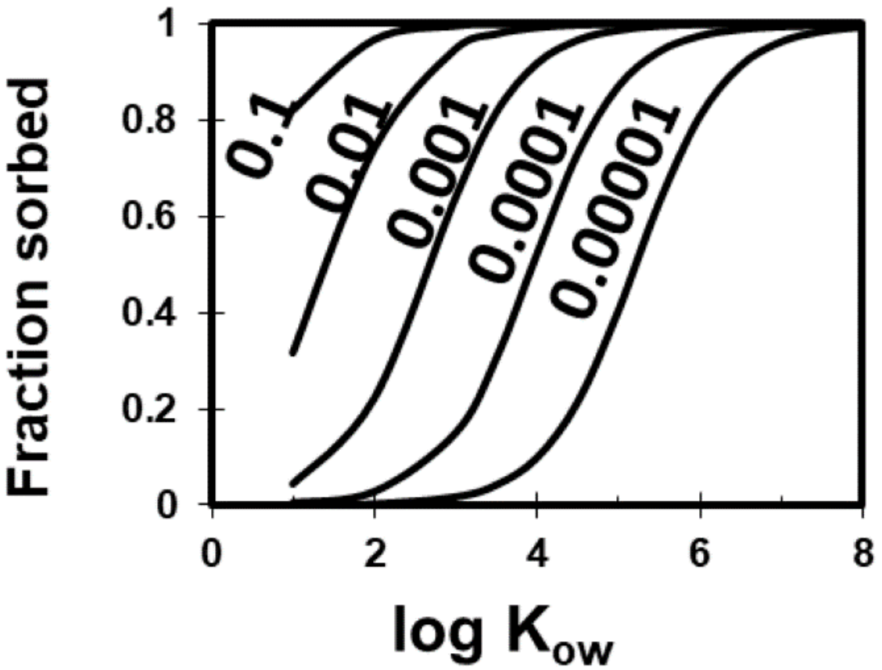


Figure 64 - The fraction of an HOC (hydrophobic organic contaminant) that would be sorbed as a function of the logarithm of the contaminant's octanol water partition coefficient (K_{ow}) for various assumed organic carbon contents of the geosorbents (f_{oc}). For this graphic, we assumed the medium is saturated with water, the total porosity is 0.3, the grains are sand, the SOM is soft, and the bulk density is 1.855 g/cm^3.

12.10 Summary Regarding Sorption of HOCs by Geosorbents

Sorption of HOCs by granular geosorbents is significant in many cases. Sorption can deplete the water of much if not most of the HOC at equilibrium, which can have profound effects on the rate of groundwater transport of the HOC (Mackay et al., 1986; Roberts et al., 1986; Fetter, 1999) and some contaminant transformation reactions. Regarding the latter, Ogram and others (1985) found in lab tests that sorbed 2,4-D (an herbicide depicted in Figure 10) was protected from biodegradation. The acknowledged importance of sorption and the ease of incorporating the simplified approach into transport simulations are two reasons that the simplified models we have shown are in wide use, along with the methods for estimating the sorption distribution coefficients, even though the idealized model of sorption assumes it is rapid, linear, and reversible.

Having defined the sorption partition coefficient using an ideal example, we must again point out that in reality the geosorbent and the sorption phenomenon may rarely fit the ideal assumptions outlined herein. The myriad complexities of sorption in the subsurface environment are explored in a variety of references for the interested reader (Allen-King et al., 2002; Luthy et al., 1997; Weber et al., 2001; Cornelissen et al., 2005). In some situations, sorption of organic contaminants, even HOCs, can be nonlinear (Allen-King et al., 1996; Chiou & Kile, 1998; Cornelissen et al., 2005; Allen-King, 2022), not rapid—that is, slow to sorb or desorb (Farrell & Reinhard, 1994; Grathwohl & Reinhard, 1994;

Huang & Weber, 1997), or practically irreversible, also called sequestered (Steinberg, et al., 1987; Luthy et al., 1997).

Furthermore, some organic contaminants, such as ionizable compounds and surfactants, may interact with inorganic surfaces; in this case, solution conditions ignored in the simple HOC sorption model may be important (pH, ionic strength and composition, among other factors). However, despite all the evidence that sorption is often not rapid, linear, or reversible, the simplicity of the idealized definition of sorption in Equation (9) is often used in practice for HOCs (Newell et al., 1996; Bedekar et al., 2016).

13 Wrap-up

While there are many properties of organic contaminants with which a geohydrologist needs to be familiar, the discussions in this book show that important simplifications can be made in many circumstances. If you know enough about the situation and contaminants you are dealing with, you may be able to reduce the number of complications you have to address to make estimates of contaminant behavior under natural or engineered remediation conditions. Typically, available simulations and general guidance documents may omit some processes of importance, and the information in this book should help you determine whether they will give you over- or under-estimates of the parameters you seek to quantify.

For everything discussed in this book, there are references that will give you deeper insight. We have included many such references, but we recommend that you frequently check to see if there are any newer publications that can aid you in your work.

14 Exercises

Exercise 1

What atom is present in all organic molecules?

Solution to Exercise 1↴

Return to where text linked to Exercise 1↥

Exercise 2

What organic molecules can enter tiny cracks or pores of molecular dimension (*nano scale*) within geologic media? Why?

Solution to Exercise 2↴

Return to where text linked to Exercise 2↥

Exercise 3

What atoms are present in all hydrocarbons?

Solution to Exercise 3↴

Return to where text linked to Exercise 3↥

Exercise 4

What is the difference between an alkane and an alkene possessing the same number of carbon atoms?

Solution to Exercise 4↴

Return to where text linked to Exercise 4↥

Exercise 5

What structure is present in all aromatic hydrocarbons?

Solution to Exercise 5↴

Return to where text linked to Exercise 5↥

Exercise 6

Name an atom that is referred to as a halogen.

Solution to Exercise 6↴

Return to where text linked to Exercise 6↥

Exercise 7

What atom is found in all amines?

Solution to Exercise 7⤵

Return to where text linked to Exercise 7⤴

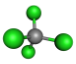
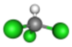
Exercise 8

Do any organic chemicals boil at temperatures below 25 °C?

Solution to Exercise 8⤵

Return to where text linked to Exercise 8⤴

Exercise 9

Which compound is more polar: carbon tetrachloride (CCl_4)  or chloroform ($CHCl_3$) ? Why?

Solution to Exercise 9⤵

Return to where text linked to Exercise 9⤴

Exercise 10

Is a hydrogen bond permanent? Why or why not?

Solution to Exercise 10⤵

Return to where text linked to Exercise 10⤴

Exercise 11

What does it mean if two phases of a compound are in equilibrium?

Solution to Exercise 11⤵

Return to where text linked to Exercise 11⤴

Exercise 12

What does vapor pressure describe?

Solution to Exercise 12⤵

Return to where text linked to Exercise 12⤴

Exercise 13

What does mole fraction refer to?

Solution to Exercise 13⤵

Return to where text linked to Exercise 13⤴

Exercise 14

What does it mean if a multicomponent mixture of organic liquids has ideal behavior with respect to vapor pressures? Are all mixtures ideal?

Solution to Exercise 14⤵
Return to where text linked to Exercise 14⤴

Exercise 15

Raoult's law applied to multicomponent mixtures of organic liquids allows you to estimate what? What parameters would you need to know to do so?

Solution to Exercise 15⤵
Return to where text linked to Exercise 15⤴

Exercise 16

What is a completely miscible organic solvent (CMOS)? Give one example.

Solution to Exercise 16⤵
Return to where text linked to Exercise 16⤴

Exercise 17

What is a partially miscible organic solvent (PMOS)? Give one example.

Solution to Exercise 17⤵
Return to where text linked to Exercise 17⤴

Exercise 18

What is an HOC? Define H, O, and C in the abbreviation. Give one example.

Solution to Exercise 18⤵
Return to where text linked to Exercise 18⤴

Exercise 19

What is the macroscopic difference between an LNAPL and a DNAPL in behavior when poured into water?

Solution to Exercise 19⤵
Return to where text linked to Exercise 19⤴

Exercise 20

A common saying is that "oil and water" don't mix; that is, they often exist in two phases when combined in a vessel. Why is that generally true? Are there any conditions in which it might not be true?

Solution to Exercise 20↴

Return to where text linked to Exercise 20⮥

Exercise 21

Which would be expected to affect the solubility of an organic contaminant more: an organic co-solvent or an organic co-solute?

Solution to Exercise 21↴

Return to where text linked to Exercise 21⮥

Exercise 22

In general, which can lead to the greatest increase in solubility of a nonpolar organic compound: rise in temperature within environmental ranges in groundwater, rise in pH within typical ranges in groundwater, rise in concentration of inorganic solutes, or rise in concentration of organic solutes.

Solution to Exercise 22↴

Return to where text linked to Exercise 22⮥

Exercise 23

What is an HIOC? Define H, I, O, and C in the abbreviation. Give one example.

Solution to Exercise 23↴

Return to where text linked Exercise 23⮥

Exercise 24

Can a pH change affect the solubility of an HOC or HIOC?

Solution to Exercise 24↴

Return to where text linked to Exercise 24⮥

Exercise 25

The most abundant halogenated contaminant in leachate from the hazardous waste site known as the Stringfellow Acid Pits in Southern California was identified in the 1980s as *para chlorobenzene sulfonic acid*, or p-CBSA, after extensive analytical work by the California Department of Health Services Hazardous Materials Laboratory. According to the California Environmental Protection Agency (2015, p. 6):

> *p-CBSA is a byproduct of the production of dichloro-diphenyl-trichloroethane (DDT). Years of DDT production released p-CBSA into the environment and contaminated the groundwater at the former plant site (the Montrose Chemical Corp Superfund site) as well as at the neighboring land (Del Amo Superfund site). Other sites of p-CBSA contamination across the country include the Stringfellow Acid Pits in California, the Basic Management Incorporated Complex in Nevada, and the Velsicol Superfund site in Michigan.*

Since this is a significant contaminant at many hazardous waste sites, we should try to understand what it is and how it may behave in groundwater.

Draw the structure of this compound in 2D (atoms and bonds). Does the molecule have polar and nonpolar portions? If so, circle the polar and/or nonpolar parts. Is it surprising that this compound would be in the leachate, assuming it was in the waste materials in the pit? Why? Would you expect this compound to form a groundwater plume? Why?

Solution to Exercise 25⤵

Return to where text linked to Exercise 25⤴

Exercise 26

In general terms, what is the Effective Solubility Model?

Solution to Exercise 26⤵

Return to where text linked to Exercise 26⤴

Exercise 27

In general terms, what does Henry's law describe?

Solution to Exercise 27⤵

Return to where text linked to Exercise 27⤴

Exercise 28

What is the K_{ow} of a contaminant? Why might you need to know the K_{ow}? Where might you find a K_{ow} if not in this book?

Solution to Exercise 28⤵

Return to where text linked to Exercise 28⤴

Exercise 29

What does "amphiphilic" mean, in general terms? Give an example of one well-known and commonly used amphiphilic organic compound.

Solution to Exercise 29⤵

Return to where text linked to Exercise 29⤴

Exercise 30

What is the primary characteristic of all surfactants?

Solution to Exercise 30⤵

Return to where text linked to Exercise 30⤴

Exercise 31

What is a micelle? What does “CMC” refer to?

Solution to Exercise 31⤵

Return to where text linked to Exercise 31⤴

Exercise 32

Under what conditions does a surfactant have the most pronounced effect on solubility of an HOC?

Solution to Exercise 32⤵

Return to where text linked to Exercise 32⤴

Exercise 33

What does “DOM” stand for? Name two components of DOM in natural uncontaminated groundwater.

Solution to Exercise 33⤵

Return to where text linked to Exercise 33⤴

Exercise 34

Why is DOM generally present as coiled or aggregated molecules?

Solution to Exercise 34⤵

Return to where text linked to Exercise 34⤴

Exercise 35

Can organic contaminants partition into microbes in groundwater environments? Under what conditions would a significant fraction of the total contaminant mass in a unit volume of the subsurface be partitioned into microbes?

Solution to Exercise 35⤵

Return to where text linked to Exercise 35⤴

Exercise 36

What do the porosity and bulk density of a geologic medium refer to?

Solution to Exercise 36⤵

Return to where text linked to Exercise 36⤴

Exercise 37

You receive laboratory determinations of PCE soil concentration (total extraction) for soil samples collected from the aquifer (saturated zone) beneath a contaminated site at which you are the project manager. Assume that the samples are collected without any loss of liquids, solids, or contaminant. The former business that operated at this location is a dry-cleaning facility and, based on historical records and patterns of typical contamination at this type of facility, you have correctly assumed that pure PCE was released into the ground. However, you wonder if there is any liquid PCE in the samples or whether the sample values indicate only dissolved and sorbed phases. Thus, the task is to evaluate the samples to determine whether they indicate the presence of NAPL. To be efficient and provide work applicable to future projects, you decide to develop a general solution to this problem using variables that represent data for the compound of interest and relevant field site properties. This exercise is based on the method of Feenstra and others (1991).

a) In addition to the total soil concentration, what field properties do you need to measure (or make reasonable approximations of) to provide a site-specific answer to the problem?
b) What assumptions are inherent in your analysis and are they well or poorly supported?
c) Make a conceptual sketch of the problem to facilitate thinking through the approach.
d) Derive a general equation to determine if a liquid single-component NAPL is present in a sample based on the known total concentration of the compound. Apply the equation to determine if there is liquid PCE in a sample reported as containing 150 mg/kg PCE.

Solution to Exercise 37⤵

Return to where text linked to Exercise 37⤴

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16 Boxes

Box 1 - Density, Melting Point and Boiling Point for Selected Compounds

Table Box 1-1 summarizes information for many examples of the listed classes of organic compounds. The background shading indicates chemicals that, if present in their pure state, would typically exist as gases (white background), liquids (blue background) or solids (gray background) in the subsurface at 20 °C and one atmosphere total pressure. Gases that are denser than air and liquids or solids that are denser than water at 20 °C have their names and densities in bold type. The chlorinated organic gases are much denser than air. Also, the listed chlorinated organic liquids and polyaromatic hydrocarbon solids are denser than water, whereas the rest of the organic liquids listed are less dense than water. This summary is provided for convenience and for use in the exercises of this book. We recommend using online or peer-reviewed summaries if you can find them, as they are more likely to be updated and used by others.

Table Box 1–1 - Densities, Melting Points and Boiling Points for Selected Compounds. The text explains the meaning of shading and bold type. The table is divided into parts focusing on different classes of organic compounds. Air and water are included for comparison.

Class	Compound	Formula	Molecular weight	Density (g/cm^3) at 20 °C	Phase at 20 °C	Melting point (°C)	Boiling point (°C)
	Air	NA	NA	0.0012	gas	NA	NA
	Water	H_2O	18	1	liquid	0	100
Chlorinated alkanes and alkenes							
	Chloromethane	CH_3Cl	51	**0.92**	gas	-98	-24
	Chloroethene (vinyl chloride)	CH_3Cl	63	**0.91**	gas	-160	-14
	Chloroethane	C_2H_5CL	65	**0.89**	gas	-136	12
	Dichloromethane (methylene chloride)	CH_2Cl_2	85	**1.36**	liquid	-95	40
	Trichloromethane (chloroform)	$CHCl_3$	119	**1.48**	liquid	-64	61
	Tetrachloromethane (carbon tetrachloride)	CCl_4	154	**1.59**	liquid	-23	77
	1,1-dichloroethane	$C_2H_4Cl_2$	99	**1.17**	liquid	-97	58
	1,2-dichloroethane	$C_2H_4Cl_2$	99	**1.26**	liquid	-35	83
	1,1,1-trichloroethane	$C_2H_3Cl_3$	133	**1.34**	liquid	-30	74
	1,1-dichloroethene	$C_2H_2Cl_2$	97	**1.22**	liquid	-122	37
	***cis* 1,2-dichloroethene**	$C_2H_2Cl_2$	97	**1.28**	liquid	-81	60
	***trans* 1,2-dichloroethene**	$C_2H_2Cl_2$	97	**1.26**	liquid	-50	48
	Trichloroethene	C_2HCl_3	131	**1.46**	liquid	-73	87
	Tetrachloroethene (perchloroethene)	C_2Cl_4	166	**1.63**	liquid	-19	121
Aromatic hydrocarbons							
	Benzene	C_6H_6	78	0.88	liquid	6	80

Class	**Compound**	**Formula**	**Molecular weight**	**Density (g/cm^3) at 20 °C**	**Phase at 20 °C**	**Melting point (°C)**	**Boiling point (°C)**
	Toluene	$C_6H_5CH_3$	92	0.87	liquid	-95	111
	Ethylbenzene	$C_6H_5(C_2H_5)$	106	0.87	liquid	-95	136
	o-Xylene	$C_6H_4(CH_3)(CH_3)$	106	0.88	liquid	-25	144
	m-Xylene	$C_6H_4(CH_3)(CH_3)$	106	0.86	liquid	-48	139
	p-Xylene	$C_6H_4(CH_3)(CH_3)$	106	0.86	liquid	13	138
	n pentyl benzene	$C_{11}H_{16}$	148	0.86	liquid	-75	205
	1,3,5, trimethylbenzene	C_9H_{12}	120	0.86	liquid	-44.5	165
Halogenated aromatics							
	Chlorobenzene	C_6H_5Cl	113	**1.11**	liquid	-45	131
	1,2 dichlorobenzene	$C_6H_4Cl_2$	147	**1.3**	liquid	-17	180
	1,3 dichlorobenzene	$C_6H_4Cl_2$	147	**1.23**	liquid	-25	173
	1,4 dichlorobenzene	$C_6H_4Cl_2$	147	**1.25**	solid	53.5	174
	1,3,5 trichlorobenzene	$C_6H_3Cl_3$	181	**1.46**	solid	63	208
	Hexachlorobenzene	C_6Cl_6	285	**2.04**	solid	231	326
Polycyclic aromatic hydrocarbons							
	Naphthalene	$C_{10}H_8$	128	**1.16**	solid	80	218
	Anthracene	$C_{14}H_{10}$	178	**1.25**	solid	218	340
	Phenanthrene	$C_{14}H_{10}$	178	**1.18**	solid	101	332
	Tetracene	$C_{18}H_{12}$	228	**1.65**	solid	357	437
	Chrysene	$C_{18}H_{12}$	228	**1.27**	solid	254	448
	Benzo(a)pyrene	$C_{20}H_{12}$	252	**1.24**	solid	179	495
PCBs							
	2-chlorobiphenyl	$C_{12}H_9Cl$	189	**1.28**	solid	77	375
	Decachlorobiphenyl	$C_{12}Cl_{10}$	499	**1.82**	solid	306	566
Aliphatic hydrocarbons							
	Methane	CH_4	16	0.0007	gas	-182	-162
	Ethane	C_2H_6	30	**0.0014**	gas	-182	-88
	Propane	C_3H_8	44	**0.0020**	gas	-188	-42
	Butane	C_4H_{10}	58	**0.0025**	gas	-137	0
	Pentane	C_5H_{12}	72	0.626	liquid	-130	36
	n-hexane	C_6H_{14}	86	0.66	liquid	-95	69
	Hexadecane	$C_{16}H_{34}$	226	0.77	liquid	18	287
	Heptadecane	$C_{17}H_{36}$	240	0.78	solid	22	302
	Octadecane	$C_{18}H_{38}$	255	0.77	solid	29	317
Alcohols							
	Methanol	CH_3OH	32	0.79	liquid	-98	65
	Ethanol	C_2H_5OH	46	0.79	liquid	-117	78
	Propanol	C_3H_7OH	60	0.8	liquid	-126	97
	Isopropanol (propan-2-ol)	C_3H_7OH	60	0.79	liquid	-89	82
	Butanol	$C_4H_9O\ H$	74	0.81	liquid	-90	118
	tert-Butanol (TBA)	$C_4H_9O\ H$	74	0.78	solid	25	82

Class	**Compound**	**Formula**	**Molecular weight**	**Density (g/cm^3) at 20 °C**	**Phase at 20 °C**	**Melting point (°C)**	**Boiling point (°C)**
	Octanol	$C_8H_{17}OH$	130	0.83	liquid	-17	194
Ketones							
	Acetone	C_3H_6O	58	0.79	liquid	-95	56
	Methyl ethyl ketone (MEK)	C_4H_8O	72	0.81	liquid	-86	80
	Methyl isobutyl ketone (MIBK)	$C_6H_{12}O$	100	0.8	liquid	-85	117
	2-heptanone	$C_7H_{14}O$	114	0.8	liquid	-35.5	151
Ethers							
	Methyl *tert*-butyl ether (MTBE)	$C_5H_{12}O$	88	0.74	liquid	-109	55
	Ethyl *tert*-butyl ether (ETBE)	$C_6H_{14}O$	102	0.74	liquid	-94	70
	tert-amyl methyl ether (TAME)	$C_6H_{14}O$	102	0.77	liquid	-80	86

Return to where Section 1.4 *Alkanes and Halogenated Alkanes* linked to Box 1⮥

Return to where Section 1.6 *Aromatics and Halogenated Aromatics* linked to Box 1⮥

Return to where Section 2.4 *Melting and Boiling Points* linked to Box 1⮥

Return to where Section 2.5 *Densities* linked to Box 1⮥

Box 2 - Calculating Vapor Concentration from Vapor Pressure

Equation (Box 2-1) is the method to calculate vapor concentration from vapor pressure and other parameters based on the ideal gas law (PV = NRT).

$$\boldsymbol{C_{i_{vapor}}} = \frac{\boldsymbol{Mn}}{\boldsymbol{V}} = \frac{\boldsymbol{MP_i}}{\boldsymbol{RT}} \qquad \text{(Box 2-1)}$$

where:

$C_{i_{vapor}}$ = vapor concentration (grams/liter)

M = molecular weight of chemical (grams/mole)

n = number of molecules in vapor (moles)

V = volume of vapor phase (liters)

P_i = vapor pressure of chemical (atm)

R = universal gas constant (0.082054 liters atm/degree(K)mole)

T = absolute temperature (K, degrees kelvin = degrees C + 273.15)

Often, vapor concentrations are reported in parts per million by volume (ppmv). This refers to the fraction of the total gas volume occupied by the chemical and is calculated as in Equation (Box 2-2).

$$ppmv_i = \frac{V_i}{V_T} = \frac{n_i}{n_T} = P_i/P_T \qquad \text{(Box 2-2)}$$

where:

$\boldsymbol{ppmv_i}$ = vapor concentration (ppmv)

V_i = volume of chemical in vapor phase (liters)

V_T = total volume of vapor phase (liters)

n_i = number of molecules of chemical in vapor (moles)

n_T = total number of molecules in vapor (moles)

P_i = vapor pressure of chemical (atm) at system temperature, T

P_T = total vapor pressure (atm) at system temperature, T

Return to where text linked to Box 2↥

Box 3 - Dependence of Vapor Pressure on Temperature

Figure Box 3-1 shows that vapor pressure is strongly dependent on temperature for the depicted classes and examples of organic compounds. The vapor pressure axis is on a log scale. If you need specific values for a particular chemical and temperature, they can be calculated from information about the chemical or found in reference books (e.g., Poling et al., 2001; Mackay et al., 2006).

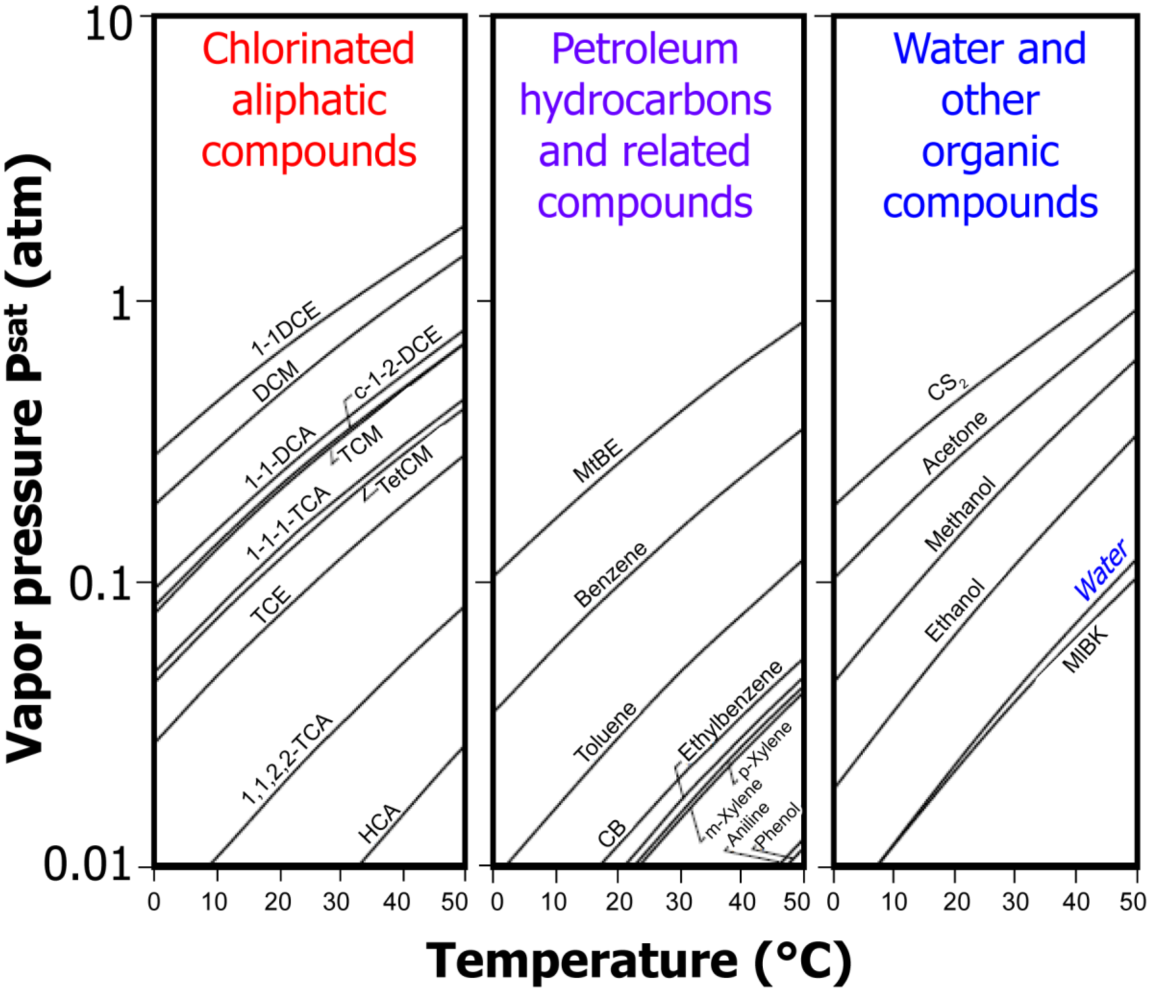


Figure Box 3-1 - Vapor pressure (log scale) versus temperature for three groups of compounds. Water is included for comparison.

Return to where text linked to Box 3↑

Box 4 - Hydrophobic Ionizable Organic Chemicals (HIOC): Prevalence of Neutral and Ionized Species

An acid–base pair has an acidity constant or acid dissociation constant (K_a) that, when the system is at equilibrium, which is a reasonable expectation for fast H^+ transfer, can be described as presented in this Box.

Organic acids

One example is discussed in Section 7.8 of this book: pentachlorophenol. The structures of this compound and its deprotonated form are presented in Figure Box 4-1.

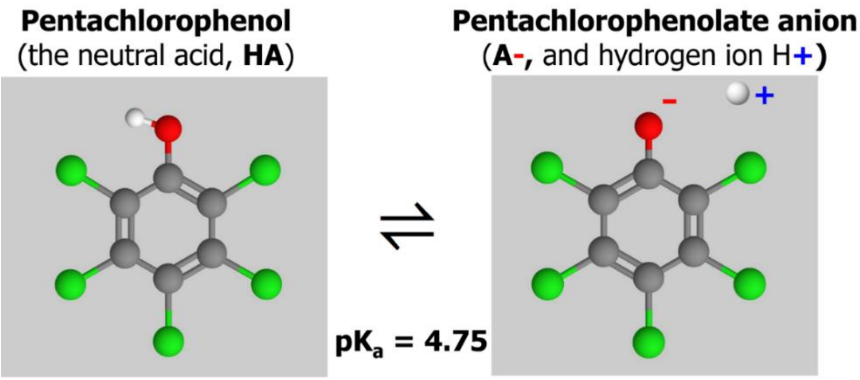


Figure Box 4-1 - Example of speciation of an organic acid that loses an H^+ to become a negatively charged ion.

The acidity constant K_a is defined as shown by Equation (Box 4-1).

$$K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}} \qquad \text{(Box 4-1)}$$

where:

$\{\boldsymbol{H^+}\}$ = activity of the hydrogen ion (dimensionless)

$\{A^-\}$ = activity of the anionic species (dimensionless)

$\{HA\}$ = activity of the neutral species (dimensionless)

For organic compounds present at low concentrations in low ionic strength aqueous solutions, the activities are approximately equal to the concentrations (the activity coefficients are approximately 1). Thus, the previous equation may be rewritten as Equation (Box 4-2).

$$K_a \approx \frac{\{H^+\}[A^-]}{[HA]} \equiv K_a^*(mixed\ acidity\ constant) \qquad \text{(Box 4-2)}$$

where:

$\{\boldsymbol{H^+}\}$ = activity of the hydrogen ion (dimensionless)

$[A^-]$ = concentration of the anionic species (ML^{-3})

$[HA]$ = concentration of the neutral species (ML^{-3})

The mixed acidity constant is what is typically reported in the literature or web sources (Schwarzenbach et al., 2017); such values are derived by measurement of organic species concentrations and pH ($\text{pH} = -\log\{H+\}$). Inspection of Equation (Box 4-2) shows that the concentrations of anionic and neutral species are equal when the hydrogen ion activity (pH) is equal to K_a (or when the negative logarithm of both are equal—that is, pH = pK_a)—as shown by Equation (Box 4-3).

$$[A^-] = [HA] \text{ when } pH = pK_a \qquad \text{(Box 4-3)}$$

In Figure (Box 4-1) the pK_a for pentachlorophenol is 4.75. In general, the pH controls the fraction of the organic acid molecules that are neutral (α_{HA}) according to Equation (Box 4-4), which can be derived from Equation (Box 4-3).

$$\alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + 10^{(pH - pK_a^*)}} \qquad \text{(Box 4-4)}$$

The anionic fraction (α_{HA}) is as shown in Equation (Box 4-5).

$$\alpha_{A^-} = 1 - \alpha_{HA} \qquad \text{(Box 4-5)}$$

For pentachlorophenol, most of the compound is the pentachlorophenolate ion ($\alpha_{HA} \leq 0.01$; $\alpha_{A^-} \geq 0.99$) at circumneutral or greater pH (at pH ≥ 6.75).

Organic bases

One example of an organic base is depicted in Figure Box 4-2 and discussed in Section 7.8 of this book: 4-methyl aniline. The structures of another neutral base (B) and its protonated form (BH^+) are presented in Figure Box 4-2.

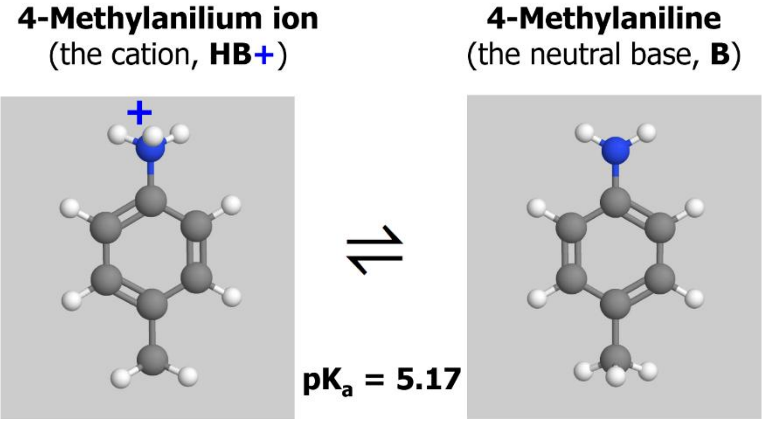


Figure Box 4-2 - Example of speciation of an organic base, which gains an H^+ at low pH.

As discussed above, this acid–base pair forms in aqueous solution, and the speciation is determined by the pH and the acidity constant. As for the organic acids, tabulated values are generally mixed acidity constants. Figure Box 4-2 shows the negative logarithm of the mixed acidity constant (pK_a^*) for 4-methyl aniline is 5.17.

The fraction of organic base molecules that are protonated (α_{BH+}) is given by Equation (Box 4-6).

$$\alpha_{BH^+} = \frac{[\mathrm{BH^+}]}{[\mathrm{BH^+}] + [\mathrm{B}]} = \frac{1}{1 + 10^{(\mathrm{pH\text{-}pK_\alpha^*})}} \qquad \text{(Box 4-6)}$$

The deprotonated (neutral) fraction (α_B) is as shown in Equation (Box 4-7).

$$\alpha_B = 1 - \alpha_{BH^+} \qquad \text{(Box 4-7)}$$

For 4-methyl aniline, most of the compound is the neutral species ($\alpha_B \geq 0.99$; $\alpha_{BH^+} \leq 0.01$) at circumneutral or greater pH (at pH ≥ 7.17).

Return to where text linked to Box 4⮥

Box 5 - Additional Information about Henry's Constant

Variation of Henry's constant with temperature

Like vapor pressures, Henry's constants vary significantly with temperature over the environmental temperature range. Figure Box 5-1 depicts a method for estimating Henry's constant of TCE for a range of temperatures. Gossett (1987) provides parameters for other compounds.

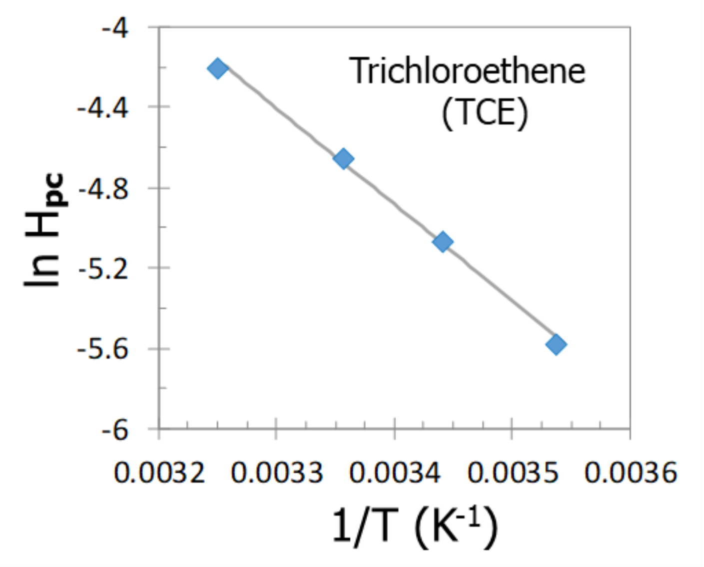


Figure Box 5-1 - Linear regression of four data points to estimate Henry's constant with temperature. TCE H_{pc} observations (m^3-atm/mole) are shown as diamonds and the linear regression as a solid line. TCE regression coefficients: A = 11.37, B = 4780, r^2 = 0.996 (Gossett, 1987).

Over the environmentally relevant temperature range, the change in Henry's constant with temperature is approximately linear when plotted as the log (or ln) transformed H versus 1/T (where T is in degrees kelvin, i.e., K). As a reminder, *log* refers to the base 10 logarithm, whereas *ln* refers to the base e logarithm. Compound-specific coefficients for use in Equation (Box 5-1) are tabulated in the literature for most compounds of interest in studies of groundwater contamination and remediation.

$$\ln H_{pc} = A - \frac{B}{T} \qquad \text{(Box 5-1)}$$

Estimation of contaminant loss to headspace in sample bottle

Here we provide the details for the example mentioned in Section 8.2 of this book and make a calculation to see how important a bubble might be if left in a sample bottle not quite filled with a water sample containing a volatile compound. We follow the approach outlined by Pankow (1996) and use Henry's law to make this calculation. We chose vinyl chloride (VC), also known as chloroethene, for this example because it has one of the highest

Henry's constants of chlorinated groundwater contaminants. As illustrated in Figure 46b, we assume water containing vinyl chloride (VC), also known as chloroethene, at 1 mg/L is collected in a 40-mL sample bottle at 20 °C, but the sampling team left 2.0 mL headspace (filled with air) when they sealed the bottle. That is a pretty big bubble—5 percent of the interior volume, which should have easily been noticed and corrected. Nevertheless, it is an instructive example.

Our inputs:

- $C_0 = 1$ mg/L (initial water concentration of VC)
- $V_w = 38.0$ mL (volume of water) = 0.0380 L
- $V_a = 2.0$ mL (volume of air) = 0.002 L
- M_{tot} = total mass of VC = V_wC_0 = 0.0380 mg
- $H_{cc} = 0.91$ for VC (20 °C)

The H_{pc} was calculated at 20 °C using Equation (Box 5-1) with constants A = 7.385 and B = 3286 for VC determined by Gossett (1987); H_{pc} = 0.0218 m^{3}atm/mol. The H_{pc} was converted to an H_{cc} using the ideal gas law.

After the sample bottle is sealed and VC partitioning from water to air comes to equilibrium, there will be a lower concentration and mass of VC in the water, which we will term C_w and M_w, respectively. The air bubble, of course, will gain VC and have an equilibrium concentration and mass, which we will call C_a and M_a. The sum of M_w and M_a must be M_{tot} if no VC mass is lost from the bottle after it is sealed, which we will assume.

We make the following calculations, using values listed above, as shown in Equation (Box 5-2).

$$\frac{M_a}{M_w} = \frac{C_aV_a}{C_wV_w} = H_{cc}\frac{V_a}{V_w} = 0.91\ \frac{2.0}{38.0}\ =\ 0.0480.91\ \frac{2.0}{38.0}\ =\ 0.048 \qquad \text{(Box 5-2)}$$

Rearranging and substituting are shown in Equation (Box 5-3) and Equation (Box 5-4).

$$M_a = 0.048M_w \qquad \text{(Box 5-3)}$$

$$M_{tot} = M_a\ +\ M_w = (1 + 0.048)\mathrm{M_w} = 1.048M_w \qquad \text{(Box 5-4)}$$

Rearranging again gives Equation (Box 5-5).

$$M_w = \frac{M_{tot}}{1.048} = \frac{0.0380}{1.048} = 0.0363\,mg \qquad \text{(Box 5-5)}$$

Since we now know M_w, we can calculate C_w as shown in Equation (Box 5-6).

$$C_w = \ \frac{M_w}{V_w}/= \frac{0.0363\ \mathrm{mg}}{0.0380\ \mathrm{L}} = 0.954\ \mathrm{mg/L} \qquad \text{(Box 5-6)}$$

The concentration of vinyl chloride in the water is 0.954 mg/L (95.4 percent of the original C_0). So, for vinyl chloride, generally considered a very volatile contaminant, even a fairly big bubble changes the water concentration by less than 5 percent at 20 °C.

Return to where text linked to Box 5↥

Box 6 - Bioconcentration: Macro- and Micro-

Bioconcentration to macro-organisms

For fish—the organisms of most interest in the original deliberations about bioconcentration—a large portion of the contaminant enters their bodies via ingestion of various items including

a) other organisms,
b) suspended solids either intentionally or unintentionally, and
c) sediment, either intentionally or unintentionally.

It is reasonable to expect that the total mass of contaminant in the fish would be affected by the contaminant concentration in the ingested items, the contaminant concentration in the water, the rate at which the fish can detoxify or remove the contaminant from its body, and so on. However, there has been fair success at predicting total contaminant load by assuming the following:

a) the major control is the contaminant concentration in the water,
b) contaminant concentration in the water (C_w) is constant,
c) when equilibrium is reached for partitioning of contaminant between fish and water, the contaminant in the fish can be considered to be uniformly distributed throughout the body at a constant concentration (C_B), and
d) at a given temperature, the concentration in the fish is equal to the concentration in the water multiplied by a constant termed the bioconcentration factor (often denoted K_B or BCF, but which we here term the biota-water partition coefficient, or K_{BW}, for consistency with terminology used elsewhere in this book).

This is illustrated by Equation (Box 6-1).

$$C_B = K_{BW}\, C_w \qquad \text{(Box 6-1)}$$

This simple relationship assumes that the contaminant concentrations are uniform within the organism and constant over time. It has been discovered that K_{BW} values range over almost six orders of magnitude for organic chemicals of environmental concern. It has also been discovered from laboratory studies that K_{BW} values correlate relatively well with octanol-water partition coefficients (K_{ow}).

For example, Veith and others (1980) collected and analyzed bioconcentration data from a number of studies by a range of investigators, with a total of 84 chemicals, subsets of which were tested with one or more of four species (fathead minnow, bluegill sunfish, rainbow trout, and mosquitofish). Veith et al. (1980) reported the regression equation relating K_{BW} and K_{ow} shown in Equation (Box 6-2).

$$\log K_{BW} = 0.76 \log K_{ow} - 0.23 \qquad \text{(Box 6-2)}$$

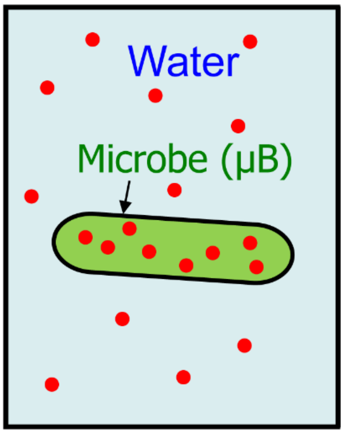
The correlation coefficient (r^2) is 0.83. There are many other such correlations reported in the literature for estimating K_{BW} for chemicals of interest from their octanol–water partition coefficient, water solubility, and other properties.

Micro-bioconcentration

Just as for bioconcentration to macroscopic biota, for our deliberations about what we call micro-bioconcentration, we assume the following:

a) the microbes are not transforming the contaminant, just storing it in their biomass;
b) the major control is contaminant concentration in the water;
c) contaminant concentration in the water (C_w) is constant;
d) when equilibrium is reached for partitioning of contaminant between microbes and water, the contaminant in the microbes can be considered to be uniformly distributed throughout each microbe at a constant concentration ($C_{\mu B}$); and
e) at a given temperature, the concentration in each microbe is equal to the concentration in the water multiplied by a constant termed the micro-bioconcentration factor (which we call $K_{\mu BW}$).

We also make the overly broad assumption that all microbes bio-concentrate to the same extent, that is, that the micro-bioconcentration factor does not depend on the species of microbe. Figure Box 6-1 illustrates our assumptions.



C_w = Concentration in water (mg/kg = mg/L_w)

$C_{\mu B}$ = Concentration in microbe (mg/$kg_{\mu B}$)

Figure Box 6-1 - Illustration of partitioning of a compound (red dots) between water and microbe (green shape).

The mass balance for the contaminant in a unit volume containing water and biomass is shown in Equation (Box 6-3).

$$M_{total} = M_w + M_{\mu B} \qquad \text{(Box 6-3)}$$

where:

M_w = mass of contaminant in the water (M)

$M_{\mu B}$ = mass of contaminant partitioned into the microbial biomass (M)

In an early critical review of bioconcentration, Baughman and Paris (1981) started from this mass balance and presented a series of useful equations using the terminology we adopt in Equation (Box 6-4) for consistency with their original analysis. The two terms on the right side of Equation (Box 6-3) are replaced as shown in Equation (Box 6-4).

$$M_{total} = C_w m_w + C_{\mu B} m_{\mu B} \qquad \text{(Box 6-4)}$$

where:

C_w = concentration of contaminant in the water (ML^{-3}) expressed in mg/L_w which is equivalent to mg/kg_w

m_w = mass of water (M) expressed in kg_w

$C_{\mu B}$ = concentration of contaminant in the microbes (ML^{-3}) expressed in mg/$kg_{\mu B}$

$m_{\mu B}$ = mass of microbiota (M) expressed in $kg_{\mu B}$

Microbial biomass is generally determined on a dry basis, and thus the micro-bioconcentration factor is defined on a dry mass basis, as shown by Equation (Box 6-5).

$$K_{\mu BW} = \frac{C_{\mu B,dry}}{C_w} \qquad \text{(Box 6-5)}$$

where:

$K_{\mu BW}$ = microbial bioconcentration factor (L^3M^{-1}) expressed in L_w/$kg_{\mu B,dry}$

$C_{\mu B,dry}$ = concentration of contaminant in the microbes on dry mass basis (MM^{-1}) expressed in mg/$kg_{\mu B,dry}$

C_w = concentration of contaminant in the water (ML^{-3}) expressed in mg/L_w

We thus rewrite the mass balance as shown in Equation (Box 6-6).

$$M_{total} = C_w m_w + C_{\mu B,dry} m_{\mu B,dry} \qquad \text{(Box 6-6)}$$

where:

C_w = concentration of contaminant in the water (ML^{-3}) expressed in mg/kg_w

m_w = mass of water (M) expressed in kg_w

$C_{\mu B,dry}$ = concentration of contaminant in the microbes on dry mass basis (MM^{-1}), expressed in $mg/kg_{\mu B,dry}$

$m_{\mu B,dry}$ = mass of microbiota on dry mass basis (M), expressed in $kg_{\mu B,dry}$

Replacing $C_{\mu B,dry}$ in the mass balance, we get Equation (Box 6-7).

$$M_{total} = C_w m_w + K_{\mu BW} C_w m_{\mu B,dry} \qquad \text{(Box 6-7)}$$

The first term is the mass of contaminant in the water and the second term is the mass of contaminant partitioned to the microbes. Therefore, the fraction of the total contaminant mass that is partitioned into the microbial biomass is shown by Equation (Box 6-8).

$$\begin{aligned}\frac{M_{\mu B}}{M_{total}} &= \frac{K_{\mu BW} C_w m_{\mu B,dry}}{C_w m_w + K_{\mu BW} C_w m_{\mu B,dry}} \\ &= \left(1 + \frac{m_w}{K_{\mu BW} m_{\mu B,dry}}\right)^{-1}\end{aligned} \qquad \text{(Box 6-8)}$$

Baughman and Paris (1981) presented an early analysis of data from many published sources. Figure Box 6-2 is a replot of one of their figures, drawing on data from a number of references they cited, showing their estimated log $K_{\mu BW}$ versus the log K_{ow}.

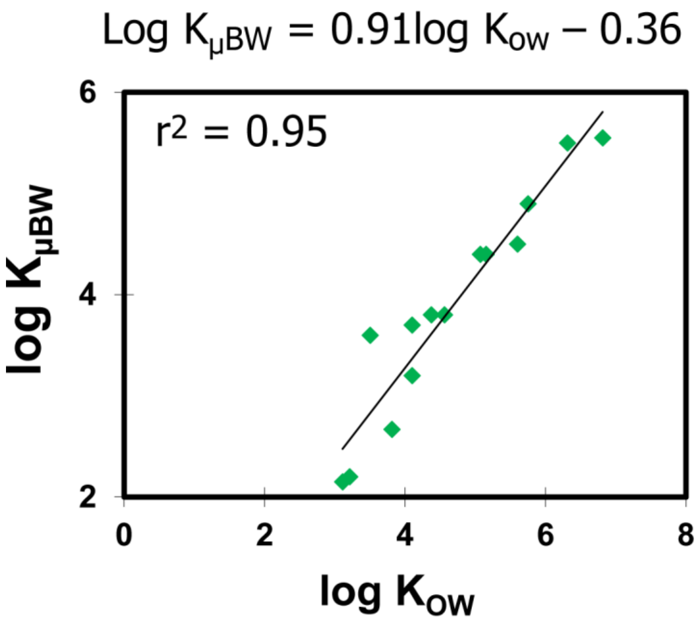


Figure Box 6-2 - Graph of bioconcentration by microbial biomass versus octanol water partition coefficient (redrawn, modified, and annotated after Baughman and Paris, 1981). Partition coefficient is on a dry microbial mass basis.

The solid regression line, whose equation is at the top of the figure, fits the data reasonably well. This suggests there is some justification for accepting the hypothesis that the partitioning to microbes on a dry weight basis can be predicted based on the octanol-water partition coefficient of the contaminant. There are other newer studies of micro-bioconcentration, which we leave to the curious reader to seek out.

Here we use the equation in Figure Box 6-2 to estimate how important micro-bioconcentration may be in typical porous media, which might have microbial populations ranging from 10^6 to 10^9 cells per gram of solids (Ferris et al, 2021). To make this calculation, we assume a typical sandy porous medium with porosity of 0.3 and density of the particles of 2.65 g/cm^3, and that the dry mass of each typical microbe is 1.3×10^{-12} g. The curves shown in Figure Box 6-3 were created by calculating the fraction of the mass of a compound in a closed system, as shown in Figure Box 6-1, if the only phase the compound can partition to is the microbial biomass. This will rarely be true, as we discuss in the main text of this book, since compounds can also partition to the solid particles. But for now, we focus on getting a sense of the impact of partitioning to microbial biomass, which is not involved in degrading or transforming the compound.

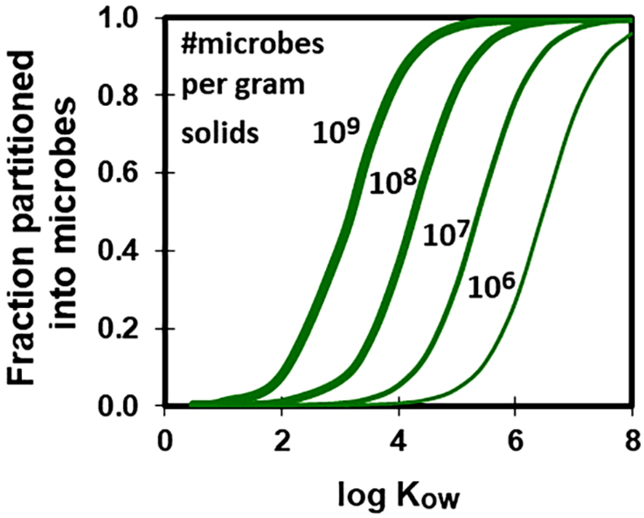


Figure Box 6-3 - Plot of bioconcentration by microbial biomass versus log K_{ow}. Curves for four different biomass concentrations are shown.

Figure Box 6-3 indicates that, unless the compound has a very high log K_{ow} or the porous medium has a high number of microbes in it, the fraction of compound that will partition to the microbes is likely to be quite small. For this reason, we are generally justified in ignoring micro-bioconcentration in other calculations regarding the transport and fate of organic contaminants in the subsurface.

Return to where text linked to Box 6↥

17 Exercise Solutions

Solution Exercise 1

Carbon.

Return to Exercise 1↥

Return to where text linked to Exercise 1↥

Solution Exercise 2

Organic molecules with single `C-C` bonds, such as TCA can enter and move within cracks or pores of molecular dimension because the ends of the molecule can rotate, allowing some flexibility during the movement. Molecules with double carbon bonds are flat and cannot rotate, reducing their ability to move within nonplanar or twisted pores.

Extra information: This is important when considering diffusion of contaminants into constricted spaces—for example, very small pores in aquifer particles.

Return to Exercise 2↥

Return to where text linked to Exercise 2↥

Solution Exercise 3

Carbon and hydrogen.

Return to Exercise 3↥

Return to where text linked to Exercise 3↥

Solution Exercise 4

Alkanes have single bonds between carbon atoms, whereas alkenes have at least two carbon atoms sharing a double bond.

Extra information: Molecules with two sets of double-bonded carbons are called *dienes*.

Return to Exercise 4↥

Return to where text linked to Exercise 4↥

Solution Exercise 5

Aromatic hydrocarbons contain one or more aromatic rings, also often called benzene rings.

Extra information:

- If they have more than one ring, they are called polycyclic aromatic hydrocarbons or PAHs; some are illustrated in Figure 10.
- Examples of one ring aromatics: benzene, toluene, ethylbenzene, chlorobenzene (Figure 8).
- Examples of two ring aromatics: naphthalene, dibenzofuran (Figure 10), biphenyl, 1,8-dimethylnaphthalene.
- Examples of three ring aromatics: anthracene (Figure 10), phenanthrene.
- Example of four ring aromatics: pyrene.
- Example of five ring aromatics: benzo(a) pyrene (Figure 10).

Return to Exercise 5⮥

Return to where text linked to Exercise 5⮥

Solution Exercise 6

Chlorine.

Extra information: A halogen is an element that readily reacts with alkali metals and alkaline earth metals to form halide salts. Some other examples: bromine, fluorine, and iodine.

Return to Exercise 6⮥

Return to where text linked to Exercise 6⮥

Solution Exercise 7

Nitrogen.

Extra information: There are many other organic compounds that contain nitrogen, including pyridine, quinoline, and nicotine.

Return to Exercise 7⮥

Return to where text linked to Exercise 7⮥

Solution Exercise 8

Yes, some organic chemicals are gases at or near 25 °C, meaning their boiling temperature is lower. Examples include methane, ethane, propane, butane, chloromethane, and vinyl chloride as shown in Figure 14 and Table Box 1-1.

Return to Exercise 8⮥

Return to where text linked to Exercise 8⮥

Solution Exercise 9

Chloroform is more polar. Carbon tetrachloride has four chlorine atoms, arranged symmetrically around the carbon, so the overall molecular dipole is zero, and thus it is nonpolar. Chloroform has three chlorines and one hydrogen, so the overall molecular dipole is non-zero, and thus the molecule is somewhat polar.

Return to Exercise 9⮥

Return to where text linked to Exercise 9⮥

Solution Exercise 10

No. Hydrogen bonds form due to mutual attractions between two molecules, but they can break and reform.

Return to Exercise 10⮥

Return to where text linked to Exercise 10⮥

Solution Exercise 11

When referring to two phases in one container, equilibrium is the state attained when the transfer of molecules to or from one phase from or to the other is balanced—that is, there is no net transfer over time (example: water and water vapor in a container). When referring to partitioning of a compound between two phases in a specific volume of interest, equilibrium is the state attained when the transfer of the compound to or from one phase from or to the other phase is balanced—that is, there is no net transfer over time (an example is partitioning of TCE between water and air).

Return to Exercise 11⮥

Return to where text linked to Exercise 11⮥

Solution Exercise 12

Vapor pressure refers to the pressure attained in a previously evacuated container when a pure compound in liquid or solid form is introduced to, but does not fill, it (Figure 28).

Return to Exercise 12⮥

Return to where text linked to Exercise 12⮥

Solution Exercise 13

In a multicomponent phase (such as a mixture of gases or a mixture of liquids), the fraction of each component is called a *mole fraction* when it is expressed as the moles (or molecules) of that component divided by the total number of moles (or molecules) of all components.

Return to Exercise 13⮥

Return to where text linked to Exercise 13↑

Solution Exercise 14

Ideal behavior occurs for mixtures for which the activity coefficient of all components is 1 (Figure 33a). This occurs when the components are structurally similar. However, not all mixtures are ideal, as shown in Figure 33b.

Return to Exercise 14↑

Return to where text linked to Exercise 14↑

Solution Exercise 15

Raoult's law, shown in Equation (1), allows calculation of the vapor pressure of a component as a function of the component's saturated vapor pressure, its mole fraction in the mixture, and the activity coefficient of the component in the mixture.

Return to Exercise 15↑

Return to where text linked to Exercise 15↑

Solution Exercise 16

A CMOS is a solvent that can combine with water in all proportions and thus does not form a separate phase. Examples include methanol, ethanol, acetone, and 1,4 dioxane.

Return to Exercise 16↑

Return to where text linked to Exercise 16↑

Solution Exercise 17

A PMOS is a solvent that cannot combine with water in all proportions and thus does not form a separate phase. It can dissolve into water. Examples include cooking oil, aromatic hydrocarbons (e.g., benzene), and chlorinated solvents (e.g., TCE).

Return to Exercise 17↑

Return to where text linked to Exercise 17↑

Solution Exercise 18

HOC stands for hydrophobic organic chemical (or contaminant). Examples of HOCs include benzene, TCE, and anthracene.

Return to Exercise 18↑

Return to where text linked to Exercise 18↑

Solution Exercise 19

An LNAPL will float on the water whereas a DNAPL will sink.

Return to Exercise 19↥
Return to where text linked to Exercise 19↥

Solution Exercise 20

Oil and water have low solubilities in each other, so while some of each can dissolve into the other, there is usually oil and water left in separate phases. However, if the amount of oil is small enough so that it all can dissolve into the water without exceeding its solubility in the water, then the oil phase will disappear.

Return to Exercise 20↥
Return to where text linked to Exercise 20↥

Solution Exercise 21

A co-solvent since it would be present in a much higher concentration in solution than a co-solute and thus is able to affect the structure of water around the contaminant (Figure 39).

Return to Exercise 21↥
Return to where text linked to Exercise 21↥

Solution Exercise 22

Organic solutes.

Extra information:

- Surfactants are particularly influential in increasing solubility.
- A rise in inorganic solutes may decrease the solubility of a nonpolar organic compound, although this is often insignificant and thus ignored in groundwater settings.
- Temperature has a very small effect on the solubility of nonpolar compounds that are liquids in their pure form.

Return to Exercise 22↥
Return to where text linked to Exercise 22↥

Solution Exercise 23

HIOC stands for hydrophobic ionizable organic chemical (or contaminant). Examples of HIOCs include organic acids such as pentachlorophenol and bases such as 4-methyl aniline (Figure 42).

Return to Exercise 23↥
Return to where text linked to Exercise 23↥

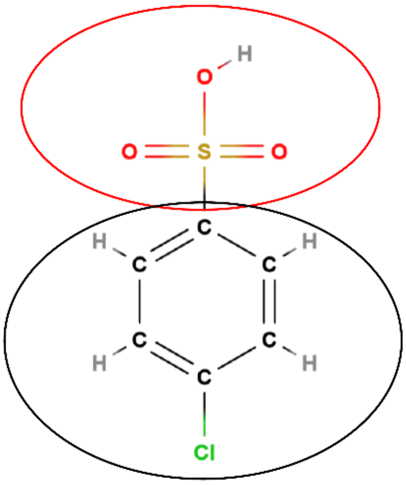
Solution Exercise 24

Change in pH in typical ranges has little effect on the solubility of HOCs but can have large effects on solubility of HIOCs (Figure 42).

Return to Exercise 24↥

Return to where text linked to Exercise 24↥

Solution Exercise 25



The chlorine and sulfonic acid groups are in para position—that is, on opposite sides of the benzene ring. Because of the sulfur and oxygens, the sulfonic acid portion is polar (red oval) whereas the rest of the molecule is nearly nonpolar (black oval). Additionally, the sulfonic acid group would be ionized at typical pH values. Thus p-CBSA would be expected to have high solubility in water, and therefore it should not be surprising that it was present in the aqueous leachate from the pits. Since it is so soluble, it would also be expected to migrate with groundwater that contacted the leachate, thus the formation of a groundwater plume is expected.

Extra information: p-CBSA has the basic characteristics of a surfactant. In fact, unpublished work by Mackay and others conducted in 1990 showed that the high concentrations of p-CBSA found in the groundwater plume at the Stringfellow site (3.3 g/l) significantly reduced the sorption of hexachloroethane (HCA) to the aquifer solids. Although not a contaminant of common concern, HCA has sorption and migration properties similar to more commonly detected contaminants such as lindane, dichloro- and trichlorobenzene.

This work indicated that if p-CBSA was present, then HCA or a similar contaminant would migrate at about one-fifth the velocity of groundwater at the Stringfellow site. However, their migration rate was predicted to increase by roughly a factor of 3 when p-CBSA was present at 3.3 g/l. Thus, while very low-toxicity groundwater contaminants such as p-CBSA may be of little public health concern on their own, they may still be important if they affect the behavior of more toxic materials in the same plume.

Return to Exercise 25↥

Return to where text linked to Exercise 25↥

Solution Exercise 26

The Effective Solubility Model (ESM) can be used to estimate the aqueous concentration of a component in equilibrium with a multicomponent organic liquid mixture; it is similar to Raoult’s law for vapor pressures of components in an organic liquid mixture.

Return to Exercise 26⮥

Return to where text linked to Exercise 26⮥

Solution Exercise 27

Henry’s law describes the air–water partitioning behavior of a compound, allowing for calculation of the compound's concentration in the air as its concentration in the water multiplied by Henry’s constant, a parameter specific to the component.

Return to Exercise 27⮥

Return to where text linked to Exercise 27⮥

Solution Exercise 28

The K_{ow} describes the equilibrium partitioning of a compound between water and octanol. Other environmental behaviors of a compound can be estimated using the compound’s K_{ow}. Examples include water solubility, microbial bioconcentration, and soil-water partitioning.

Values of K_{ow} are compiled online (https://pubchem.ncbi.nlm.nih.gov↗) and available in various books and scientific literature, although the online compilation is the most convenient to use.

Return to Exercise 28⮥

Return to where text linked to Exercise 28⮥

Solution Exercise 29

Amphiphilic compounds have both water-loving hydrophilic portions and fat-loving lipophilic (also called hydrophobic) portions. Well-known examples are surfactants, detergents, and soaps.

Return to Exercise 29⮥

Return to where text linked to Exercise 29⮥

Solution Exercise 30

Surfactants have polar and nonpolar portions, so they are soluble in water (polar or hydrophilic end) and their nonpolar (or hydrophobic) portions can solubilize oils, grease, and other low-solubility materials.

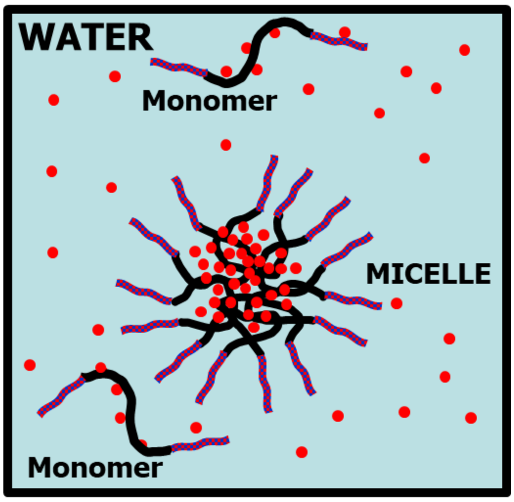
Return to Exercise 30⮥

Return to where text linked to Exercise 30⮥

Solution Exercise 31

A micelle is a self-assembly of amphiphilic molecules. In other words, amphiphilic molecules, when present in sufficient concentration, will form 3D structures in solution with their hydrophilic portions on the outside surrounded by water and their hydrophobic portions on the inside away from the water. Micelles form when the total concentration of a particular amphiphilic molecule exceeds what is called its critical micelle concentration, or CMC.

Extra information: Figure 52 illustrates one structure of a micelle formed from surfactants with a polar and a nonpolar end. Some surfactants have more complex structures, with both ends hydrophilic and a middle portion that is hydrophobic, such as illustrated below (two-tone textured hydrophilic ends, black hydrophobic middle). The micelle that forms when such a linear amphiphilic compound of this type exceeds its CMC is illustrated in the image shown here, with the black hydrophobic middle sections attracted to one another in the interior of the micelle. The red dots illustrate contaminant molecules that are dissolved in the water, sorbed to the middle portion of the monomeric surfactants, and sorbed to and held within the interior of the micelle.



A linear amphiphilic compound exceeds its CMC (redrawn, modified, and annotated from Rana et al., 2017).

The core of the micelle formed by the hydrophobic portions of the surfactants is the volume within which a relatively hydrophobic drug could be loaded, being released slowly once ingested. Perhaps you can imagine that similar uses might arise in groundwater remediation when there is some advantage to distributing in a water flush a hydrophobic remediation additive throughout a contaminated portion of the saturated zone or desorbing or dissolving sorbed or NAPL contaminants from within such a zone.

Return to Exercise 31↥

Return to where text linked to Exercise 31↥

Solution Exercise 32

The effect is most pronounced when the surfactant concentration exceeds its CMC (Figure 53 and Figure 54).

Return to Exercise 32⤴

Return to where text linked to Exercise 32⤴

Solution Exercise 33

DOM stands for dissolved organic matter. In uncontaminated groundwater, the two primary components of DOM are fulvic acids (FA) and humic acids (HA).

Return to Exercise 33⤴

Return to where text linked to Exercise 33⤴

Solution Exercise 34

Because the DOM molecules have hydrophobic and hydrophilic portions, the former can hydrogen bond with each other to pull the molecules into an aggregate, and the latter can be shielded from the surrounding water by this structure.

Return to Exercise 34⤴

Return to where text linked to Exercise 34⤴

Solution Exercise 35

Yes, but relatively weakly compared to other phases onto or into which they could partition (e.g., sorption to solid media). Microbes that are not transforming the contaminant are likely to be a minor sink for the contaminant unless the contaminant is very hydrophobic and the microbial population very large.

Return to Exercise 35⤴

Return to where text linked to Exercise 35⤴

Solution Exercise 36

Porosity refers most commonly to the fraction of the total volume of a geologic medium that is not filled with solids so would be filled by water when fully saturated or water and air when the medium is partially saturated. Or, if NAPL were present, NAPL would occupy some fraction of the total porosity, the rest being water or air.

Bulk density is the mass per total volume of medium.

Return to Exercise 36⤴

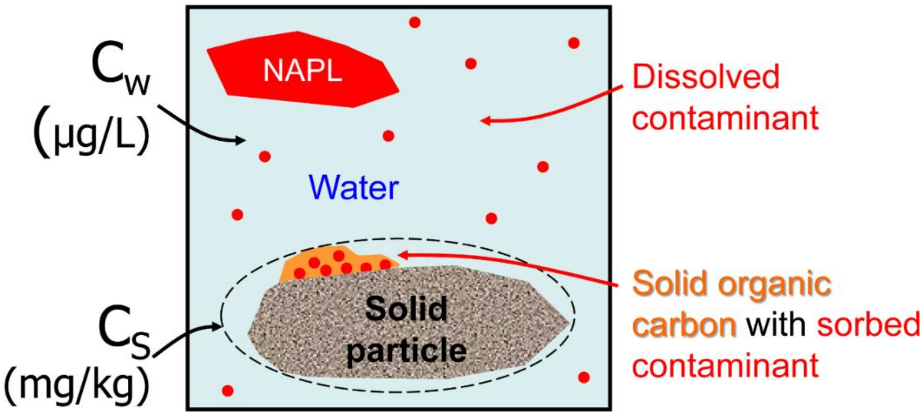
Return to where text linked to Exercise 36⤴

Solution Exercise 37

a) In addition to the total soil concentration, it would be necessary to measure or estimate site-specific values of f_{oc}, bulk density, and porosity. Compound-specific values needed are the K_{oc} and solubility.

b) We assume that site values of bulk density, porosity, and f_{oc} are applicable to the soil sample collected, although they probably are not measured on that specific soil sample. Because soil properties are heterogeneous, this introduces some uncertainty. However, if the bulk density and porosity are from the same geologic unit, uncertainties caused by these two properties will usually be modest. The f_{oc} distribution is also heterogeneous and its uncertainty contribution to the result could be the most significant of the site-specific properties. The uncertainty in the K_{oc} is probably within a factor of two or three and the uncertainty on tabulated compound solubility measurements can be significant. The assumption given in the exercise, that no contaminant is lost, may not be correct because it is easy to lose volatile contaminants while samples are manipulated in the field; by taking proper precautions a low proportion of VOC is lost.

c) The following image was created to help think through the solution.



d) The table shown here describes the steps taken and the equations used for each step of evaluating the presence of NAPL.

STEP	The concept of the step	Equation
1	If the total contaminant mass (M_T) is more than the mass in the water (M_w) at solubility and the mass sorbed (M_s) in equilibrium with the water, then there must be NAPL in the sample. So our start is to write the mass balance for when the total mass is only dissolved and sorbed phases.	$M_T = M_W + M_S$
2	The soil contaminant concentrations (C_T) are reported as the mass of contaminant per mass of the aquifer solids (m_s).	$C_T = \frac{M_T}{m_s} = \frac{M_w + M_s}{m_s}$
3	Next, we break down the total masses into their components of contaminant concentration in each phase and volume or mass of the phase. In this case, V_w is the water volume and C_w and C_s are the dissolved and sorbed concentrations. We do not need the volume of the solids because the C_T has units of mass of contaminant per mass of solids.	$C_T = \frac{C_w V_w + C_s m_s}{m_s}$
4	We translate the variables on the right-hand side (RHS) to quantities as they are measured and reported. We multiply numerator and denominator on the RHS by $1/V_T$, where the V_T is the aquifer volume sampled. And we substitute the definitions of the porosity ($\theta = V_w / V_T$) and bulk density ($\rho_b = m_s / V_T$).	$C_T = \frac{(C_w V_w + C_s m_s)/V_T}{m_s/V_T}$ $= \frac{C_w \theta + C_s \rho_b}{\rho_b}$
5	We relate the sorbed to dissolved concentrations using the sorption distribution coefficient ($K_d = C_s/C_w$). And we estimate the K_d from the compound K_{oc} and aquifer (or site-specific) fraction organic carbon content (f_{oc}) by this equation: $K_d = K_{oc} f_{oc}$.	$C_T = \frac{C_w \theta + K_{oc} f_{oc} C_w \rho_b}{\rho_b}$ $= C_w \left(\frac{\theta}{\rho_b} + K_{oc} f_{oc}\right)$
6	When C_w (in the Equation of step 5) > aqueous solubility, then NAPL must be in the sample. So, we solve for C_w.	$C_w = \frac{C_T}{\left(\frac{\theta}{\rho_b} + K_{oc} f_{oc}\right)}$
7	Determine whether there is liquid PCE in the sample with C_T =150 mg/kg PCE. Using values typical of a sandy aquifer and chemical property data for PCE from Broholm and Feenstra (1995) for the solubility (*S*) and the US EPA log K_{oc} reported in Mackay and others (1993), we calculate, in the next step, the expected concentration in solution as if there was no NAPL present.	$\theta =$ 0.31 [-] $\rho_b =$ 1.83 [kg/L] $f_{oc} =$ 0.10 [%] $log K_{oc} =$ 2.56; $K_{oc} =$ 363 [L/kg] $C_w^{sat} =$ 242 [mg/L]
8	We find that the result, 282 mg/L, exceeds the solubility (C_w^{sat}) of PCE in water and conclude that NAPL must be present.	$\frac{150}{\left(\frac{0.31}{1.83} + 363 * 0.0010\right)} =$ 282 mg/L

Return to Exercise 37↥

Return to where text linked to Exercise 37↥

18 About the Authors

Douglas M. Mackay is an Adjunct Professor Emeritus, who retired from the University of California, Davis, in 2017. His research addressed the transport and fate of organic contaminants and their transformation products in the vadose and saturated zones via field, laboratory, and numerical studies. His research team conducted controlled field experiments to explore constraints and opportunities for groundwater remediation technologies including methods for release and mixing of solutes (remediation amendments, tracers) into groundwater. His team also proposed and evaluated methods for estimating total mass discharge of, and thus risk presented by, contaminants flowing in groundwater, and identified a sensitive NAPL-detecting tracer. Field experiments illustrated factors limiting natural attenuation of organic contaminants in the vadose and saturated zones, including crude oil, refined petroleum products, ethanol-blended gasoline, gasoline oxygenates, pesticides, and halogenated solvents.

Richelle M. Allen-King is a Professor in the Departments of Geology and Environment and Sustainability at University at Buffalo, State University of New York. Her research has focused on the hydrogeochemical aquifer properties that control the fate and transport of contaminants in water. She led teams that conducted paired aquifer and outcrop analog mapping studies that provided insights on how the heterogeneous distributions of aquifer properties affect contaminant plume movement. In collaboration with colleagues, her teams have conducted extensive laboratory experimental work to decipher the effects of aquifer organic matter geologic maturity on contaminant retention by sorption. A recent collaborative field experiment provided a demonstration of how high sorbed concentrations in low permeability porous media can retain contaminants, and thus serve as a secondary source of contamination to more permeable media, which frustrates clean up and can limit natural biodegradation. While much of her work has focused on chlorinated solvents, she has also studied the fate and transport processes of pesticides, hydrocarbons, and most recently, selected per- and polyfluorinated alkyl substances (PFASs). She is also involved in numerous service roles within her university and the broader hydrogeologic community.

William G. Rixey is an Associate Professor in the Department of Civil and Environmental Engineering at the University of Houston. His research interests involve physicochemical processes, particularly mass transfer and phase equilibria, applied to fate and transport, remediation, and environmental risk assessment of chemicals in soil and groundwater. His research has included laboratory and large-scale experimental investigations of source generation and groundwater impacts associated with subsurface spills of MTBE, ethanol, and other organic compounds used in reformulated gasoline and other hydrocarbon-based fuels. He also teaches courses in water and wastewater treatment, hazardous waste treatment processes, and mass transfer in environmental systems.

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Modifications to Original Release

Changes from the Original Version to Version 2

Original Version: May 8, 2024, Version 2: September 19, 2024

Page numbers refer to the original PDF.

page i, added Version 2

page 4, corrected formula for acetylene in Figure 4

Changes from the Version 2 to Version 3

Version 2: September 19, 2024, Version 3: January 31, 2025

Page numbers refer to the version 2 PDF.

page iii, change version number and date

page 131, changed “research by Mackay and others (1990) has shown” to “unpublished work by Mackay and others conducted in 1990 showed”