Contaminant Sorption by Soil and Bed Sediment
Is There a Difference ?

Rapid industrialization since the mid-19th century has produced a large quantity and a wide variety of chemical wastes. Many relatively non-biodegradable chemicals originating from these wastes have spread throughout the environment, into water, soil and sediment. These chemicals may persist for indefinite periods, depending on their chemical properties and their interactions with the environment. Some of these chemicals are known to be harmful to humans and other species, either by direct exposure or by intake of contaminated water and food. Soils and sediments are important "sinks" for such contaminants because of their enormous quantities and their abilities to pick up, or sorb, large amounts of a wide variety of contaminants. It is essential to understand the mechanism by which the contaminant is sorbed to soil and sediment.

CORE SAMPLING

Collecting bed-sediment samples in the Mississippi River.

Drilling for soil samples near Bemidji, Minnesota

Sorption to soils and sediments is probably the most influential factor on the transport and fate of organic contaminants in the environment. The extent of the sorption to soil and sediment affects not only the contaminant level in an ecosystem, but the movement and fate of the contaminant as well. For example, in a hydrogeologic system, the increased sorption of a contaminant to soil and sediment reduces its level in the adjacent water column, and thus decreases its exposure and transport to other parts of the ecosystem, such as fish and plankton.

## Soil mineral matter versus soil organic matter

The way in which contaminants are sorbed into soil or sediment varies with the nature of the contaminant and the makeup of the soil and sediment (Chiou and others, 1979; Karickhoff and others, 1979). The composition of soil and sediment includes both mineral matter and organic matter as the primary constituents. Under relatively dry conditions, the soil/sediment mineral matter acts as an *adsorbent*, where the sorbed organic compounds are held on the surface of the mineral grains. The soil/sediment organic matter (SOM) acts as an *absorbent*, or a partition medium, where the sorbed organic compounds dissolve (partition) into the matrix of the entire SOM. The soil or sediment, then, is characterized as a dual-function sorbent, in which the mineral matter sorbs the contaminant by adsorption while the SOM sorbs the contaminant by a partition process (Chiou and others, 1983; Chiou and Shoup, 1985; Chiou and others, 1985).

Adsorption versus partition process

Consider a natural water system with many organic contaminants present. Adsorption to soil/sediment mineral matter occurs as a consequence of the competition between all species, including water. In the presence of water, the soil/sediment mineral matter prefers to *adsorb* water

In the presence of water with many contaminants, water is adsorbed on the surface of mineral matter, whereas, contaminants are absorbed into the organic matter by a partition process.
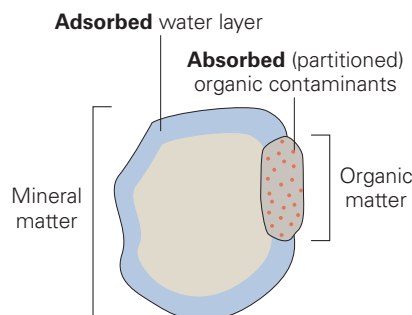
Adsorbed water layer

Absorbed (partitioned) organic contaminants

Mineral matter

Organic matter

because of their similar molecular polarities, while the soil organic matter prefers to *absorb* the contaminants (organic solutes) in water. This means that the (nonionic) organic contaminants are not significantly adsorbed to minerals, and that the partition of a contaminant is not affected by water or by other contaminants. So two processes are at work: (1) the organic contaminants are competitively prevented by water from adhering to the surface of the soil mineral matter, while at the same time, (2) the organic contaminants are able to partition independently into the SOM. Because so many environmental contaminants are transported by ground water and surface water, it is important to understand the unique function of the soil organic matter within these aquatic systems and how the partition processes affect the fate of common environmental contaminants.

Calculating the distribution of contaminants

In aquatic systems, a linear relationship exists between the concentration of a contaminant solute in soil/sediment and the concentration of the contaminant in water at equilibrium. In other words, when the concentration of a contaminant in water is increased, the concentration of that contaminant in the soil/sediment will also increase by a constant factor. This linear relationship is expressed mathematically via the solute distribution coefficient, which is the ratio of the solute concentration in soil (C_s) to the solute concentration in water (C_w).

$$K_d = \frac{C_s}{C_w}$$

K_d is the solute distribution coefficient, C_s is the solute concentration in soil/sediment, and C_w is the solute concentration in water. Knowing the concentration of a contaminant in one compartment, either water or soil/sediment, thus allows scientists to predict the concentration of a contaminant in the other compartment. Because the contaminant sorption occurs predominantly by partition into the soil organic matter, it is more useful to express the distribution coefficient in terms of the SOM content.

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

In this equation, K_{oc} is the partition coefficient normalized to the organic carbon of the soil/sediment, and f_{oc} is the organic carbon fraction of the soil (or sediment). By normalizing the partition coefficient to the soil organic matter (organic carbon) content, scientists can then compare the relative partition properties of the organic matter from different geographic sources. Any variation between soils (or sediments) from different geographic sources can then be attributed to the variation in SOM properties.

Study objective and approach

To what extent do the soil organic matter properties differ among soils and sediments of diverse geographic origins? If it is found that the contaminant sorption to organic material in different soils or sediments varies widely, then it would be necessary to study each soil individually. This would be a time-consuming process. On the other hand, if the contami-

nant sorption to the organic material in different soils or sediments shows only minor variation, then contaminant sorption could be quantified collectively, at a great savings of time and effort. A study was undertaken by the U.S. Geological Survey to provide the answer by comparing the organic-carbon normalized partition coefficients (K_{oc}) of selected organic contaminants on a large number of soils and sediments (Kile and others, 1995).

Sampling

The organic carbon partition coefficient (K_{oc}) values were measured for carbon tetrachloride (CT) and 1,2-dichlorobenzene (DCB), on 32 soil samples from widely diverse geographic regions in the United States and People's Republic of China, and 36 bed-sediment samples from widely diverse aquatic systems within both countries. All U.S. soils and some Chinese soils were taken from the soil layer (or zone) that lies near the surface and is characterized to be the zone of maximum water leaching.

All other Chinese soils were taken from depths about 1 meter below the land surface to minimize the impact of agricultural practice. The bed-sediment samples were taken from the top 0–20 centimeters of the sediment surface. Sediment samples include those from rivers, freshwater lakes, and marine bays or harbors. Soil and sediment samples were dried, ground, and homogenized to pass a 35-mesh sieve (U.S. samples) or a 200-mesh sieve (Chinese samples).
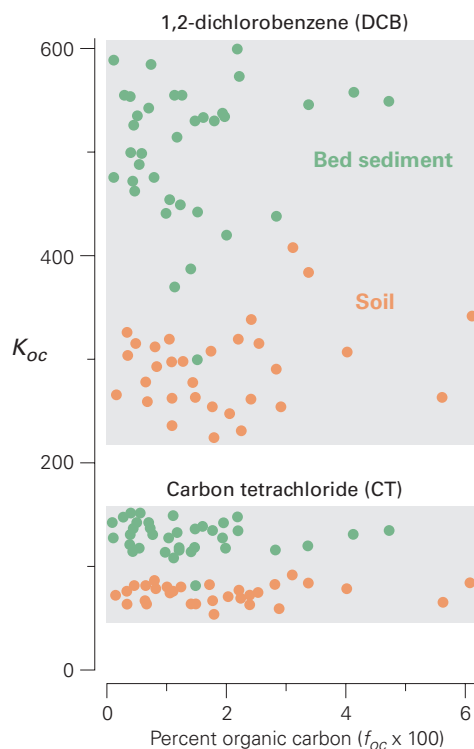
Five river-suspended solids were also collected for the sorption experiments. Suspended solids were collected in June 1989 from the Illinois River at Hardin, Illinois, during a low-to-normal river flow and from the Missouri River at Herman, Missouri, during a moderately high flow. Suspended solids from the Mississippi River at Thebes, Illinois, and St. Louis, Missouri, were collected during a high river flow in June 1990. The collected water was processed by filtration through a 63-micrometer sieve to remove the sand fraction, followed by continuous-flow centrifugation.

		K_{oc}	
Soil samples	%OC	CT	DCB
1. Oliver Co., N. Dakota (USEPA* reference soil 3)	1.43	53	277
2. West-central Iowa (USEPA reference soil 10)	2.04	58	248
3. Manchester, Ohio (USEPA reference soil 12)	2.25	57	230
4. Anoka, Minnesota	1.08	61	261
5. Spinks soil, East Lansing, Michigan	1.03	65	318
6. Woodburn soil, Corvallis, Oregon	1.26	65	296
7. Anda, Heilongjiang, China	2.83	67	288
8. Nanjing, Jiangsu, China	1.08	61	236
9. Gangcha, Qinghai, China	1.12	62	295
10. Luochuan, Shanxi, China	0.46	66	315
11. Xuwen, Guangdong, China	0.64	55	257
12. Qiongzhong, Hainan, China	0.34	62	304

Bed-sediment samples	%OC	CT	DCB
1. Isaacs Creek at Ohio River, Ripley, Ohio (USEPA reference sediment 11)	1.50	66	301
2. Illinois River, near Lacon, Illinois (USEPA reference sediment 22)	2.20	116	572
3. Mississippi River, Helena, Arkansas	1.60	109	534
4. Mississippi River, St. Francisville, Louisiana	0.40	119	549
5. Lake Charles, adjacent to the Calcasieu River, Lake Charles, Louisiana	1.97	112	536
6. Marine sediment from Suisin Bay, northern San Francisco Bay, California, site 416	1.48	107	532
7. Tumen River, Helong, Jiling, China	1.99	93	420
8. Xuanwu Lake, Nanjing, Jiangsu, China	4.12	103	557
9. Zhujiang River, Guangzhou, Guangdong, China	3.37	95	545
10. Yellow River, Zhengzhou, Henan, China	0.11	112	589
11. Sangonghe River, Fukang, Xinjiang, China	0.38	103	499
12. Lake Pumo, Langkazi, Tibet, China	1.94	101	539

*USEPA—United States Environmental Protection Agency

This table is a partial list of the K_{oc} values calculated from the soil/sediment samples. They are plotted on the figure to the right.

%OC = Percent of soil/sediment organic carbon content
K_{oc} = Measured partition coefficient
CT = carbon tetrachloride
DCB = 1,2-dichlorobenzene

32 Soil samples
Mean K_{oc} for CT is 60 (SD = ± 7).
Mean K_{oc} for DCB is 290 (SD = ± 42).

36 Bed-sediment samples
Mean K_{oc} for CT is 102 (SD = ± 11).
Mean K_{oc} for DCB is 502 (SD = ± 66).

The means for the bed sediments are about 1.7 times the means for the soil samples.

The suspended solid from the Yellow River, near Zhengzhou in Henan Province, People's Republic of China, was collected in August 1991 during the high-flow season from a depth of 0.5 meters below the water surface. The water samples were pooled, and the suspended solids were separated by gravitational settling over night.

Study results

The finding that K_{oc}'s for DCB are generally about five times the K_{oc}'s for CT on all soil and bed-sediment samples is consistent with the difference in water solubility of CT (800 milligrams per liter) and DCB (154 milligrams per liter), which is also approximately a five-fold difference, and with the similarity of their solubilities in soil organic matter (Rutherford and others, 1992).

The high degree of invariance of the K_{oc} values of CT and DCB between most soils or between most bed sediments is striking, since these samples came from widely dispersed locations in the United States and the People's Republic of China. This invariance suggests that the properties of the soil or sediment or-

1,2-dichlorobenzene (DCB)

Bed sediment

Soil

K_{oc}

Carbon tetrachloride (CT)

Percent organic carbon (f_{oc} × 100)

These plots show the K_{oc} values of CT and DCB on the studied soils and bed sediments.

K_{oc} values of both DCB and CT from most soils do not vary much between regions, which suggests similar properties for relatively uncontaminated soils.

Higher K_{oc} values of DCB and CT in bed sediments suggests that the process that turns soils into bed sediments results in a change of the organic properties.

The variation in K_{oc} within bed sediments reflects the extent of conversion of soils to bed sediments—the older sediments have higher K_{oc} values.

A noncontaminating Isokinetic sampler (made entirely of Teflon®) was used to collect samples of bed sediment, water, and suspended sediment.

ganic matter that control nonpolar solute solubility are quite similar for a wide variety of uncontaminated shallow soils and also likely for relatively pristine surficial bed sediments. It appears that there may not be much variability in the soil organic matter polarity and composition between soils of relatively shallow depths from diverse geographic locations. This speculation will be further tested.

The fact that most soil K_{oc}'s are distinct from bed sediment K_{oc}'s suggests that the process that turns eroded soils into bed sediments brings about a noticeable change in the property of the organic constituent. A possible cause for this change is that the sedimentation process fractionates soil organic constituents such that the more polar and more water-soluble organic components in soil organic matter are separated out to form dissolved organic matter and colloids in water, and hence the less polar organic constituents in soils are preserved in the bed sediment. The time scale required to bring about a complete soil-to-sediment conversion should depend, among other factors, on river depth and flow dynamics.

Part of the variation in K_{oc} within bed sediments may reflect the extent of conversion of the eroded soils to bed sediments. Recently eroded soil retains most

of its soil organic composition and has significantly lower K_{oc} values. The difference between soil and bed-sediment K_{oc} values as detected by relatively nonpolar solutes provides a basis for identifying the source of suspended solids in rivers. For instance, the K_{oc} values for CT and DCB in the suspended solids for the rivers sampled at high water are typical of those for soils, whereas the K_{oc} values for CT and DCB in the suspended solids for the one river sampled at low-to-normal flow are more representative of bed sediments. The assumption can be made that the suspended solids from high-water flows consist mainly of newly eroded soil, and the suspended solids from low-to-normal flows consist largely

This table is a list of the K_{oc} values for river-suspended solids. K_{oc} values can serve as an indicator of the source of suspended soils. For example, K_{oc} values for CT and DCB for the rivers at high water, such as the Yellow and Mississippi, are typical of those for soils.

Suspended-solid samples	%OC	K_{oc}	
		CT	DCB
1. Mississippi River, Thebes, Illinois	1.82	60	296
2. Mississippi River, St. Louis, Missouri	1.78	58	283
3. Illinois River, Hardin, Illinois	2.60	89	423
4. Missouri River, Herman, Missouri	2.87	49	231
5. Yellow River, Zhengzhou, Henan, China	0.38	63	300

of resuspended bed sediment. Thus, sorption data serves as a simple indicator of the source and time history of the suspended solids.

Comparison with contaminated sites

Marine bed sediment samples were collected from Fort Point Channel of Boston Harbor, which is known to be severely contaminated by hydrocarbons. Bed sediments were collected from the Bayou d'Inde, which drains industrial wastewaters into the Calcasieu River downstream from Lake Charles, Louisiana, and is contaminated by chlorinated hydrocarbons. From Bemidji, Minnesota, soil was collected from an oil-spill site. In comparison with the K_{oc} values with normal soils and sediments, the Bayou d'Inde sediments yield noticeably higher K_{oc} values, and the sediment from Fort Point Channel of Boston Harbor and the soil from Bemidji exhibit exceptionally high K_{oc} values, which are 5–10 times the values for uncontaminated soils and sediments. A

> The K_{oc} data may serve as an effective sensor for contamination in soils and sediments.

This soil sample was taken from Bemidji, Minnesota.

similar effect was reported by Sun and Boyd (1990), who noted that nonpolar solutes exhibit unusually high K_{oc} values on soils contaminated by petroleum and/or polychlorinated biphenyl (PCB) oils. The sorption data may serve as an effective sensor for relatively high levels of contamination in soils and sediments.

Implications and environmental applications

The K_{oc} data of both CT and DCB on most normal soils from shallow depths are shown to be quite invariant, suggesting that soil organic matter at such depths from diverse geographic sources maintains a comparable polar-to-nonpolar balance and possibly a comparable composition. However, soil samples are genuinely different from bed-sediment samples in terms of their K_{oc} values. The average K_{oc} values for nonpolar solutes on bed sediments are about twice those on soils, suggesting that sediment organic matter is in general less polar in nature than soil organic matter. This unique geochemical disparity has not been documented until now. The observed difference in K_{oc} between the soil and bed sediment samples must be taken into account in future studies. Because it has now been shown that K_{oc} values for soils are largely consistent worldwide, just as K_{oc} values for sediments are largely consistent worldwide, K_{oc} values can be used to assess the sorption of nonpolar contaminants to

the organic matter of different soils/sediments. This finding should result in considerable savings in cost and time for contamination studies.

—C.T. Chiou and D.E. Kile

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