Chapter 7 Synthetic Organic Chemicals in Biosolids

Society produces and consumes immense quantities of organic chemicals. Synthetic organic chemicals are made in the laboratory and as by-products of manufacturing, burning, or other human activities. "Organic" once described anything that was originally living matter; in the scientific world, however, any substance containing carbon molecules is organic. Here, synthetic organic chemicals are referred to simply as organics to distinguish them from organic matter derived from plants and animals. Natural processes do not create organics of general environmental concern.

The differences between organics and trace metals are important. In particular, concentrations of organics are extremely low in biosolids – industrial pretreatment and household hazardous waste programs are working well. Metals can be measured at 10 to 1000s of parts per million (ppm, 10-1000s of mg/kg), but organics seldom reach concentrations of 1 ppm and often are either below detection levels or measured in the parts per trillion (ppt) range. Their toxic potential in biosolids is thus remote, even though they are far more toxic than metals at similar concentrations. A few of the more common organics are listed in Table 7.1, and some are present in biosolids because households and industries continue to discharge minute amounts as sewage.

The levels of organics are very low in biosolids for two reasons. First, increased awareness of their dangers has led to regulations eliminating persistent ones in favor of others that are more easily degraded. Second, many organics are volatile. Compounds such as benzene, trichloroethylene, and chloroform are lost to the atmosphere in sewers and aeration basins of wastewater treatment facilities. Also, unlike metals, organics degrade with time. Some degrade very slowly, but many of the most persistent are no longer produced (e.g., polychlorinated biphenyls -- PCBs -- once commonly used in transformers). Because current organics are designed to degrade relatively quickly, they do not linger in the environment. PCBs are no longer made, so their concentrations in sewage and the environment continue to decline, as do those of pesticides and herbicides such as DDT, dieldrin, eldrin, and 2,4,5-T.

Table 7.1. Examples of synthetic organic compounds and their origin (taken from NRC 2003).

Class	Origin	Examples
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene Phenanthrene Benzo[a]pyrene Pyrene	Combustion of coal, oil, and wood Asphalt, creosote Automobile emissions, fuels, and lubricating oils
Nitroaromatics	2,4,6-trinitrotoluene (TNT) Trifluralin Benefin Ethalfluralin Methyl parathion	Military installations Bombing ranges Bactericides Pesticides
Phenols, anilines	Pentachlorophenol (PCP) Phenylamide herbicides: phenylureas, phenylcarbamates, and acylanilides	Wood preservatives Biocides Dyestuff wastewater Phenylamide herbicides
Halogenated aromatics	Polychlorinated biphenyls (PCBs) Dioxins	Hydraulic oils, capacitor dielectrics Pesticide applications Incineration of medical/municipal waste, hazardous waste, and sewage sludge Forest fires and volcanic eruptions Cement kilns and boilers Petroleum, coal, and tire combustion Draft black liquor boilers Secondary lead smelting
Halogenated aliphatics	Chloroform Bromomethane Carbon tetrachloride Vinyl chloride 1,1-dichloroethene Trichloroethene (TCE) Tetrachloroethene (PCE)	Degreasing solvents Former dry-cleaning facilities Plastics manufacturing
Pesticides and herbicides	Alachlor Aldicarb Atrazine BHC Carbofuran Chlordane 2,4-D Toxaphene DDT (DDD, DDE)	Agriculture Residential and industrial pest control
Petroleum hydrocarbons	Benzene Xylenes Toluene Ethylbenzene Alkanes	Oil recovery and refining industry Automobiles and other forms of transportation Oil tankers, pipelines, and other modes of transporting oil Industry

Synthetic organics have numerous origins, such as the phthalates used as binders in plastics, which are so ubiquitous that inevitably some gets into wastewater. Similarly, the most important source of dioxins is the textile industry, which uses dyes containing dioxin. These dyes wash out of fabrics in laundering; however, dioxin levels are far lower in newer fabrics, so wastewater dioxin levels are declining.

Degradation of synthetic organics

Most organics break down in wastewater treatment and continue to do so after they are applied to land. When a compound decomposes it breaks into molecularly smaller, more innocuous compounds by one or more of three different processes: photochemical, chemical, and biological.

The photochemical process involves the energy of light, usually from the sun. In some cases this energy is sufficient to break a molecule; an example is the effect of sunlight on certain plastics, which may discolor, crack, and lose strength. A similar process – chemical decomposition – takes place when other chemicals react with a compound, resulting in breakdown of the organic molecules into simpler compounds usually having different, less toxic chemical properties than the original, more complex molecules.

Biological degradation is by far the most common natural process attacking these chemicals. Biodegradation involves microorganisms such as bacteria and fungi naturally living in soils; they are part of the soil's ecosystem and are necessary for its overall health. These microorganisms break down organic compounds for energy; in so doing they literally consume organic pollutants, ultimately reducing them to carbon dioxide, water, and methane. As synthetic organics are spilled, deposited, or otherwise used in the environment, microorganisms have adapted to degrade them in exchange for energy; for example, strains of bacteria have evolved to degrade PCBs and dioxins (Pearce 1994).

Many factors influence the amount of biodegradation taking place in soils: absence or presence of oxygen, pH (or acidity), amounts of other necessary nutrients available to microorganisms (e.g., nitrogen, phosphorus, potassium), and whether the structures and types of compounds are amenable to biodegradation. Complex chemicals are more difficult for soil microbes to degrade and thus remain in the environment longer. Two are important to consider: PCBs and dioxin.

Contaminant entry into an organism

Any synthetic organics in the soil are potentially invasive and, once inside an organism, may be toxic. However, not all organics can invade nor are they all harmful. Active chemicals capable of direct impact are termed bioavailable. Each step a contaminant must take to cause harm has a different bioavailability. A contaminant bound to a soil particle can invade an organism only by direct ingestion of soil; once ingested, only a very small portion is available and the remainder passes through and is eliminated.

In contrast, a contaminant that has been released from a soil particle can enter an organism by direct ingestion, plant uptake followed by consumption of the plant, leaching into water that is then consumed, or inhalation after volatilization. Once in an organism, a contaminant likely is bioavailable and may accumulate to toxic levels, even though much of it may still be eliminated.

The fate of PCBs and dioxins

PCBs are found occasionally in biosolids, although in ever-decreasing concentrations. Industry has curtailed their manufacture, but some are still present in the urban environment in older electrical equipment and in industrial outputs; because they are persistent, measurable quantities are sometimes found in sewers and biosolids. In the National Sewage Sludge Survey conducted in 1988-1989, four of the different PCB compounds were absent from all 198 biosolids wastewater treatment plants sampled; low concentrations of the other three PCB compounds were present in only 10% of the treatment plants.

Dioxins and furans are general names of two classes of synthetic organic compounds called polyhalogenated aromatic hydrocarbons (PCDD/Fs). They are found everywhere in the environment – water, soil, and air – principally as byproducts of other processes, such as PCB synthesis, bleaching wood pulp, diesel fuel, burning materials like wood that has chloride in it and municipal waste -- even forest fires and volcanic eruptions. Once airborne, they disperse readily and are re-deposited on the soil and water. Many manufacturing processes that inadvertently created dioxins have been changed or eliminated to reduce their incidence.

There are 210 different compounds (called congeners) making up these classes, distinguished by the number of chlorine atoms each has and how the atoms are arranged around the eight positions available. Seventeen are considered toxic, and those 17 vary in toxicity. Toxic equivalents (TEQs) were devised to compare concentrations of these compounds. The concentration of a particular compound is multiplied by how toxic it is compared to the most toxic congener (2,3,7,8 TCDD). All the compounds are then be added together to yield a single TEQ value.

Recent analysis of biosolids from several US wastewater treatment plants showed ranges of 6 to 3600 pg/g TEQ (a picogram/g equals 1 g in 1,000,000,000,000 g of dry biosolids, or 1 part per trillion), although half the samples tested were below 15 pg/g TEQ. As with other toxic organics, these concentrations have decreased from their peaks in the 1950s. For example, archived biosolids show concentrations peaked in 1956 (Sewart et al. 1995), decreasing to near-background levels in 1992.

Concentration of dioxins in biosolids (parts per trillion)

Year	1942	1944	1949	1953	1956	1958	1960	1992
Conc	18	36	61	127	402	229	166	0.4-29

Both PCBs and PCDD/Fs are potent carcinogens. For this reason, PCBs have long been the focus of studies of organics in biosolids (MMSD 1988, Furr et al. 1976, Moza et al. 1979), while investigations of dioxins and their behavior in biosolids and soils are more recent. However, the majority of studies on the fate of PCBs and dioxins have centered on sites with far higher levels of these compounds than are present in biosolids. The results thus reflect a situation that exaggerates their overall concentration and behavior when compared to actual concentrations in biosolids intended for land application.

Soils and plants. In most cases, PCDD/F and PCB concentrations in biosolids are higher than those in soils. Repeated applications can increase the soil concentration, but very slowly. At a median concentration of PCDD/F of 15 pg/g and with a yearly application of 3 dry tons per acre, the concentration in the top 6 inches of soil would still be less than 1.0 pg/g after 100 years. The concentration stays so low after repeated applications because some decomposes each year. The estimated half-life (the time it takes half to decompose) of PCDD/F is 10-20 years. If a 15-year half-life is assumed, 91% remains after 1 year, 61% after 10 years, and only about 8% after 50 years. At these relatively low concentrations, background levels in the soil profile may exceed the amounts added; in fact, atmospheric deposition of PCDD/Fs typically adds more TEQs than are added by biosolids amendments.

PCDD/Fs typically are highly adsorbed by soil organic matter, do not volatilize, and are relatively insoluble in water -- all reasons why they decompose slowly and linger in the soil (GAO 2002). Field studies have shown that these compounds remain in the soil for many years, corroborating evidence of long half-lives. By contrast, volatile compounds or those that decompose readily may decline to background levels in less than a year.

Plant uptake of these compounds is minimal for the same reasons they do not degrade. Very small amounts have been found in plants, other than by adherence of soil particles to plant parts (e.g., peels of root crops) or water splashing soil particles onto them (Chaney et al. 1996). Also, small amounts have been found in crops with oily roots (e.g., carrots) (Muller et al. 1994). Most of the relevant research has been conducted on soils contaminated by forms of these compounds more pure than those found in biosolids where the compounds are far less available to plants due to strong adsorption by organic matter. Plant uptake of PCBs applied to soils generally is also very minimal; for example, only small percentages have been reported in agricultural crops, although root crops may have concentrations higher than those of other crops (Duarte-Davidson and Jones 1996). Plant uptake depends upon compound solubility, as more soluble compounds are taken up more readily. In the case of PCBs and PCDD/Fs, those with fewer chlorine atoms are more soluble and taken up more easily than those with four or more chlorine atoms. (Compounds with fewer chlorine atoms are also less toxic.)

Humans. Estimates of human exposure to PCDD/Fs are based almost solely on food consumption. Infants have the highest estimated daily intake followed by children, the major reason being the high daily milk consumption and low body weight of both groups. For the general US population, the EPA estimates that 62% of PCDD/F intake is from meats, eggs, and fish, 35% from milk and dairy products, and 3% from fruits and vegetables; however, all PCDD/F levels are in decline due to reduced emissions.

A risk assessment study predicted total dioxin exposure to be 2.6 ppt per kilogram per day, based on the very conservative parameter of someone whose food was entirely derived from biosolids-amended soil (Jackson and Eduljee 1994). The limit in the United Kingdom (where the study was made) is 10 ppt per kilogram per day. According to this model and its assumptions, application of biosolids to agricultural lands presents no significant health risk, and other studies report similar findings. Despite the presence of some PCBs and dioxins in biosolids and their potential migration into the food chain, current research has demonstrated that land application of such biosolids poses no significant risk to humans who eat the resulting agricultural crops (Jackson and Eduljee 1994).

Other animals. PCBs and PCDD/Fs from biosolids reach animals via plant uptake followed by consumption, splashes of PCBs and PCDD/Fs on plant shoots followed by ingestion, or direct ingestion of soil. Because plant uptake is minor, by far the most important exposure pathway for grazing animals is direct ingestion of soil and biosolids particles. Ingestion is a problem for grazers such as cattle, which regularly consume soil along with plant matter. When cattle were given PCDD/Fs in their feed, only small amounts were absorbed; feces and milk were important excretion routes -- about 20% of that taken up by a cow was excreted in her milk (McLachlan 1990).

Studies on wildlife failed to find chemically induced health problems after heavy applications of pulp and paper waste residuals to pine plantations and reclaimed mine sites (McFadden et al. 1995). Biosolids with PCDD/F concentrations as high as 50-80 ppt TEQ were evaluated in studies that included several species of birds, small mammals, and soil fauna. There were no bioaccumulations in rodents, insects, or earthworms nor were levels detectable in fish, algae, and back-vegetation in a lake receiving runoff.

Regulations

When the EPA analyzed a large number of treatment plants in 1988-1989 (the National Sewage Sludge Survey), the organics in biosolids were lower than expected, especially compared to the 40-Cities survey done in the late 1970s (Table 7.2, note that pollutant limits are in parts per million, while concentrations are in parts per trillion). At that time, a policy decision was made to delete synthetic organics from biosolids regulations because the risk was so insignificant. The reasoning for exempting organics is as follows.

1. The pollutant has been banned from use, has restricted use, or is no longer being manufactured for use in the US.
2. The pollutant was not detected in many of the biosolids (less than 5%) in the National Sewage Sludge Survey.
3. The concentration of the pollutant in biosolids is already so low that, when applied to soils, it would be less than that determined safe by the exposure risk assessment.

Table 7.2. Chemical organics in biosolids evaluated for risk to humans and the environment (modified from NAS 1996 and EPA 1995).

Pollutants	Limiting pathway (ppm)	Pollutant limit (ppm)	1970 Conc[1] (ppt)		1988 Conc[2] (ppt)	
Aldrin/Dieldrin	adult eating animal products	2.7	6.4	(16%)	1.9	(3%)
Benzo(a)pyrene	child eating biosolids	15	138	(21%)	-	(3%)
Chlordane	child eating biosolids	86	6.4	(16%)	-	(0%)
DDT	adult eating fish/drinking water	120		(0%)	-	(0%)
Heptachlor	adult eating animal products	7.4	6.4	(16%)	-	(0%)
Hexachlorobenzene	adult eating animal products	29	155	(16%)	-	(0%)
Hexachlorobutadiene	adult eating animal products	600	23	(5%)	-	(0%)
Lindane	child eating biosolids	84	6.4	(16%)	-	(0%)
Dimethylamine	child eating biosolids	2.1	57	(5%)	-	(0%)
Toxaphene	adult eating animal products	10	6.4	(16%)	-	(0%)
Trichloroethylene	child eating biosolids	10000	8139	(84%)	-	(1%)

[1]Averages from the 40-Cities Study conducted in the late 1970s.
[2]Averages from the National Sewage Sludge Survey conducted in the late 1980s.
Numbers in parentheses are the percentage of wastewater treatment plants in which a compound was detected.

The EPA is now in the process of adding numeric concentration limits for PCDD/Fs and PCBs in biosolids applied to land. As an example of the magnitude of concentration limits that may be proposed, in 1994 the EPA entered into a

Memorandum of Understanding with the pulp and paper industries (which at the time had significant concentrations of dioxins in their residuals). This memorandum states that residuals with less than 10 ppt TEQ would be unregulated; for those exceeding 10 ppt TEQ to a maximum concentration of 50 ppt TEQ, the soils to which waste residuals were incorporated must not exceed 10 ppt TEQ in the soil/residual mixture.

Summary

Society produces large amounts of synthetic organic compounds. Because of widespread use, some find their way into sewer systems, survive wastewater treatment, and reappear in low concentrations in biosolids. In general concentrations are extremely low and most organics eventually degrade.

In the rule-making process for biosolids, the EPA sought those organics that presented the greatest risk to humans and the environment. An exposure risk assessment indicated that concentrations in current biosolids were far below accepted limits. In addition, concentrations of many organics in biosolids were dramatically decreasing as the result of industrial pretreatment, household hazardous waste programs, and halting production of the most toxic chemicals (such as PCBs). Synthetic organics also pose little risk because they are difficult to assimilate. The main exposure route for humans and other animals is by direct ingestion of soil containing biosolids or consumption of fat from animals that ate soil. Plants take up insignificant amounts of organics and those that are taken up are strongly adsorbed to soil particles, especially by the organic fraction of biosolids. Studies have shown that PCBs and dioxins/difurans pose little risk, despite their high toxicity.