Organic chemical contaminants in Biosolids

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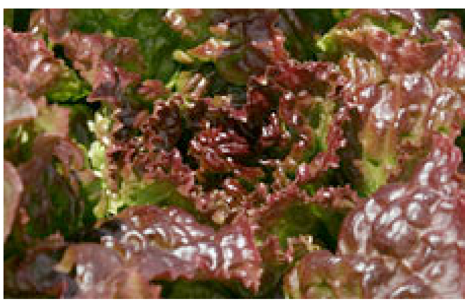
What are organic chemicals?

"Organic chemicals" (or "organics") is the name for an enormous range of chemicals that have in common one central characteristic: they contain the element carbon. Like all things that are made out of carbon, organic contaminants will degrade over time to simple carbon dioxide. The time required to turn these compounds back to carbon dioxide will vary , depending on the complexity of the compound. For example, both a head of lettuce and the plastic bag that you put it in at the supermarket are organic, carbon based materials. The lettuce will break down in a matter of days or weeks - as those of us who have been asked to clean out the vegetable bin in the refrigerator can attest. Plastics, on the other hand, can persist in the environment for decades.




There are a wide range of chemicals that can be classified as organic. For example, all plants, animals, and people are carbon based and can be classified as organic. Perfume, shampoo, and laundry detergent are also classified as organic. Carbon can bind to both itself as well as to other elements. Organic chemistry is the science that deals with the different types of organic compounds and explains their behaviors and persistence. The names of different organic chemicals are often derived from their differing carbon structures. For example, trichloroethylene, or TCE, is an organic contaminant that, in the past, was commonly used as a solvent for industrial cleaning, as well as by your neighborhood dry cleaner. The hazards associated with too much TCE in the environment were brought to light in the book 'A Civil Action' by Jonathan Harr. The name of this chemical simply describes its structure: it is an ethylene group with three chloride atoms attached to it ("trichloro").

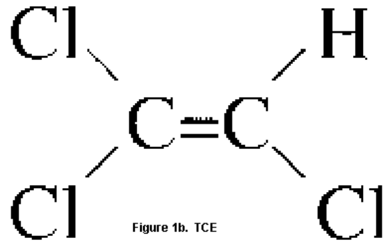


Figure 1b. TCE

The chemical trichloroethylene is drawn above

In many cases, names of different organic chemicals are representative of different families of compounds. This is the same as names for different styles of homes. A colonial is a home that has two stories with a central staircase. All homes that fall under this classification will share some properties, but they won't all look exactly alike. One example of this is the broad class of organic compounds that fall under the general classification "dioxins." Dioxins are one of the well known dangerous organic chemicals. Dioxins had commercial uses, primarily in the pulp and paper industry, but have been outlawed due to their toxicity. They can also occur naturally when different organics are burned when chloride ions are present. There are many types of dioxins. "Dioxin" is actually a general term for a large number of compounds that contain two oxygen atoms that substitute for carbon in one of their ring structures. Within this class of compounds, the different forms are generally referred to as "congeners." The dictionary definition of congener is a 'member of the same class or group'. If you go back to the home analogy, different congeners are the equivalent of colonial houses, one with 3.5 baths, one with a Jacuzzi tub, one with stall shower, and so on. All fit under the general umbrella "colonial, but each has a distinct feature. In the case of chemical congeners, such distinct features can potentially create different properties and toxicities. For example, while there are 75 forms of dioxins, only 7 of them are sufficiently toxic to merit concern for human health. These are the congeners that have chlorine atoms attached to the carbons at the 2, 3, 5, and 7 positions.

Toxic organic chemicals

Once an organic chemical is labeled as a contaminant, the implication is that it is potentially dangerous, or toxic. In some cases, these chemicals were created by scientists to *be* toxic; examples here include different herbicides and pesticides. However, in many instances, these compounds were synthesized for specific purposes and the potential dangers associated with their use have only been recognized over time. One example of this involves a class of compounds called poly-brominated di-phenol ethers, or PBDEs. (A translation of this name: "poly-brominated" means that these compounds have a varying number of bromine atoms attached. "Diphenol" means that there are two phenol groups, with a phenol group being a ring of carbon atoms with a hydroxyl group attached. Finally, an "ether" consists of two carbons with an oxygen in the middle.) These compounds were developed to be used as flame retardants. They are very effective at reducing the potential for fire and the spread of fire. They have proven to be so effective that they are currently in use in a wide range of common household products including furniture cushions, infant pajamas, TV sets, and computers. Because they are so common in the home, as well as in industry, they are found in biosolids, household air, food products, wild fish, and human breast milk (Hale et al., 2001; Schecter et al., 2004; Stapleton et al., 2005). Because of their utility for modern society, PBDEs have become ubiquitous in the environment. As trace concentrations of PBDEs have been found in a wide range of environments where they were not intended to be, there has been increasing concern about potential environmental and health effects of these compounds. In some countries, as well as in parts of the US, particular types of PBDEs have been banned.

The danger posed by any organic chemical – its toxicity – depends on three things:

1. its concentration – how much of it there is
2. the susceptibility of the organism that is exposed to that concentration – some organisms are not affected by some chemicals, while others are; for example, some people are highly affected by the natural organic chemical in poison ivy, while others are not
3. the exposure – whether or not and for how long the susceptible organism has contact with the chemical.

In the example of PDBEs, while there are significant concentrations of PDBEs around us all the time, we are not exposed to them because they are bound in the cushions, computers, etc. to which they are added. Only when these things break down and release very small particles of PDBEs, does exposure become possible, and, then, much smaller amounts can apparently cause harm to living organisms.

Furniture cushions typically contain 100,000 to 300,000 parts per million flame retardants (PBDEs).

How different organics behave in the environment

Organic chemicals can be placed into two broad groups: hydrophilic and hydrophobic. The hydrophobic chemicals are not generally soluble in water. Oil falls into this class. As the saying goes: “oil and water don’t mix.” Other organics are hydrophobic and will readily dissolve in water. This is why you are able to mix sugar into your coffee. When different types of organic chemicals enter a wastewater treatment plant, the ones that are soluble in water will most likely be broken down by the microorganisms that decompose the human waste and other organic matter in the wastewater. (Small quantities will exit the plant in the effluent.) The compounds that are insoluble in water will be decomposed in the treatment process or will end up in the biosolids.

When these hydrophobic organic chemicals are added to soil with biosolids, they will most likely stick (partition) onto either the organic compounds in the biosolids or the soil organic matter. When these different chemicals bind to the organic matter, there is the potential that their structure will change as a result of the bonding. This bonding may either accelerate or retard their decomposition by soil microorganisms. But, as noted before, all organic compounds will eventually break down to simple molecules, including carbon dioxide, over time. Time here may be several hours or several centuries. A rough way to gauge whether a compound is likely to break down quickly or slowly is to look at how large it is, how many ring structures it has, and how many chlorides are attached to it. The larger and more complex it is, and the higher the number of rings and chlorides it has, the harder it will be to decompose .

It is important to remember that soil is an overcrowded condominium for soil microorganisms. The standard estimate is that about 1 million microbes call each gram of soil their home (Brady and Weil). These microbes eat organic matter. While they do have taste preferences for the compounds that are easier to decompose, they are generally willing to eat just about anything. If it is possible, they will figure out a way to eat any organic chemical – including ones that may, in sufficient quantity, be toxic to humans or other forms of life. Two examples that include different degrees of digestibility will clarify this point. Scientists have studied the decomposition of synthetic hormones in biosolids amended soils. These hormones are in biosolids because women that take birth control pills excrete a fraction of the hormones. The scientists found that these organic compounds in biosolids are "eaten" by microorganisms (decomposed) within 48 hours after they have been added to soil (Colucci, 2001a; Colucci, 2001b). In contrast, PBDEs are insoluble, and one study indicated that they persist in soils for years, although they are likely tightly bound to soil particles and, therefore, are not likely to create significant exposure to larger organisms, including plants and people.

The compounds that will tend to persist are generally those that have the lowest water solubility (i.e. those that are hydrophobic). These are also the compounds that will bind most tightly to soil organic matter. When these compounds are added to soil with biosolids, they are effectively added with "glue" to hold them in place. What does this mean about the hazards and risks associated with these compounds? To figure out if a chemical has the potential to do harm in the environment, you have to first think about how it can come into contact with the animals and plants that it potentially poses a threat to – creating exposure. For example, DDT (a pesticide that was widely used in the 1950s and 1960s) caused damage to birds because earthworms accumulated DDT from soils. The birds that ate the worms also ate the DDT. Once in a bird's system, the DDT interfered with calcium metabolism, reducing the bird's ability to make strong shells for their eggs (Rachel Carson, Silent Spring). The pathway for the DDT was then soil→earthworm → bird. The DDT did not harm the worm, it harmed the bird that ate the worm.

There are three groups of living things that could potentially be at risk from organic chemicals in biosolids amended soils. Plants, soil organisms, and animals that eat either the soil or something that could get the chemical from the soil (including plants and bugs). These comprise the potentially at-risk population. In order for a potentially toxic chemical to affect any of them, there must be a route of exposure.

Plants take up most of the nutrients they need from the water in soils. In order for potentially toxic chemicals to harm a plant, they would need to get into the plants. In order for these chemicals to get into the plants, they would first need to be soluble in water. They would then need to pass through the plants cell walls or through the ion channels that let in the nutrients. Here it can't be both ways. If the chemicals are in solution, they will be too hydrophilic to get through cell walls. If they were lipophillic (liking lipids, which also means insoluble in water) enough to get into cell walls, they wouldn't be in solution. For the chemicals to pass through the ion channels they would need to be very small: the channels are only big enough to let in nutrients that are generally single ions. This means that the threat to plants from potentially toxic organic chemicals (or to animals that eat the plants) is very low.

Plant uptake of organic chemicals added to soils in biosolids is expected to be generally very low

Animals have the potential to come into contact with potentially toxic chemicals applied in biosolids either through eating the soil or eating other animals that have eaten the soil. Here you have to think about the persistence of the chemical, the concentration of the chemical in the soil, and whether the chemical would be absorbed from the soil that is being eaten into the gastric system of the consumer. For many potentially toxic chemicals in biosolids, the concentrations may be above current sensitive tests' detection limits, but are very low. When biosolids are applied at the required agronomic rate, the concentrations in the biosolids amended soil usually fall below detection limits. For example, one study found concentrations of PBDEs in biosolids averaging about 1.5 ppm (Hale et al., 2001). If biosolids are applied at fertilizer rates, that means that about 5 tons of biosolids are tilled into the top 6 inches, or 1000 tons of soil, on an acre of land. This would dilute that 1.5 ppm concentration of PBDEs 200 fold, bringing the concentration of PDBEs into the low parts per billion range.

For chemicals that have been traditionally considered to be highly toxic, concentrations in biosolids are generally in the parts per billion range. The process behind setting regulatory limits for such chemicals will be discussed next. For newer organic chemicals of concern, including pharmaceutical compounds and things like detergents and shampoos, research is just beginning. The potential hazards associated with those compounds will also be discussed below.

Organics and the Part 503 biosolids regulations

When research was being carried out to evaluate the safety of land application of biosolids, a range of different organic compounds was included in the studies. At the time that this risk assessment was being carried out, concern was focused on the categories of compounds that were considered to be directly hazardous to human health. The scientists who developed the regulations determined the concentrations of each contaminant that could be present in biosolids without causing a potential risk to human health. This list was then compared to the concentrations of these compounds in biosolids. The concentrations in biosolids were taken from the EPA sponsored National Sewage Sludge Survey. The problem was, that of the 11 compounds considered, only 3 of them were detected in all of the different biosolids surveyed. Of these, one was found in 1% of the biosolids sampled, and the other two were found in 3% of the biosolids tested. In all cases, when these compounds were found in biosolids, they were present at less than 1/1000 of the proposed regulatory limit. This was because the scientists primarily considered compounds whose hazardous properties had resulted in a ban on use. It was decided that it didn't make sense to include limits for these organic chemicals in biosolids regulations because they just weren't there to begin with. Their absence does not reflect negligence, but rather no real need to set limits on compounds that aren't there even .

Organic chemicals in biosolids evaluated for risk to humans and the environment (modified from NAS 1996 and EPA 1995). Chemical concentrations are expressed in parts per trillion and potential limits for biosolids are expressed in parts per million

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.

This decision was recently revisited when EPA went through the process of determining appropriate limits for dioxins in biosolids (US EPA 2003). EPA considered the potential for increased cancer risk from dioxins for those that eat a majority of their food (including meat) from biosolids amended soils. For these targeted individuals, EPA found that the increased cancer risks were 0.22 potential cases of cancer over a 50-year period. Due to the very low risk and to decreasing concentrations of dioxins in biosolids, EPA decided that limits for this class of compounds wasn't necessary.

It should also be noted that the source control or pretreatment divisions of municipalities routinely monitor for a number of organic chemicals that are not currently regulated. At King County, WA, these include toluene, benzene, and other polyaromatic hydrocarbons. When an industry moves into an area, they are required to notify the wastewater treatment division regarding the volume and content of what they will discharge into the municipal system. This includes compounds that aren't regulated in biosolids in addition to those that are. In the same way that the treatment police begin their detective work when they see an increase in metals coming into the plant, they do the same for a range of organic chemicals.

New organics of concern

Recently there has been a lot of attention in both the scientific literature and popular press about a new class of organics in biosolids. The general term for these compounds is pharmaceuticals and personal care products, or "PPCPs." Although these compounds have scientific names like the hazardous compounds looked at in the biosolids rule-making process, they also have names that are familiar to most adults. For example biphenylol is a bactericide in dishwashing detergent. Musk xylene is a fragrance commonly found in perfumes and shampoos. Dextromethorphan will relieve your cough and can be purchased over the counter (Xia et al., 2005).

A recent cover of *Environmental Science and Technology* (the most widely cited journal reporting environmental science) makes clear the interest in personal care products in the environment.

The vast majority of these new organic chemicals of concern are ingredients in common, everyday products. These chemicals don't enter the treatment plant from industries. They come from private homes and hospitals. For these compounds, the potential for them to cause harm to people because they are in biosolids is really not an issue. For example, should you be more concerned about flame retardants in biosolids at 1 ppm or in your infants' pajamas at 100,000 ppm? Not only is the concentration much higher (5 orders of magnitude) in the pajamas, there is also direct contact with your baby's skin and the potential for oral absorption if he or she is teething. The current concerns about these "new" organic chemical compounds is entirely focused on the effects of these compounds in the environment – not on direct human health impacts. The reason for the concerns is the fact that some of these compounds can interfere with the endocrine and/or reproductive systems of fish and other organisms.

Interest in these "new" compounds increased dramatically after the release of a US Geological Survey report that measured concentrations of a wide range of them downstream from wastewater treatment plants and confined animal feeding operations (Kolpin et al., 2002). At least a portion of all of the chemicals were found in the vast majority of sampling locations. Although not toxic to humans, even with the direct contact that most of us have with these products, in a river or stream, very low levels (parts per billion) can harm aquatic organisms. In a soil system, it is not clear if they have any effect at all. One report claimed that sheep grazing on plants grown on biosolids amended soils exhibited more feminine behavior (a difficult thing to measure), but another found no changes in sheep at all, nor traces of these chemicals in their organs (Erhand and Rhind, 2004; Rhind et al, 2005).

As awareness and concern over these new chemicals has increased, research on their fate and behavior in the environment has also increased. Studies are being reported in the scientific literature on the fate of these compounds in wastewater treatment plants and in land-applied biosolids (e.g. DiFrancesco et al., 2004;North, 2004). Many of these compounds degrade very quickly in the environment. In fact, it may be possible to alter the wastewater treatment plant process to encourage their decomposition within the plant itself (Xia et al., 2005). For those that persist in the environment (the most hydrophobic compounds), it is likely that the same properties that make them persistent will make them unable to cause harm to the environment. This is a topic that is of concern for biosolids programs, and research is being funded by these programs to ensure better understanding of the fate and impacts of these organic chemicals, so that biosolids programs can be sure that biosolids recycling to land does not harm the environment.

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