**Metals in Biosolids**

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## Heavy metals in the environment

There is no question that certain heavy metals are very toxic to people and animals. In excess, others can kill plants. Some examples of toxic metals include lead, mercury and arsenic. Exposure to lead can result in brain damage to children. When leaded gasoline and leaded paints were commonplace, many kids in urban areas suffered from excess lead. Even today, a large portion of children in inner cities have blood lead levels above the recommended level of 10 ug dL-1. Many people still remember the horrible images of deformed children born to parents who had been exposed to excess mercury in their diets. Minimata disease has seared an understanding of the dangers of mercury poisoning into the minds of the general public. Today, excess arsenic in drinking water has caused millions of people in Bangladesh to develop cancers. A recent report by the National Academy of Sciences recommended that standards for arsenic in drinking water in the United States be lowered to protect public health.

## Utility of Heavy Metals

With these horrible risks associated with the use of heavy metals one might question why these elements are still in use and still have commercial value. For many of these elements, the recognition of their hazards is tempered by their utility. One example is lead. Lead was very widely used and could be found in every household. Lead based paints were the standard because lead helped the paint retain its color. Lead solder on pipes and cans was also very effective. Lead was added to gasoline as an anti-knock agent. As the understanding of the hazards of lead has grown, the impetus to find substitutes has also gained momentum. Today it is no longer possible to purchase lead based paints or gasoline in the United States. Methyl tertiary butyl ether (MTBE) is now added to gasoline as a substitute. However, the utility of lead is still a factor: car batteries are a prime example.


Lead is still a standard material for car batteries.

Another example is mercury. Mercury was widely used for a range of purposes including extracting gold from ores, felting hats, thermometers and the amalgam that fills cavities in your teeth. As with lead, as the hazards of mercury become understood, the search for substitutes gains momentum. Gold is now mined using cyanide and it is now possible to get your teeth filled with an organic resin.

Amalgam (high mercury) and resin fillings for teeth
www.robinspool.co.uk/composite.htm

**Form and Hazard**

Mercury is an extreme example of what is true for all of the heavy metals. One of the problems with metals, and also one of the benefits of metals is that their toxicity depends on both their form and their ability to reach a receptor. Lead and mercury are both good examples of this point. The form of the mercury is what determines how dangerous it is. So, a very small amount of methyl mercury in fish was enough to cause terrible birth defects to children whose mothers ate the contaminated fish. However, very high (up to 50%) concentrations of mercury in dental amalgam is not considered to be a hazard. Mercury will only methylate under highly anaerobic (without oxygen) conditions. In your mouth highly anaerobic conditions would be indicative of a much more acute problem then any caused by mercury: it would mean that you had stopped breathing. It is only when mercury enters an environment like the ocean that it is likely to transform into methyl mercury and become a potential hazard. Even here, it is only when the fish consume the mercury and store it in their fatty tissue and then people eat the fish that the mercury becomes a hazard. If there was no exposure pathway for the mercury in the ocean to reach people and cause harm, it would not pose a danger to people. The lead in the paint posed no danger to people living in the house. The only case where the lead on the walls posed a hazard was when the paint started chipping off the walls and little children played with the peeling paint and ate the paint chips. Lead in gasoline was a hazard as lead was released in car exhaust and entered the environment where it had many different ways of contacting potential receptors. With lead and mercury having so many commercial uses, they were unintentionally released to the environment where they had the potential to alter form and become highly toxic. As both currently have fewer commercial uses, the amount of each that is released into the environment has dramatically decreased. With the decrease in use, there is a decreased potential for these metals to cause harm. While there is still a pool of mercury and lead in the environment as a result of previous use, additional inputs continue to go down.

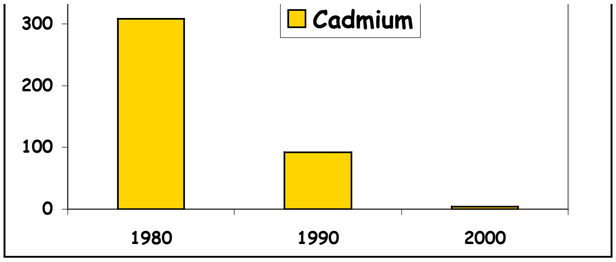
**What this has to do with biosolids**

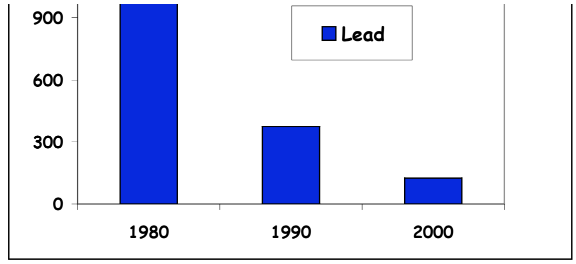
When land application of biosolids was initially being studied for potential hazards, the scientists tasked with determining the safety of this practice considered both heavy metals and toxic organic compounds. Both categories of contaminants can be found in biosolids and there was concern that by land applying biosolids, there was the potential for these contaminants to enter the food chain and cause harm. The scientists ended up endorsing land application of biosolids as an environmentally sound and beneficial practice. Although they determined that concentrations of toxic organics in biosolids were too low to merit regulation, they did set limits on how much metals biosolids could contain and still be considered safe. These limits are outlined in the National regulations on biosolids, US EPA CFR Part 503. The scientists developed a pathway approach to predict whether the regulated metals in the biosolids had the potential to cause harm. Here they considered animal and plant health in addition to human health. Details of this process are presented in another chapter. At any rate, what they concluded was that there are certain concentrations of metals that can be present in biosolids and have only 1 chance in 10,000 for an increased risk of danger to human health for a person that eats over half of their food from gardens where the soil consists almost completely of biosolids for a 50 year period. These concentrations are included in the regulations as the exceptional quality limits and are presented in the table below. Only under very limited conditions can biosolids be land applied if the biosolids have metals exceeding these concentrations. If the metals in the biosolids are lower than the limits set in this table, they can be land applied based on the fertilizer demands of the crop.

Now, the scientists that developed these regulations have been criticized for the metal limit numbers because the numbers were based on safety and did not take into account what metal concentrations were possible to achieve in municipal wastewater treatment. And in fact, over time, metal concentrations in biosolids have been drastically reduced. This happened because pre treatment regulations were put into place at about the same time that the biosolids quality regulations were established. The goal of the pre treatment regulations was to protect the quality of the water leaving the wastewater treatment plants. As a result of the pretreatment regulations, industries were forced to monitor amounts of targeted compounds (including metals) that entered the wastewater stream. Improved metal recovery at industrial sites resulted in dramatically lower metal concentrations in both effluent and biosolids. Pre treatment has been successful enough that it is hard to find biosolids in the United States that have metal concentrations anywhere near the regulatory limits for exceptional quality material. A few examples from across the country are presented below to illustrate this point.

**Chicago-**

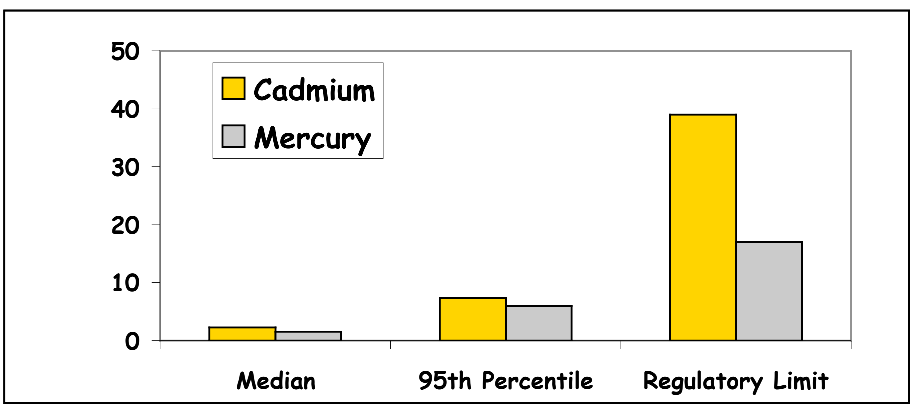
The Metropolitan Wastewater District of Greater Chicago produces 200,000 dry tons of biosolids each year. Initially, metal concentrations in the biosolids in Chicago were much higher than current regulatory limits (see figures 1a and 1b). In fact, Chicago biosolids have been used by scientists across the country to understand the behavior and risk of metals in biosolids ( eg Brown et al., 1998; Granato et al, 2004)). However, an aggressive pre-treatment program has reduced metal concentrations in Chicago biosolids by several orders of magnitude. Metals in Chicago biosolids are now low enough that it would be impossible to reach the soil cadmium concentrations in the biosolids regulations by land applying these materials. In Chicago, biosolids are used as a soil amendment on golf courses and football fields. They are also used as soil for municipal landfills and as a fertilizer for agricultural soils.




Cadmium and lead concentrations in biosolids produced by the City of Chicago have decreased dramatically since 1980.

**Pennsylvania**
Metals concentrations in Philadelphia biosolids, and in Pennsylvania as a whole have also decreased as a result of aggressive enforcement of pretreatment regulations as well as a general decrease in the use of these elements. In a study published in the Journal of Environmental Quality, Stehouwer et al., examined both nutrient and metal concentrations at 177 publicly owned treatment plants from 1978 to 1997. The authors noted that while concentrations of nutrients in the biosolids have remained stable, there have been large decreases in the concentration of cadmium, chromium, copper, lead, mercury, nickel and zinc over the 20 year period. In addition to the decreases that have resulted from enforcement of the pre-treatment regulations, metal concentrations in biosolids have decreased as many municipalities are treating their drinking water to make it less acidic and more alkaline. This reduces the metals such as copper, zinc and lead, that leach into water from water pipes. In Philadelphia, biosolids are used to reclaim coal mined lands. They are also made into compost for use in gardens.




**Cadmium and mercury concentrations in biosolids in Pennsylvania**. The median value is the average concentration across all of the treatment plants. The 95$^{th}$ percentile is the metal concentration that 95% of all treatment plants sampled fall below. Finally the regulatory limit is the cadmium and mercury concentrations that scientists determined were safe for unlimited biosolids applications over time (Stehouwer et al., 2000)

**Seattle**
Biosolids in Seattle have followed the same trend as biosolids in Chicago and Pennsylvania. Cadmium concentrations are currently 10% of what they were in 1981 (49 ppm in 1981 and 4 ppm in 2000). Lead in biosolids has also been reduced by 90% from 1981 concentrations.

While mercury concentrations are half of what they were in 1981 (6.2 ppm in 1981 and 2.7 in 2000), the King County Wastewater treatment program is working to bring that number down further. They are targeting dentists' offices in this effort. Dentists are the largest source of mercury to the wastewater system. Every time someone has a filling replaced or gets a new amalgam filling, the mercury in the rinse water goes down the drain. In King county dentists are now required to install special settling chambers to capture the mercury so that it can be recycled and does not enter the wastewater treatment system.

Biosolids from King County are used to fertilize commercial and State owned forests and agricultural lands. A portion of the biosolids are also composted and used by landscaping contractors. In a new project, King County biosolids are being used to fertilize canola. The oil from canola is then being processed into biodiesel for use in municipal fleets.

**Pre-treatment Police**

One of the reasons that metal concentrations in biosolids have fallen so dramatically is that each municipality has employees whose job is to make sure that no illegal discharges are made into the municipal wastewater system. Pre treatment regulations have given these officials a set of rules to enforce and they have taken these rules and their jobs seriously. One concern about biosolids has been the perception that anyone can dump any number of dangerous chemicals into the sewer and that these will end up in the biosolids. Due to the pre-treatment police, that is just not the case. Jim Sifford of the King County Source Control (pre-treatment) program explained how they do their job.

Everyday in King County, a composite sample is collected from all of the water entering the wastewater treatment system. This sample is analyzed for both metals and organics of concern. The Source Control program at King County has developed a spreadsheet model that mimics the path of the influent through the treatment plant. The model can predict the concentration in biosolids of a particular compound based on its concentration in the water coming into the plant. This model is used to alert Source Control when concentrations in the influent threaten to compromise biosolids quality: 'if we (based on historical data) see an elevated metal concentration in the influent above normal range, we can take that analytical data and plug it into model and predict what change in concentration for the biosolids- if we do get a metals slug- it will tell if it is high enough to affect the biosolids and if it would put it to the limit and for how long- this assures that all of the biosolids will meet the regs. We have seen slugs- but we have never seen one big enough or of sufficient duration that has forced a stop to the process, nothing to stop the trucks, never have exceeded the EQ standards for application.'

**Chromium and the Aircraft Manufacturer**

The Source Control program begins their detective work when metal concentrations deviate from normal over an extended time period or at regular intervals. Mr. Sifford gave an example of how the Source Control division found that a local, large aircraft manufacturing company was dumping chromium into the wastewater system:

'We have had a few cases where we have had to do detective work. The aircraft case- we did notice an increase in influent concentration levels of Cr that over a short period of time. They seemed to be occurring on regular intervals, not every day but a couple of times a week. Once that got our attention, we checked the next biosolids sample that followed that initial notice and it had elevated Cr in it. And that was a kind of a check, to see if the influent numbers were real or not. We continued to monitor the influent and keep an eye on the biosolids but we also then did a quick check by phone of our known Cr dischargers to see if anyone had an accident. The permit process give us a list of known point sources, they are supposed to call if they have an accident but they don't always call. In this case it turns out that their (Boeing) large solids clarifier was malfunctioning and they didn't know it. We were able using a series of auto-samplers, to narrow down geographically where the Cr was coming from. Then we noticed what area, we called people we knew in the area, all denials. We used the auto-samplers again, we started an upstream /downstream scenario and we just keep narrowing the potential sources. We had one close to the plant and one upstream, the upstream was clean, downstream dirty. We kept narrowing the distance between the samplers till we were able to really narrow it down. We said we think you are having a problem, they (the company) said no we're not, they finally checked and it was them. We then levied big fines. We also continued close monitoring to make sure the discharges had stopped. In addition to the fines, we published their name in the newspaper: we advertise. This makes them madder than the fine. They just want to be under the radar on that stuff.'

All industrial dischargers are required to notify the POTW of intent and what is expected to be in the wastewater. For organics that are not regulated nationally, King County will work with the industry to determine an expected concentration in discharge from the plant. If this is above levels that are acceptable to the treatment works, the Source Control will work with the industry to help reduce discharge or limit entry of the compounds of concern into the wastewater treatment system.

**Metals in Biosolids Today**

Because of the low metal concentrations in current biosolids, it is impossible to reach soil metal concentrations that are considered safe in the biosolids regulations. For example, scientists that developed the regulations set 39 ppm as the safe limit for cadmium in biosolids. If you went out and built a soil from biosolids and biosolids alone (equivalent of 200 years worth of annual applications) using biosolids from the city of Chicago, the highest cadmium concentration you would ever achieve would be between 4 and 8 ppm. The biosolids from Chicago has 4 ppm cadmium. The biosolids consists of about 50% organic matter and 50% inorganic matter (sand and clay particles). The organic matter will decompose over time. In theory, this decomposition could reach 100%. In the real world, as soil organic matter decomposes, additional organic matter is added to the soil by plants and animals. If all of the organic matter decomposed, the total cadmium in a soil made up entirely of Chicago biosolids would reach 8 ppm. In all likelihood, the actual cadmium concentration would be somewhere between 4 and 8 ppm. This is about 10 and 20% of what was determined to be safe for someone who ate over half of their food for over 50 years from a biosolids garden. Another thing to consider is that cadmium concentrations in biosolids are likely to keep going down over time. Like lead and mercury, it is now recognized that the hazards associated with cadmium can outweigh the benefits. Cadmium is no longer used for yellow pigment. Other commercial uses such as the cadmium nickel battery may also become obsolete. If this occurs, it is likely that cadmium concentrations in biosolids and in the environment in general will continue to decrease over time.

In an ideal world, the concentrations of metals in biosolids would be the same as those in native soils. Unfortunately while we still use copper pipe, steel cookware, batteries and other metal items, this is unlikely to be the case. What is fortunate is that a great body of knowledge has been developed about the behavior of metals in soils as a result of the research that was begun to determine what concentrations of metals in biosolids would be safe. The methods used by the researchers became more sophisticated as the understanding of the behavior of metals in soils systems became more sophisticated. This greater sophistication showed itself in two ways: both in understanding metal behavior in soils and in understanding that evaluating the hazards for each potential pathway to each receptor requires a measure uniquely suited to that pathway and receptor.

**Behavior of Metals in Biosolids**

For the initial stages of research on biosolids, scientists added metal salts to soils in pots and grew plants to see how much of the metal in the soil would be taken up by plants and at what point the plants would start to die. From these studies, the initial metal limits for biosolids were established. However, when the same tests were repeated using biosolids and metal actually in the biosolids rather than added as salts, results were very different. The same metal concentrations that killed plants when added as salts had no affect on plant yield and plant metal concentrations were often orders of magnitude lower when the plants were grown in biosolids amended soils. This brought home an important point that was recently reiterated in a National Academy of Science publication on 'Bioavailability of Contaminants in Soils and Sediments' (NRC, 2003). To understand the behavior of a contaminant like heavy metals, it is essential that you test the contaminant in the matrix, or in the form that it will occur in the environment. The metals in biosolids behaved very differently than metals added to soils as salts. As additional research was done on metals in biosolids amended soils, this observation was repeated again and again. Biosolids were able to complex metals in such a way that they were less available to plants and to animals that were exposed to the biosolids amended soils. Jim Ryan, a scientist with US EPA National Risk Management and Research Lab has termed this phenomena 'Biosolids Magic'. His group has worked to understand this phenomena. Their research has shown that both biosolids organic matter and the high surface area iron and manganese minerals that form during biosolids stabilization are responsible for this 'magic'. This understanding coupled with reduced metal concentrations in biosolids has opened up a new use for these materials. Municipal biosolids have now been used at over 5 mining sites on US EPA's Superfund list as a way to restore plant growth and reduce the danger posed by highly metal contaminated soils. In addition, high iron biosolids compost is being tested as a means to reduce the hazard associated with high lead soils in inner cities. In Baltimore, MD and E. St. Louis, Missouri, high iron biosolids have been added to home gardens and abandoned lots to reduce the hazards associated with high soil lead and help restore a grass cover to the sites.

A truck spreading biosolids to farmland in Eastern Washington State. The biosolids were used to fertilizer a crop of canola. The canola being harvested is shown below.

What this research has shown for average biosolids applied to farms, is that even when biosolids are applied at high rates (100 tons per acre or 20 annual applications), biosolids do not cause increases in metals for food crops grown on the amended soils (Brown et al., 1998). Lettuce was grown on both high biosolids soils and untreated soils. The biosolids used for this study had 13.4 ppm cadmium which is at least double the concentrations of cadmium for biosolids produced in Chicago, Seattle and the State of Pennsylvania. Lettuce in the soil that had had biosolids applied had between 0.5 and 1.2 ppm cadmium when the soil was pH 6.2. The lettuce grown in the same soil without biosolids had between 0.9 and 1.8 ppm cadmium at the same pH.

**Restoring soil in Leadville, CO**

At the turn of the 20$^{th}$ century, Leadville, CO was the center of a mining boom. Rich deposits of gold, lead and zinc were discovered and a mining industry developed overnight. This was well before the advent of regulations on disposal of mine wastes. It was also at a time when ores were high in metals and extraction efficiencies were much lower than in current mining operations. As a result of both of these factors, soils in Leadville became heavily contaminated with mine-wastes. Mine wastes would wash into the Arkansas River. Soils along an eleven -mile stretch of the Arkansas became toxic to plants as a result of the tailings deposits.


In 1997, US EPA Region 8 began an effort to restore plant growth to the tailings using biosolids from Denver in combination with lime. The goal of this effort was two-fold: to restore the soil ecosystem and to stop the contaminated tailings from eroding back into the river. As this was a new technology for EPA, the treated areas were put through an extensive range of tests to evaluate the success of the biosolids amendment. In addition to standard soil extracts including the toxics characteristic leaching procedure (TCLP) and multiple extraction procedure (MEP), a range of tests of ecosystem function were carried out. These included measures of soil microbial activity, earthworm survival and metal uptake, plant germination tests, small mammal metal body burden and a fat head minnow assay to see what affect re-entrainment of the tailings would have on the fish in the Arkansas River. Adding biosolids and lime to the tailings restored both a plant cover to the tailings and ecosystem function. By all of the indices used, the biosolids and lime amendment brought the soils back to life (Brown et al, 2005).

**Lead in Baltimore**

Like all older cities, many soils around homes in Baltimore, MD have high lead concentrations. Older cities tend to have more older homes than newer suburbs and that means more homes painted with lead based paints. In addition, soils in these cities are contaminated from car exhaust from the time when cars still used leaded gasoline. Baltimore has a program to identify homes with high lead soils that includes testing of kids who live in these houses to monitor their blood lead levels. The standard way to remediate high lead soils is to excavate them and replace them with clean soil. But there isn't sufficient funding or soil to do this in inner cities.

Research conducted at the USDA in Beltsville, MD added different composts made from biosolids to lead contaminated soil from a home in Baltimore. The goal of the research was to see if adding the compost would reduce the dangers associated with the lead. After incubation, the soils were fed to rats to see if less lead would be absorbed by the rats who ate the soils with compost added. In fact, a high-iron biosolids compost produced from Baltimore biosolids was very effective, reducing lead absorption by the rats by close to 40% over the untreated soil (Brown et al., 2003).

As a follow up to this lab study, home gardens in Baltimore were treated with compost from the wastewater treatment plant in Baltimore, For the treated areas highest in total lead, adding compost to the soil reduced the availability of the lead (as measured by a lab extraction) by 64-67% compared to the soil that did not have compost added (Farfel et al., 2004).

Compost being raked in to soil in garden in Baltimore MD. A lawn before and after compost addition (pictures from Farfel et al., 2004).

This is one example of biosolids being used to fix metal contamination that also illustrates that the metals in biosolids are not a concern for public health.

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