Public Health Assessment Questions Toxaphene Analysis Method

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Overview

The Agency for Toxic Substances and Disease Registry, part of the U.S. Department of Health and Human Services, reviews environmental sampling data as part of the Superfund process. The purpose of the review—called the Public Health Assessment—is to determine human health threats from chemicals found at the site.

The Glynn Environmental Coalition received for review the Public Health Assessment for Terry Creek Dredge Spoil Areas/Hercules Outfall Site, Brunswick, Glynn County, Georgia, dated August 12, 2002. The report summarizes site and testing history; discusses characteristics of toxaphene, the main chemical threat found at the site; outlines health assessment models; and, gives recommendations for the site. The Environmental Protection Agency (EPA) is then expected to act on those recommendations.

This Public Health Assessment (PHA) provides an unusually candid assessment of toxaphene testing methodology. EPA and Hercules, the potentially responsible party for the site, contend that toxaphene is a difficult chemical to measure. EPA/Hercules argue that only very special methods of treating the analytical data can accurately measure toxaphene. However, most laboratories doubt that toxaphene is more difficult to quantify than any other substance. Further, the EPA Region 4 methods for quantifying toxaphene are apparently not accepted for testing anywhere else but in Brunswick, Ga. This PHA discusses toxaphene under-quantification (toxaphene present, but not detected) as a potential source of risk to Glynn County, Georgia subsistence fishers.

Discussion

The Terry Creek Superfund site is a contaminated marsh formed by the confluence of Terry and Dupree Creeks in Glynn County, Georgia. The site received runoff of toxaphene—a banned pesticide—from a drainage ditch connecting the marsh to the Hercules Inc. manufacturing plant where the company made toxaphene. The runoff contained toxaphene wastes and off-grade product. Dredging operations by the U.S. Army Corps of Engineers to open the waterways spread toxaphene contaminated marsh sediments when dredged sediments were deposited in spoil islands and impoundments.

Toxaphene was a broad spectrum poison marketed as an insecticide, although toxicity was not limited to insects. “Insecticides” are usually only toxic to bugs; however, toxaphene is a biocide that kills animals, and causes a specific type of tumor in laboratory animals. Toxaphene is classified as a possible human carcinogen. Toxaphene is a mixture of about 200 similar chemicals; only about 20 have been isolated for more study, and the principle toxins and carcinogens (“cancer-causers”) are not known. Toxaphene is properly called “PCC” for “polychlorinated camphene.” The Hercules Plant produced camphene (a chemical formed into a complex “ring” shape) from pine stump oils, and then added chlorines to the camphene. Generally, the more chlorines added to the rings of the camphene, the more toxic it is, and the longer the chemical stays in the environment. “Toxaphene” was a brand name for the

Hercules product made by chlorinating camphene until a sample could kill a certain number of flies during a certain time period. PCC that passed the test was labeled as “toxaphene” product. Process water, sludge, and material that failed the “toxaphene” product test went into the Terry Creek marsh via the drainage ditch. The marsh is contaminated with waste PCC, not toxaphene product.

The Terry Creek disposal area is a “Superfund” site, meaning that the EPA found the area to be highly toxic. For all Superfund sites, environmental testing is required to determine the types of chemicals, the amounts of toxic chemicals and the distribution of toxins. Simply put, if toxins are not found, the area is not cleaned up.

Environmental sample media include air, soil, sediment, surface water, groundwater, and animal and plant tissue. When measuring a complex mixture it is typical for media to show different chemical patterns. For example, the pattern of chemicals found is different for mud than it is for analysis of fish fat.

PCC is a complex mixture of about 200 different chemicals (called “isomers”) with varying amounts of chlorine. The lightly chlorinated PCC isomers are more soluble in water than the heavily chlorinated isomers; and the more chlorines on the molecule the more tightly the PCC can stick to soil and sediment. Biota, such as plants and fish, also show different “uptake” of PCC isomers. With complex mixtures such as PCC, each media has a unique isomer “fingerprint” pattern.

To measure a chemical in water, soil or other media the sample is mixed with another chemical—a solvent known from experimentation to dissolve PCC’s. Then the extracted sample is filtered so that the solvent contains the PCC, but not the media. Then the amount of each PCC isomer (or other chemical) is measured on an instrument called a gas chromatograph. Essentially, all of the chemicals in the sample extract are bound to an analytical column; then each specific chemical is precisely removed from the column and measured. The sequence in which the PCC chemicals are removed usually relates directly to the amount of chlorine on the camphene rings. In theory, there are 600 different combinations of chlorine and camphene. Each chemical combination is a PCC isomer. However, some PCC isomers are easier to make than others, so about 200 isomers typically occur in the PCC.

Gas chromatography (usually just called “GC”) can be extremely precise. The technique has been used for decades and thousands of publications attest to the reliability of GC to detect and quantify chemicals. On a GC chromatograph of toxaphene, (the printed record of the analysis) each of the nearly 200 isomers appears in a series of “peaks” on a graph. From the width and height of the triangle-shaped peak the amount of the isomer can be calculated. From its position (early to late) on the graph the amount of chlorine in the isomer can also be inferred. The EPA has established methods for collecting, extracting, and measuring chemicals by GC. Each method is a set of rules that are followed so that all laboratories get the same result regardless of who performs the test. For PCC the main method is 8080. However, the EPA in Region 4 uses a non-standard variation of method 8080 for PCC in Georgia. In contrast to the standard EPA method for PCC, Region 4 EPA uses a method that bases cleanup decisions using only the commercial grade of toxaphene sold by the plant 20 years ago. Although toxaphene has not been made or sold at the facility since the 1970’s, and numerous studies indicate environmental PCC is substantially different from commercial toxaphene, EPA Region 4 has insisted on using the old toxaphene standard. The modified method, the so called “toxaphene-task force” methodology, allows the technician performing the test to override EPA guidelines on complex

mixtures and choose only a few of the isomers in the late portion of the chromatograph. Since methods are designed to eliminate bias, subjective peak picking for toxaphene analysis raises questions of accuracy. “Bias” is the term used by scientists to define conditions that lead to erroneous results. Bias can cause both false positives-- a detection of toxaphene when it is not present, or false negatives—failure to detect toxaphene when it is there. The consequence of a false positive bias is Hercules may have to perform a cleanup when it is unnecessary. The consequence of a false negative is that toxaphene is illegally left in the environment.

The Agency for Toxic Substances and Disease Registry subjected a 1997 Toxaphene Task Force (TTF) analysis to a third-party independent audit. That review found six instances of under-reporting where the TTF method failed to detect the correct concentration of toxaphene, and one instance of a potential false-positive where the toxaphene was reported at a higher concentration than actually present (Tables 1-5 of the Appendix E). There are 57 total samples reported in these tables, 7 incorrect samples represents an error rate of greater than 12%, a very high rate of incorrect conclusions. The ATSDR report also noted that toxaphene standards were under-quantified by the Toxaphene Task Force methodology. In Appendix D of the report, ATSDR noted that a commercial toxaphene standard was correctly assayed using the EPA’s Total Peak Area method, but was not correct with the TTF method. A 5 Part-Per-Million standard was read as 5.19 PPM using total area analysis, but the same 5 PPM standard was read as 1.42 PPM using the combined peak areas of seven components in the late half of the chromatogram (the Toxaphene Task Force method). Generally, analytical chemists prefer at least a 95% confidence level in quantification. Therefore, values in the range of 4.75 to 5.25 PPM are within the calibration standard. The 3.5-fold under-quantification using TTF methodology is not acceptable, and indicates the TTF method is not scientifically reliable.

The ATSDR PHA review also provided a number of recommendations related to measurement of PCC in fish tissue. First and foremost the ATSDR report stated that gas chromatography with electron capture detection (GC-ECD), the basis for the Toxaphene Task Force method, is “¼not the most accurate and conclusive method” for monitoring PCC. The author of the study suggested several other techniques would have a greater likelihood of providing unbiased PCC data. Secondly, if the GC-ECD method is used, the study’s authors recommended using “¼as many single peak areas as possible¼” in the chromatograph, as opposed to the bias introduce by selecting certain peaks in the late half of the chromatograph, as in the TTF method. Note also, this recommendation is different from EPA’s “total peak area” methodology. It is a case for using all clearly found isomers, rather than all material that elutes (Total Peak Area method), or some subjectively chosen isomers (TTF method). The study’s authors also had several recommendations related to sample and standard treatment, and use of other techniques to measure toxaphene.

Conclusions

The ATSDR Public Health Assessment concluded the Toxaphene Task Force method used by Region 4 EPA produces false-negative sample analyses. The consequence of these false-negative readings is that some marsh areas may be unsafe and require cleanup, but are missed with the Region 4 modification of EPA’s standard method.

This area of toxaphene analysis has long been controversial. This study shows the value of a third-party (not Hercules and not EPA) review of the testing methods. The Toxaphene Task Force

methodology should be abandoned and ATSDR's recommendations on testing should be adopted immediately. Previous studies should be reanalyzed, or resampled, to accurately determine PCC presence in Terry Creek.

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