



Fact or Fiction?

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How Toxic Are Toxic Chemicals in Soil?★

Bioavailability and chirality are two words that should be in your vocabulary, if they aren't already. They both mean that amounts that are actually available to do harm aren't necessarily the amounts that are reported in a chemical analysis. In other words, tests currently used to detect some pollutants in soils may overestimate the risk to living organisms. Let's look at each of these, because they are both receiving more and more coverage in technical literature.

Bioavailability

Bioavailability is the amount of toxins available to harm organisms. Considerable evidence exists to show that the extent of reduction in the bioavailability of chemicals is greatly affected by soil properties.

Cornell researchers reported that tests currently used to detect old DDT and other pollutants may overestimate the risk to living organisms, and the real issue for government regulators at toxic cleanup sites should be "biological availability" of aging toxins. "Recent research has cast doubt on the validity of current analytical methods for assessing the risk from organic pollutants in soils," says Martin Alexander of Cornell, co-author of a number of recent reports on bioavailability.¹⁻⁶

He further states: "Current methods determine the total concentration of compounds, not the amounts that are actually available to do harm. If we are not measuring bioavailability, we are overestimating, sometimes appreciably, the risk to biological organisms. Age can be an important factor

because the compounds might be sequestered in the soil and are less likely to be absorbed by living organisms."^{4,7}

Some Results

- An extensive decline in bioavailability to earthworms as a result of aging of DDT, DDE, DDD and dieldrin in field soils was reported by Morrison, *et al.*² The findings indicated that more than half to >85 percent of the pesticides were not in a form accessible to the test species.
- Short-term sorption of a variety of mutagens including benzo(a)pyrene, 7, 12-dimethylbenz(a)anthracene, 9-phenylanthracene, captan and aldicarb by six markedly different soils resulted in a 28.2 to >99 percent decline in availability for genotoxicity.³ This reduced bioavailability varied markedly with the soil and the compound. Considering individual chemicals, the bioavailabilities differed by factors of 5.4, 7.1, 4.2, >4.0 and 3.2 among the tested soils for DMBA, BaP, PA, captan and aldicarb, respectively. These findings emphasize the key role of soil properties in determining the amount of a substance that will be available for genotoxicity.
- Chung and Alexander confirmed that sequestration and the time-dependent decline in bioavailability of phenanthrene and 4-nitrophenol to bacteria and of phenanthrene to earthworms were quite different in soils with dissimilar properties.⁵
- Many toxicants become less hazardous to test mammals within a short time after they are added to soil or aquifer solids, regardless of whether exposure is by oral or dermal route, *e.g.*, trichloroethylene, benzo(a)pyrene, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), and m-xylene.¹
- The biological availability of lead was shown to vary with the nature and different form of lead matrices present in contaminated soils and dusts.⁸ Conclusions were that with current models used by EPA, bioavailability of lead from some environmental samples may be overestimated, while from others it may be underestimated.
- The bioavailability of pure soil vs. adsorbed benzene on adult male rats showed that the adsorption capacity of soil for benzene correlated inversely with organic matter content and directly with clay content.⁹
- Dioxin contaminated soil from two manufacturing sites in New Jersey was unable to produce toxic effects in orally exposed guinea pigs compared with similar amounts of pure dioxin.¹⁰

Summarizing on bioavailability: Assessment of exposure of living organisms to toxic chemicals in soil requires information on the concentration that is available to those species. Yet the current approach to exposure assessment commonly relies not on the level that is biologically available but rather on the total concentration as determined by vigorous extraction. However, considerable evidence exists that the amount that is available to mammals, invertebrates, plants, and microorganisms is less, and sometimes appreciably less, than that anticipated by analytical procedures based on vigorous extraction.⁴ The very fact that the organic compounds in Superfund

*With thanks to M. Alexander, who used this same title in a paper published in Environmental Science & Technology in 1995.¹

and most other hazardous waste sites have been in contaminated soils for long periods of time emphasizes the need for assessing the significance of aging to toxicity.¹

Chirality

Chirality is a characteristic exhibited by chemicals with asymmetric molecules. Chiral compounds are those that have mirror image structures, called enantiomers.¹¹ One-fourth of all commercial pesticides are chiral, and in some cases, the biological activity of a pesticide may be attributed to one enantiomer, while the other enantiomer has little or no activity.¹² Half of the top best-selling drugs, including barbiturates, Ritalin®, and Ibuprofen® are marketed as single enantiomers to avoid adverse side effects. Thalidomide® illustrates how complex the chiral world can be. With this chiral drug, one enantiomer is beneficial and the other is highly toxic. The drug that caused the horrible birth defects in the 1960s was responsible for the problems. Now there are proposals to remanufacture the beneficial enantiomer in pure form.¹¹

Caste¹³ points out that everything in nature has a mirror image, and all the amino and nucleic acids come in both left-handed and right-handed forms. While these two forms are chemically identical in the sense of being formed from exactly the same atomic constituents, the chemical actions of the two forms are quite different as a result of their "twisting" in opposite directions. He further discloses, "All like forms on Earth use exclusively left-handed amino acids to form proteins and right-handed nucleic acids to form the genetic material. As a consequence of this puzzling fact, we could starve to death on a planet where the steaks were made out of right-handed proteins, since our body chemistry would be unable to break these proteins down to extract their energy."¹³

Back to pollution—A recent study published in *Nature*¹⁴ uncovered what Cohen¹⁵ calls "a hole in our knowledge of the chemicals we regulate that is so deep that what has passed for reliable data about them are flawed at best, and perhaps even entirely useless." Much of the historical environmental data collected on pollutants are unreliable because so many of the chemicals are chiral, and the data do not distinguish which mirror images of certain chemicals were present and which were harmless. Says Dr. David Lewis, co-

author of the *Nature* report, "The good news is that trace amounts of many of the environmental pollutants EPA is most worried about, including some DDT derivatives, PCBs and plasticizers, aren't as bad as previously thought. On the other hand, measures intended to protect the environment such as using treated sewage sludge as a fertilizer, will likely increase the persistence of the more toxic forms of some pesticides."¹⁴

The problem with pollutants is two-fold. First, very few chemicals now considered major pollutants have been evaluated for their chirality at all. Second, environmental changes appear to alter which mirror images persist in the environment by affecting the soil microbes responsible for breaking down the chemicals. The *Nature* study further points out that the EPA has never considered the fact that many of the chemicals it regulates are chiral, with each individual form having completely different effects on living organisms.

Because EPA does not include chirality in its risk assessments, this raises a question about the validity of the agency's findings on, for example, pesticides, of which approximately one-fourth are chiral. As the authors point out, current methods of determining which chemicals pose threats to the environment may be worthless in many cases.¹⁴

This work¹⁴ and others¹² also demonstrate that significant environmental changes, such as tropical deforestation and global warming, may substantially alter the relative persistence of enantiomers of chiral pollutants, exacerbating the adverse effects of some while ameliorating the effects of others. It calls into question the accuracy and future relevance of current risk assessments for numerous pollutants, and underscores the need to better incorporate science in efforts aimed at protecting public health and the environment.¹⁶ *P&SF*

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