The K_{ow} CONTROVERSY

Doubts about the quality of basic physicochemical data for hydrophobic organic compounds could be undermining many environmental models and assessments.

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Environmental risk assessments, fate and transport models, and sediment quality guidelines may be on shaky foundations because some of the basic data needed to predict the fate of a contaminant have large errors, according to a detailed analysis by United States Geological Survey (USGS) physical chemists James Pontolillo and Robert Eganhouse (pubs.water.usgs.gov/wri01-4201/) (*1*). Other scientists say that the problem is nothing new and doesn't significantly affect models and policy decisions.

The USGS report claims that there is an alarming level of uncertainty in reported octanol–water partition coefficients (K_{ow}s) and aqueous solubilities (S_ws) for the notorious insecticide DDT and its primary metabolite, DDE. These variables are conventionally reported as their logarithms. In a detailed review of some 700 publications from 1944 to 2001, Pontolillo and Eganhouse found up to 4 orders of magnitude variation with no convergence over time. They conclude that the reliability of the entire DDT and DDE K_{ow} and S_w database is questionable and believe that the problems "are probably indicative of a more general problem in the literature of hydrophobic organic compounds." (*1*)

Most of the controversy focuses on the quality of K_{ow} data and the coefficient's role as an environmental science workhorse. A key parameter for estimating toxicity, bioaccumulation, and sorption to soils and sediments, K_{ow} is used for projects that range from small-scale investigations, such as estimating contaminant pore water concentrations in sediments, to large-scale research, such as the global transport of persistent organic pollutants. Environmental agencies in the United States, Europe, and Japan require K_{ow} measurements or calculations for new compounds entering commerce, according to Albert Leo, a quantitative structure–activity relationship (QSAR) specialist at Pomona College in California and one of the principal scientists in BioByte Corp., Claremont, Calif.—a company that develops software for estimating physicochemical properties and maintains an extensive database of such measurements.

The USGS claims are especially significant because of new U.S. federal data quality guidelines issued by the White House Office of Management and Budget in January that establish new benchmarks for the scientific data used by federal agencies to craft regulations and policy. Although agencies are still grappling to interpret and implement the new guideline, some observers suggest that the uncertainties uncovered by the USGS report may not withstand this unprecedented scrutiny.

"K_{ow} is so important," says University of Toronto environmental scientist Frank Wania. "For example, very simple criteria, including K_{ow}, are often being used to decide whether chemicals are sufficiently bioaccumulative to be persistent organic pollutants or not," he says. "The difference between a [log] K_{ow} of four or five can be the difference between being classed as a pollutant of concern or not."

Most scientists using readily available physical–chemical databases have not previously been aware of the extent of this problem, says environmental consultant Peter Chapman of EVS Consultants in Vancouver, British Columbia, Canada. "While experts in the fate and transport of hydrophobic organic compounds have apparently been aware of this problem and have dealt with it by either using selected data or probabilistic assessments, these approaches do not resolve the basic problem, are of arguable efficacy, and have not been generally applied in the published literature," he adds.

But other experts disagree about whether the uncertainties exist and whether they are significant. For S_w, Pontolillo and Eganhouse are pretty much correct, but for K_{ow}, "they haven't done their homework and the uncertainties they cite just don't exist," says Leo. Don Mackay at Trent University in Canada, often regarded as the "father" of multimedia fate and transport modeling, also takes this viewpoint. "Of course, good data are always better than bad data," he says, but "I believe it's quite unlikely that [in risk assessment] wrong decisions could be made because of this. Instead, the significance is in the relative level of risk. Perhaps the risk assessment comes out and says there's a 10% chance of something happening when it really turns out to be 30%."

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Three concerns

To appreciate why these experts disagree about the significance of uncertainties in K_{ow}, it is important to first break down the USGS survey into three parts: questions about K_{ow}, questions about S_w, and questions about the peer-reviewed literature and the compilation volumes that are "data bibles" for many environmental scientists.

Practically everyone interviewed for this article agreed that there are significant uncertainties in S_w values, because of a lack of good analytical methods and because QSAR programs fail to yield "good" estimates. The work-around for these problems is to estimate solubilities from K_{ow}s. However, the USGS study says that there are "egregious errors in reporting data and references" for K_{ow}, and the original measurements are of poor quality or have procedures that are inadequately documented (*1*).

K_{ow} measurements sound simple but turn out to be tricky. Mix water, octanol, and the chemical of concern, wait a while, and then measure the contaminant, usually in both phases. Gas chromatography is the most common analytical method. Scientists initially did just that with a shake-flask method, until they found that the approach leaves enough octanol in the water phase to act as a detergent. Slow stir is now the method of choice (*2, 3*). Among the best slow-stir log K_{ow} values for DDT are 6.91 and 6.22, according to ecotoxicologist Johannes Tolls at Utrecht University's Institute for Risk Assessment Sciences in the Netherlands, who has just finished an interlaboratory comparison for determining K_{ow} values for highly hydrophobic organic compounds. Tolls, Eganhouse, Pontolillo and many other scientists argue that having only two well-documented, "good" values with this much spread is just not good enough.

Others disagree. "This spread in values is not that important for environmental hazard assessment," says Leo. "What is the water phase being modeled in the environment? The Mississippi River, for example, has suspended solids that will adsorb DDT, making it appear less lipophilic than the slow-stir values. Pine tree pollen drops into the pristine lakes in northern Canada, making a foam along the shoreline. This also would make DDT appear less lipophilic. Models are useful, but we should not expect more than what they can deliver," he says.

Recycled data

Pontolillo and Eganhouse started looking for K_{ow} and S_w values for DDT and DDE when they were researching the fate of these compounds in the sediments of the Palos Verdes Shelf, off southern California (*4*). "We expected that studies reporting physicochemical properties for DDT and DDE would be very well documented because DDT has a long history and its widespread application and biological effects are well known," says Eganhouse. To their surprise, the USGS scientists found that their assumption couldn't have been more wrong.

In an investigation that consumed two years, they pored through more than 700 publications including databases, handbooks, review articles, and bibliographies. They also carried out computerized searches using the Chemical Abstracts Search Service Index (CASSI) database and the Web.

What they found surprised them. The percentage of original S_w and K_{ow} data for DDT and DDE in literature and book compilations decreased with time, and in the most recent publications surveyed—1994 to 1997—original data make up only 6–26% of the reported values (*1*). This means that numbers are being recycled and cited as original data when, in fact, they aren't. For example, a measurement reported in 1967 might get cited in papers published in 1970, 1972, and 1975. Then the compilation quotes the three later papers as if they are reporting original measurements so that it looks as though three different researchers obtained the same value. "These tabulations become bibles that have a certain authority," says Eganhouse. "Scientists go to these and depend on them, assuming that the compiler has checked the numbers. Top people in the field all realize that there are problems with the some of the numbers, but there are many environmental scientists who don't," he says.

The recycling leads to a significant flaw in important environmental data, say several scientists involved in data quality assurance or in fate and transport modeling. Several fate and transport modelers contacted for this article say that they account for the uncertainties in the K_{ow}s of hydrophobic organic compounds by using probabilistic risk assessments. In other words, they use a distribution of values from a compilation. "This is worse than misleading," according to Robert Huie, group leader of the Experimental Kinetics and Thermodynamics Group at the National Institute of Standards and Technology (NIST) in Gaithersburg, Md., because the values in the compilation include measurements reported again and again rather than all original data. Unless you do lots of searching, you can't tell which are repeats, he adds.

But Mackay, whose compilation volume is among the most widely used (*5*), says that such works would not exist if all of the data had to be tracked back to original sources to meet the standards advocated by the USGS analysis. "The USGS report is useful, but it took years of digging. Sadly, there are some 1000 substances in these compilations. No one can afford the time to do such a detailed search for all these compounds," he says.

Wania agrees that what Pontolillo and Eganhouse have unearthed is a flaw in environmental science. "We all know it's important to generate good, reliable data. But such work is least likely to get money, and least likely to be published." To begin to address the problem, he says reviewers have to be tougher about data citations. "We all have to be tougher about data quality."

Stirred, not shaken

After sorting through the recycled data, the USGS chemists say that the verifiable, published original DDT and DDE data consist of 100 K_{ow} values—64 for DDT and 36 for DDE. These data span 2 to 4 orders of magnitude, respectively, and there is little indication that the uncertainty in these measurements has declined over the past 50 years. "Consequently, the practice of using physicochemical data without carefully assessing its reliability is inappropriate," Pontolillo and Eganhouse write.

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Even values recommended in the compilations fall within a range of more than 2 orders of magnitude (log K_{ow} DDT, 4.9–6.9; log K_{ow} DDE, 4.3–7.0). This makes the task of selecting a value somewhat simpler, but no more reliable than scrutinizing the database itself, according to the USGS scientists.

Using data evaluation systems that assess the reliability of scientific literature in terms of the quality of the analytical, experimental, and statistical data presented, the USGS scientists found that 95–100% of the database literature provides so little information that it cannot be evaluated. Indeed, there has been only one interlaboratory comparison involving determination of K_{ow} values for DDT and DDE (*6*).

Dominic DiToro, a pioneer in water quality-monitoring methods who is based at Manhattan College outside New York City and one of the developers of EPA's partially completed sediment quality criteria, calls the concern over K_{ow} values an "old story". "It pretty well has been resolved in favor of using structure–activity methods to compute K_{ow}," he adds. David Mount, branch chief of ecotoxicology analysis at EPA's National Health and Environmental Effects Research Laboratory in Duluth, Minn., goes further, saying that good data are available if you know where to look. "[The USGS scientists] looked at the data out of context," he says. Many different analytical methods were used to obtain the data, and some of those methods are no longer credible, he says. EPA, as part of its effort to develop sediment quality guidelines, conducted an expert review of K_{ow} values and was able to find satisfactory data, says Mount.

But the USGS scientists and many other experts interviewed for this feature say that there is too much uncertainty in the measured data to even evaluate the quality of the structure–activity methods used to calculate K_{ow}s. Ecotoxicologist Tolls agrees. As part of the round-robin laboratory study of K_{ow} values for hydrophobic organic compounds, he wanted to include DDT but couldn't settle on a reference value. "There are only five or six good original data, and the value we think may be the best is higher than the others. It was too tricky to derive a reference value," he says.

Orphaned data

Whether knowledgeable environmental scientists believe that uncertainties in K_{ow} are a significant problem or not boils down to a difference between those who see uncertainties in the variable as a problem that can be worked around and those who see it as a problem that affects the foundations of environmental sciences. At this point, neither group can quantify the effects of this uncertainty.

"K_{ow} is a data orphan," says Stephen Stein, deputy director of NIST's Physical and Chemical Properties Division. "There's no big organization looking after the quality of these data. Look at the vigorous research into atmospheric data. This is coordinated and watched over by NASA." Environmental science needs something similar, he says.

"In a perfect world, that would be great," said one environmental scientist contacted for this article. "But NASA's like a Rolls Royce and environmental sciences is a VW van—an old, beat-up VW van. We have to do the best with what we've got." However, the new data quality legislation could force a federal agency to step in and ensure that K_{ow} for hydrophobic compounds is better measured. Until then, environmental scientists should think twice about the basic data they use.

Rebecca Renner is a contributing editor to ES&T.

References

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