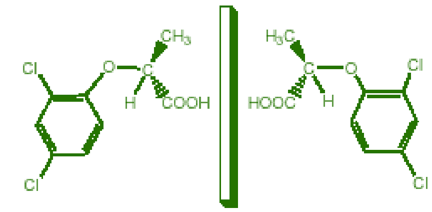
U.S. Environmental Protection Agency

MIRROR IMAGES

Chiral Chemistry: the ultimate in pollutant speciation

What's in a molecule? We ordinarily think that the diagram of a molecule's structure shows everything about the way the atoms connect to make a specific chemical with defined properties. *However,* with some molecules, a careful look at their three dimensional structure offers a surprise – there are two ways to connect the atoms. These are called *chiral* molecules, or chiral chemicals, from the Greek *cheir* (hand), because, like hands, the two forms of the molecule are non-superimposible mirror images of each other. These two species are called *enantiomer*s.



(R)-(+)-dichlorprop (S)-(-)-dichlorprop

Enantiomers of the chiral herbicide dichlorprop

Objective: Enantiomers have identical physical and chemical properties except when they interact with enzymes or with other chiral molecules; then they usually react differently, or selectively. This *enantioselectivity* results in different rates of microbial transformation and differences in activity and toxicity of the two enantiomers. Up to 25% of pesticides are chiral molecules, as are some PCBs and many other pollutants. However, almost all chiral pesticides are manufactured and applied as mixtures of equal amounts of the two enantiomers. On the other hand, the agrochemical industry and government regulators are beginning to take enantioselectivity into account. For example, the (R)-(+)-enantiomer of the herbicide dichlorprop (as well as the (R)-(+)-enantiomers of all the phenoxypropionic acid herbicides) is the active enantiomer, killing the weeds, while the (S)-(-)-enantiomer is inactive (see the dichlorprop structures above); so, to reduce the amount of herbicide used and avoid the possibility of the unnecessary enantiomer causing some adverse impact, several European countries have decreed that only the (R)-enantiomers will be used. To make more accurate risk assessments of chiral pesticides, it is necessary to understand the relative persistence and effects of their enantiomers. **The objective of our research is to determine the environmental occurrences, fate and effects of the enantiomers of selected chiral pesticides and other chiral organic pollutants.**

Our research approach

Separation: develop analytical techniques (GC, HPLC or CE) to separate enantiomers *(*1).

Occurrence: analyze water, soil, sediment, biota and food samples expected to contain chiral pollutants to determine occurrences and ratios of the enantiomers

Transformation: conduct degradation experiments in selected environmental matrices to measure enantioselectivity and rates of enantiomer degradation

Effects: for especially important pollutants, separate and collect enough of each enantiomer for individual toxicity testing.

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Some results

- The enantioselectivity occurring during microbial transformation of chiral pesticides in soils may be substantially altered by environmental changes imposed on the soils, thus changing the relative persistence of the enantiomers *(2*).
- Bromochloroacetic acid, formed by chlorination of drinking waters containing naturally occurring bromide, degraded enantioselectively in all six natural waters and a municipal wastewater effluent into which it was spiked.
- o,p'-DDD, a chiral residue that remains in fish tissue after exposure to DDT, occurs primarily as the (S)-enantiomer.
- The (R)-enantiomer of o,p'-DDT was shown by endocrine disrupter screening tests to have much more estrogenic activity than the (S)-enantiomer.
- Several chiral PCB congeners occur enantioselectively in lake and river sediments (3), indicating the biotransformation has occurred, as well as in associated biota.

Useful publications

1. Garrison, A.W. "Analysis of Chiral Pesticides and Polychlorinated Biphenyl Congeners in Environmental Samples" in *Encyclopedia of Analytical Chemistr*y, R.A. Meyers, ed., pp. 6147-6158, John Wiley & Sons, 2000. (A general reference to chiral chemistry in the environment.)
2. Lewis, D.L., Garrison, A.W., Wommack, K.E., Whittemore, A., Steudler, P., Melillo, J. "Influence of environmental changes on degradation of chiral pollutants in soils" *Natur*e, 1999, 401, 898-901.
3. Wong, C.S., Garrison, A.W., Foreman, W.T "Enantiomeric composition of chiral polychlorinated biphenyl atropisomers in aquatic bed sediment" *Environmental Science and Technolog*y, 2001, 35, 33-39.

Selected milestones

June 2001 - APM 127: Characterize the enantiomeric ratios of selected organophosphorus (OP) and other widely used and less persistent pesticides in environmental and food samples
2001 – Measure the endocrine disrupting activity of the enantiomers of selected persistent organochlorine (OC) pesticides
2002 – Measure the degradation rates and endocrine disrupting activity of the enantiomers of selected OP and other less persistent pesticides
2003 -- Measure the relative microbial degradation rates of the enantiomers of selected OC pesticides and PCBs in soil and sediment systems

Expected Benefits

- **Risk assessment –** increased accuracy of environment and human risk assessment will result from consideration of enantioselectivity in exposure and effects of chiral pollutants
- **Pollution prevention –** use of only the target-active enantiomer of pesticides will reduce the pollutant load and avoid any adverse effects of the other enantiomer.

Participants/affiliations

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