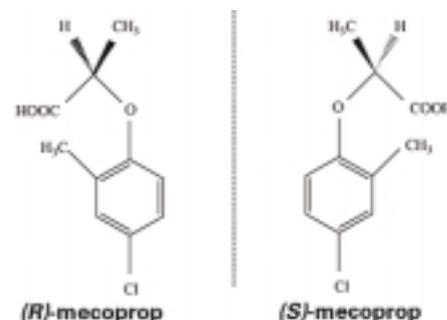


Chiral compounds

Clues for natural attenuation in groundwater

by Geoff Williams & Ian Harrison, *Keyworth*



The two enantiomers of mecoprop.

The release of man-made organic compounds into the environment is a potential threat to ecosystems and to human health. Agricultural pesticides are used in large quantities to improve crop yields, yet are extremely toxic and their long-term fate in groundwater needs to be understood. Pesticides are ubiquitous in groundwater in many countries, albeit at low concentrations, but the EC recommended limit of 0.1 micrograms per litre in drinking-water is also very low.

In the past, agrochemicals were relatively simple molecules having gross effects on the target organism but, with a subtler understanding of biochemical processes at a cellular level, chemists now design biocide molecules to block specific metabolic steps. Many are modified forms of natural biocides such as pyrethrins which are chiral, that is they exist as 'left-handed' and 'right-handed' mirror image forms. However, usually only one form (called an enantiomer) is biologically active. Consequently many of the new biocide molecules which are successful metabolic blocking agents are also chiral.

Chiral molecules are identical chemically and physically, but they may behave differently in biological systems. Thalidomide is a well-known chiral compound; one form is an anti-emetic, while the other is teratogenic, causing severe malformations in the developing foetus (although it is now proving useful in cancer treatment).

Our interest in the chiral pesticide mecoprop stems from extensive groundwater pollution that has arisen from the disposal of an estimated 40 tonnes of pesticide tank washings into a landfill in the Lincolnshire Limestone aquifer. A

public water supply borehole 2.5 kilometres away contains eight micrograms of mecoprop per litre of water and has to be treated. When deposited, the mecoprop contained equal amounts of the (*R*) (rectus, or right-handed) and the (*S*) (sinister, or left-handed) enantiomers. Previous studies have shown that the enantiomers degrade at different rates but only in aerobic conditions, so changes in their ratio with distance from the landfill might indicate biological changes associated with mecoprop's natural 'clean-up' (or natural attenuation) in the aquifer.

Measurements show that the enantiomeric ratio does not change in the landfill where conditions are sulphate reducing, suggesting that no degradation has occurred even though disposal ceased ten years ago. However, as the mecoprop migrates along with biodegradable compounds also from the landfill, inversion of the (*R*)-mecoprop to (*S*)-mecoprop appears to take place in anaerobic conditions, but without degradation. This may be initiated by enzymes

released by bacteria, which metabolise the more degradable organic compounds present. Further east along the flow path the groundwater becomes aerobic; the (*S*)-mecoprop degrades faster than (*R*)-mecoprop, and the (*R*)-enantiomer predominates. Further east still, water in the Lincolnshire Limestone is naturally anaerobic and sulphate reducing, so mecoprop stops degrading and the enantiomeric ratio stays constant (see table).

This evaluation is being confirmed by laboratory work involving microcosms to identify the conditions under which inversion and degradation occur, the microbial consortia present, and the enzymes responsible for inversion.

Preliminary results suggest that enantiomeric ratios provide insight into mecoprop degradation/inversion in relation to the geochemical conditions in the groundwater. There are many other chiral compounds of environmental concern and the knowledge gained from this study may help in assessing their fate.

| Zone | Organic Content | Redox state | EF* | Inferred processes |
|-----------------------|-----------------|--------------------------------|-------------------|---|
| Close to the landfill | High | Sulphate reducing/methanogenic | EF = 0.5 | No degradation or inversion |
| Landfill plume | Intermediate | Iron & nitrate reducing | EF < 0.5 | Inversion of (<i>R</i>)- to (<i>S</i>)-mecoprop |
| Unconfined aquifer | Background | Aerobic | trend to EF > 0.5 | (<i>S</i>)-mecoprop degrades faster |
| Confined aquifer | Background | Sulphate reducing | EF constant | No degradation or inversion |

*We use the Enantiomeric Fraction $EF = [R]/([R] + [S])$ to avoid infinite values of $[R]/[S]$ where $[R]$ and $[S]$ are the concentrations of the two enantiomers.