

Soil-air exchange of legacy organochlorine pesticides

T.F. BIDLÉMAN¹, P.B. KURT-KARAKUS², F. WONG³,
L. M. JANTUNEN⁴, H.A. ALEGRIA⁵ AND K.C. JONES⁶

^{1,2,4}Centre for Atmospheric Research Experiments,
Environment Canada, 6248 Eighth Line, Egbert, ON,
L0L 1N0 Canada

³Environment Canada, 4905 Dufferin St., Downsview, ON,
M3H 5T4 Canada

⁵Dept. of Environmental Science, Policy and Geography,
University of South Florida St. Petersburg, 140 Seventh
Avenue South, St. Petersburg, FL, 33701 U.S.A.

⁶Dept. of Environmental Science and Centre for Chemical
Management, Lancaster University, Lancaster, LA1 4YQ,
U.K.

Of the dozen persistent organic pollutants (POPs) to be eliminated under the Stockholm Convention, eight are organochlorine pesticides (OCPs: DDT, aldrin, dieldrin, endrin, heptachlor, chlordane, mirex and toxaphene). Residues of OCPs remain in agricultural soils and are continually emitted into the atmosphere, thereby buffering atmospheric concentrations and slowing rates of decline. OCPs also contaminate background soils, presumably as a result of atmospheric deposition. "Chemical markers" for identifying sources and tracing soil-air exchange include pesticide isomers, parent/metabolite pairs and enantiomers of chiral compounds. Elevated concentrations of OCPs in air over agricultural soils confirm their emissions and, when coupled with micrometeorological techniques, such measurements can determine fluxes. The relative volatilities of soil residue components can be used to reliably predict their proportions in air. Campaigns in southern Mexico show much higher concentrations of DDT in air compared to temperate North America, yet proportions of DDT/DDE in air of the Great Lakes region implicate emissions from regional soils rather than transport from Mexico. Profiles of toxaphene constituents in soil and air of the southern U.S.A. and Mexico show characteristic depletion of certain labile congeners. These congeners are also depleted in surface water samples from the Atlantic Ocean during the 1990s, however sample profiles from the 1980s more closely resemble technical toxaphene. Enantiomers of two chiral components of technical chlordane, *trans*- and *cis*-chlordane, are in nonracemic ratios in present-day ambient air samples, but were racemic in atmospheric deposition samples from Sweden in the early 1970s. Background soils contain residues of DDT which vary over four orders of magnitude and are poorly correlated with latitude or percent soil organic matter. Residues of chiral OCPs in these soils show much more variability in enantiomer composition than do the same compounds in ambient air. These observations indicate the dual role of soils in supplying OCPs to and receiving them from the atmosphere, the changing role of agricultural application vs. soil emission sources and postdepositional diagenesis of OCPs in background soils.

Experimental investigation of the behaviour of CO₂ droplets rising in seawater under hydrate forming conditions

N. BIGALKE¹, G. REHDER² AND G. GUST³

¹(nbigalke@ifm-geomar.de)

²(gregor.rehder@io-warnemuende.de)

³(gust@tu-harburg.de)

We present comprehensive experimental results on the upward motion of CO₂-droplets in simulated deep-sea environments. A cooled high pressure tank was used to establish conditions along a natural oceanic hydrotherm. At pressures and temperatures well inside the CO₂ hydrate stability field, observed rise rates were in accordance with predictions based on empirical equations developed to match momentum of hydrate-covered, deformed droplets. In contrast, droplets rising at P,T conditions closer to the phase boundary deviated from model predictions in numerous instances. This was related to a partially incomplete or missing hydrate skin due to insufficient thermodynamic forcing. To support this relationship, additional experiments outside the field of hydrate stability were carried out and compared to the erratic data. The results confirm expectations and show that non-hydrated droplets have a markedly different rising behaviour and rise rates of up to 40% higher than equally buoyant droplets with a hydrate skin. This might have a significant impact on the vertical distribution of dissolved CO₂ in the ocean and has to be taken into account when assessing CO₂ sequestration at mid water depth.