Environmental Fate and Distribution of Lindane

CHEM 331: Environmental Organic Chemistry
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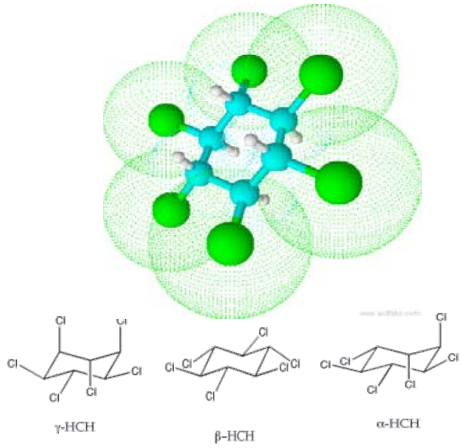
INTRODUCTION[1]

Hexachlorohexane's (HCH) are among the most distributed and frequently detected organochlorine contaminants in the environment. Production of HCH began in 1943 and due to their low cost, world wide use reached about 10 million tones between 1948 and 1997. More acutely toxic then DDT, Lindane has been shown to interfere with the cation flux across nerve cells resulting in motor and mental impairment, convulsions, and violent seizures for example.

There are 8 isomers of hexachlorocyclohexane (HCH) and technical grade HCH consists of 5 isomers: α-HCH, β-HCH, γ-HCH, δ-HCH, ε-HCH. Lindane refers to refined technical grade HCH that is >99% γ-HCH, which is the only isomer with strong insecticidal properties. As one of Canada's top 10 insecticides, Lindane was used until 2003 in Canada primarily for canola seed treatments in the prairie region, as well as, insect control of grain, fruit and vegetable crops throughout the world. Furthermore, the pharmaceutical industry utilizes Lindane for treatment of scabies and lice. Over 14 countries have banned the use and 16 others have restricted use however, unused stockpiles still exist to this day.

Although the use of technical grade HCH has decreased there are many places throughout the world that still use Lindane. The continued use of γ-HCH is a concern not only for the release of Lindane itself, but it has been shown to attribute to the accumulation of α– and β–HCH through isomerization reactions that occur within the environment; both which are arguably more detrimental to the environment.



POSSIBLE REMEDIATION TECHNIQUES

Although the use of Lindane and other HCH's have been banned in many areas, they are still currently used in some places resulting in many contaminated places. Phytoremediation is a possible way to clean up contaminated site through the uptake of HCH's into plants. As the plant matter degrades accumulation occurs at the soil surface however, as humification of organic matter occurs the bioavailability of the contaminant decreases as a "bound-residue" is formed (7). This remediation technique is arguably not long term since the contaminant is not removed from the environment.

Another remediation technique is the use to zero-valent iron nanoparticles. By passing contaminated water through the nanaoparticles, the iron acts as a strong electron donor for the removal of chlorine atoms. Lindane is degraded by this technique is via dechlorination or dehydrochlorination. This technique is very promising but not without its problems. Two examples of the problems encountered are the precipitation of metal hydroxides on the iron decreasing the reactivity, as well as, the possible increase in toxicity and persistence of the released products (8).

ENVIRONMENTAL DISTRIBUTION AND SIGNIFICANCE

TABLE 1: Comparison of the physical properties and partition constants for the three environmentally significant HCH isomers and DDT.

	log K_{OW}[2]	-log C^{w}_{SAT} (M)[2]	log P^{0} (atm)[2]	-log K_H[2] (calculated)	log BCF[3]
γ–HCH	3.78	4.60	-7.16	3.94	3.00
α-HCH	3.81	5.28	-7.53	3.63	2.85
β-HCH	3.80	6.46	-9.41	4.33	2.82
DDT	6.36	7.80	-9.71	3.30	4.71

- the most environmentally significant isomers are γ-HCH, α-HCH, and β-HCH
- all three isomers have moderately high vapor pressures and high water solubility compared to other organochlorine contaminates therefore, generally detected in the atmosphere or bodies of water (1)

- the log K_{OW} value represents the partitioning between an organic phase, such as soil, and the water phase
- all three isomers have values in the same order of magnitude indicating a preference to partition into the soil from the water

- the vapor pressure is a direct measurement of the strength of intermolecular forces
- γ-HCH and α-HCH have vapor pressures about one order of magnitude larger than β–HCH and DDT due to weaker intermolecular forces
- α-HCH and γ-HCH have slightly larger K_H values and therefore, would be more prevalent in the atmosphere than in the water compared to β-HCH

When lindane and other HCH's are applied to the soil, the major loss is though volatilization into the atmosphere. Remaining HCH's are removed via abiotic or biotic degradation. Depending on the environmental conditions in the atmosphere or the soil, γ-HCH can be transformed into other HCH isomers, some which are more persistent and more toxic.

Being the most frequently detected organochlorine contaminant in the environment and more acutely toxic than DDT, the use of HCH as insecticides has decreased. However, stock piles of technical grade HCH still exist throughout the globe resulting in the contamination by HCH's for many years to come. Furthermore, Lindane is still used in many places and through isomerization reactions within the environment accumulation of α-HCH and β-HCH will occur both which are arguably more detrimental than γ-HCH.

LITERATURE CITED

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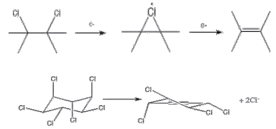
VICINAL DEHALOGENATION

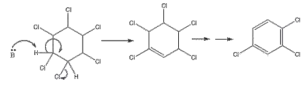
- important reaction in environments such as flooded rice soils and anaerobic sewage sludge
- the dehalogenation products are generally less toxic and more degradable



- the reaction requires two electrons resulting in the loss of two chlorines (4)
- within the environment, naturally occurring humic material and metal ion complexes can act as electron donators thereby becoming oxidized themselves as the reaction proceeds (4)

DEHYDROCHLORINATION

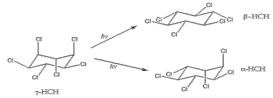
- in basic aqueous solutions, HCH dehydrochlorinates forming pentachlorocyclohexene then to trichlorobenzene
- half-life for Lindane at pH 8 and 5°C was found to be 42 years (5)
- at pH 7 and 25°C, the half-life was found to be 241 days (k_H = 1.2E-04 hr^{-1}) (5)



- in slighly basic environments, dehydrohalogenation results in 1,2,4-trichlorobenzene forming 3 molecules of hydrochloric acid per 1 molecule of lindane (5)
- the dehydrochlorination is an elimination reaction where the carbon-hydrogen bond and carbon-chlorine bond are in the antiperiplanar conformation ensuring the σ bonds are in the correct alignment to form a π bond (6)

PHOTOISOMERIZATION AND BIODEGRADATION

- Lindane can be transformed into α–HCH and β-HCH
- the absorption of Lindane in the troposphere is weak so the photochemical rate constant of the isomerization would be low (1)



- in most soils, Lindane is biodegraded to γ-pentachlorocyclohexene, benzene and chlorobenzene (3)
- anaerobic soil conditions lead to the microbial transformation into α-HCH, tetrachlorobenzene, tetrachlorocyclohexane, and pentachlorobenzene for example (3)
- several grass species have shown the ability to metabolize γ-HCH to β-HCH (3)