# Pre-Feasibility Study on Environmental Photolysis of *p,p′*-DDT and *γ*-HCH

Hanari, N.[1], Falandysz, J.[2], Saba, M[2], Yamazaki, E[3], Yamashita, N[3]

[1]National Institute of Advanced Industrial Science and Technology (AIST) Tsukuba Central 3, Tsukuba, Ibaraki, Japan, 305-8563; [2]University of Gdansk, Gdansk, Poland; [3]AIST Tsukuba West, Tsukuba, Ibaraki, Japan, 305-8569

## Introduction

*p,p′*-DDT [1,1-*bis*(4-chlorophenyl)-2,2,2-trichloroethane] and gamma (*γ*)-HCH (hexachlorocyclohexane, lindane) are the examples of organochlorine compounds used in a massive scale as agricultural insecticides from the 1940s [1]. Apart from the appliances in agriculture, the *p,p′*-DDT was also used in human hygiene and epidemiology, and relatively widely in forestry - until the 1980s in the former Eastern Germany [1,2]. Both *p,p′*-DDT and *γ*-HCH are easily spread via the atmospheric transport and diffused worldwide, and they are readily adsorbed to soils and sediments where can persist for a long-term [3]. Similarly to them, the environmentally persistent and toxic are polychlorinated naphthalenes (PCNs), which are industrial chemicals. PCNs occur in trace as by-products in some synthetized organochlorine compounds and are produced unintentionally in thermal processes such as combustion, incineration, and others [4]. PCNs were manufactured and used as the technical formulations of several types that become known under the brand name of Halowax from 1914 until the 1970s [4-5]. DDT, HCH, and PCNs, because of their proven toxicity, persistency, accumulation and transfer via food web are in the recent decades of years almost continuously studied and monitored in the environmental media, food and human [3]. Moreover, they are registered in the Stockholm Convention on Persistent Organic Pollutants (POPs) as listed chemicals in Annex A or B [6].

DDT, HCH, and PCNs like many other POPs possess similar physical and chemical properties such as lipophilicity and low vapor pressure. Hence, they are expected to behave roughly similar in the air, water, soils or sediments. Nevertheless, when studying a fate of POPs in the "abiotic" environmental media as mentioned above, the unique characteristics of a medium and its biological activity also have to be taken into account. The insecticides DDT, HCH, and industrial chemical PCNs are hydrophobic and all they possess high affinity to surfaces of a different type, while all the surfaces containing an organic component have the greatest adsorption capacity for POPs [7].

An insight into possible atmospheric fate and some photolytic characteristics of several POPs has been obtained recently in controlled experiments performed in the high mountain environment, and from a study of real water media samples collected from the Himalayan region of the Eastern Tibetan Plateau. The experiments performed *in vitro* and the study of glacial samples from a region of the peak of Minya Konka (Mt. Gongga) from the Eastern Tibetan Plateau showed on induced by sunlight degradation of several perfluoroalkyl substances (PFASs) containing PFCAs (perfluorocarboxylic acids) and PFSAs (perfluorosulfonic acids). An exposure to sunshine resulted in degradation (probably via de-alkylation) of longer chain compounds and formation of shorter chain compounds or

disappearance of some PFASs [8,9]. Also, PCNs contained in the Halowax when exposed to sunlight in a mountain environment (at the top of the Mt. Mauna Kea in Hawaii, USA) [10] or an environment of other type (campus of the Yuxi Normal University in Yuxi, Yunnan Province, China) [11] undergo a widespread photolytic degradation but some isomers of hexachloronaphtahelene, *i.e.* 1,2,3,4,6,7-HxCN/1,2,3,5,6,7-HxCN (PCN #66/67), survived.
Aim of this study was to examine in field a possible photodegradation by sunshine of *p,p'*-DDT and *γ*-HCH dissolved in water. The sunlight conditions in the experiment were the same as in a mentioned experiment with PCNs.

## Materials and methods

The sites selected for the field experiments were the campus of the Yuxi Normal University, Yuxi, Yunnan Province (China) and the Mt. Mauna Kea in Hawaii Island (USA). Experiment in Yunnan was carried out for 149 days (from June 22, 2015 to November 17, 2015) at elevation of 1700 m above sea level [11] and experiment in Hawaii was carried on for 106 days (from September 10, 2010 to December 24, 2010) at elevation of 4200 m [10]. The *p,p'*-DDT (Sigma-Aldrich Japan, Japan) and γ-HCH (Tokyo Chemical Industry, Japan) standards were dissolved in a mixture of methanol and acetone, and then diluted with Milli-Q water. Methanol and acetone amounts in the test solutions were at concentrations of around 1 %. The solutions made were divided into three tubes and amount was 3 mL for each sample. The test tubes were made of the Pyrex glass (capacity 5 mL) equipped with a butyl rubber septum cap at the top. One solution in set of three tubes (containing *p,p'*-DDT or γ-HCH) was randomly selected as a control sample and kept under darkness at –20 °C immediately after preparation. The remaining two solutions in the tubes were transported under darkness within 2 days from preparation to the sampling locations. During the solar irradiation, the test tubes were kept in a clear polyethylene container without a cover from the top. An initial concentration each of the studied compounds was approximately 1 $\mu g\ mL^{-1}$. After the photolysis experiments, the compounds were extracted with *n*-hexane and separated by capillary gas chromatography coupled to quadrupole mass spectrometry (GC-MS, Agilent Technologies 6890 GC and 5973 MS, USA) [9]. The analytes were monitored with electron ionization in the selected ion monitoring mode (*p,p'*-DDT, *m/z* 235 and 237; *γ*-HCH, *m/z* 181 and 219).

## Results and discussion

The total ion chromatograms of intact and exposed *p,p'*-DDT and *γ*-HCH solutions prepared in Pyrex tubes were examined and compared. The *p,p'*-DDT and *γ*-HCH concentrations decreased significantly after the experiments. The *p,p'*-DDT in the sunshine exposed solutions almost disappeared since a degradation rate noted was over 75% in both experiments (Fig. 1). A high rate of disappearance of *p,p'*-DDT in tested solutions can be explained as a result of direct exposure to UV [12]. An intact sample apart from *p,p'*-DDT originally contained by-side *p,p'*-DDE [1,1-*bis*(4-chlorophenyl)-2,2-dichloroethylene] at concentration of approximately 0.30 % and *p,p'*-DDD [1,1-*bis*(4-chlorophenyl)-2,2-dichloroethane] at 0.15 %. Interestingly, the amounts of *p,p'*-DDE and *p,p'*-DDD arising from degraded *p,p'*-DDT were in exposed solutions in similar proportion in both experiments. In experiment by Chu, a photodegradation of *p,p'*-DDT resulted in formation of its principal degradation products such as *p,p'*-DDD and *p,p'*-DDE, which both initially increased in concentrations, while highly decreased in course of the experiment [13]. In the experiments performed with *γ*-HCH, the result was a little bit different from that observed in the experiments with *p,p'*-DDT. In the experiment performed in the Yunnan site, exposed *γ*-HCH disappeared almost entirely from the irritated solution, while *γ*-HCH survived in the Hawaiian site (Fig. 1). A lack of the degradation of *γ*-HCH in the Hawaiian site when compared to the Yunnan site can be because of a difference in the environmental conditions between the sites due to different localization, duration of the experiment, season and/or UV pattern. A residual abundance of *γ*-HCH can be higher than that of *p,p'*-DDT under similar irradiation condition [14].

In our experiment with *p,p'*-DDT has not been found any of its known degradation products such as DDD and DDE. For HCH, characteristic degradation products were not detectable in this study. In contrast to the results from this study a part of PCNs survived in exposed Halowax samples [10,11]. In the Halowax irradiated under the Hawaiian condition some congeners of PCN survived, while PCN #66/67 dominated after irradiation, and under the Yunnan experiment condition survived only PCN #66/67. Hence, the ultraviolet rays energy from the sunshine in the region of Yunnan in China was stronger than at the Hawaiian site and this can be read from the results obtained after irradiation experiments with *p,p'*-DDT, *γ*-HCH, and PCNs. Moreover, the photolysis pathway of the analytes may be significantly different for the sites. Those experiments are continued and more results can be known later.

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## References

1. Guzzella L, Roscioli C, Vigano L, Saha M, Sarkar SK and Bhattacharya A (2004) *Environment International*, **31**, 523-534.
2. Heinisch E and Wenzel-Klein S (1994) Produktion und Anwendung von Chlorkohlenwaserstoff-Pestiziden in der ehemaligen DDR, Schadstoffatlas Osteuropa. *Okologisch-chemische und okotoxikologische Fallstudien iiber organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa* (Heinisch E, Kettrup A, and Wenzel-Klein S, Eds.). Ecomed, Landsberg am Lech.
3. Falandysz J, Brudnowska B, Kawano M and Wakimoto T (2001) *Archives of Environmental Contamination and Toxicology*, **40**, 173-178.
4. Falandysz J (2003) *Food Additives & Contaminants*, **20**, 995-1014.

5. Taniyasu S, Horii Y, Hanari N, Yamashita N, Pan J, Yang Y and Loganathan BG (2011) *Global Contamination Trends of Persistent Organic Chemicals* (Loganathan BG and Lam PKS, Eds.) pp 215-258, CRC Press, Florida.
6. Stockholm Convention on Persistent Organic Pollutants (POPs), Programmes, New POPs, Overview. <http://chm.pops.int/Programmes/New%20POPs/Overview/tabid/667/language/en-US/Default.aspx>.
7. Elder G and Weber K (1980) *Chemosphere*, **9**, 111-118.
8. Taniyasu S, Yamashita N, Yamazaki E, Petrick G and Kannan K (2013) *Chemosphere*, **90**, 1686-1692.
9. Yamazaki E, Falandysz J, Taniyasu S, Hui G, Jurkiewicz G, Yamashita N, Yang YL and Lam PKS (2016) *Journal of Environmental Science and Health, Part A*, **51**, 63-69.
10. Hanari N, Falandysz J, Petrick G, Nakano T and Yamashita N (2013) *Organohalogen Compounds*, **74**, 32-35.
11. Hanari N, Falandysz J, Yamazaki E and Yamashita N (2016) *Organohalogen Compounds*, **78**, 1030-1033.
12. Keum Y-S and Li QX (2004) *Bulletin of Environmental Contamination and Toxicology*, **72**, 999-1005.
13. Chu W (1999) *Environmental Science & Technology*, **33**, 421-425.
14. Zaleska A, Hupka J, Wiergowski M, Biziuk M (2000) *Journal of Photochemistry and Photobiology A: Chemistry*, **135**, 213-220.

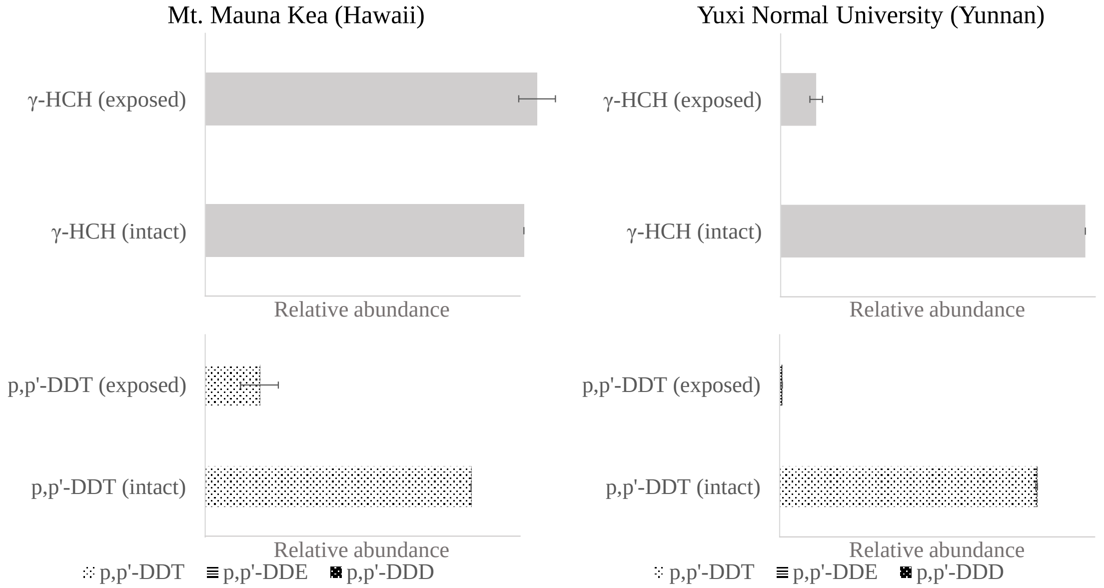

Fig. 1 Relative abundances of *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, and *γ*-HCH in intact and exposed solutions prepared in Pyrex tubes from the Mt. Mauna Kea (Hawaii, USA) and Yuxi Normal University (Yunnan, China) photodegradation experiments.