

## Degradation of organochlorine agrochemicals by mechanochemical treatment

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### Introduction

The sale and use of persistent and toxic organochlorine agrochemicals such as  $\gamma$ -hexachlorocyclohexane have been banned in most countries. However, for economic reasons,  $\gamma$ -HCH is still used in some countries, and there are many  $\gamma$ -HCH-contaminated sites around the world. Large quantities of organochlorine compounds were produced in Japan, and unused products have been buried and stockpiled at various sites under the control of the Ministry of Agriculture, Forestry, and Fisheries (MOAFF). The Stockholm Convention on Persistent Organic Pollutants (POPs) requires that signatories take measures to decompose and detoxify POPs, including not only organochlorine agrochemicals and PCBs but also by-products such as dioxins.

As one experimental technology for treating stockpiles of POPs and other organochlorine agrochemicals, MOAFF selected mechanochemical (MC) treatment. MC treatment has been demonstrated to efficiently degrade organochlorine compounds such as DDT<sup>1</sup>, PCB<sup>2, 3</sup>, chlorobenzenes<sup>3, 4</sup>, and dioxins<sup>2</sup>. Although MC treatment is expected to be a good technology for the remediation of POPs and other organochlorine agrochemicals, the degradation efficiency of MC treatment may depend on the structures of the target compounds. In addition, information about degradation pathways is essential for determining whether these hazardous compounds can be degraded safely. Here, we report on the applicability of a MC treatment method for several types of organochlorine agrochemicals and their degradation behaviors.

### Methods and Materials

The MC reactor used was a planetary ball mill (Pulverisette-7, Fritsch, Germany) with two stainless-steel pots (45 cm<sup>3</sup>) in which seven steel balls (15-mm diameter) were arranged. The pots were situated on a rotating disk that permitted the pots and the disk to rotate in opposite directions. Heptachlor,  $\gamma$ -hexachlorocyclohexane (HCH), and pentachloronitrobenzene (PCNB) were used as representative organochlorine compounds. Heptachlor and HCH are two of the twelve compounds that were assigned high priority in the POPs convention, and PCNB contains dioxins as impurities.

Each target compound (200 mg) was milled with 2 g of CaO. To confirm mineralization of chlorine, a portion of each milled mixture was extracted with water. The filtrates were analyzed for chloride ions by means of ion chromatography (IC 7000, Yokogawa Analytical Systems Co., Japan). A second portion of each milled mixture was extracted with hexane and dichloromethane using reciprocal shaking according to the standard analytical method for analysis of organic compounds using low-resolution gas chromatography/mass spectrometry (LR-GC/MS; HP 5973 MS selective detector, Agilent, USA).

### Results and discussion

#### 1. Degradation of organochlorine agrochemicals by MC treatment

After 2 h of MC treatment, the amounts of chloride ions in the milled mixtures of CaO and heptachlor, PCNB, and  $\gamma$ -HCH were measured. The dechlorination ratios (defined as the ratio of the amount of chloride ions after milling to the amount of chlorine in the initial quantity of the parent compound) were approximately 100% for all three compounds, and no organochlorine compounds were detected by LR-GC/MS (Table 1). These results confirmed that the three organochlorine agrochemicals were completely dechlorinated by the MC process and implied that they could be safely treated by means of the process without the production of other organochlorine compounds. Note that no

organic compounds were detected in the milled samples after 2 h of MC treatment, which indicates that low-molecular-weight organic or inorganic compounds undetectable by LR-GC/MS may have been produced.

Table 1: Dechlorination ratio of organochlorine agrochemicals after MC treatment (2 h)

Target compound	heptachlor	PCNB	$\gamma$ -HCH
Dechlorination ratio (%)	99.4	100.8	99.4

## 2. Degradation behavior of $\gamma$ -HCH

A mixture of  $\gamma$ -HCH and CaO (1:10 molar ratio with respect to chlorine bound to  $\gamma$ -HCH and calcium) was milled for 2 h. During the milling period, the degradation products of  $\gamma$ -HCH were analyzed by LR-GC/MS in scan mode over the mass range of 50–550  $m/z$  for identification of the products and in selective ion monitoring mode for quantification of the identified compounds.

Many degradation products appeared in the total ion chromatogram of  $\gamma$ -HCH after 15 min of MC treatment (Fig. 1). By comparing the mass spectrum patterns with data stored in the U.S. National Institute of Standards and Technology mass spectral library (ver. 2) and by carrying out spike tests with standard materials, we identified the degradation products as monochlorobenzene (MCBz), dichlorobenzenes (DiCBzs), trichlorobenzenes (TriCBzs), tetrachlorobenzenes (TeCBzs), and 1,2,4,5,6-pentachlorocyclohexene (PCCH). (Note that we synthesized PCCH from  $\gamma$ -HCH and used it for the spike test because a commercial standard was not available.)

$\gamma$ -HCH was completely degraded after 30 min, and the amounts of DiCBzs and TriCBzs increased and reached their maximum values at 30 min (Fig. 2). Throughout the MC treatment, CBz and TeCBzs levels remained quite low. Although quantification of PCCH was impossible, owing to the lack of an analytical standard, the area of the PCCH peak suggested that PCCH was a major product of  $\gamma$ -HCH degradation (data not shown). This result indicates that MC treatment of  $\gamma$ -HCH using CaO caused dehydrochlorination at first, resulting in the production of PCCH.

At longer milling times, chlorobenzenes were the major degradation products. The mechanism for the production of TriCBzs from PCCH is also likely to be dehydrochlorination; dehydrochlorination of PCCH may produce tetrachlorocyclohexadiene, which subsequently undergoes dehydrochlorination to produce TriCBzs. The instability of tetrachlorocyclohexadiene may be the reason that it was not detected. The rate of dehydrochlorination of tetrachlorocyclohexadiene is expected to be higher than that of PCCH.

As far we know, this is the first paper to report the production of a benzene ring by means of mechanochemically induced dehydrochlorination of polychlorinated cyclohexane, although some studies have shown dechlorination of organochlorine compounds by MC treatment<sup>1, 2, 3, 5</sup>. Note that pentachlorocyclohexane, a dechlorination product of  $\gamma$ -HCH, was not detected. This result indicates that MC degradation of  $\gamma$ -HCH proceeded by means of dehydrochlorination.

The dechlorination of  $\gamma$ -HCH by MC treatment was confirmed by the 100% recovery of inorganic chlorine, although some organochlorine compounds were produced as intermediates.

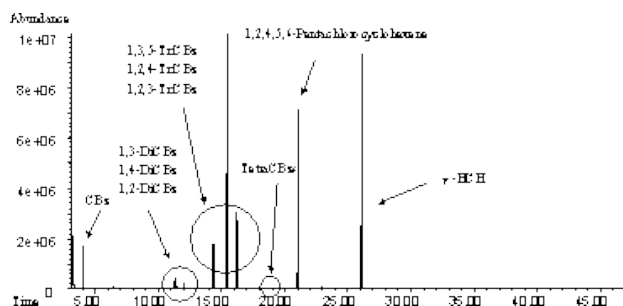


Figure 1. LR-GC/MS chromatogram of the degradation products obtained by MC treatment of  $\gamma$ -HCH for 15 min

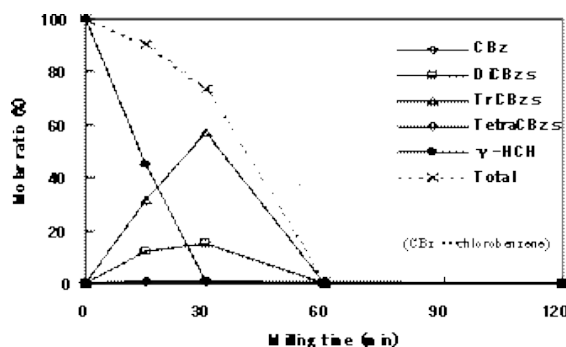


Figure 2. Time dependence of the molar ratio of chlorobenzenes produced during MC treatment of  $\gamma$ -HCH

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### References

1. Hall, A. K., Harrowfield, J. M., Hart, R. J., Maccormick, P. G.; (1996) *Environ. Sci. Technol.*, 30, 3401-3407.
2. Nomura, Y., Nakai, S., Lee, B-D., Hosomi, M.; (2002) *Kagaku Kogaku Ronbunshu*, 28, 5, 565-568.
3. Birke, V., Mattik, J., Runne, D.; (2004) *J. Material Sci.*, 39, 5111-5116.
4. Loiselle, S., Branca, M., Mulas, G., Cocco, G.; (1997) *Environ. Sci. Technol.*, 31, 261-265.
5. Zhang, Q.; Saito, F.; Shinme, K.; Masuda, S.; (1999) *J. Soc. Powder Technol. Japan*, 36, 468-473.