

# 広島県の河川水中における残 薬 に 関する水 その消滅および除去機構

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## Contamination, Fate and Elimination Kinetics of Pesticide Residues in River Water, Hiroshima Prefecture

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### Abstract

#### Chapter 1

#### General Introduction

This chapter focuses on the importance of pesticides for increasing the agricultural effects of their extensive use on the environment. Since these pesticides became universal contaminants found in all segment of our environment especially water. Furthermore, this chapter describes the fate of these pesticides in the contaminated water, the techniques used to eliminate these compounds and finally the aims of this study.

#### Chapter 2

#### Distribution, Seasonal pattern and Flux of Pesticides and Nonylphenol Residues in Kurose River water, Higashi-Hiroshima, Japan

In this chapter distributions, seasonal variation, flux, and contaminati and n n n n a d d ring the period from April 2001 to January 2002 at 5 sites (Namitakiji, Tokumasa-Kami, Izumi, Ochiai, and Hinotsume) in Kurose River water, Higashi-Hiroshima, Japan. The results show that, nineteen pesticide compounds were detected and isoprothiolane (37 ng/l), fenitrothion (35) and iprodione (34) showed the e e concentrations (as 5 site averages), while pencycuron (5), diazinon (6), tolclofos-m t l dithiopyr (8) were the compounds of lowest mean concentrations. Nonylphenol, which is a degradation product of a NPEOs that are used in a wide range of industrial and household product . c u d . p t c d . d n average concentration of 305 ng/l. At each of the five sites, its concentration was greater than individual pesticides. The concentration levels of pesticides

and nonylphenol were highest at Izumi (the downtown site of Higashi-Hiroshima) and were lowest at Namitakiji and Tokumasa-Kami (urban and rural sites, respectively) and fluxes of both compounds tended to be higher in spring to summer and low during fall to winter at most of the sites. The total pesticides concentration was poorly correlated with nonylphenol concentration. A statistical analysis of water quality data suggested that their main sources appear to be different such as agricultural activity for pesticides and wastewater discharge for nonylphenol.

### Chapter 3

#### Photodegradation Kinetics of Fenitrothion in Various Aqueous Media and Its Effect on Steroid Hormones Biosynthesis

The photodegradation kinetics of fenitrothion (common river water pollutant over Japan) in various water media under both direct and indirect photolysis with respect to degradation rate, and phototransformation kinetics of fenitrothion was examined in this chapter. Furthermore, the effect of fenitrothion and its photoproducts on steroid hormone biosynthesis was also investigated. The results show that, the degradation rate of fenitrothion under indirect photolysis to which nitrate was added was faster than that of direct photolysis, in both pure and natural water. The phototransformation kinetics of fenitrothion in pure water showed that the identified photoproducts, such as fenitrooxon and 3-methyl-4-nitrophenol, under both direct and indirect photolysis were almost the same. This is evidence that there is no specific degradation pathway with hydroxyl radicals under indirect photolysis in fenitrothion transformation. The  $\mu\text{M} \sim 50 \mu\text{M}$  levels of fenitrothion and two of its

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si  $\text{H}_2\text{O}_2/\text{UV-VIS}$  system than the  $\text{Fe}^{3+}/\text{UV-VIS}$  and  $\text{H}_2\text{O}_2/\text{UV-VIS}$  systems in natural waters. Subsequently, the mineralization rate of fenitrothion was much faster under the  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-VIS}$  system than other two systems. The high generation rate of hydroxyl radicals measured under  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-VIS}$  system was the key to the fast degradation of fenitrothion. Increases of

hydrogen peroxide and iron concentration level lead to better final degradation of fenitrothion. These results suggest that the photo-Fenton reaction ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-VIS}$ ) system is likely to be an effective method for fenitrothion removal in contaminated natural waters.

## Chapter 5 General Discussion and Conclusion

This chapter summarizes a discussion on the most important results obtained in this study. Numerous pesticide compounds and nonylphenol were detected in Kurose River waters from both agricultural and urban areas at the ppt level. Indirect photolysis affected significantly the degradation rate of fenitrothion. Fenitrothion and its photodegraded products (fenitrooxon and 3-methyl-4-nitrophenol) perturbed steroid hormones biosynthesis in adrenal glands. Photo-Fenton reaction is suggested to be a powerful method for removal of low concentration levels of fenitrothion in contaminated agricultural water.