た。硫酸イオン 100mg/l では過塩素酸イオンのピーク面積に影響を与えなかったが、150mg/l では過塩素酸イオンのピークを半ば飲み込む形になり定量は不可能であった。内部標準過塩素酸-$^{18}O_4$ のピークも、後半はイオンの取り込みが阻害されていた。通常の河川水の硫酸イオン濃度は数十mg/l 程度であり、分析上問題となることは少ないと思われる。炭酸水素イオンに関しても 200mg/l までは過塩素酸イオンのピーク面積に影響が現れず、前処理で除去しなくても分析上問題はないと思われた。

実際の河川水に過塩素酸イオンを添加した結果を図 4 に示す。過塩素酸イオンの添加(0-15μg/l)により、傾き 1.02 でピーク面積が増加しており、マトリックスの影響はほとんどないと考えられる。標準添加法による計算値は 13.7μg/l であり、定法で求めた 14.2μg/l と良く一致していた。

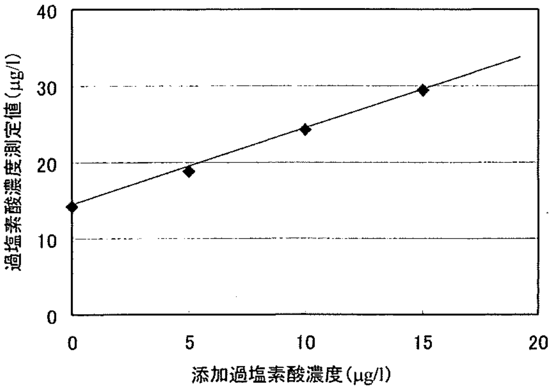


図4　河川水への過塩素酸イオンの添加例

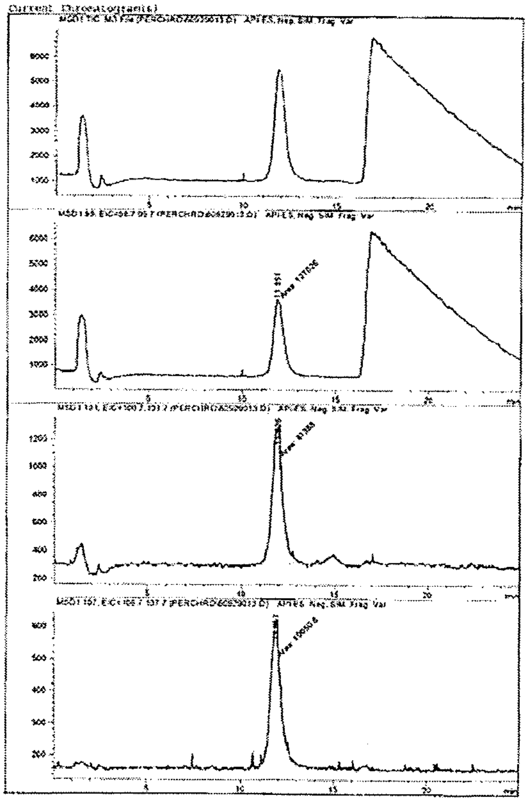
3. 河川水中過塩素酸イオンの分析

群馬県内の河川水 11 地点で半年間分析し、本法が、河川水のモニタリングに適用できるか検討した。

クロマトグラムの例を図 5 に示す。上段は利根川福島橋 2006 年 9 月、下段は谷田川合の川橋 2006 年 8 月である。過塩素酸イオンの定量用 m/z 99 のマスクロマトグラムには、河川水中に存在する硫酸イオンの大きなピークが見られるが、硫酸イオンのピークが過塩素酸イオンのピークに覆い被さることはなかった。

河川水の測定結果を表 1 に示す。河川水 66

利根川 福島橋 2006 年 9 月



谷田川 合の川橋 2006 年 8 月

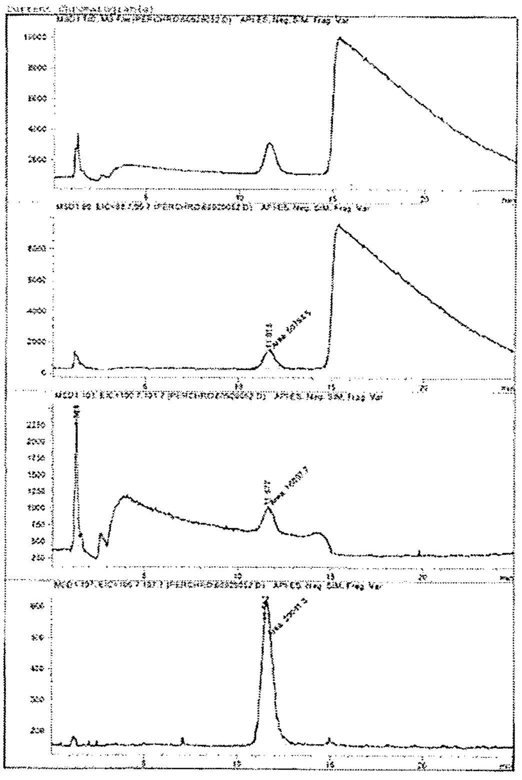


図5　河川水のクロマトグラム

表1　河川水中の過塩素酸イオン濃度

地点	8月	9月	10月	11月	12月	1月
福島橋	9.90	14.21	6.32	8.66	6.52	5.78
中島橋	(0.20)	(0.24)	0.55	0.52	0.44	0.51
保泉橋	4.33	(0.25)	(0.29)	0.34	(0.26)	(0.23)
早川橋	(0.25)	(0.16)	0.36	(0.19)	(0.28)	0.41
前島橋	0.31	0.30	0.44	0.42	0.49	0.45
大川合流前	0.55	0.41	0.61	0.73	0.91	0.63
古利根橋	0.37	0.46	0.52	0.63	1.11	0.80
泉大橋	0.87	0.33	(0.25)	(0.29)	0.38	(0.29)
落合橋	(0.16)	nd	0.34	0.43	0.36	0.44
合の川橋	5.35	3.52	0.73	1.28	1.13	0.83
岩田橋	1.30	1.11	0.33	(0.24)	(0.26)	1.20
当所水道水	－	0.33	(0.25)	0.32	0.32	0.35

単位：g/lμ、（　）内は定量下限値以下、nd < 0.1μg/l、
－：測定せず

検体中約 1/4 の 16 検体が定量下限値以下、1 検体が検出下限値以下であった。人為的な過塩素酸汚染のないと見られる河川水の多くも定量出来ており、本法は河川水のモニタリングに利用可能と思われる。また、得られた過塩素酸イオン濃度は、ND ～ 14.2μg/l であり、全て USEPA が飲料水等価濃度として採用した 24.5μg/l[11]以下であった。日本人は欧米人とは異なり、海草を多量に摂取しているためヨウ素摂取量が多く、過塩素酸イオンの影響は受け難いと考えられる。調査した河川水中の過塩素酸イオンに関しては懸念する必要はないであろう。

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Using precise data sets on farming and pesticide properties to verify a diffuse pollution hydrological model for predicting pesticide concentration

Y. Matsui*, K. Narita*, T. Inoue and T. Matsushita***

*School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
(E-mail: *matsui@eng.hokudai.ac.jp*; *n_exodus_k@yahoo.co.jp*; *taku-m@eng.hokudai.ac.jp*)

**Department of Architecture and Civil Engineering, Toyohashi University of Technology, Tempakucho, Toyohashi, Aichi 441-8580, Japan (E-mail: *inoue@tutrp.tut.ac.jp*)

Abstract Verification of a diffuse pollution model involves comparing results actually observed with those predicted by precise model inputs. Acquisition of precise model inputs is, however, problematic. In particular, when the target catchment is large and substantial estimation uncertainty exists, not only model verification but also prediction is difficult. Therefore, in this study, rice-farming data were collected for all paddy fields from all farmers in a catchment and pesticide adsorption and degradation rates in paddy field soil samples were measured to obtain precise model inputs. The model inputs successfully verified the model's capability to predict pesticide concentrations in river water. Sensitivity analyses of the model inputs elucidated the processes significantly affecting pesticide runoff from rice farms. Pesticide adsorption and degradation rates of the soil did not significantly affect pesticide concentrations, although pesticide discharge to river water accounted for less than 50% of the total quantity of pesticide applied to fields, possibly owing to pesticide adsorption and degradation. The timing of increases in pesticide concentrations in river water was affected mostly by the farming schedule, including the time of pesticide application and irrigation, and secondarily by rainfall events.

Keywords Adsorption; degradation; isoprothiolane; pollutograph; uncertainty

Introduction

Pesticide release from agricultural fields and contamination of surface waters are major threats to human health as well as local ecology in many regions, because surface waters are a primary source of drinking water (e.g. Gilliom *et al.*, 1999). Although pesticide usage in Japan has recently begun to gradually decrease (Ministry of Agriculture, Forestry and Fisheries of Japan, 2005), coinciding with changes in farming practices, the more stringent, recently promulgated drinking water quality guidelines have caused concern at local, regional, and national scales. In general, the amount of pesticide transported to surface waters depends on several factors, including pesticide and soil properties, agricultural practices, watershed characteristics, and weather conditions. Pesticides that are sufficiently resistant to degradation in water and soil and are adequately soluble may be transported readily and may reach water bodies in significant amounts. Various mathematical models have been developed to describe quantitatively pesticide runoff as a function of the factors mentioned above and to predict pesticide concentrations in surface waters (Borah and Bera, 2003, 2004). However, pesticide runoff and the processes by which pesticides are distributed environmentally are complex, and their modelling inevitably involves uncertainty associated with model shortcomings (structural errors or model inadequacy) as well as model inputs and parameters (Dubus *et al.*, 2003). The ability or inability of a model to represent reality and the accurate determination of significant processes affecting pesticide fate can be tested if adequate and precise model inputs and

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parameters are used. However, precise model inputs and parameters are hard to obtain, and substantial estimation uncertainty also exists, in particular for large, basin-scale catchments, making not only model prediction but also model testing difficult (Matsui *et al.*, 2005, 2006). Pesticides applied to rice paddies are the main types of pollutant pesticides in Japan and some other countries, because pesticides used in rice farming add pollutants to surface waters at higher rates than do those used in upland fields (Matsui *et al.*, 2002). Rice-farming pesticides may be transported from rice paddy fields to surface waters primarily by spill-over during or after rainfall or by rice-paddy drainage.

In this study, a daunting task is undertaken: collection of precise information on the farming work schedules of all farmers in a river basin and obtaining pesticide adsorption/decomposition rates for rice-paddy soils in the catchment. Our objective was to test the ability of a diffuse pollution hydrological model to reproduce experimental observations of rice-farming pesticide concentrations in river water by using adequate and precise model inputs. The sensitivity of the model is also analysed to elucidate rice-farming pesticide runoff phenomena.

Materials and methods

Site description and modelling

The Kakkonda River basin (191 km^2), consisting mainly of forest and rice-paddy fields cultivated by 372 farmers (Figure 1), was selected to test the model and to predict pesticide concentrations. In the model, the river basin was divided into a grid of 1 km by 1 km grid cells. Each grid cell was subdivided into 12 or more compartments: several rice-paddy ponding compartments (W compartments), rice-paddy soil compartments (X and Y compartments), a river-water compartment (R compartment), a riverbed compartment (S compartment), and so on, as shown in Figure 2. The paddy fields in the river basin were divided into a total of 686 W compartments. The size of each compartment varied, depending upon the land cover of the grid cell containing the compartments, allowing the heterogeneity of the watershed characteristics to be taken into account. Areas of the W compartments were obtained from the Iwate Agricultural Research Center, and those of

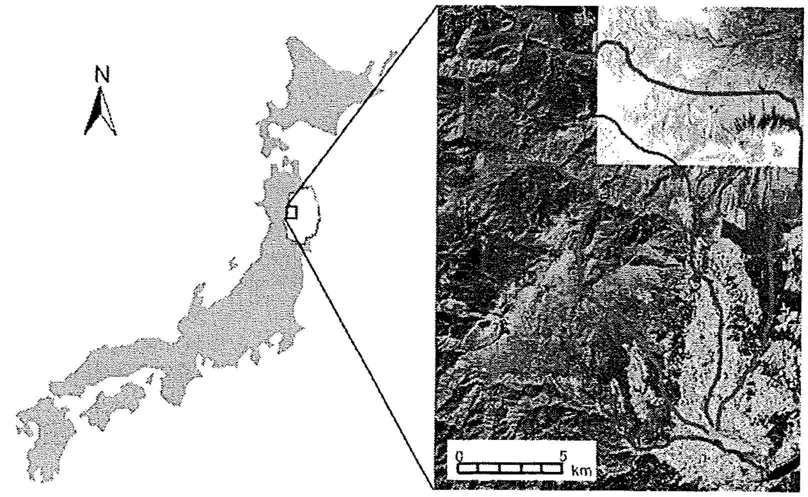

Figure 1 The target catchment area. The red dot indicates the water sampling point, where pesticide concentrations were measured (composed using Google satellite map). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst

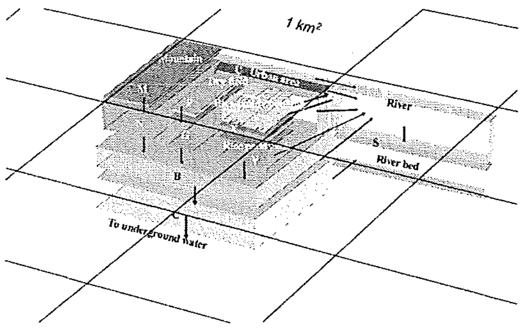

Figure 2 Compartments in a 1-km^2 grid cell and flow directions

the other compartments were determined from a Geographic Information System (GIS) land-cover data file (Geographical Survey Institute, Tokyo, Japan). Water flow directions among grid cells were determined from GIS data and a 1:50 000 topographic map (Geographical Survey Institute, Tokyo, Japan). In modelling, the solute concentration and water level were assumed to be uniform within a compartment, and each was represented by a single variable. Therefore, a set of differential mass-balance equations describing the dynamics of a solute (pesticide) and water in each compartment was defined, based on the law of conservation (i.e. mass balance) for the solute and the water. The details of the model have been published elsewhere (Matsui *et al.*, 2002, 2005, 2006).

Target pesticide and farming data

The target pesticide was a fungicide, isoprothiolane, one of the most applied pesticides in the rice-paddy fields of the target catchment area. The data on pesticide concentrations, observed at a site close to Kakkonda Bridge, were provided as a courtesy by A. Nakano and used for the comparison with the model predictions. Data from the Cultivation Management Register, which contains the complete farming schedule, including irrigation and pesticide application dates and the quantity of pesticide applied for each paddy field, for the years 2003 and 2004 for all 372 farmers cultivating the 686 paddy fields, were compiled, and a database was constructed for use as model input.

Soil map and sampling

Rice paddy field soils in the target watershed belong mainly to six soil groups or subgroups: three types of wet Andosol and Brown Lowland, Gray Lowland, and Peat soils (Iwate Agricultural Research Center 1997). In the model, therefore, paddy soils were categorised into six types: three subgroups of wet Andosols (wet Andosol 1, wet Andosol 2, and wet Andosol 3), Brown Lowland soils, Gray Lowland soils, and Peat soils, and the soil types present in each paddy field were determined. Twenty-seven soil samples representing all soil types were collected on 1 July 2005 from nine paddy fields (three soil samples were collected from each paddy field) and stored at 4 °C in a refrigerator. Batch pesticide adsorption and degradation tests were conducted on the individual soil samples in a laboratory maintained at 20 °C to estimate the soil adsorption coefficient (K_d) and the degradation rate constant for the pesticide.

Estimation of K_d

Batch tests for estimation of K_d were conducted according to the Organisation for Economic Co-operation and Development (OECD) guidelines (OECD, 2000), with some modifications as follows. Four grams (dry weight) of wet soil was added to a glass tube containing 20 mL of 0.01 M $CaCl_2$ and 2.0 mg/L isoprothiolane. The tube was shaken at 100 rpm for 12 h at 20 °C in the dark; it was confirmed that shaking for 12 h resulted in an equilibrium distribution of isoprothiolane between the soil and water. After shaking, the water phase was separated from the soil by centrifugation at 3500 rpm for 10 min, followed by filtration through a glass filter (GF/F, $\phi = 0.7\,\mu m$, Whatman Japan K. K., Tokyo, Japan). The water phase was then extracted with 10 mL of *n*-hexane. The extract was dried over anhydrous sodium sulphate and subjected to gas chromatography–mass spectrometry (GC–MS) analysis for quantification of isoprothiolane.

Estimation of the degradation rate constant

Ten grams (dry weight) of wet soil was added to a glass tube. Ultrapure water was then added to the tube to a water depth of 1–2 cm, which was maintained during the batch test by adding additional ultrapure water as needed. The soil–water mixture was pre-incubated for 3 days at 20 °C in the dark for conditioning. After 3 days, isoprothiolane was added to the tube at a final concentration of 7.2 mg/kg-dry soil, which is the average application dose recommended for actual paddy fields (Japan Plant Protection Association, 1994). The soil was then incubated again at 20 °C in the dark. Samples were withdrawn on days 0, 5, 10, and 20 for quantification of residual isoprothiolane as follows. The samples were centrifuged at 3500 rpm for 10 min to separate the water and soil. The procedure used for the extraction of the isoprothiolane from the water phase was the same as that described in the previous section, and the extract was subjected to the GC–MS analysis. To extract the isoprothiolane from the soil, 10 mL of acetone was added to the soil and the mixture was vortexed for 20 min. After vortexing, the mixture was centrifuged at 3500 rpm for 10 min, and the supernatant was subjected to the GC–MS analysis.

Analytical methods

Isoprothiolane was quantified by GC–MS (Agilent 6890N gas chromatograph, Agilent 5973 mass spectrometry detector) equipped with a capillary column (Agilent HP-5MS, 5% diphenyl 95% dimethylsiloxane; i.d., 0.25 mm; length, 30 m). The temperature of the ion source, injector, and transfer line was 250 °C. GC–MS was performed in selected ion monitoring mode; the fragment ions of isoprothiolane were detected at m/z 118. The relative contents of organic compounds in the soil were measured by NC analyzer (Sumigraph NC-800, Sumika Chemical Analysis Service, Ltd., Tokyo, Japan) so that the adsorption coefficient of soil organic compounds (K_{OC}) could be calculated from K_d.

Other model inputs and parameters

The time-series hydrological input for the model was precipitation after subtracting evapotranspiration; these data were calculated from published meteorological data (Japan Meteorological Agency, Tokyo) by a method described elsewhere (Matsui *et al.*, 2005). The model takes into account 23 hydrologic parameters. The values of 13 parameters are provided a priori or a posteriori from observation data (Matsui *et al.*, 2005), and those of the remaining 10 parameters are adjustable. Their values are searched for during model simulation so as to give the best fit to observed water flow rates (Ministry of Land, Infrastructure and Transport of Japan, 2005) in accordance with the minimum error criterion of the Nash–Sutcliffe coefficient (Nash and Sutcliffe, 1970).

Results and discussion

Isoprothiolane adsorption and degradation in soil

The isoprothiolane concentration changes in the soils due to degradation were well described by first-order reaction kinetics (data not shown), and the degradation rate was parameterised by the first-order reaction constant (k). The degradation rate constant (k) varied greatly depending on the soil type (Figure 3). Even within the same soil group (wet Andosols), rate constants differed by a factor of 12. For soil samples within the same soil subgroup (for example, wet Andosols 2) collected from different paddy fields, the difference in rate constants became smaller. The adsorption coefficient of the soils sampled from various paddy fields, expressed as the ratio of the amount of pesticide adsorbed per unit weight of organic carbon (K_{OC}), also varied depending on the soil type. However, in soils of the same soil subgroup, K_{OC} was roughly similar. The organic carbon contents of soils from the same soil subgroup were similar. Since soils of the paddy fields in the target catchment area were mostly wet Andosols, we assumed that in the model, the isoprothiolane degradation rate could be described by a first-order reaction with the degradation rate constant determined in accordance with the soil type. K_{OC} and OC values in the model were also determined in accordance with soil type. In addition, we confirmed that the literature-reported values of the degradation rate (half-life) and the soil adsorption coefficient (Uchida, 1978; Kuwatsuka and Yamamoto, 1998; Kishimoto *et al.*, 1999) were in the same range as our values.

Predicting isoprothiolane concentration in river water

Agricultural records were collected for all 372 farmers engaged in paddy-rice cultivation in the river basin, including dates of rice transplanting, dates and amounts of herbicide, fungicide, and insecticide applications, irrigation practices and water level of rice-paddy pondings, and harvest time. From these, a model input data set for all of the farmers were created. Model inputs for isoprothiolane adsorption and degradation in the soil were developed from the above mentioned observational data. Uncertainty in model inputs was minimised by using these data, making it possible to test the predictive capability of the model. Predicted and observed time variations in the isoprothiolane concentrations in river water are compared and given in Figure 4. In 2003, the concentration was predicted to peak on July 20, but regrettably there were no observed data on that day. Therefore, the ability of the model to predict peak concentration could not be confirmed. In 2004, fairly good agreement was obtained for both concentration peak height and timing between predicted and observed values, because adequate water samples had been collected at suitable times. Overall, the predicted concentrations were close to observed values. These results suggested that the model was capable of predicting pesticide concentration in river water when precise model inputs and parameter values were provided. In other words, the model realistically predicted pesticide fate without neglecting significant processes such as pesticide transport and decomposition.

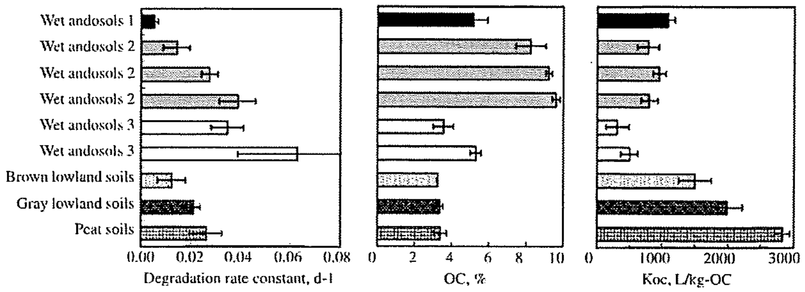

Figure 3 Soil characteristics for isoprothiolane degradation and adsorption in soils sampled from nine paddy fields. Error bars were calculated from data of three soil samples from each paddy field

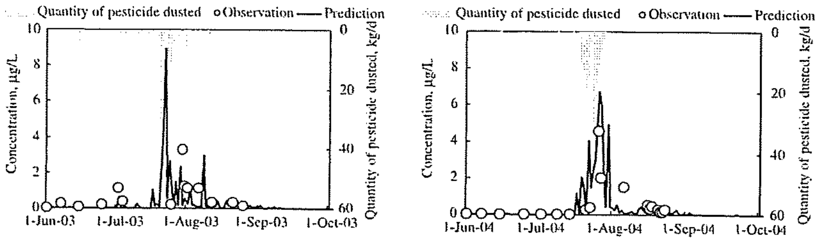

Figure 4 Comparison of observed time-series isoprothiolane concentrations with those predicted by the model

Sensitivity analysis

A sensitivity analysis of the model was conducted to elucidate pesticide runoff phenomena.

Effects of pesticide application and precipitation date accuracy. The pesticide concentration in the runoff increased several days after pesticide application to the rice paddy (Figure 4). Therefore, the effect of the accuracy of input dates of pesticide application and irrigation was studied by model simulation. The pesticide concentrations predicted with imprecise input data, when the pesticide application dates input were either 1 week ahead or 1 week behind the actual schedule, did not yield accurate predictions (Figure 5). However, the concentration variation pattern is shifted 11 days forward when the input date was shifted forward by 1 week, whereas it is shifted back by 1 week when the input date was shifted back by 1 week. Thus, although the date of pesticide application was the dominant factor determining the period of pesticide runoff, the shift in the runoff dates did not correspond simply to the shift in pesticide application timing.

Pesticide runoff can be caused by spill-over of rice-paddy water during or after a rainfall or by artificial drainage of rice-paddy water. To investigate the effect of the timing of rainfall, model simulations were conducted with time-series model inputs in which weather (precipitation) events were shifted by 1 week either backward or forward. A 1-week delay or acceleration of the weather pattern changed both the peak height and time-course variation in pesticide concentration (Figure 6). However, the pattern did not shift forward or back by 1 week, suggesting that pesticide runoff was not caused primarily by

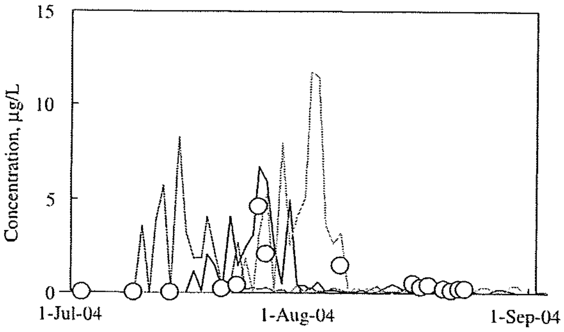

Figure 5 Effect of the accuracy of agricultural practice data on model prediction. Black line, prediction with accurate input data; blue line, prediction with agricultural schedule inputs moved forward by 1 week; red line, prediction with inputs moved back by 1 week. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst

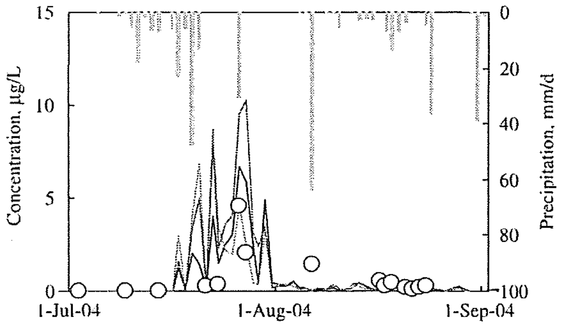

Figure 6 Effect of precipitation dates on model prediction. Green bars, actual precipitation; black line, prediction with actual precipitation data; blue line, prediction with precipitation input moved forward 1 week; red line, prediction with precipitation input moved back 1 week. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst

spill-over of rice-paddy water during or after rainfall but was probably related to artificial drainage of rice-paddy water.

Effects of pesticide adsorption and decomposition. Pesticide adsorption coefficient and degradation rate constant did not greatly affect pesticide concentration in the river water (Figures 7 and 8). In general, the smaller the K_{OC} value was, the larger the pesticide concentration was, but an increase in K_{OC} had a smaller effect than a decrease. An increase in the degradation rate constant by a factor of 10 decreased the pesticide concentration in river water by about 30%, but a decrease in the degradation rate constant changed the pesticide concentration by a lesser amount. These results suggest that the pesticide isoprothiolane is somewhat hydrophobic and persistent, so further enhancement of these tendencies would not affect the runoff of the pesticide. Overall, the effects of pesticide adsorption and degradation was not linear, and a parameter value change in the direction of constraining pesticide runoff likely is characterised by diminishing returns. These parameters did not significantly influence peak height of time-varying concentrations in the pesticide pollutograph (data not shown), but instead

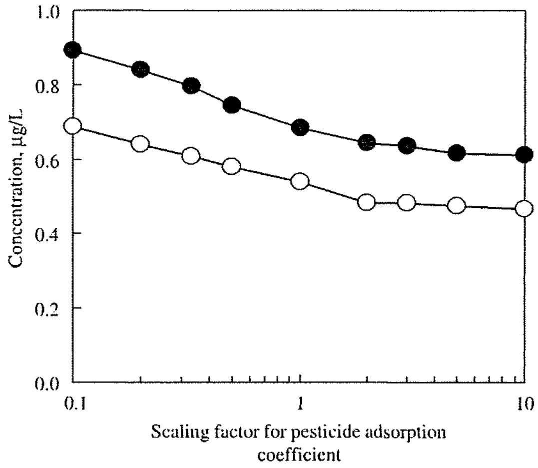

Figure 7 Effect of the pesticide adsorption coefficient (K_{OC}) on average and peak concentrations in July and August

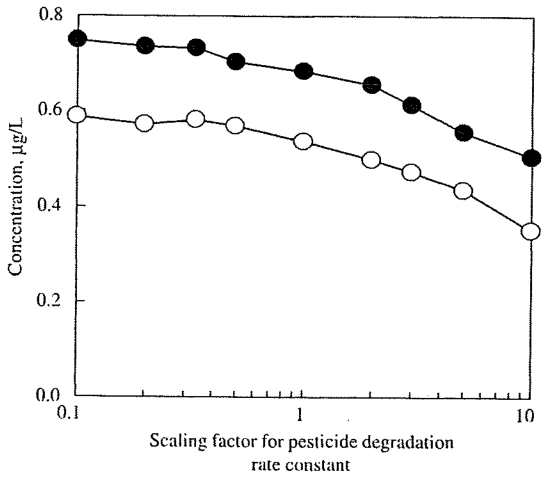

Figure 8 Effect of the pesticide degradation rate constant on average and peak concentrations in July and August

affected the low concentrations of the decreasing limb of the concentration peaks. Pesticide runoff at these low concentrations probably occurs through soil and groundwater percolation, leading to greater dependence on the values of the pesticide decomposition and adsorption parameters.

Effect of quantity of pesticide applied and runoff rate. The quantity of pesticide applied directly affects the pesticide concentration in the river water. As expected, an explicit linear relationship was obtained between concentration and applied quantity. The total pesticide discharge to the river was also linearly proportional to the total quantity of pesticide applied to the paddy field (data not shown). However, all of the pesticide applied to the paddy fields was not discharged to the river water. The pesticide discharge rate, defined as the annual pesticide discharge in the river flow divided by the annual quantity of pesticide applied to the paddy fields in the catchment, was 28% in 2003 and 42% in 2004

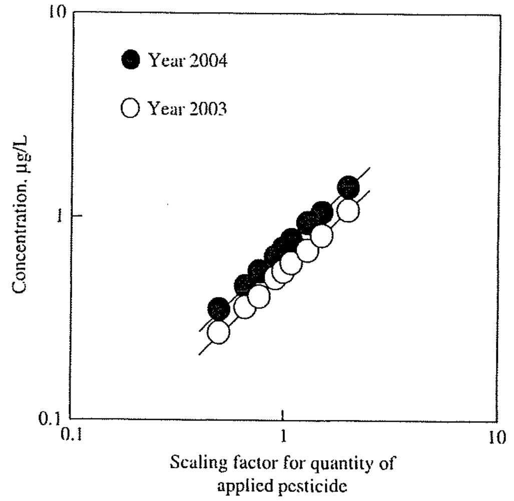

Figure 9 Effect of quantity of pesticide applied on average river water concentrations in July and August

(see Figure 9), indicating that more than half of the pesticide applied to the paddy fields did not reach the river. Nonetheless, the rates of adsorption and degradation of pesticide in the soil did not significantly affect the concentration in the river water. Further study is needed to elucidate the significant pesticide runoff processes.

Conclusions

Pesticide concentration in river water was successfully predicted by a diffuse pollution model provided with precise model inputs, including agricultural practices of individual farmers and experimentally derived data on pesticide adsorption and degradation rates in paddy field soils. Although rates of both pesticide adsorption and degradation differed, depending on soil type, similar values were obtained for soils belonging to the same soil subgroup. The timing of concentration increases in river water was determined mostly by agricultural practices (pesticide application and irrigation) and not greatly by weather (precipitation) patterns. These results suggest that artificial drainage of paddy water may be a significant process affecting pesticide runoff. However, the pesticide discharge rate was less than 50%, possibly because of loss from pesticide degradation. Nonetheless, the pesticide concentration in river water was not greatly affected by pesticide adsorption and degradation rates in paddy field soils.

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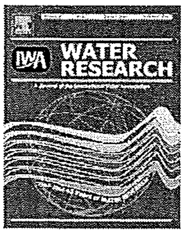

Effects of chlorine on organophosphorus pesticides adsorbed on activated carbon: Desorption and oxon formation

Koichi Ohno[a,*], *Takehiro Minami*[a], *Yoshihiko Matsui*[a], *Yasumoto Magara*[b]

[a]*Department of Socio-Environmental Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan*
[b]*Creative Research Initiative "Sousei", Hokkaido University, N21W10, Sapporo 001-0021, Japan*

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ABSTRACT

We investigated effects of chlorination on four organophosphorus pesticides (diazinon, isoxathion, malathion, and tolclofos-methyl) adsorbed on powdered activated carbon (PAC). Following adsorption of each pesticide on 10 mg/L of PAC in water, chlorine was added. After 30 min of chlorination, the corresponding oxons were detected in the water, but the parent compounds were not detected. Molar ratios of the oxon concentration in solution after 30 min of chlorine addition to the initial pesticide concentration before the adsorption process were 4.1% and 7.9% for diazinon, 3.9% and 5.8% for isoxathion, 1.2% and 1.7% for malathion, and 1.4% and 1.4% for tolchlofos-methyl, in the case of 2 and 5 mg/L of chlorine addition. The results suggested that the oxons were desorbed from the PAC by chlorination. The concentrations of the desorbed oxons gradually decreased with time, apparently owing to their readsorption by the PAC. Results from additional experiments suggest the following sequence of events: (i) adsorbed pesticides are oxidized by chlorine on the surface of the PAC and transformed into corresponding oxons; (ii) the oxons are released from the PAC; (iii) the released oxons are gradually readsorbed by the PAC, decreasing their concentrations in the water phase.

1. Introduction

Organophosphorus pesticides are widely used throughout the world and are frequently detected in surface and ground waters (Gomezgomez et al., 1995; Tanabe et al., 2001; Sankararamakrishnan et al., 2005; Gilliom et al., 2006). These pesticides are mostly dissolved in water and cannot be easily removed by solid/liquid separation processes such as coagulation and sand filtration. An effective and simple method for removing pesticides is the addition of powdered activated carbon (PAC) at the inlet of a water purification process train.

To prevent the growth of algae in a sedimentation basin with plate or tube settlers and in a rapid sand filter, chlorine is sometimes also added at the inlet. This process, known as pre-chlorination, is also used to oxidize iron, manganese, ammonia, and other compounds. Intermediate chlorination, which is the addition of chlorine between sedimentation and filtration processes, is used as an alternative to pre-chlorination.

Thus, it is likely that chlorine will come into contact with PAC in both pre-chlorination and intermediate chlorination, although the contact time and degree will differ. This contact between chlorine and PAC is undesirable, because chlorine reacts with the surface of the PAC and decreases its capacity to adsorb targeted pollutants (Sontheimer et al., 1988). Furthermore, Gillogly et al. (1998) showed that a taste- and

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*Corresponding author. Tel./fax: +81 11 706 7282.
E-mail address: ohnok@eng.hokudai.ac.jp (K. Ohno).

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odor-causing compound, 2-methylisoborneol, that was initially adsorbed on PAC could be released back into the water following the addition of chlorine. Huang and Yeh (1999) showed that chlorination of natural organic matter adsorbed on PAC caused the appearance of chlorination byproducts such as trihalomethanes and adsorbable organic halogens in the aqueous phase. Also, Voudrias et al. (1985) found that the addition of chlorine to water containing phenols adsorbed on granular activated carbon caused the formation of a variety of chlorinated derivatives in the aqueous phase. These reactions might also occur with organophosphorus pesticides that are adsorbed on PAC.

Organophosphorus pesticides containing phosphorus–sulfur double bonds (P=S) are oxidized to their corresponding oxons, with phosphorus–oxygen double bonds (P=O), by chlorination (Magara et al., 1994; Wu and Laird, 2003). These oxons are relatively persistent by chlorination although some of the oxons degrade further (Magara et al., 1994; Arai et al., 2005; Kamoshita et al., 2007). *In vitro* assays, such as analysis of acetylcholinesterase (AChE) inhibition, show that these oxons are more potent AChE inhibitors than their parent compounds (Monnet-Tschudi et al., 2000; Tahara et al., 2005). A survey of source water and finished water collected from 12 community water systems found that organophosphorus insecticides detected in source water were not detected in the finished potable water (Coupe and Blomquist, 2004). Although this could be due to complete removal by the water treatment processes, Duirk and Collette (2006) suggest that the parent pesticides were transformed into the more potent AChE inhibitors, oxon forms, which were not measured in the survey. Therefore, it is important to understand the behavior of not only organophosphorus pesticides, but also their corresponding oxons.

In the present study, we investigated the effects of chlorination of organophosphorus compounds adsorbed to PAC. We also investigated the mechanisms of the desorption and the readsorption of the pesticides and their oxons from PAC.

2. Materials and methods

2.1. *Reagents and materials*

Four organophosphorus pesticides (diazinon, isoxathion, malathion, and tolclofos-methyl) were used as adsorbates in this study. Diazinon, diazinon oxon, isoxathion, isoxathion oxon, malathion, and tolclofos-methyl were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Malaoxon came from Dr. Ehrenstorfer-Schäfers (Augsburg, Germany), and tolclofos-methyl oxon came from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan). The physico-chemical and toxicological properties of these compounds are listed in Table 1. Acceptable daily intake values for the oxons are not available because they are unintended chemicals and oxidative transformed substances of the parent pesticides. All

Table 1 – Physico-chemical and toxicological properties of the organophosphorus pesticides and their corresponding oxons

Compound	CAS #[a]	Molecular weight	Logarithm of octanol–water partition coefficient ($\log K_{ow}$)		Water solubility at 25 °C (mg/L)		ADI[b] (mg/kg bw per day)
			Tomlin (2006)[c]	USEPA (2007)[c]	Tomlin (2006)[c]	USEPA (2007)[c]	
Diazinon	333-41-5	304.35	3.30[d]	3.81[d]	60[d,e]	40[d]	0.002[f,g]
Diazinon oxon	962-58-3	288.29		2.07[d]		245[h]	
Isoxathion	18 854-01-8	313.31	3.88[d]	3.73[d]	1.9[d]	1.9[d]	0.003[g]
Isoxathion oxon	32 306-29-9	297.25		2.13[i]		192[h]	
Malathion	121-75-5	330.35	2.75[d]	2.36[d]	145[d]	143[d,e]	0.3[f], 0.02[g]
Malaoxon	1634-78-2	314.29		0.52[i]		7500[d,j]	
Tolclofos-methyl	57 018-04-9	301.13	4.56[d]	4.56[d]	1.1[d]	1.1[d]	0.064[g]
Tolclofos-methyl oxon	97 483-08-4	285.07		3.00[i]		41[h]	

[a] Chemical Abstracts Service number.
[b] Acceptable daily intake.
[c] See references.
[d] Experimental value.
[e] At 20 °C.
[f] Joint meeting on Pesticide Residues (JMPR) (2002).
[g] Japanese Ministry of Health, Labour and Welfare (2004).
[h] Estimated by WSKOW v.1.41.
[i] Estimated by KOWWIN v.1.67.
[j] At 22 °C.

other reagents were purchased from Wako Pure Chemical Industries, Ltd.

To suppress fluctuations in the pH, we prepared raw water for experiments by adding 20 mg/L of sodium hydrogen carbonate to ultra-pure water (18.2 MΩ cm resistivity) obtained by reverse osmosis using an Osmoclear system (Organo Corp., Tokyo, Japan) followed by a Puric MX-II water purification system (Organo Corp.). Stock solutions of individual pesticides were prepared at 1 g/L in acetonitrile, and the standard working solutions were obtained by dilution with 0.15% acetic acid in water. Individual pesticide solutions for adsorption and chlorination experiments were prepared by the direct addition of each pesticide reagent to the raw water without assistance of organic solvent, followed by sonication for about 0.5 h by use of an ultrasonic bath, Model 8210 (Branson Ultrasonics Corp., Danbury, CT, USA). Next, the solution was filtered through a 0.45-μm hydrophilic polytetrafluoroethylene (PTFE) membrane filter (Advantec, Tokyo, Japan) to remove any undissolved residue. These pesticide solutions were prepared for every experiment. For adsorption and chlorination experiments, the solution was diluted with the raw water. The targeted pesticide concentration for experiments was basically around 100 μg/L, but the concentration was not constant because the dissolution of pesticide reagents fluctuates without the help of organic solvent. Therefore, we measured the initial pesticide concentration for every experiment prior to PAC and chlorine addition.

Thermally activated, wood-based PAC (Taikou-W; Futamura Chemical Industries Co., Ltd., Nagoya, Japan) was used as an adsorbent. The BET surface area and median particle diameter of the PAC were 862 m^2/g and 7.6 μm. The PAC was dried in an oven at 105 °C for 20 min and stored in a desiccator before use.

2.2. *Experimental procedures*

2.2.1. *Chlorination of PAC following adsorption of organophosphorus pesticide*

PAC (10 mg) was added to 1 L of pesticide solution in a beaker. The solution was then stirred with a mixer at 300 rpm for 1 h. Next, the pre-determined amount of sodium hypochlorite was added to the solution, and the solution was stirred again. The pH of the solution was maintained at 7.4 ± 0.1, although it rose to ~8.0 for a few minutes following the addition of the chlorine. Water samples were collected before (initial concentration) and after the adsorption process and every 30 min for 2 h after the addition of chlorine.

2.2.2. *Extraction of pesticides and their oxons adsorbed on PAC*

Compounds adsorbed on PAC were extracted as follows. First, 500 mL of the PAC solution was filtered through a 0.45-μm hydrophilic PTFE membrane filter to capture the PAC on the filter. The filter and the attached PAC were placed in a beaker, covered with 20 mL acetonitrile, and sonicated for 10 min in the ultrasonic bath. After the sonication, the suspension and the filter were transferred to a test tube with a ground stopper, mixed with 30 mL of acetonitrile, and shaken for 10 min. The suspension was then filtered through a 0.2-μm hydrophobic PTFE membrane filter (Advantec), and the concentrations of the parent pesticide and its oxon were measured in the filtrate.

2.3. *Analytical methods*

Residual chlorine was analyzed by the DPD colorimetric method (Standard Method 4500-Cl G (APHA, 2005)) using DPD total chlorine reagent packs (Hach Company, Loveland, CO, USA). Pesticides and their corresponding oxons were analyzed using a liquid chromatography (LC)—tandem mass spectroscopy (MS–MS) system. LC was carried out with an Agilent 1100 high-performance LC system (Agilent Technologies, Inc., Palo Alto, CA, USA) with a Mightysil RP-18 column (150 mm × 2.0 mm internal diameter; Kanto Chemical Co., Inc., Tokyo, Japan). The mobile phases were 0.15% acetic acid in water (eluent A) and 0.15% acetic acid in acetonitrile (eluent B). The gradient elution programs were as follows. For the analysis of diazinon, malathion, and their oxons, the initial composition was 40% B. This was followed by a linear gradient to 90% B over 7 min and maintenance at 90% B for 5 min. For the analysis of isoxathion, tolclofos-methyl, and their oxons, the initial composition was 50% B. This was followed by a linear gradient to 95% B over 2 min and maintenance at 95% B for 5 min. The flow rate was 0.2 mL/min, the injection volume was 5 μL, and the column temperature was maintained at 40 °C. Mass analysis was performed with an API 3000 MS–MS system (Applied Biosystems, Foster City, CA, USA). The operating parameters of the electrospray-ionization-positive mode were optimized by evaluating the sensitivity and fragmentation of each compound. For each compound, the precursor and product ions were chosen for quantitation (Table 2).

3. Results and discussion

3.1. *Effect of chlorine on PAC following adsorption of an organophosphorus pesticide*

Before chlorination, 10 mg/L of PAC was added to each pesticide solution. After 1 h of adsorption, 0.5–1.1% of the diazinon remained in the water, and the concentrations of the other pesticides (isoxathion, malathion, and tolclofos-methyl) were below the detection limits (0.03 μg/L). Following

Table 2 – Precursor and product ions in LC-MS-MS analysis

Compound	Precursor ion (m/z)	Product ion (m/z)
Diazinon	305.2	169.2
Diazinon oxon	289.2	153.2
Isoxathion	314.0	105.3
Isoxathion oxon	298.3	242.1
Malathion	331.1	127.1
Malaoxon	315.1	127.1
Tolclofos-methyl	301.1	125.1
Tolclofos-methyl oxon	285.0	109.0

adsorption, chlorine was added to the PAC solution. After 30 min of chlorination, the parent pesticides were not detected in the water, but their corresponding oxons were detected (Fig. 1). When 2 mg/L of chlorine was added, molar ratios of oxon concentration in water after 30 min of chlorine addition to the parent pesticide concentration before PAC and chlorine addition were 4.1% for diazinon, 3.9% for isoxathion, 1.2% for malathion, and 1.4% for tolclofos-methyl, and when 5 mg/L of chlorine was added, the ratios were 7.9%, 5.8%, 1.7%, and 1.4%, respectively. The ratios were therefore higher at 5 mg/L than at 2 mg/L chlorine for each pesticide except for tolclofos-methyl, the ratio was the same in this case. Subsequent samples ($t>30$ min) showed that the concentrations of the released oxons decreased with time. This result implies that the peak concentration of oxon in water was reached after less than 30 min of chlorination.

3.2. *Mechanism of decrease in the level of released oxon with chlorination time*

As mentioned above, the concentration of the released oxon decreased with chlorination time. There are two possible explanation for this finding: that the oxons were further degraded, and that the oxons were readsorbed on the PAC. To determine which of these explanations is correct, we divided the solution into two parts, one with and the other without PAC, after 30 min of chlorination. To prepare the solution without PAC, the suspension was filtered through a 0.45-μm hydrophilic PTFE membrane filter. The oxon and residual chlorine concentrations were measured over time (Fig. 2). The oxon concentrations decreased with time in the solutions with PAC, but not in the solutions without PAC (but with residual chlorine). This was true of all four pesticides, although the trend was weaker for malathion and tolclofos-methyl. Therefore, the progressive decrease in oxon levels in water appeared to be due to the readsorption of the oxons by PAC rather than to further degradation. Kamoshita et al. (2007) added about 1.0 mg/L of chlorine to a number of single oxon solutions, of which concentration was 5.7–12 μg/L. The residual ratios of the four oxons by 24-h contact with chlorine were 76% for diazinon oxon, 61% for isoxathion oxon, 99% malaoxon, and 104% for tolxlofos methyl oxon. Diazinon oxon and isoxathion oxon appeared to relatively degrade, but they degrade only a little, less than 10%, by 4-h contact with chlorine. These results supported our results.

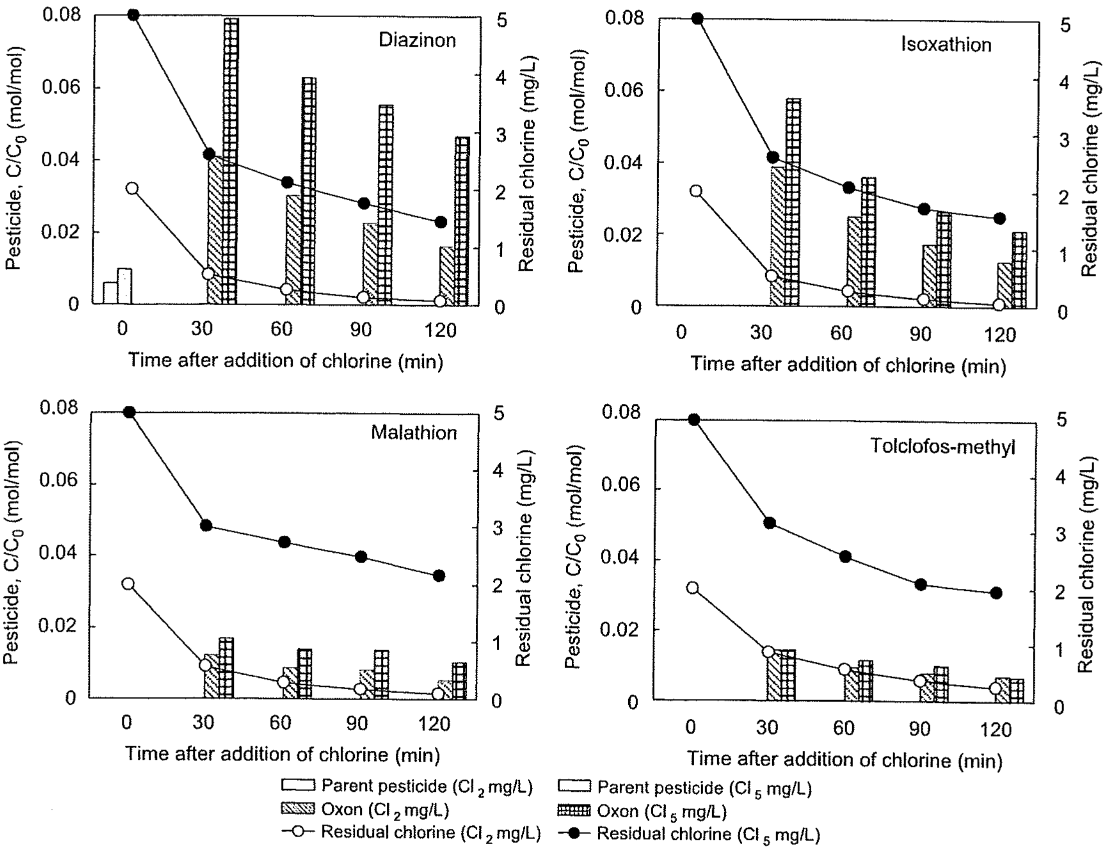

Fig. 1 – Aqueous pesticide and chlorine concentrations following chlorination of suspensions containing PAC with pre-adsorbed parent pesticide. Initial pesticide concentrations (C_0) in the solutions were 0.44 μM (135 μg/L) for diazinon, 0.38 μM (118 μg/L) for isoxathion, 0.65 μM (216 μg/L) for malathion, and 1.27 μM (383 μg/L) for tolclofos-methyl. C, measured concentration.

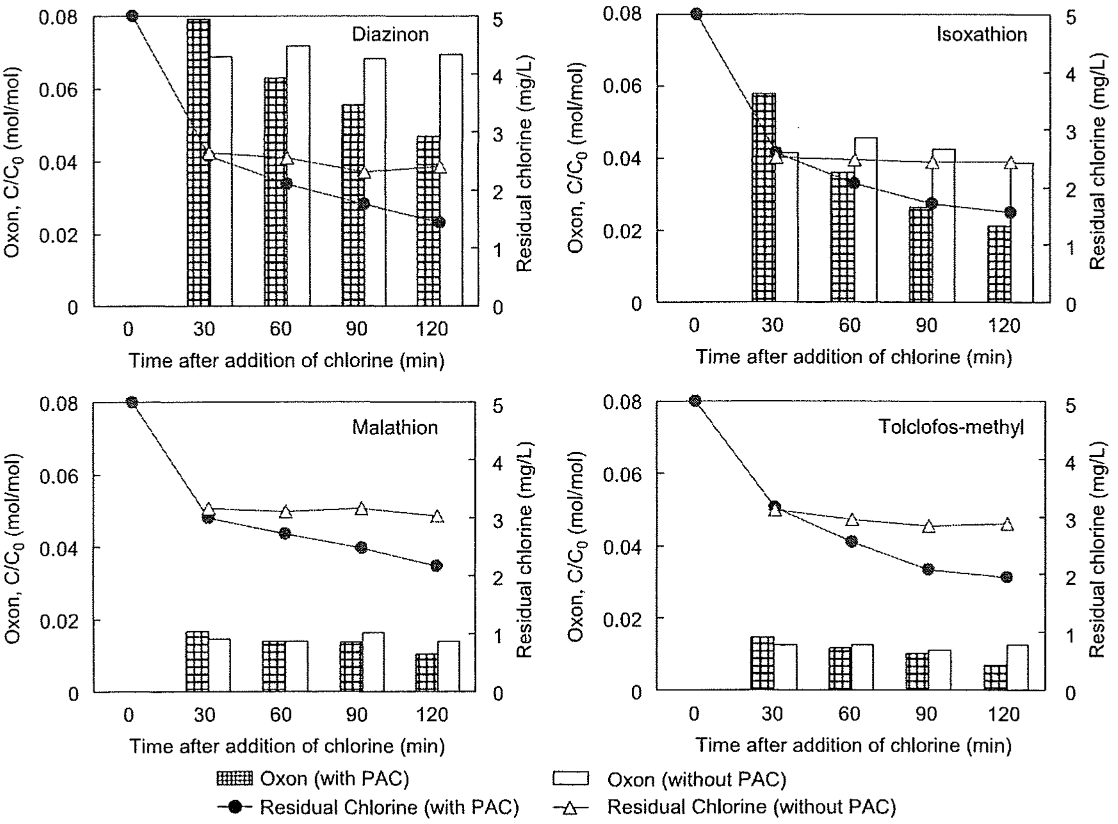

Fig. 2 – Effects of PAC on the decrease in the concentration of released oxons with chlorination time. To produce solutions without PAC, PAC was removed by filtration following 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentrations of the parent pesticide solution were the same as in Fig. 1.

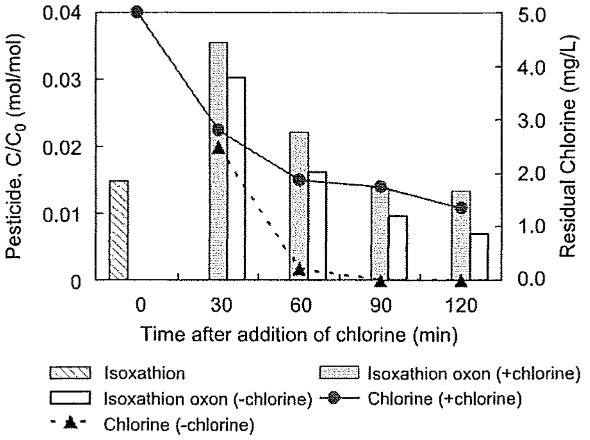

Fig. 3 – Effect of chlorine on isoxathion oxon concentrations released during 30 min of chlorination. For the condition without chlorine, chlorine was quenched after 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentration of isoxathion in the solution was 2.8 μM (880 μg/L).

As shown in Fig. 2, the residual chlorine decreased with time in the solutions with PAC but not in the solutions without PAC. This is due to progressive oxidation of the PAC by chlorine. This oxidation causes a decrease in the number of adsorption sites, which may reduce the rate of oxon readsorption. To examine this effect, we performed the chlorination experiment using isoxathion, and after 30 min, we divided the solution into two parts, one of which was treated with sodium thiosulfate to quench the residual chlorine (Fig. 3). Owing to the action of PAC as a catalyst (Sontheimer et al., 1988), the oxon could be further degraded when both PAC and chlorine are present, but we found that the oxon concentration in water decreased faster when chlorine was absent. These results indicate that the dominant factor in the decrease in the released oxon concentration is not the further degradation of the oxon, but rather its readsorption to the PAC. The results also show that the residual chlorine continues to oxidize the surface of the PAC, decreasing the adsorptive capacity.

We considered that the desorption of oxons was due to the decrease of the adsorptive capacity of PAC by chlorination. The observed data also suggested that readsorption rate of oxons was slower than adsorption rate of the parent pesticides (Figs. 1–3), for almost all the parent pesticides were adsorbed on PAC for 1 h as mentioned in the result of the first experiment. This slower adsorption rate of oxons can be also explained by the decrease of the adsorptive capacity. There are, however, other possible explanations for the slower adsorption rate and for the dominant desorption of the oxons: the oxons may have slower adsorption rates. The lower adsorption capacity is consistent with the physicochemical data (Table 1): the oxons have lower octanol–water partition coefficient (K_{ow}) than the parent pesticides. Therefore, the slower readsorption rate of the oxons was considered to be due to the combination of the decrease of adsorption capacity and the lower adsorption capacity of the oxons.

3.3. *Mechanism of the desorption of oxon forms from PAC*

Our results showed that chlorination of the PAC caused the desorption of previously adsorbed organophosphorus pesticides. The desorbed substances, however, were not the parent pesticides but the oxon forms (Fig. 1). One possible explanation for these results is that chlorine oxidizes the sites where the parent pesticide was adsorbed, causing the pesticide to be released back into the water, where it is oxidized to the corresponding oxon. A second possibility is that the adsorbed parent pesticide is first oxidized to the corresponding oxon on the PAC and then released from its adsorption site. To examine these two possibilities, we performed the chlorination experiment using isoxathion solution, and measured the levels of isoxathion and its oxon after 30 min (Fig. 4). After the chlorination, ~80% of the isoxathion was degraded to the isoxathion oxon. Following the chlorination of isoxathion-adsorbed PAC, the parent isoxathion was not detected (Fig. 1). If the first explanation were correct, the parent isoxathion should have been detected. Therefore, it appears that the second explanation is correct.

To investigate the reaction of isoxathion on the PAC surface during chlorination, we extracted the compounds adsorbed on the PAC after 30 min of contact with chlorine. We found that 53% of the compound adsorbed on the PAC was isoxathion oxon and 47% was isoxathion (Fig. 5). Thus, approximately half of the isoxathion adsorbed on the PAC remained untransformed, and the remaining half was transformed to the oxon form. These findings support the idea that organophosphorus pesticides are oxidized to their oxon forms on the PAC and then released. Furthermore, if the isoxathion was released from the PAC and then transformed to the oxon form in the water phase, both the isoxathion and the oxon should have been detected in the water phase, because not all of the isoxathion in the water phase was transformed to the oxon form after 30 min of chlorination (Fig. 4). In the experiment in which isoxathion was adsorbed by PAC and chlorinated, however, isoxathion was not detected in the water phase. Thus, it is unlikely that isoxathion adsorbed on the PAC surface was released and then transformed to the oxon form in the water phase.

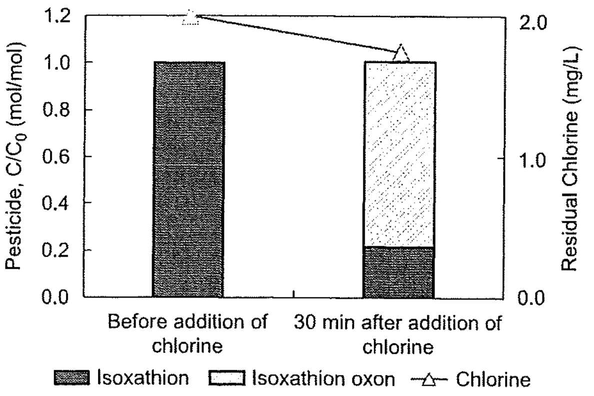

Fig. 4 – Concentrations of isoxathion and its oxon after direct chlorination in aqueous solution. The initial concentration of isoxathion in the solution was 0.20 µM (62 µg/L), and the chlorine dose was 2.0 mg/L.

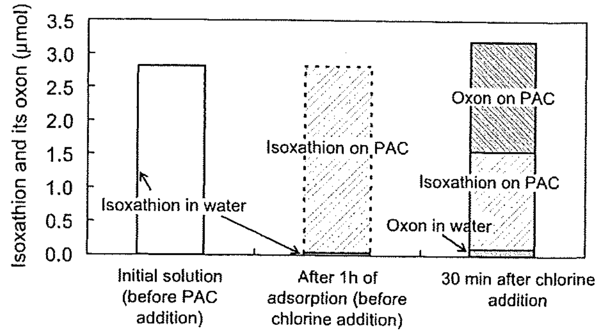

Fig. 5 – Change in the state of isoxathion and its oxon during the adsorption and chlorination experiment. The initial chlorine dose was 5 mg/L. The amount of isoxathion adsorbed on PAC after 1 h of adsorption was an estimate, whereas the amounts of isoxathion for the other samples were experimentally measured.

4. Conclusions

We investigated the effects of chlorination of organophosphorus compounds adsorbed to PAC. The oxons rather than the parent pesticides were detected in the water phase after chlorination. In addition, the concentrations of the desorbed oxons decreased with chlorination time. This result can be explained by the readsorption of oxons in the water phase by PAC. Results from additional experiments suggest that the parent pesticides adsorbed to PAC are first oxidized to the corresponding oxon, then released from the adsorption sites. In the case of isoxathion, after 30 min of chlorination, approximately half of the parent compound adsorbed to the PAC surface was converted into the corresponding oxon.

In this study, we focused on the clarification of mechanism of desorption and oxon formation of organophosphorus pesticides that were pre-adsorbed on PAC by contact with chlorine. To elucidate the mechanism more clearly, we conducted the chlorination experiments with the pesticide solutions at much higher concentrations than environmentally relevant concentrations. The reactivity of chlorine and the pesticides that are adsorbed on PAC at lower concentrations remained unrevealed. As a result of this study, however, we may provide the following recommendations for water purification facilities that have a possibility for contact between PAC and chorine: oxon concentrations in addition to those of the parent pesticides should be monitored in finished water, and longer contact time between PAC and the desorbed oxons for readsorption should be taken.

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フガシティモデルを利用した流出農薬プライオリティの評価

Evaluation of Priority of Pesticides Runoff using Fugacity Model

池貝　隆宏*
Takahiro IKEGAI

要旨：農薬に関する水道水質管理を的確に行うには，流域における農薬の流出状況を判定できる基礎情報が不可欠である。本稿では，流域別の流出農薬のプライオリティを判別するため，農薬の流出をモデル化し，レベルⅡフガシティモデルを用いて流出可能性を表す時期別の指標値を算出する手法を検討した。この方法を用いて，神奈川県の相模川及び酒匂川の農薬流出状況を評価した。その結果，流域別流出量は農薬流出可能性を表す指標として利用可能であり，ADI あたりの流域別流出量である RRI 値を用いて流出農薬のプライオリティが詳細に判定できることを示した。

キーワード：農薬流出，フガシティモデル，流出量推定，流域

Abstract：In order to carry out a precise water-purity control regarding pesticides, it is essential to judge the pesticides runoff situation of the river basin. In this paper, we modeled a mechanism of pesticide runoff by using level Ⅱ fugacity model in order to decide the priority of runoff pesticides on each basin, and constructed a method of calculating the index which indicated pesticide runoff potential on each period. We evaluated the pesticides runoff situation of Sagami-river and Sakawa-river in Kanagawa prefecture by using this method. As a result, estimated runoff volume of pesticides could be used as an index which indicated runoff potential, and RRI value which indicated runoff volume per ADI could be used as an index deciding the priority of runoff pesticides in detail.

Key Words：pesticide runoff, fugacity model, spillage estimation, basin

はじめに

農薬の使用実態は，農作物の耕作状況の地域差を反映し，同一県内でも地域により大きく異なっている。安全な水道水を供給するため，水道事業体には水源河川や浄水場において農薬に対する的確な水道水質管理を行うことが求められているが，これには周辺地域で使用される農薬の種類，量，流域への流出状況等を的確に判定できる基礎情報が不可欠である。平成16年4月に施行された現在の水道水質基準では，農薬は水質管理目標設定項目に位置付けられており，総農薬方式により水質管理が行われている。総農薬方式は，水道事業体が地域の状況を勘案して測定対象農薬を選定し，その実測データから検出指標値を算出し，管理を行う仕組みである。効率的な水質管理を行うには，対象流域で流出可能性が高い農薬を事前に予測し，リストアップすることが重要となる。

農薬の流出は，実測（川嵜ら，2006；海老瀬ら，2006）や予測モデルを用いた推定（永淵ら，2006；稲生，2004）により現況把握や評価が行われている。これら既往研究の手法は，特定の農薬の河川中における挙動を知るのに適しているが，多種類の農薬を対象に行う前述のリストアップの手段には必ずしもなじまない。農薬の流出状況予測には，流出可能性を表す指標値を比較的単純化した方法で包括的に算出できる手法を設定する必要がある。

これを満足する手法として，既報（池貝，2006）において農薬の散布と流出をモデル化し，レベルⅠフガシティモデルを用いて求めた散布農薬の分配量から流域別流出量を推計する方法を検討した。フガシティモデル（Mackay，1979；Mackay *et al.*，1981）は，大気，水，土壌等の環境媒体中の物質の分配を表すモデルで，物質が媒体の外に出ようとする傾向を表すフガシティを変数に持つ。モデルの型式は4種あるが，レベルⅠは定常状態を仮定した単純平衡モデルである。既報では，流域別流出量と実際の検出頻度の傾向が概ね整合し，これが流出可能性を表す指標値として利用できることを示した。

本稿では，より実態に近い指標値を算出するために上位のフガシティモデルを利用し，時期別の流出状況が把握可能な手法について検討した。この手法を用いて，神奈川県の相模川と酒匂川における監視対象農薬のプライオリティの評価を行ったので，その結果を報告する。

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* 神奈川県環境科学センター　企画部