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
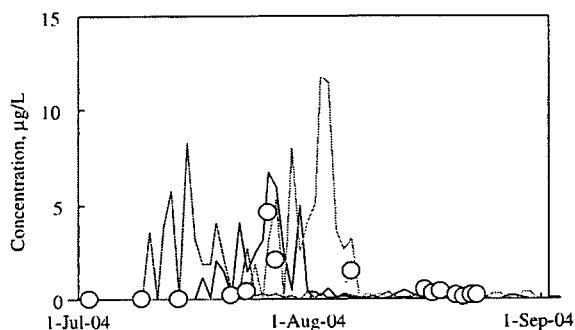

Figure 5 Effect of the accuracy of agricultural practice data on model prediction. Black line, prediction with accurate input data; blue line, prediction with agricultural schedule inputs moved forward by 1 week; red line, prediction with inputs moved back by 1 week. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from http://www.iwaponline.com/wst
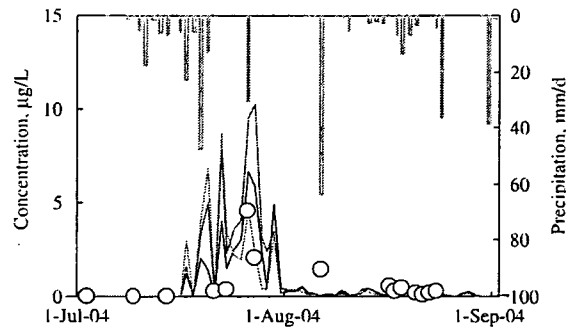
Figure 6 Effect of precipitation dates on model prediction. Green bars, actual precipitation; black line, prediction with actual precipitation data; blue line, prediction with precipitation input moved forward 1 week; red line, prediction with precipitation input moved back 1 week. Subscribers to the 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
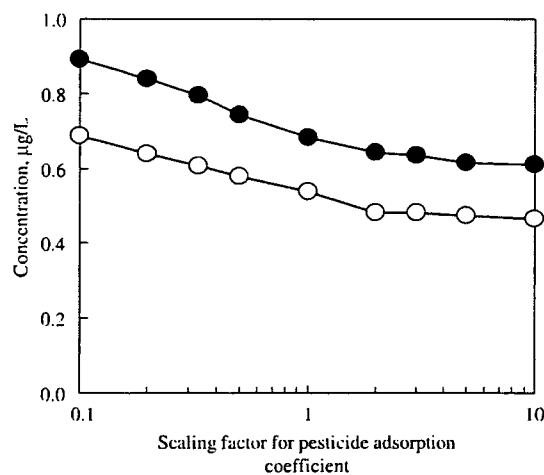

Figure 7 Effect of the pesticide adsorption coefficient (K_{OC}) on average and peak concentrations in July and August
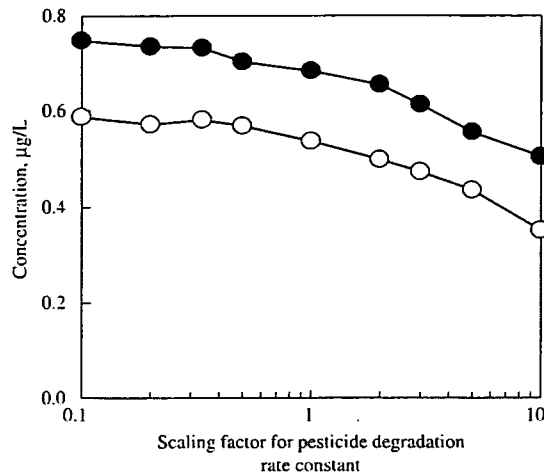
Figure 8 Effect of the pesticide degradation rate constant on average and peak concentrations in July and August

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
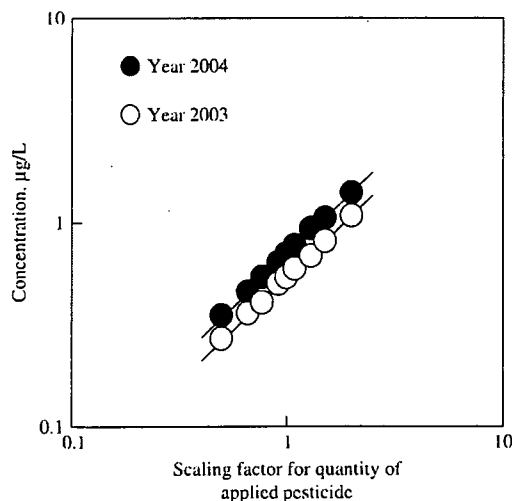

Figure 9 Effect of quantity of pesticide applied on average river water concentrations in July and August

(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.
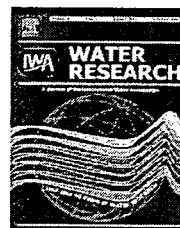
Acknowledgements

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WATER
RESEARCH

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

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ARTICLE INFO

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 tolclofos-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

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	18854-01-8	313.31	3.88[d]	3.73[d]	1.9[d]	1.9[d]	0.003[g]
Isoxathion oxon	32306-29-9	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	57018-04-9	301.13	4.56[d]	4.56[d]	1.1[d]	1.1[d]	0.064[g]
Tolclofos-methyl oxon	97483-08-4	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 m²/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.
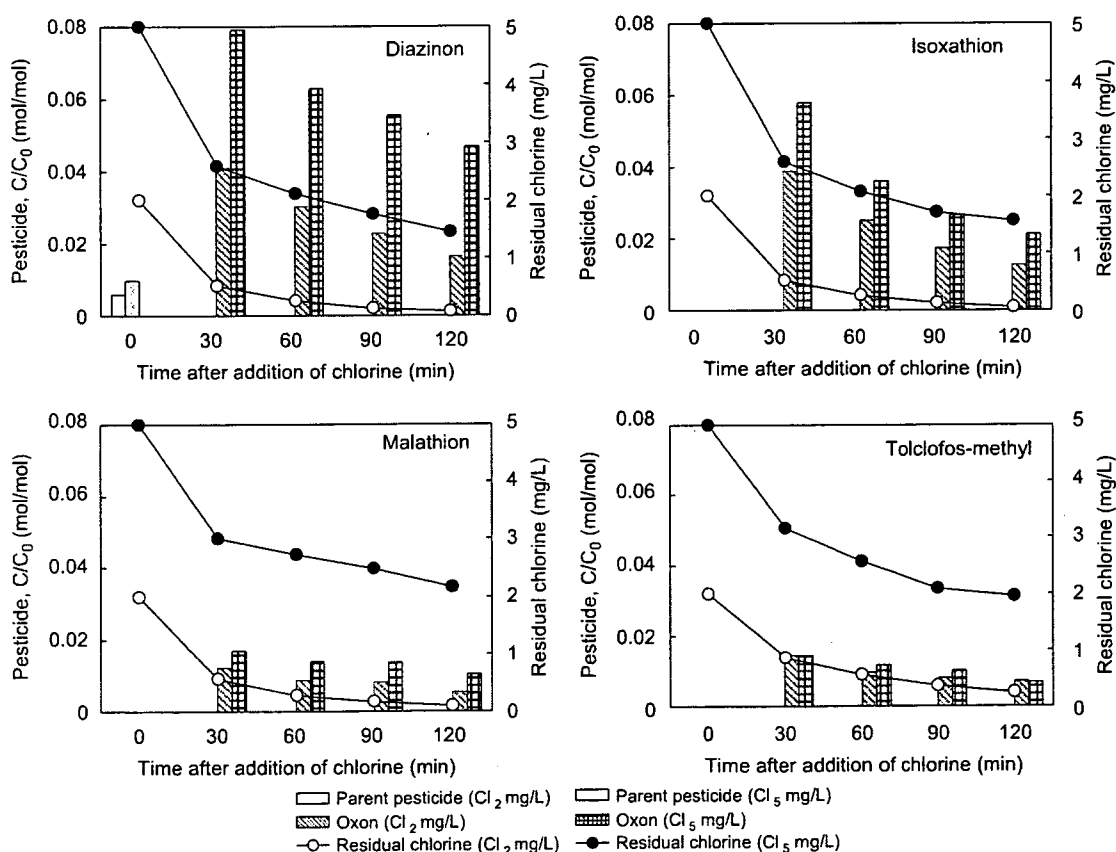

Fig. 1 – Aqueous pesticide and chlorine concentrations following chlorination of suspensions containing PAC with pre-adsorbed parent pesticide. Initial pesticide concentrations (C_0) in the solutions were 0.44 μM (135 μg/L) for diazinon, 0.38 μM (118 μg/L) for isoxathion, 0.65 μM (216 μg/L) for malathion, and 1.27 μM (383 μg/L) for tolclofos-methyl. C, measured concentration.
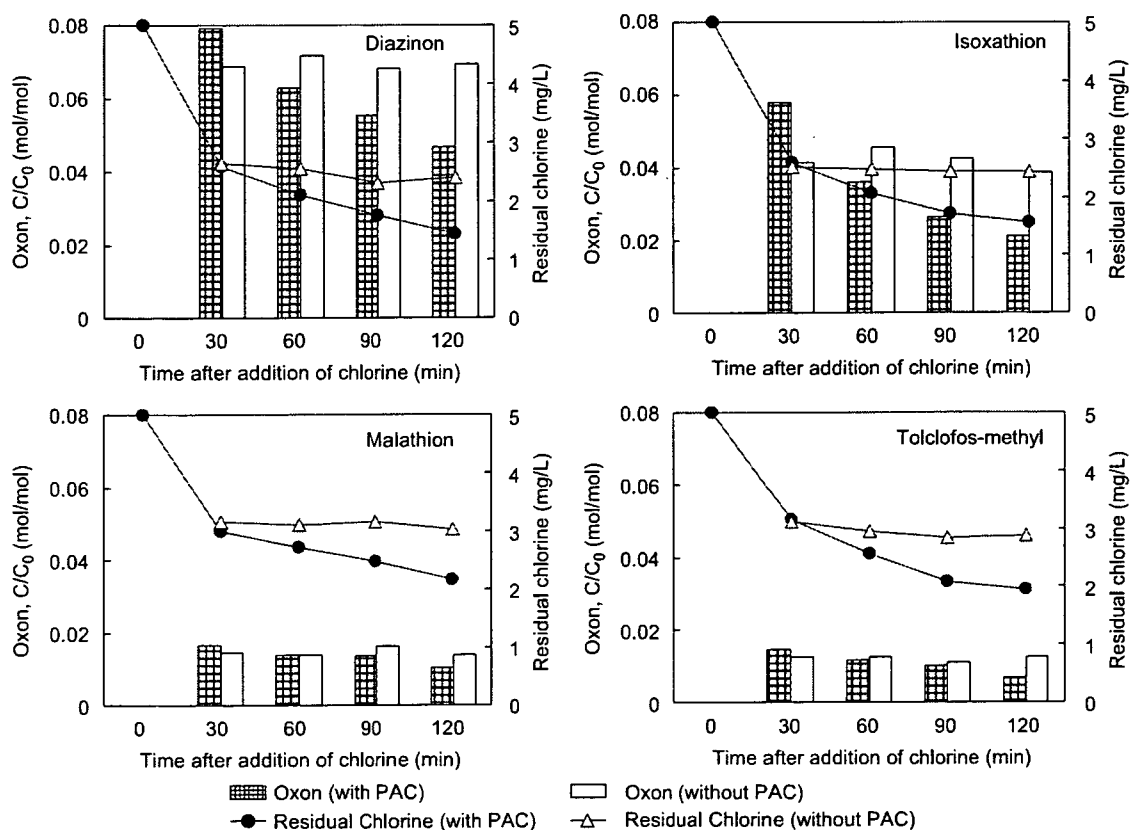
Fig. 2 – Effects of PAC on the decrease in the concentration of released oxons with chlorination time. To produce solutions without PAC, PAC was removed by filtration following 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentrations of the parent pesticide solution were the same as in Fig. 1.

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
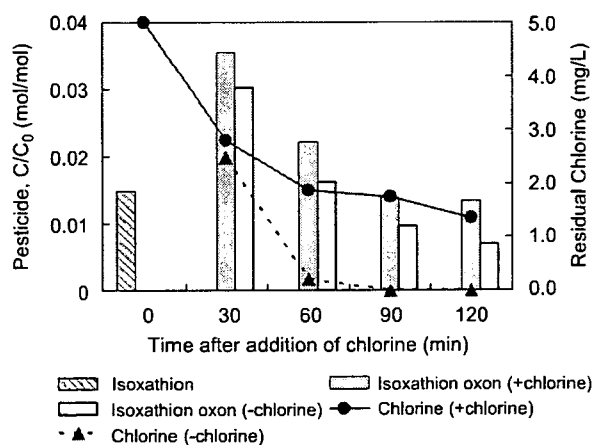

Fig. 3 – Effect of chlorine on isoxathion oxon concentrations released during 30 min of chlorination. For the condition without chlorine, chlorine was quenched after 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentration of isoxathion in the solution was 2.8 μM (880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

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 physico-chemical 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
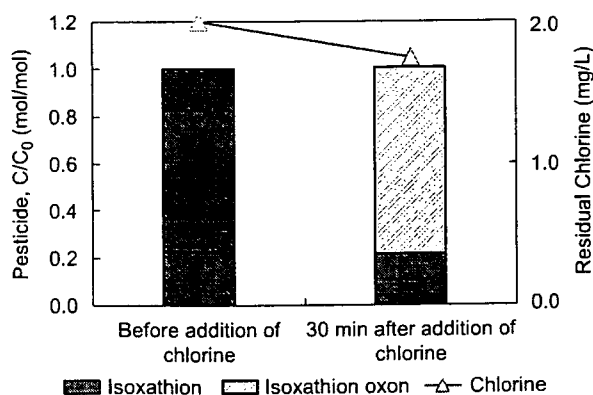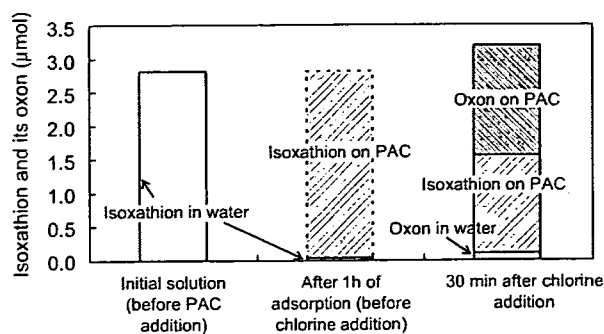

Fig. 5 – Change in the state of isoxathion and its oxon during the adsorption and chlorination experiment. The initial chlorine dose was 5 mg/L. The amount of isoxathion adsorbed on PAC after 1 h of adsorption was an estimate, whereas the amounts of isoxathion for the other samples were experimentally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

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.

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

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.

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.

Acknowledgment

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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（川嶋ら，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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1．研究の方法

1．1 流出可能性を表す指標値算出の考え方

本研究では，農薬の流出可能性を表す指標値として，流域別流出量及びADI（許容一日摂取量）あたりの流域別流出量を算出した。後者は，人健康リスクからみた流出負荷の指標値であり，後述する(9)式に示すように，無次元数のRunoff Risk Index（RRI値）と定義した。

流域別流出量は，まず流域別散布量を算出し，この散布量に対し，移流を考慮せず，環境中での分解過程を組み入れた定常平衡モデルであるレベルIIフガシティモデルをあてはめ，分解後の残留量と媒体別存在比を推定した。フガシティモデルを適用するため，農薬の散布と流出に関して次のモデル化条件（池貝，2006）を設定した。

(1) 農薬の流出しやすさを「平衡時における農薬の水相への存在しやすさ」であるととらえ，水相に分配する農薬量を水域への流出量とみなす。

(2) 農薬の散布環境を図1のように水田型と畑地型に区分する。

(3) 畑地型では，流出を安全側で評価するため，降水量1mm以上の降雨時に土壌中水分に分配する農薬が水域に流出するとみなす。

ここで，水田型散布環境は大気相，水相及び土壌相の三相構成，畑地型散布環境は大気相及び土壌相の二相構成とした。畑地土壌は30%の含有率で土壌水分を含むものとし，後述するようにこの土壌水分量から流出に寄与する有効土壌水相厚を定義した。なお，非湛水期に使用される水田農薬は，畑地型で推定した。

対象とした農薬は，化学物質排出把握管理促進法に規定する第一種と第二種指定化学物質に含まれる農薬並びに水道法の水質管理目標設定項目として対象農薬リストに掲載されたもの（第一群）及び厚生科学審議会生活環境水道部会が作成した今後の検討対象農薬リストに該当するもの（第二群，第三群）あわせて249種である。

1．2 流域別散布量の算出方法

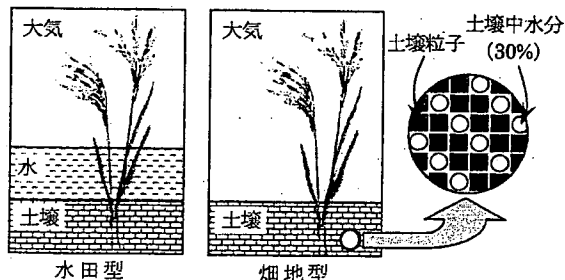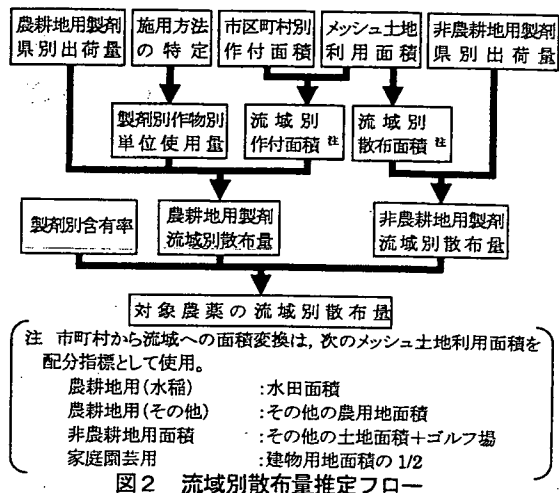流域別散布量の算出フローを図2に示した。流域別散布量は，農地散布製剤については単位使用量（10アール

図1 散布環境モデル

図2 流域別散布量推定フロー

あたり施用量）と作付面積の積の比，それ以外の製剤については散布面積の比で県内出荷量を配分して求めた。流域別の作付面積は，市区町村別作付面積を基準地域メッシュ（一辺約1km）に分解し，これを流域単位に再編成して算出した。したがって，各流域はこのメッシュの組み合わせとしてその境界を特定することとなる。製剤の施用方法は，登録内容から，①製剤の希釈倍率，②散布回数，③散布液量及び④適用病害名または除草剤の使用時期区分を32種の作物ごとに特定した。このうち，④は標準的な散布時期と対応させ，「3-4月」，「5-6月」，「7-8月」及び「9-11月」の4期に分けた指標値が算出できるようにした。非農耕地用製剤については，④に関する適当なデータがないため，4月から9月までの6ヶ月間に均等に散布されるものとした。

1．3 流域別流出量の算出方法

移流を考慮しないレベルIIフガシティモデルでは，農薬の散布量Iを系への投入量と考えると，(1)式が成立する。さらに，同一面積の散布環境モデルを考えた場合，(2)式から平衡後の各相の農薬量$M(p)$は，フガシティ容量・媒体相厚積$Z(p)L(p)$に比例するので，媒体別の分配比はこのフガシティ容量・媒体相厚積の比に相当する。媒体別のフガシティ容量$Z(p)$は後述の(3)～(5)式（Mackay, 1979；Mackay et al., 1981）で求められるため，媒体相厚$L(p)$を適切に設定すれば2種の散布環境の水相への分配比が算出できる。流域内の各散布環境に対する分解後の残留農薬量を求め，これに前述の分配比を乗じることにより，流域別流出量を算出した。媒体相厚$L(p)$は，大気相厚200m，水田の水相厚5cm，土壌相厚5cm，畑地の土壌相厚を20cmとし，畑地の有効土壌水相厚は，気象庁の地域気象観測システム海老名観測所における過去5年間の降雨頻度をもとに1.81cmに設定した（池貝，2006）。土壌吸着定数は，非イオン性農薬はオクタノー

ル/水分配係数から推定し (Karickhoff, 1981；Karickhoff, 1985)，イオン性農薬は有機炭素吸着定数から算出した。分解過程は水中の微生物分解のみを考慮し，分解の速度定数は(8)式 (Kanazawa, 1987) により算出した。

$$I = \sum_p C(p)V(p)K(p) = f\sum_p Z(p)V(p)K(p) \tag{1}$$

$$M(p) = C(p)V(p) = f \cdot S \cdot Z(p)L(p)$$
$$= \frac{I \cdot S}{\sum_p Z(p)L(p)K(p)} \times Z(p)L(p) \tag{2}$$

$$Z(air) = \frac{1}{RT} \tag{3}$$

$$Z(wat) = \frac{1}{H} \tag{4}$$

$$Z(soi) = \alpha \cdot \frac{Kp \cdot psoi}{H} \tag{5}$$

$$Kp = 0.48 \cdot \gamma \cdot Kow \quad (\text{イオン性農薬以外の場合}) \tag{6}$$

$$Kp = \gamma \cdot Koc \quad (\text{イオン性農薬の場合}) \tag{7}$$

$$\log \frac{K(wat)}{8.76} = -1.02(\log Kow)^2 + 4.96(\log Kow) - 5.23 \tag{8}$$

ここで，C は平衡時濃度 (mol·m^{-3})，f はフガシティ (Pa)，H は Henry 定数 (Pa·m^3·mol^{-1})，I は散布量 (mol·year^{-1})，K は分解速度定数 (year^{-1})，Koc は有機炭素吸着定数 (10^{-3}·m^3·kg^{-1})，Kow はオクタノール/水分配係数 (－)，Kp は土壌吸着定数 (10^{-3}·m^3·kg^{-1})，L は媒体相厚 (m)，M は平衡後の媒体別農薬量 (mol)，p は媒体，R は気体定数 (8.31Pa·m^3·mol^{-1}·K^{-1})，S は面積 (m^2)，T は絶対温度 (K)，V は媒体体積 (m^3)，Z はフガシティ容量 (mol·m^3·Pa^{-1})，α は土壌固相率 (畑地は 0.4，水田は 0.5)，γ は土壌有機炭素含有率 (0.05)，$psoi$ は土壌粒子比重 (2700kg·m^{-3}) である。なお，媒体相厚及びα，γ，$psoi$ の設定値は，既報 (池貝，2006) による。

2．結果と考察

2．1　流出可能性の指標としての流域別流出量の妥当性

2005 年度出荷量を用いて推計した流域別流出量を県内水道事業体が実施した 2005 年度のモニタリング結果 (真柄，2007) と比較した。モニタリングは，河川ごとに選定した 80〜90 種の測定対象農薬の濃度を散布期を中心に年間 5〜20 回程度測定したものである。流域別流出量は県内で散布された農薬を対象に推計するため，上流県からの流下がない河川として相模川水系の中津川，小鮎川，鳩川，玉川及び酒匂川水系の狩川を対象に，流域別流出量の年間値と検出状況の関係を調べた。結果を図 3 に示した。図の縦軸の検出率は，測定対象農薬のうち検出された割合を示すが，どの流域においても流域別流出量が多くなると検出率が高くなる傾向が見られた。このことから，流域別流出量は，流出可能性を判定する指標値として利用できると考えられる。なお，本研究で
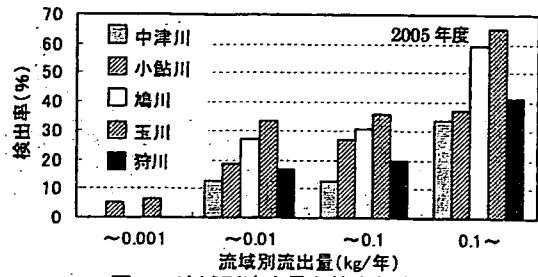

図3　流域別流出量と検出頻度の関係
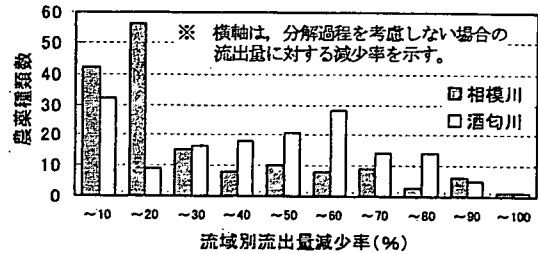
図4　分解による流出量減少率と農薬検出状況の関係

は分解過程として考慮できたものは，前述のように水中の微生物分解のみである。そのため，土壌分解性の大きい農薬については過大推計の可能性が大きい。

この方法により推計した流域別流出量は，分解を考慮しているため，レベルⅠフガシティモデルを適用して算出した場合に比べて数値は小さくなる。県内に出荷実績のあった 158 種の農薬を対象に，相模川と酒匂川についてその状況を比較した結果を図 4 に示した。図 4 の横軸は，レベルⅠフガシティモデルによる流出量に対する分解による減少量の割合を示している。これによると，流域別流出量減少率が 20%未満の農薬は，相模川では全体の 62%を占めたが，酒匂川では 26%に過ぎず，分解過程の有無による違いは酒匂川の方が大きかった。特に，プロピネブ (減少率は相模川 11%，酒匂川 77%)，イミダクロプリド (相模川 11%，酒匂川 46%) はその傾向が顕著であった。この流域間の違いは，流域に分布する 2 種の散布環境の比率の差異に起因するものと考えられる。

県内出荷量の確定値を用いて推計を行う場合，算出される流域別流出量は年度遅れ値となる。年度遅れの流出量を用いて次の年の流出予測の可能性を検討した。図 5

図5　前年度流域別流出量と検出頻度の関係

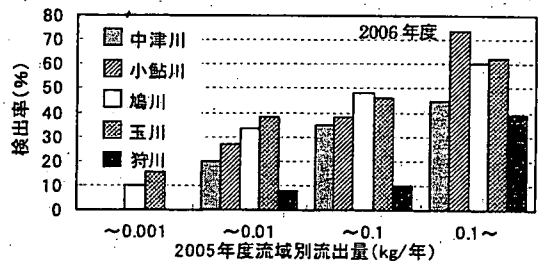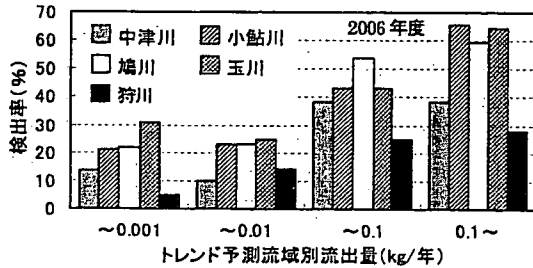図6 トレンド予測流域別流出量と検出頻度の関係
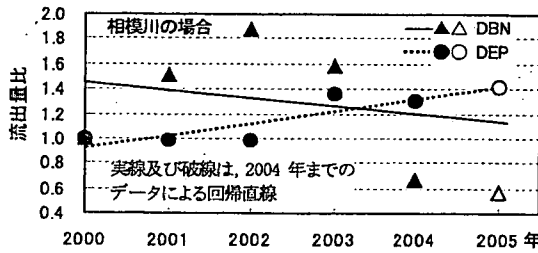

図7 トレンド予測における直線回帰の例

に，図3と同じく2005年度出荷量を用いて算出した年間の流域別流出量と2006年度のモニタリング結果による検出状況の関係を示したが，この場合も図3と同様の傾向が認められた。比較のため，過去5年間の出荷量から毎年の年間の流域別流出量を算出し，対象農薬ごとに直線回帰式を作成，これを外挿して2006年度のトレンド予測流出量を算出した。図6は，このトレンド予測流出量と2006年度のモニタリング結果を比較したものであるが，低流出農薬ではトレンド予測値の推定精度が悪くなり，実際の流出状況との乖離が大きくなる傾向が認められた。この状況は，他年度のデータで比較を行った場合にも同様に確認された。

図7に相模川におけるトレンド予測の回帰直線の例を示した。図の縦軸は2000年度を基準とした流出量の比を表している。DEPのように経年的な出荷量変動の少ない農薬は外挿したトレンド予測値が白抜きプロットで示した2005年度出荷量に基づく流出量と良く一致したが，DBNのように変動幅が大きい場合はトレンド予測流出量の推定誤差が大きくなった。このような経年変動の大きな農薬は，出荷量が比較的少ない農薬に多かった。2005年度出荷量に基づく流出量に対する前年度（2004年度）流出量及びトレンド予測（2005年度）流出量との相関を調べたところ，相関係数はトレンド予測流出量（r=0.92〜0.95）より前年度の流域別流出量（r=0.95〜0.99）の方が高かった。

曲線近似を行うなどトレンド予測流出量の精度を上げる方法はあるが，水質管理の現場において簡易な操作で次年度の流出可能性を予測するには，トレンド予測流出量より前年度の流域別流出量を指標値に用いることが適

切と考えられる。

2．2 時期別流出状況の推定

2005年度出荷量に基づく流域別流出量を2006年度の流出可能性を表す指標値として利用し，モニタリング結果との比較から時期別流出状況の評価を行った。前述の5河川について，モニタリングで検出された農薬の期別最大濃度と期別流出量から流出パターンを比較した。その結果，最大流出期がモニタリング結果と指標値で一致した割合は，中津川79%（年間の検出農薬数は24種），小鮎川64%（同36種），鳩川72%（同36種），玉川75%（同36種）及び狩川88%（同16種）となった。図8に，最大流出期が一致した例として，小鮎川のベンタゾン及び鳩川のダイアジノン，最大流出期が1期分ずれた例として鳩川のMEP，玉川のDBNの状況を示した。また，最大流出期が2期ずれたものは，5流域の検出農薬延べ148種中，中津川のNAC，鳩川のベノミルとNACとアセフェート，玉川のシマジンとイソキサチオンの6種のみであった。一部の農薬で最大流出期が一致しなかった原因は，実際の散布時期が適用病害名または除草剤の使用時期区分から特定した製剤別の標準的な散布時期とずれていたためと考えられる。
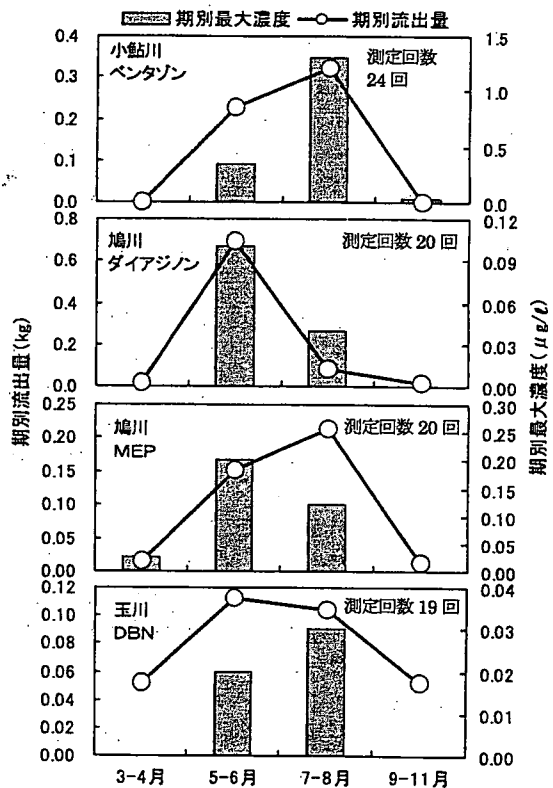

図8 期別流出量と検出濃度の関係

以上のように，対象5河川平均で74%の検出農薬で最大流出期が一致したことから，期別流出量は時期別の流出状況を予測する指標値として十分利用できると考えられる。

2．3　2006年度プライオリティの評価

現在，いくつかの水道事業体では，「監視農薬プライオリティリスト」を作成し，これをもとに監視対象農薬の選定を行っている。プライオリティリストは，農薬出荷量，ADI，Kow及び生分解性をパラメータとし，これらを数値の大きさによって5段階にスコア化し，これを合算した総スコア値によって監視対象農薬としてのプライオリティを決定しようとするものであり（眞柄，2002），神奈川県でも相模川酒匂川水質協議会により作成されている。そこで，流域別流出量をもとに相模川と酒匂川に関する2006年度における農薬のプライオリティを求め，その結果を2006年度版プライオリティリストの総スコア値による評価結果と比較した。総スコア値は，ADIを考慮した人健康リスクを意識した指標であることから，1．1で述べたRRI値を2005年度出荷量確定値による流域別流出量から算出し，プライオリティを判定した。RRI値の算出式を(9)式に示す。

$$RRI = \frac{一日あたりの流域別流出量}{50 \cdot ADI} \quad (9)$$

相模川と酒匂川に関するプライオリティが高いと考え

表1　2006年度流出農薬プライオリティ評価結果

順位	相模川			酒匂川		
	農薬名	RRI	S値	農薬名	RRI	S値
1	ダゾメット ※	28	16	マンネブ	16	12
2	プロピネブ	14	14	マンゼブ	6.3	16
3	マンネブ	13	12	アシュラム	3.5	14
4	DEP	5.6	15	DEP	3.4	15
5	マンゼブ	4.4	16	ダゾメット ※	2.7	16
6	MITC	3.3	14	イミノクタジン	2.5	13
7	アセフェート	2.7	15	DDVP	2.0	15
8	ホスチアゼート	2.4	14	アセフェート	1.4	15
9	DDVP	2.1	15	MITC	1.3	14
10	イミノクタジン	2.1	13	プロピネブ	1.2	14
11	アシュラム	1.9	14	グルホシネート	1.1	14
12	MCPP	1.8	14	ジネブ	0.70	16
13	ダイアジノン	1.3	14	ダイアジノン	0.67	14
14	グルホシネート	1.2	14	DMTP	0.62	15
15	ジネブ	0.77	16	ジメトエート	0.43	13
16	DCMU	0.73	15	MCPP	0.37	14
17	ジメトエート	0.71	13	ホスチアゼート	0.35	14
18	シアナジン ※	0.44	14	ACN	0.22	14
19	MCPA	0.43	11	ベンチオカーブ	0.19	14
20	ACN	0.41	14	MEP	0.17	14

（注）S値は，監視農薬プライオリティリスト総スコア値。
　　　※が付されたものは，土壌分解性が高い農薬。
　　　網掛けは，2006年度のモニタリング非対象農薬。

表2　総スコア値ごとのＲＲＩ値の分布

総スコア値 / RRI値		16	15	14	13	12	11
相模川	1~	40%	60%	32%	3 %	2 %	5 %
	~1	40%	40%	32%	18%	2 %	5 %
	~0.1	20%	—	18%	37%	19%	10%
	~0.01	—	—	14%	24%	23%	5%
	~0.001	—	—	5%	13%	23%	33%
	~0.0001	—	—	—	5%	30%	43%
酒匂川	1~	40%	60%	18%	3 %	2 %	5 %
	~1	40%	40%	32%	11%	—	—
	~0.1	20%	—	32%	32%	14%	10%
	~0.01	—	—	5%	29%	26%	10%
	~0.001	—	—	9%	16%	28%	19%
	~0.0001	—	—	5%	11%	30%	57%

（注）網掛け部は，分布の多いRRI値上位2階級に該当するもの。
　　　枠付き部は，総スコア値によるプライオリティが低いと考えられるもの。

られる農薬上位20種を表1に示した。土壌分解性が高いダゾメット及びシアナジンは過大評価されていると考えられるが，概ね総スコア値の高い農薬がリストアップされた。しかし，MCPA（総スコア値11），マンネブ（同12）などはプライオリティリストの総スコア値が低かった。このプライオリティリストでは総スコア値の最高値は16であり，主として総スコア値13以上の農薬から監視対象農薬が選定されている。RRI値による判定では，これらの農薬も監視対象に加えることが望ましいと考えられる。また，どちらの流域においてもリストアップした20種のうち10種は測定対象外農薬であった。この中には，マンゼブ，ACNなど水道水に適した測定法がないとして第二群の検討対象農薬に該当するものが5種含まれていた。的確な農薬の水質管理を行うには，これらの農薬の測定法を早急に定める必要があると考えられる。

2006年版プライオリティリストでは，スコア値11以上に該当する農薬が全部で298種（スコア値16；5種，同15；7種，同14；35種，同13；53種，同12；96種，同11；102種）存在する。これらの農薬のうち，2006年度に県内に出荷実績があり，本研究で対象とした農薬は135種である。これらの農薬について，総スコア値ごとのRRI値の分布を表2に示した。表2では，分布の多い上位2つのRRI値の階級に該当する部分を網掛けで示した。どちらの流域においても，全般的に総スコア値が高い農薬ほどRRI値も大きくなる傾向が見られた。また，相模川では，総スコア値14に該当する農薬について，RRI値が大きい領域に分布する農薬が酒匂川より多かった。網掛けで示した部分は，前述のとおり総スコア値が多く分布するRRI値の階級であることから，ここから離れている農薬ほど総スコア値とRRI値の乖離が大きい

とみなせる。2 階級以上離れている農薬を乖離が大きいと判別すると，表中の枠付き部分に相当する農薬は，総スコア値によるプライオリティが低いため，RRI 値を用いてプライオリティを見直す必要があると考えられる。これに該当する農薬は，イミノクタジン（酒匂川 RRI 値 2.5，総スコア値 13），マンネブ（相模川 RRI 値 13，酒匂川 RRI 値 16，総スコア値 12），ピメトロジン（相模川 RRI0.14，総スコア値 12），MITC（相模川 RRI 値 3.3，酒匂川 RRI 値 1.3，総スコア値 11），MCPA（相模川 RRI 値 0.43，酒匂川 RRI 値 0.089，総スコア値 11），チオシクラム（相模川 RRI 値 0.087，酒匂川 RRI 値 0.045，総スコア値 11），プレチラクロール（相模川 RRI 値 0.011，総スコア値 11）の 7 種であった。

プライオリティリストの総スコア値は流域別の数値が算出できず，全県値としてのみ利用可能な数値であるが，以上の検討のように RRI 値を用いることによって流域による流出状況の違いが把握でき，より詳細なプライオリティの判定が行えるものと考えられる。

おわりに

流域別の流出農薬のプライオリティを判定するため，農薬使用状況の地域差を反映し，多種類の農薬を対象に比較的単純化した方法で流出可能性を表す指標値を算出する手法について検討した。農薬散布環境をモデル化し，農薬の施用方法，出荷量，散布対象面積等の公表データをもとに算出した流域別散布量にレベルⅡフガシティモデルをあてはめ，流出時期を 4 期に区分した期別の指標値を算出する手法を作成した。この手法による算出指標値は，流域別流出量及び ADI あたりの流域別流出量である RRI 値である。この手法を用いて，神奈川県の相模川及び酒匂川の流出農薬プライオリティを評価したところ，次のような知見を得た。

(1) 年間の流域別流出量をモニタリングの検出状況と比較したところ，流域別流出量が多くなると検出される農薬の割合が高くなる傾向が見られたことから，流域別流出量は，流出可能性を判定する指標値として利用できると考えられた。

(2) 県内出荷量確定値をもとに算出した前年度の流域別流出量は，翌年度のモニタリングの検出状況とほぼ一致したことから，前年度の流域別流出量を利用して翌年の流出状況を予測することが可能と考えられた。

(3) 期別の流域別流出量をモニタリングの検出濃度と比較したところ，平均で 74% の検出農薬で最大流出期が一致したことから，期別の流域別流出量は時期別の流出状況を予測する指標値として利用可能と考えられた。

(4) RRI 値を用いて，相模川と酒匂川の流出農薬プライオリティを評価したところ，上位 20 位の農薬の半数は，モニタリング対象外農薬であった。

(5) RRI 値は，人健康リスクを踏まえた流域別の流出農薬負荷の指標値として利用可能であり，プライオリティリストの総スコア値と併用することにより，より詳細な流出状況の判定が可能になると考えられた。

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ELSEVIER

Two-generation reproductive toxicity study of the rubber accelerator N,N-dicyclohexyl-2-benzothiazolesulfenamide in rats

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Abstract

Male and female Crl:CD(SD) rats were fed a diet containing rubber accelerator N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) at 0, 80, 600 or 4500 ppm throughout the study beginning at the onset of a 10-week pre-mating period and continuing through the mating, gestation, and lactation periods for two generations. At 4500 ppm, decreases in the body weight, body weight gain, and food consumption were found in F0 males and females. No changes in the estrous cyclicity, copulation index, fertility index, gestation index, delivery index, number of implantations, precoital interval, or gestation length were observed in any generation at any dose of DCBS. Delayed preputial separation at 4500 ppm as well as delayed vaginal opening and higher body weight at the age of vaginal opening at 600 and 4500 ppm were found in the F1 generation. A transient change in performance in a water-filled multiple T-maze was found at 600 and 4500 ppm in F1 females. There were no compound-related changes in number of pups delivered, sex ratio of pups, viability of pups, anogenital distance, surface righting reflex, negative geotaxis reflex, mid-air righting reflex, pinna unfolding, incisor eruption, or eye opening in the F1 and F2 generations. The body weight of F1 and F2 male and female pups was lowered at 4500 ppm. Reduced uterine weight of the weanlings was noted in the F1 generation at 4500 ppm and in the F2 generation at 600 and 4500 ppm. The data indicate that the NOAEL of DCBS for two-generation reproductive toxicity is 80 ppm (5.2 mg/kg bw per day) in rats.
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Keywords: N,N-Dicyclohexyl-2-benzothiazolesulfenamide; Rubber accelerator; Two-generation reproductive toxicity; Developmental toxicity; Rat

1. Introduction

N,N-Dicyclohexyl-2-benzothiazolesulfenamide (DCBS) is a sulfenamide accelerator. The sulfenamide accelerator class of rubber accelerators has been manufactured in the USA for over 60 years [1]. Sulfenamide accelerator compounds are widely used in the manufacture of automotive compartments and industrial rubber products such as tires, hoses, conveyer belts, bushings seals, gaskets and windshield wiper blades, and the typical usage for sulfenamide accelerators is from 0.5 to 4 parts accelerator per every 100 parts of rubber [1]. Sulfenamide accelerator materials are shipped extensively throughout the world from manufacturing plants located in North America, South America, Europe, Asia and Africa [1]. DCBS was produced

in Japan with an annual production level of about 1000 tonnes in 1990–1993 and 1900 tons in 2000–2003, and most of this amount was sold and handled domestically [2]. DCBS is used as an accelerator of vulcanization and is completely reacted in the vulcanizing process [2]. DCBS is regulated for use in articles in contact with food in Germany, but this compound is not regulated for use in FDA food contact applications [3]. Exposure of workers handling sulfenamide accelerator materials is likely to be highest in the area of materials packaging. During material packout at the manufacturing site and to a lesser degree during weigh-up activities at the consumer site, there is potential for skin and inhalation exposure. Although consumer exposure would be minimal, the most likely route of consumer exposure is skin contact from rubber or latex articles [1].

Only up to 6% biodegradation for DCBS was determined in a ready biodegradability test, and a measured log K_{ow} value of 4.8 suggests that DCBS may have a high bioaccumulation potential [2]. The possibility of such a chemical compound entering

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into biological systems has aroused great concern regarding its toxicological potential. Generally, biological effects produced by chemicals should be studied in laboratory animals to investigate their possible influences on human health, and the results of animal tests of chemical toxicity are relevant to humans [4]. However, very little information on the toxicity of DCBS has been published. Vorobera (1969) [5] reported that the oral LD50 value was 8500 mg/kg bw in male mice and that repeated inhalation exposure of male rats for 15 days, daily, 2 h/day, at 350–400 mg/m^3 caused mucous membrane irritation. Although the toxic effects of DCBS have been briefly summarized by the European Chemical Bureau [6] and EPA [1], descriptions regarding the toxicity of DCBS are insufficient to assess the adverse effects of this compound. The EPA [1] noted that the oral LD50 values were 1077–10000 mg/kg bw in rats, the oral NOAEL for 44-day repeated dose toxicity was higher than 100 mg/kg bw per day in rats, and no effects on reproduction were observed at doses up to 400 mg/kg bw per day in rats. Toxicity studies including acute toxicity, in vitro genotoxicity, and repeat dose toxicity combined with reproductive/developmental toxicity studies of DCBS were performed as a part of the Safety Examination of Existing Chemical Substances and Chemical Safety Programmes by the Japanese Government [7]. These toxicity studies are summarized in the IUCLID Data Sets [8], OECD Screening Information Data Sets [2] and the Hazard Assessment Sheet [9]. We previously reported results of repeat dose toxicity combined with a reproductive/developmental toxicity screening test of DCBS showing that DCBS at 400 mg/kg bw per day possessed a deleterious effect on reproduction and development and caused a marked decrease in the number of live pups as well as a total loss of pups until postnatal day (PND) 4 [10]. The primary effects may be on the gestation index for dams and live birth index for pups, which both appear to be affected at multiple points along the female reproductive process; the viability of neonatal pups may also be affected. The previous study was performed in compliance with the OECD guideline for a Combined Repeated Dose Toxicity Study with the Reproduction/Developmental Toxicity Screening Test [11,12], but this screening test guideline does not provide complete information on all aspects of reproduction and development due to the relatively small numbers of animals in the dose groups and selectivity of the endpoints. In order to further evaluate the reproductive and developmental toxicity of DCBS in rats, a two-generation reproductive toxicity study was conducted. We examined reproductive and developmental endpoints such as sexual development, estrous cyclicity, anogenital distance (AGD), physical and functional development, serum hormone levels, and sperm count and motility.

2. Materials and methods

This study was performed in 2006–2007 at the Safety Research Institute for Chemical Compounds Co. Ltd. (Sapporo, Japan) in compliance with OECD guideline 416 Two-generation Reproduction Toxicity Study [13] and in accordance with the principles for Good Laboratory Practice [14], "Law for the Humane Treatment and Management of Animals" [Law No. 105, 1 October 1973, revised 22 December 1999, Revised Law No. 221; revised 22 June 2005, Revised Law No. 68], "Standards Relating to the Care, Management and Refinement of Laboratory Animals" [Notification No. 88 of the Ministry of the

Environment, Japan, 28 April 2006] and "Fundamental Guidelines for Proper Conduct of Animal Experiment and Related Activities in the Testing Facility under the Jurisdiction of the Ministry of Health, Labour and Welfare" [Notification No. 0601005 of the Health Sciences Division, Ministry of Health, Labour and Welfare, Japan, 1 June 2006].

2.1. Chemical and dosing

N,N-Dicyclohexyl-2-benzothiazolesulfenamide (DCBS; CAS No. 4979-32-2) was obtained from Ouchishinko Chemical Industrial Co. Ltd. (Tokyo, Japan). DCBS in the form of off white to tan granules is very slightly soluble in water and methanol but soluble in oil, and its melting point is 100–105 °C, density at 21 °C is 1230 kg/m^3, and molecular weight is 347 [3]. The DCBS (Lot no. 508001) used in this study was 99.7% pure, and it was kept in a sealed container under cool (1–8 °C) and dark conditions. The purity and stability of the chemical were verified by analysis using high-performance liquid chromatography before and after the study. Rats were given dietary DCBS at a concentration of 0 (control), 80, 600 or 4500 ppm. The dosage levels were determined based on the results of our previous dose-finding study in male and female rats fed a diet containing DCBS at 0, 1500, 3000, 6000 or 10,000 ppm (0, 83, 172, 343 or 551 mg/kg bw per day in males and 0, 126, 264, 476 or 707 mg/kg bw per day in females) for a total of eight weeks beginning 16 days before mating in males and a total of nine weeks in females throughout the mating, gestation and lactation periods beginning 16 days before mating. In that study, we found reduced body weight gain in males at 6000 ppm and higher and females at 3000 ppm and higher, reduced number of implantations at 6000 ppm and higher, decreased absolute and relative weight of the spleen in females at 6000 ppm and higher, reduced number of pups born at 10000 ppm, lowered body weight of pups at 6000 ppm and higher, and decreased absolute and relative weight of the spleen in male weanlings at 1500 ppm and higher and female weanlings at 3000 ppm and higher [15]. Dosed diet preparations were formulated by mixing DCBS into an appropriate amount of a powdered basal diet (CRF-1, Oriental Yeast Co. Ltd., Tokyo, Japan) for each dietary concentration. The control rats were fed a basal diet only. Analysis showed that DCBS was homogeneous in the diet and stable for at least 21 days in a room temperature, and formulations were maintained in a room temperature for no more than 21 days. Generally, diet was replaced every 1 week.

2.2. Animals and housing conditions

Crl:CD(SD) rats were used throughout this study. Rats of this strain were chosen because they are the most commonly used in reproductive and developmental toxicity studies and historical control data are available. Male and female rats at 4 weeks of age were purchased from Hino Breeding Center, Charles River Laboratories Japan, Inc. (Yokohama, Japan). The males and females were acclimated to the laboratory for eight days prior to the start of the experiment. Male and female rats found to be in good health were selected for use. One hundred and ninety two rats were randomly assigned 24/sex/group and all animals were assigned a unique number and ear tattooed prior to the start of the experiment. Animals were housed individually in suspended aluminium/stainless steel cages except during the acclimation, mating and nursing periods. From day 17 of pregnancy to the day of weaning, individual dams and litters were reared using wood chips as bedding (White Flake; Charles River Laboratories Japan, Inc.).

Animals were reared on a basal diet or diet containing DCBS and filtered tap water *ad libitum* and maintained in an air-conditioned room at 22 ± 3 °C, with a humidity of 50 ± 20%, a 12-h light (8:00–20:00)/dark (20:00–8:00) cycle, and ventilation at 10–15 times/h.

2.3. Experimental design

Twenty-four rats (5-week-old males and females)/sex/group were fed a diet containing DCBS at 0, 80, 600 or 4500 ppm for 10 weeks prior to the mating period. Each female F0 rat was mated with a male rat of the same dosage group, with administration of DCBS in the diet continuing throughout the mating period. Administration of DCBS was continued throughout gestation and lactation. Twenty-four male and 24 female F1 weanlings (1 male and 1 female