

Table 2. Limit of Detection, Limit of Quantity, and Linear Range of Nine OP Oxons

Compound	Correlation coefficient (R ²)	Linear range (ng/ml)	Limit of detection (ng/ml)	Limit of quantity (ng/ml)
Butamifos oxon	0.996	1–50	2.0	10.0
Chlorpyrifos oxon	0.994	10–1000	10.0	50.0
Daizinin oxon	0.997	0.2–20	0.5	2.5
EPN oxon	0.998	5–100	5.0	25.0
Isofenphos oxon	0.995	1–100	1.0	5.0
Isoxathion oxon	0.991	20–2000	50.0	200.0
MEP oxon	0.998	5–500	5.0	25.0
Prothiofos oxon	0.996	1–100	1.0	5.0
Tolclofos-methyl oxon	0.999	0.5–50	0.5	2.5

Table 3. Average Recovery Rates of Nine OP Oxons from Tap Water Using Three Solid-Phase Extraction Cartridges

Compound	Spike level (ng/ml)	Recovery (%) (RSD%)		
		HLB	PS-2	C18
Butamifos oxon	10.0	57.3 (8.1)	60.0 (0.3)	67.3 (4.2)
Chlorpyrifos oxon	50.0	69.0 (1.9)	62.0 (0.2)	92.5 (16.7)
Daizinin oxon	2.5	96.1 (8.3)	110.5 (7.3)	107.2 (6.5)
EPN oxon	25.0	58.7 (2.6)	38.7 (4.9)	58.9 (2.3)
Isofenphos oxon	5.0	80.0 (9.0)	77.9 (7.2)	78.7 (1.0)
Isoxathion oxon	200.0	118.1 (8.0)	82.5 (1.8)	72.1 (2.9)
MEP oxon	25.0	83.6 (9.2)	84.2 (5.0)	89.9 (8.0)
Prothiofos oxon	5.0	71.1 (0.6)	68.5 (0.9)	84.6 (10.2)
Tolclofos-methyl oxon	2.5	84.7 (11.3)	120.8 (6.2)	118.2 (11.4)

ery was less than 60% with an RSD of less than 5%. To improve this, additional investigation was carried out on the pretreatment method with C18-HLB, C18-C18, and HLB-C18 cartridges. Tandem cartridges were equilibrated separately. After extraction of the water samples, tandem cartridges were dried separately and elution was carried out as described above. However, not all compounds were detected from the second of the tandem cartridge pairs. It is thus necessary to take the recovery rate into account when calculating the concentration based on the calibration curves to ensure precision in the analysis of compounds for which the recovery rate is low.

The performance of each cartridge was compared based on extraction efficiency. The cartridge packed with C₁₈ bonded to silica (Sep-Pak Plus C18) was a suitable for the extraction of oxons from water samples. Most compounds were extracted with high reproducibility and good recovery rates of more than 70%, and the RSDs for the studied compounds were 12% lower when using Sep-Pak Plus C18.

The limit of quantification (LOQ) was calculated to be 10-fold the standard deviation and as the low-

est concentration that provided RSDs of less than 10% in the recovery test. LOQ values obtained at 500-fold concentrations were 2.5 ng/ml for diazinon oxon and tolclofos-methyl oxon, 5.0 ng/ml for isofenphos oxon and prothiofos oxon, 10 ng/ml for butamifos oxon, 25 ng/ml for EPN oxon and MEP oxon, 50 ng/ml for chlorpyrifos oxon, and 200 ng/ml for isoxathion oxon. Actual sample concentrations converted those LOQ values were 5 ng/l for diazinon oxon and tolclofos-methyl oxon, 10 ng/l for isofenphos oxon and prothiofos oxon, 20 ng/l for butamifos oxon, 50 ng/l for EPN oxon and MEP oxon, 100 ng/l for chlorpyrifos oxon, and 400 ng/l for isoxathion oxon. The LOQ values of their parent compounds were obtained at 5-fold the LOD level with the Sep-Pak Plus C18 cartridge, corresponding to 1% or less of the guideline values, except for the values of isoxathion and isofenphos.

Behavior of OPs upon Chlorination

Free chlorine 1 mg/l was added to water samples containing each OP 10 ng/l. Parent compounds rapidly decomposed, and their oxons were detected as

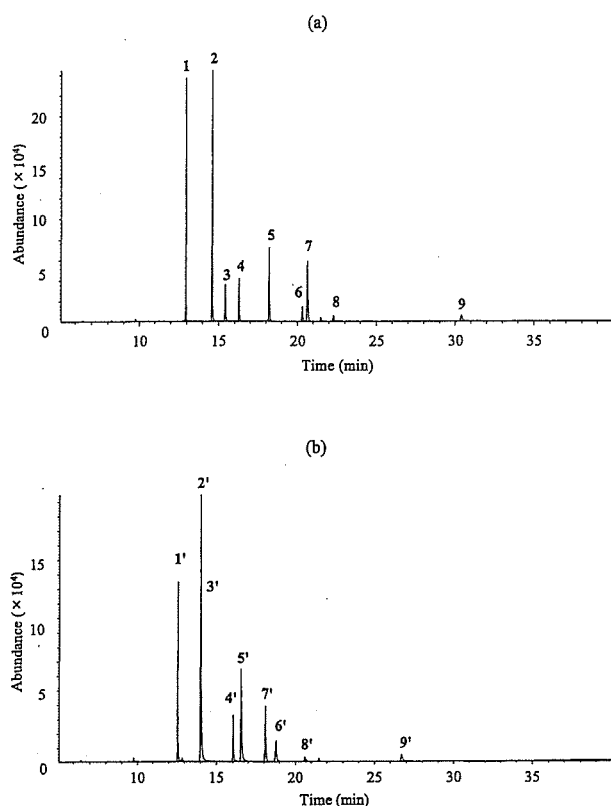


Fig. 1. Chromatograms of Nine OPs and their Products after Chlorination

(a) OPs: 1, diazinon; 2, tolclofos-methyl; 3, MEP; 4, chlorpyrifos; 5, isofenphos; 6, butamifos; 7, prothiofos; 8, isoxathion; 9, EPN. (b) Chlorinated products after 30 min: 1', diazinon oxon; 2', tolclofos-methyl oxon; 3', MEP oxon; 4', chlorpyrifos oxon; 5', isofenphos oxon; 6', butamifos oxon; 7', prothiofos oxon; 8', isoxathion oxon; 9', EPN oxon.

primary reaction products. Figure 1 shows the chromatograms of nine OPs and their oxons after chlorination at the start time and after 30 min. Figure 2 shows the time-dependent reactions of nine OPs and their oxons. The parent compounds decreased and the oxon forms increased upon chlorination in comparison with concentrations at the start time. The generation of oxons due to chlorination occurred rapidly. In addition, the effect of chlorination on diazinon was independently examined. The reaction was completed within 5 min at low concentrations of the parent compound (Figs. 3 and 4). It is known that the oxon forms of OPs are more toxic than their parent compounds.⁶⁻⁸ These results highlight the necessity of detecting both forms to trace the presence of OPs and their oxons during the water treatment process.

In conclusions, we established a selective and sensitive method for the quantitative analysis of oxon forms of OPs in water samples using GC/MS with

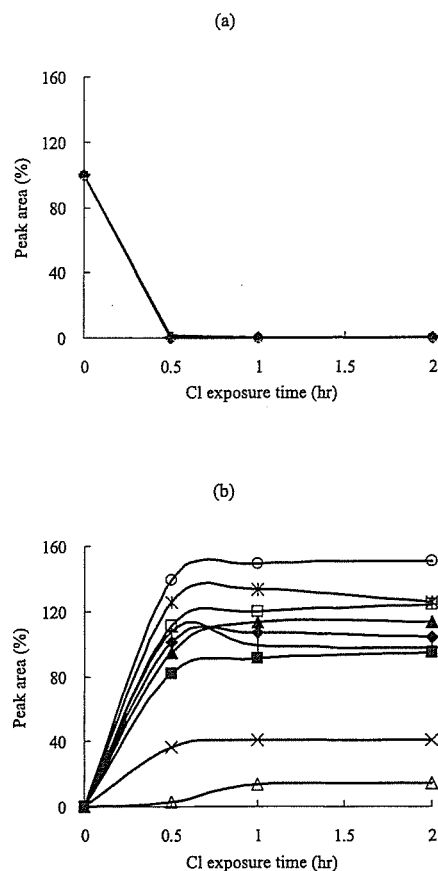


Fig. 2. Time-Dependent Behavior of OPs and their Oxon Forms after Chlorination

(a) Parent compounds, \circ —, butamifos; $*$ —, isofenphos; \square —, EPN; \blacktriangle —, MEP; \blacklozenge —, diazinon; $+$ —, prothiofos; \blacksquare —, tolclofos-methyl; \times —, chlorpyrifos; \triangle —, isoxathion. (b) Oxons, \circ —, butamifos oxon; $*$ —, isofenphos oxon; \square —, EPN oxon; \blacktriangle —, MEP oxon; \blacklozenge —, diazinon oxon; $+$ —, prothiofos oxon; \blacksquare —, tolclofos-methyl oxon; \times —, chlorpyrifos oxon; \triangle —, isoxathion oxon. The concentration at the start of the reaction was defined as 100%.

SPE. This method is suitable for the simultaneous detection and determination of OPs and their oxons and allows the tracing their reactions in water. Calibration curves for the oxons showed good linearity. The method yielded low LOD values and reproducible recovery rates for the accurate quantification, simultaneous extraction, and the determination of the concentration of 18 compounds in water. The LOD values of oxons were from 0.5 to 20 ng/ml. The LOQ values ranged from 5 to 400 ng/l in actual water samples. In addition, we found that OPs were rapidly converted to their oxon forms in the presence of chlorine.

Many OPs are highly toxic, and thus it is necessary to detect and control not only the parent compounds but also the oxon forms in the environment and after the water treatment process. Quality con-

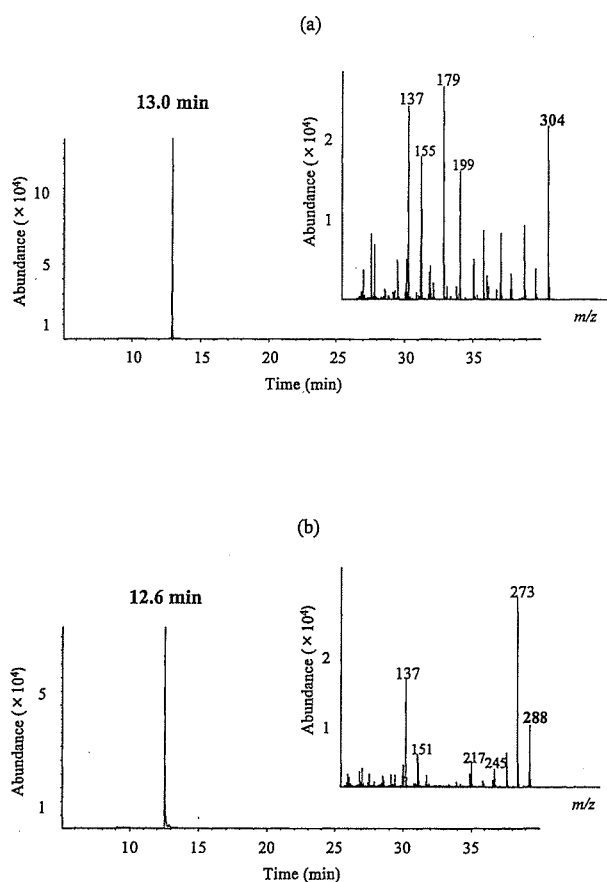


Fig. 3. Chromatogram and MS Spectra of Diazinon after Chlorination
Chlorine exposure time: (a) 0 min and (b) 5 min.

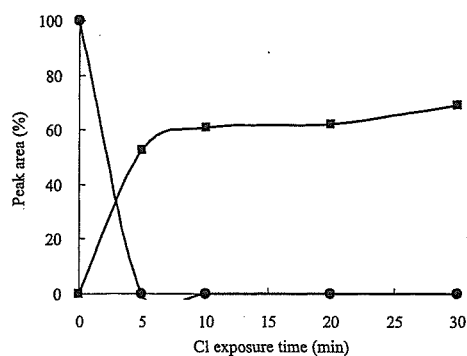


Fig. 4. Behavior of Diazinon and its Oxon after Chlorination
●, diazinon; ■, diazinon oxon.

trol of natural water has become an urgent issue. Regulations governing drinking water quality are meant to limit human risk and environmental pollution. However, regulations for OP oxons are not defined and no standard method for their detection has been given in Japan. Our approach can be applied

as a screening method for field monitoring of OP parent compounds and oxons. The risk of these compounds to human health and ecosystems can be accurately evaluated using the present method. We believe that our results will be important in enforcing the Water Quality Standard of Japan.

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流域の環境負荷評価のための農薬流出推定

Estimation of Pesticide Runoff for Evaluating Environmental Load of River Basin

池貝 隆宏

Takahiro IKEGAI

要旨：河川流域の環境評価として、事業所や家庭などの点源負荷と並び、流出農薬の負荷は重要であり、これを的確に評価する必要がある。本稿では、農薬の流出をフガシティモデルを用いてモデル化し、地域的な偏りの大きい農薬の使用状況を反映した流域別流出量推定法を検討した。この方法を用いて、神奈川県内河川における249種の農薬の流出量を算出し、環境負荷が大きなPRTR対象外農薬の寄与、排出源別の環境負荷の寄与等を流域単位で把握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 evaluate environment of river basin, it is very important to calculate load of pesticide runoff as well as load from point sources. In this paper, we modelled a mechanism of pesticide runoff by using fugacity model, and constructed a method of estimating pesticide spillage by each basin based on actual pesticide usage which had large regional deflection. We calculated the spillage of 249 pesticides into the river of Kanagawa prefecture by using this method. As a result, this method indicated that contribution of pesticide which does not belong to PRTR and contribution of environmental load of each pollution source could be calculated by each basin.

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

はじめに

近年、流域をひとつの単位として河川環境の保全を行う流域管理の重要性が広く認識されるようになった。流域管理では、水循環によって維持される自然生態系全体を保全する観点から、生態リスクに着目した対策を講じることが重要とされ、そのために河川の環境負荷の的確な評価が求められる。河川生態系に影響を及ぼす汚濁負荷として、事業所や家庭由来の物質と並び、農薬の存在は無視できない。例えば、神奈川県内の金目川ではチオベンカルブ等の高濃度検出が報告されており（大塚ら、2004）、これは河川生態系に対する影響が懸念される状況にある。一方、水道法においては平成16年度から農薬が水質管理目標設定項目に位置付けられ、水道事業体による水質管理の強化が図られている。このような状況から、流域における農薬の流出状況の把握は、河川環境の管理及び評価において不可欠の要素であると考えられる。

環境負荷の評価に利用可能なデータとして、近年PRTR（Pollutant Release and Transfer Register：化学物質排出移動量届出制度）の運用が開始され、有害性のある多種多様な化学物質について、発生源ごとの環境中

への排出量に関する情報が整備されつつある。しかし、PRTRにおいては農薬は非点源として扱われており、県単位の排出量しか算出されないため、この数値から流域単位の流出量を直接算出することはできない。農薬の使用状況は、同一県内でも農作物の耕作状況の違いによって地域的な偏りが大きいため、流出量を求めるにはこれらの地域情報を考慮した推定手段を用いる必要がある。

そこで、本稿では、農薬の登録内容からその使用方法を特定し、散布対象作物の作付面積等の土地利用面積情報と組み合わせることで流域単位の農薬散布量を算出するとともに、農薬の流域への流出をモデル化し、年間流出量を推定する手法について検討した。さらに、この推定法で算出した農薬流出量をもとに、神奈川県における流域ごとの環境負荷の評価を行ったので、その結果を報告する。

1. 研究の方法

本稿で提案する推定法では、PRTRの届出排出量と同様に排出先河川ごとの水域排出量としての農薬流出量を算出することを想定している。そのため、多種類の農薬を対象に比較的単純化した方法で包括的に流出量が計算できることを前提に推定法の組み立てを行った。本稿で

は、(1) 流域別散布量の推定と、(2) 散布量に対する流出比率の推定をそれぞれ行い、これらの数値を掛け合わせることで流域別流出量を推定する方法を検討した。ここで、流域別散布量の全県合計値は、PRTR 対象である化管法の第一種指定化学物質に該当する農薬については県別排出量公表値に一致する。

1. 1 流域別散布量の推定

農地散布剤の流域別散布量の推計フローを図1に示した。散布量の基礎数値は、登録内容から32種の作物ごとに特定した剤の希釈倍率、散布回数、散布液量と市町村別作付面積である。これらの数値から剤別作物別の基準使用量を求め、県内出荷量で補正して市町村別散布量を算出し(池貝ら, 2003)、さらに、国土数値情報の土地利用メッシュデータを用いてこれを流域別に変換した。散布量算出の基礎数値である作付面積は、流域別に把握できない。そこで、市町村別散布量を一度3次メッシュに分解し、これを流域単位に再編成することにより、流域別散布量を求めた。したがって、各流域は3次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。なお、非農耕地用剤については前述の散布回数等の情報がないため、表1に示すように出荷量を散布対象として想定される土地利用区分の面積で3次メッシュに直接配分することにより、水域別散布量とした。

評価対象流域は、流域に農地が多い神奈川県的主要河川である相模川及び酒匂川については主たる支流を一つの流域とし、他の河川は全流域をまとめて一つの流域に区分し、全51流域について流出量の算出を行った。

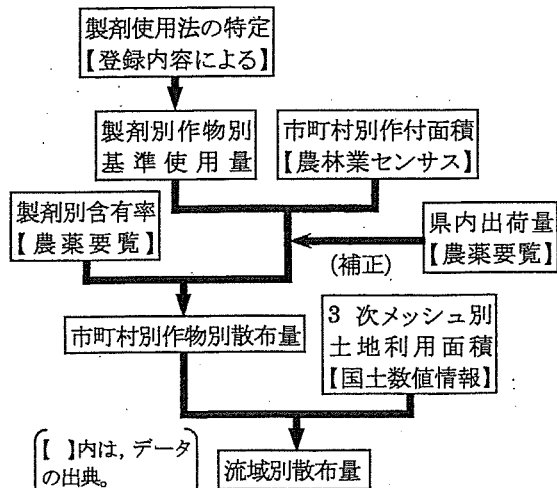


図1 農地散布剤の流域別散布量推計フロー

表1 非農耕地用剤のメッシュ配分指標

種別	配分指標とする土地利用区分	実際の散布場所
ゴルフ場用	ゴルフ場面積	ゴルフ場
家庭園芸用	建物面積の1/2	宅地周辺
他の非農耕地用	その他の土地	公園, 駐車場, のり面等

1. 2 散布量に対する流出比率の推定

流出比率は、農薬の散布及び流出の状況をモデル化し、fugacity model で算出した。Fugacity model は環境媒体間での移動過程の表現方法や、変換過程の取り扱いの違いなどにより4つのレベルがあるが、本稿では対象物質の変換過程を考慮しない平衡モデルである fugacity model (level I) を使用した。農薬の散布と流出のモデル化の条件は、次のとおりである。

- (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」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2のように水田型と畑地型に区分する。
- (3) 畑地型では、降雨時に土壤中水分に分配する農薬が水域に流出するとみなす。

図2に示すモデル環境中で一定量の農薬の散布を考えたとき、散布された農薬は各媒体へ移行し、平衡状態となる。実際の環境では生分解及び物理化学的分解過程が関与するが、本稿では安全サイドにたったワーストケースを想定し、これら散布後の消長は考慮しないこととした。この場合、平衡時の各媒体の農薬の存在しやすさはフガシィ容量のみに依存する。同一面積のモデル環境を考えた場合、平衡時は各相のフガシィが等しいので、(1)式からフガシィ容量と媒体相厚の積(以下、「 $Z(p)L(p)$ 値」という。)の比が媒体別存在比に等しいと考えることができる。

$$M = \sum_p C(p) \cdot V(p) = f \cdot \sum_p Z(p) \cdot V(p) = f \cdot S \sum_p Z(p) \cdot L(p) \dots\dots\dots(1)$$

ここで、 M は散布量(mol)、 p は媒体(水, 大気, 土壌)、 C は平衡時の濃度(mol・m⁻³)、 V は媒体体積(m³)、 f はフガシィ(Pa)、 Z はフガシィ容量(mol・m⁻³・Pa⁻¹)、 S はモデル環境面積(m²)、 L は媒体相厚(m)である。媒体別のフガシィ容量 $Z(p)$ は後述の(2)~(5)式で表されるため、媒体相厚 $L(p)$ を適切に設定すれば各媒体の

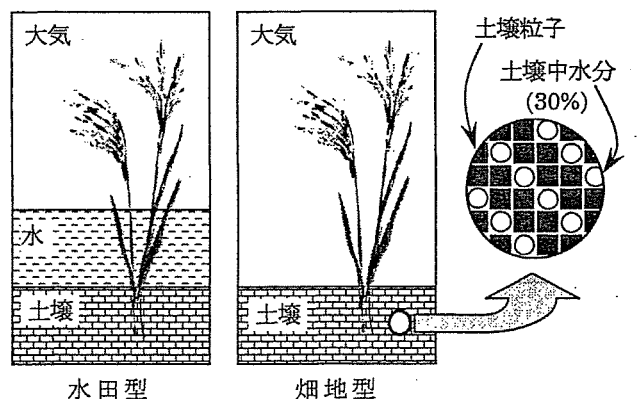


図2 散布環境モデル

$Z(p)L(p)$ 値が算出できることになる。水相存在比は、三媒体の $Z(p)L(p)$ 値の水相寄与率として与えられる。

水田型の媒体相厚は、湛水部に分配する農薬がそのまま水域に流出すると考え、水相厚を平均的な湛水部水深である 5cm とした。畑地型では、農薬は土壌中に存在する間隙水（体積含水率 30% とする）に分配するが、これが日降水量 1mm 以上の降雨時に流出するものと考え、土壌水分量に降雨頻度を乗じて流出に寄与する有効土壌水相厚を設定した。本稿では、2000~2004 年における平均降雨日数（海老名 AMeDAS による）から、降雨頻度を 110/365 とし、畑地土壌厚を 20cm とし有効土壌水相厚 1.81cm とした。そのほかの媒体相厚は、大気相厚 200m、水田土壌相厚 5cm に設定した。

流出比率は、2 つのモデル環境の水相存在比と散布比率を乗じることにより算出した。この流出比率を流域別散布量に乗じたものが流出量に相当する。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。フガシティ容量の算出式 (Mackay, 1979, Mackay et al, 1981, Karickhoff, 1981, Karickhoff, 1985) を次に示す。

$$\text{大気 } Z_{air} = \frac{1}{RT} \dots\dots\dots(2)$$

$$\text{水 } Z_{wat} = \frac{1}{H} \dots\dots\dots(3)$$

$$\text{土壌 } Z_{soi} = \alpha \cdot \frac{Kp \cdot \rho_{soi}}{H} \dots\dots\dots(4)$$

$$\text{ただし、} Kp = 0.48 \cdot \gamma \cdot Kow \dots\dots\dots(5)$$

ここで、 R は気体定数 ($=8.31\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)、 T は絶対温度 (K)、 H は Henry 定数 ($\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$)、 Kp は土壌吸着定数 ($10^{-3}\cdot\text{m}^3\cdot\text{kg}^{-1}$)、 Kow はオクタノール水分配係数 (-) である。これらの農薬物性値には、HSDB¹⁾ または PhysProp²⁾ のいずれかのデータベースの数値を用いた。また、 α は固相率 (畑地型の場合 0.4、水田型の場合 0.5)、 γ は土壌有機炭素含有率 (0.05)、 ρ_{soi} は土壌粒子密度 ($2700\text{kg}\cdot\text{m}^{-3}$) である。これら土壌環境条件の設定値は、文献値 (土質試験法編集委員会, 1990, 山根, 1990, 地学団体研究会, 1982) を参考に平均的な数値として設定した。

2. 結果と考察

2.1 推定流出量と実測データの比較

相模川及び酒匂川において県内の水道事業者が実施した農薬モニタリング結果を用いて、推定流出量の妥当性を検討した。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年数回測定したものである。本推定法は、県内で散布された農薬を対象にしているため、上流県からの流下がない河川のうち、測定が

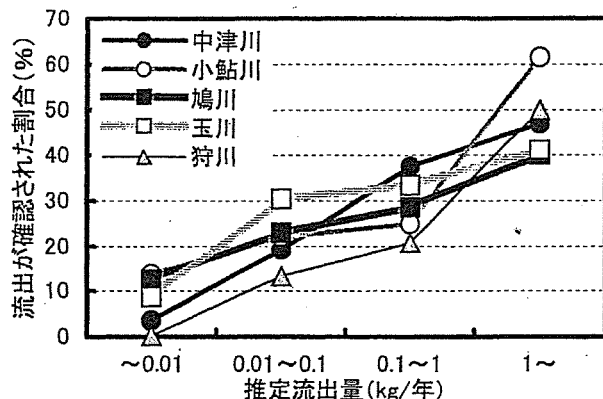


図3 流出量と検出割合 (2004年度)

年間 4 回以上行われた 5 河川 (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) を対象に検討した。流量の実測値がなく、負荷量の比較ができないため、ここでは推定流出量と検出回数 (検出割合) の関係を調べた。

2004 農薬年度 (2003 年 10 月~2004 年 9 月) の推定流出量と 2004 年のモニタリングにおいて流出が確認された割合との関係を図 3 に示した。いずれの流域においても推定流出量が多くなると測定農薬のうち流出が確認された農薬の割合が高くなる傾向が見られた。検出回数が多いことは直ちに負荷量が大いことを意味しないが、相対的に散布量が多く、河川に流出しやすい農薬であることを示している。したがって、この推定流出量は、農薬の流出しやすさを示す指標として利用できると考えられる。なお、推定流出量と検出濃度との比較も試みたが、主として以下に述べる理由により、明確な傾向は認められなかった。本推定法では、前述のとおり散布後の分解過程を考慮していないため、分解性の大きい農薬については流出量が過大評価されている。また、殺虫、殺菌剤には対象とする病害虫の発生地域でのみ散布される製剤があるが、散布方法は全県一律で計算を行っている。この推定流出量を用いて環境負荷を評価する場合には、このような推計法上の限界に起因する実態との乖離に留意する必要がある。

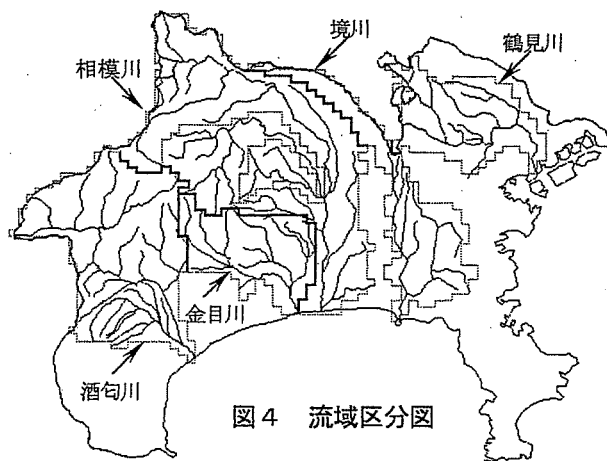


図4 流域区分図

2. 2 流域別推定流出量

PRTRの第一種及び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に係る第一群、第二群及び第三群に該当する農薬は、あわせて249種となる。これらを有効成分として含有し、2002年度以降に神奈川県に出荷実績のある製剤を特定したところ、577種が該当した。このうち、使用形態から判断して流出がほとんどないと考えられる苗・種子等消毒剤、育苗箱施用剤、塗布剤等の非散布型の製剤31種を除外した546種を対象に

前述の方法で流域別推定流出量を算出した。

農薬流出が比較的多い神奈川県内河川5流域の2003農薬年度における上位20位までの流出量を表2に示した。なお、グリホサート系農薬などのイオン性の農薬については K_p を(5)式で適切に推定することが困難であるため、除外した。表2に示す河川は、図4に示すように、相模川を中心として、鶴見川と境川が県東部、金目川と酒匂川が県西部に位置しているが、流域によって流出量の多い農薬に違いが見られた。算出結果によると、

表2 神奈川県内主要流域の農薬推定流出量(上位20位まで)

単位:kg/年

鶴見川	境川	相模川	金目川	酒匂川	
マンネブ	990	1,700	460	マンネブ	790
アセフェート	340	410	440	マンゼブ	420
マンネブ	ダノメット	370	アセフェート	マンネブ	340
ダノメット	マンネブ	350	マンゼブ	アセフェート	320
プロピネブ	240	290	ダノメット	DEP	220
マンゼブ	140	DEP	DEP	ジメトエート	110
マンゼブ	DEP	プロピネブ	マンゼブ	ホセチル	99
DEP	ホセチル	マンゼブ	プロピネブ	マンゼブ	94
ホセチル	プロピネブ	ホセチル	ジメトエート	DDVP	92
DDVP	DDVP	ジメトエート	ホセチル	マンゼブ	89
ジメトエート	ジメトエート	マンゼブ	マンゼブ	プロピネブ	68
ジネブ	ジネブ	ACN	ACN	ジネブ	64
D-D	D-D	DDVP	DDVP	マンゼブ	57
マンゼブ	マンゼブ	ジネブ	ジネブ	ダノメット	50
マンゼブ	ホスチアゼート	パクロプロトラゾール	パクロプロトラゾール	ACN	30
メチルイソチオシアネート	メチルイソチオシアネート	D-D	マンゼブ	ニテンピラム	29
ハロスルフロンメチル	マンゼブ	ピラゾスルフロンエチル	ピラゾスルフロンエチル	パクロプロトラゾール	19
マンゼブ	ハロスルフロンメチル	メチルイソチオシアネート	D-D	ピラゾスルフロンエチル	15
ホスチアゼート	マンゼブ	マンゼブ	メフェナセット	DMTP	12
DCMU	DCMU	ハロスルフロンメチル	ニテンピラム	メフェナセット	12

注)本文中に記載した農薬を網掛けで表示。

表3 神奈川県内主要流域のRRI値(上位20位まで)

単位:1×10⁶ kg-bw

鶴見川	境川	相模川	金目川	酒匂川			
ダノメット	340	ダノメット	380	ダノメット	270	マンネブ	440
プロピネブ	260	マンネブ	130	プロピネブ	240	マンゼブ	190
マンネブ	190	プロピネブ	120	マンネブ	200	プロピネブ	170
マンゼブ	84	マンゼブ	61	マンゼブ	91	マンゼブ	110
DEP	44	ホスチアゼート	51	ACN	75	ACN	32
DDVP	43	マンゼブ	38	DEP	60	DEP	53
マンゼブ	42	マンゼブ	38	DEP	60	マンゼブ	44
マンゼブ	42	DEP	33	マンゼブ	55	DDVP	40
マンゼブ	42	DDVP	32	マンゼブ	48	マンゼブ	38
マンゼブ	36	マンゼブ	31	DDVP	43	マンゼブ	25
メチルイソチオシアネート	21	メチルイソチオシアネート	18	マンゼブ	38	ジネブ	25
ジネブ	18	ジネブ	14	メチルイソチオシアネート	28	ジメトエート	21
ジメトエート	6	ACN	6	ジネブ	22	メフェナセット	19
ACN	6	ジメトエート	5	ジメトエート	19	マンゼブ	18
DCMU	5	DCMU	4	メフェナセット	17	メチルイソチオシアネート	16
ハロスルフロンメチル	4	シマジン	4	ダイアジノン	10	メフェナセット	9
ジラム	4	ハロスルフロンメチル	4	DCMU	7	シマジン	7
シマジン	3	ジラム	2	ハロスルフロンメチル	6	MPP	6
マンゼブ	3	マンゼブ	2	MPP	5	ベンチオカーブ	5
マンゼブ	2	ダイアジノン	2	シマジン	5	DMTP	5

注)本文中に記載した農薬を網掛けで表示。

除草剤のアシュラムは非農耕地に散布されるため、農作物の耕作状況の違いによらずどの流域でも推定流出量が大きかったが、特に県東部河川において顕著であった。また、主として野菜に施用される殺虫剤のメソミル、チオジカルブの推定流出量も県西部に比べて県東部の方が大きくなる傾向が見られた。一方、果樹に施用されることが多い殺菌剤のチオファネートメチルや殺虫剤のイミダクロプリドは、耕作状況の地域差を反映し、県西部地域における推定流出量は県東部より大きかった。このように、推定流出量により、流出の可能性の高い農薬を流域ごとにリストアップすることができると考えられる。

2.3 人健康リスクからみた農薬の環境負荷

推定流出量を用いて流域における農薬の環境負荷を評価するため、毒性を考慮した指標を設定し、流域ごとの評価を試みた。本稿では、推定流出量をADIで除した数値をRunoff Risk Indexと定義し、これを農薬別、流域別に算出した。RRI値は、「体重1kgあたり許容摂取量の何倍の農薬が流域から流出するか」を表す数値であり、人健康リスクからみた流域の環境負荷の指標と考えることができる。前述のとおり、推定流出量が厳密に流域の負荷量を表しているとはいえないため、この数値による定量的な比較はできないが、流出農薬に関する人健康リスクに着目した流域ごとの特徴は把握可能であると考えられる。

表2に示した5流域について、RRI値を算出した結果を表3に示した。表3にリストアップされた農薬は全部で26種あるが、このうちアシュラム(除草剤)、アセフェート(殺虫剤)、イミダクロプリド(殺虫剤)、シアナ

ジン(除草剤)、チオジカルブ(殺虫剤)、ホスチアゼート(殺虫剤)、メソミル(殺虫剤)、ACN(除草剤)の8種はPRTR対象外の農薬であった。神奈川県各流域においては、これらの物質の環境負荷にも留意する必要があると考えられた。

2.4 河川生態系の環境負荷の包括的評価

神奈川県では、生活環境の保全等に関する条例第40条の3に規定する「化学物質の安全性影響度の評価に関する指針」において、毒性係数を定めている。これは、対象物質の人健康及び生態系に対する有害性に応じ、化管法の第一種及び第二種指定化学物質を対象に物質ごとに4段階の数値として設定されている。表4には、生態影響に係る毒性係数表を示した。毒性係数を同指針に定める手順によって算出する年間排出量に乗じると換算排出量が得られる。物質別の換算排出量及びこれを合算した総換算排出量は、環境負荷としての比較が可能な量であり、事業所における化学物質排出削減対策に利用されている。本稿では、前述の推定流出量と農薬以外のPRTRデータを用いて流域別の換算排出量を算出し、2003年度における河川生態系に関する環境負荷の包括的評価を試みた。

表4 毒性係数表

総合判定	生態系への影響	毒性係数
A	LC ₅₀ 又はEC ₅₀ が0.1mg/l以下のもの	1,000
B	LC ₅₀ 又はEC ₅₀ が1mg/l以下のもの	100
C	LC ₅₀ 又はEC ₅₀ が10mg/l以下のもの	10
D	LC ₅₀ 又はEC ₅₀ が10mg/lを超えるのもの	1

化学物質の安全性影響度の評価に関する指針別表4から抜粋。

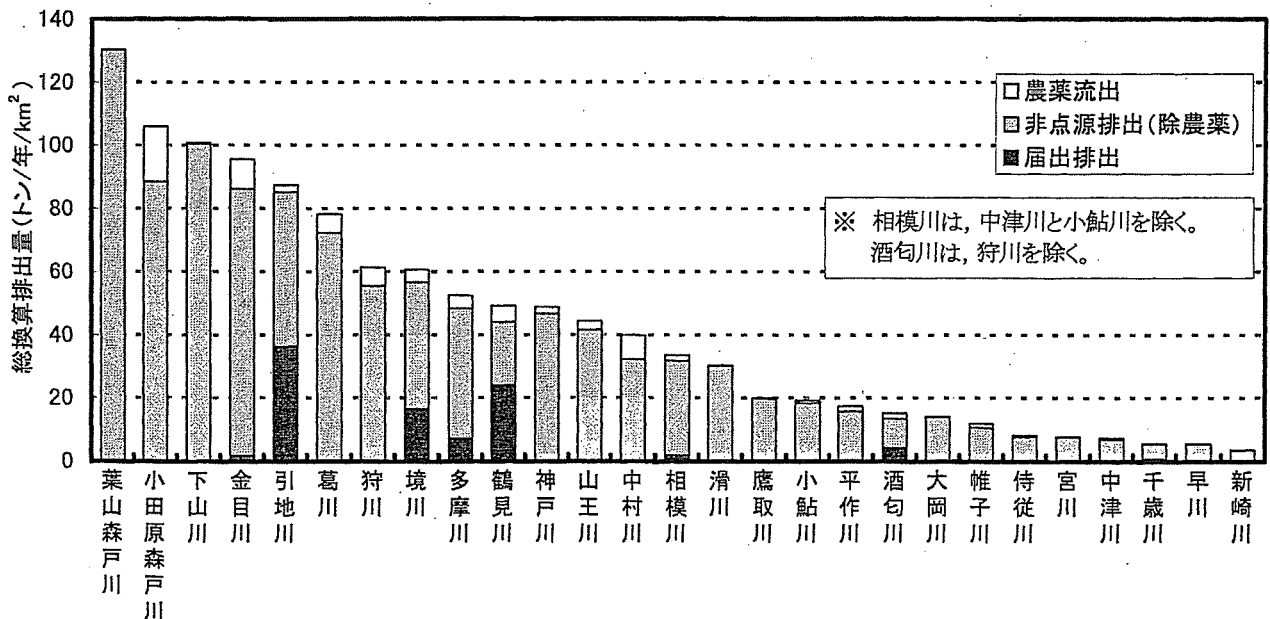


図5 神奈川県内河川の流域面積あたり総換算排出量 (2003年度)

農薬を除く非点源排出量は、市区町村別排出量を排出源の区分に応じたメッシュ統計データで3次メッシュに配分し、これを流域単位に再編成して流域別排出量とした。これを流域単位に集計した届出排出量及び前述の農薬の推定流出量と合わせて、流域ごとの排出量データとした。この排出量に表4に示す毒性係数を乗じ、これらを合算して流域ごとに流域面積あたりの総換算排出量を算出した。このような農薬流出量、PRTRデータ及び換算排出量を組み合わせた解析を行うことにより、流域における環境負荷の構造の違いを把握することができると考えられる。

図5に神奈川県内の27流域の流域面積あたり総換算排出量を示した。どの流域も農薬以外の非点源排出の寄与が大きく、平均で87%を占めた。農薬流出の寄与が10%を超えたのは、県西部に位置する中村川(19%)、森戸川(16%)、酒匂川(11%)、県東部に位置する平作川(11%)、帷子川(11%)、鶴見川(10%)の6河川であった。また、農業が盛んな県西部ばかりでなく、市街化の進んだ県東部においても農薬に起因する環境負荷が無視できない河川があることが考えられた。一方、水域への届出排出がある流域は12河川あり、その寄与が最も大きかったのは鶴見川(49%)、次いで引地川(42%)、酒匂川(28%)、境川(27%)であった。届出排出の寄与が大きい流域では、このような解析により届出事業所が排出先河川に与える負荷を具体的に示すことが可能となると考えられる。

おわりに

農薬使用状況の地域差を反映し、かつ、多種類の農薬を対象に比較的単純化した方法で流域別農薬流出量を算出する手法を検討した。農薬散布環境を fugacity model (level I) でモデル化し、流域別散布量の推定と流出比率の推定を別々に行い、これらを掛け合わせて流出量を推定する手法を作成した。この手法を用いて水道法及び化管法対象農薬249種の神奈川県内河川における流出量評価を行い、次のような知見を得た。

- (1) 推定流出量が多くなるほど実測で検出される農薬の割合が高くなる傾向が見られた。推定流出量は、農薬の流出しやすさを示す指標として利用できると考えられた。
- (2) 神奈川県東部と西部で推定流出量を比較したところ、流域の耕作状況を反映した違いが見られた。
- (3) 人健康リスクからみた流域環境の負荷指標値として

Runoff Risk Index を定義し、県内で負荷が高いと考えられる農薬26種を抽出したところ、このうち8種はPRTR対象外農薬であり、これらの農薬環境負荷にも留意する必要があると考えられた。

- (4) 神奈川県条例で規定する毒性係数と農薬以外のPRTRデータを加えて県内河川の生態系に係る包括的評価を行ったところ、各流域における環境負荷の発生源別寄与の違いを把握することができた。

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補注

¹⁾ U.S. National Library of Medicine (01/09/2006 updated) Toxicology Data Network. <<http://toxnet.nlm.nih.gov/index.html>>, 10/12/2005 referred.

²⁾ Syracuse Research Corporation (25/08/2006 updated) PhysProp database. <<http://www.syrres.com/esc/physdemo.htm>>, 10/12/2005 referred.

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Precise Data Sets on Farming and Pesticide Properties Verify a Diffuse Pollution Hydrological Model for Predicting Pesticide Concentration

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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.

Key words 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), 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 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, we undertook a daunting task: 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. We also analysed the sensitivity of the model to elucidate rice-farming pesticide runoff phenomena.

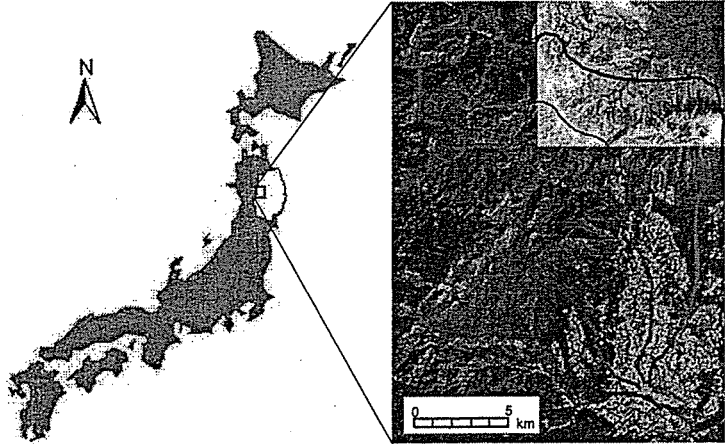


Figure 1 The target catchment. The red dot indicates the water sampling point, where pesticide concentrations were measured (composed using Google satellite map)

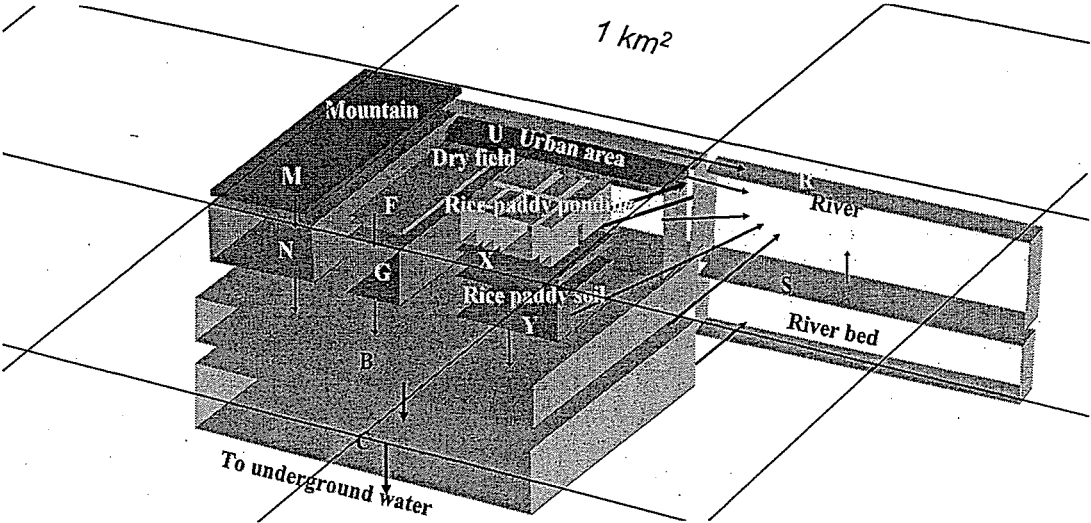


Figure 2 Compartments in a 1-km² grid cell and flow directions

MATERIALS AND METHODS

Site description and modelling

The Kakkonda River basin (191 km²), 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 the other compartments were determined from a Geographic Information System 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. 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 CaCl₂ 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, $\phi = 0.7 \mu\text{m}$, 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 less 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) 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 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.

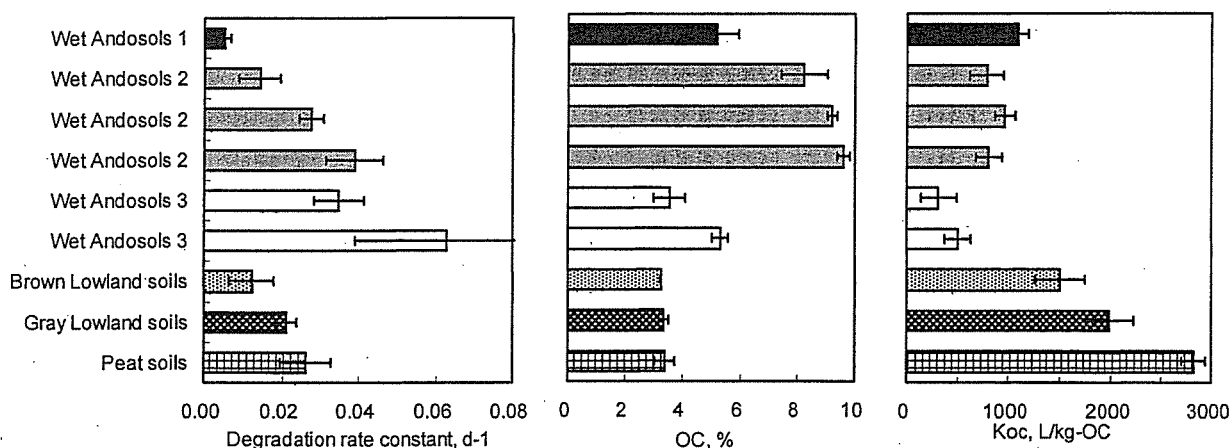


Figure 3 Soil characteristics for isoprothiolane degradation and adsorption in soils sampled from nine paddy fields. Error bars were calculated from data of three soil samples from each paddy field.

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 abovementioned observational data. Uncertainty in model inputs was minimised by using these data, making it possible to test the prediction capability of the model. We compared predicted and observed time variations in the isoprothiolane concentrations in river water (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.

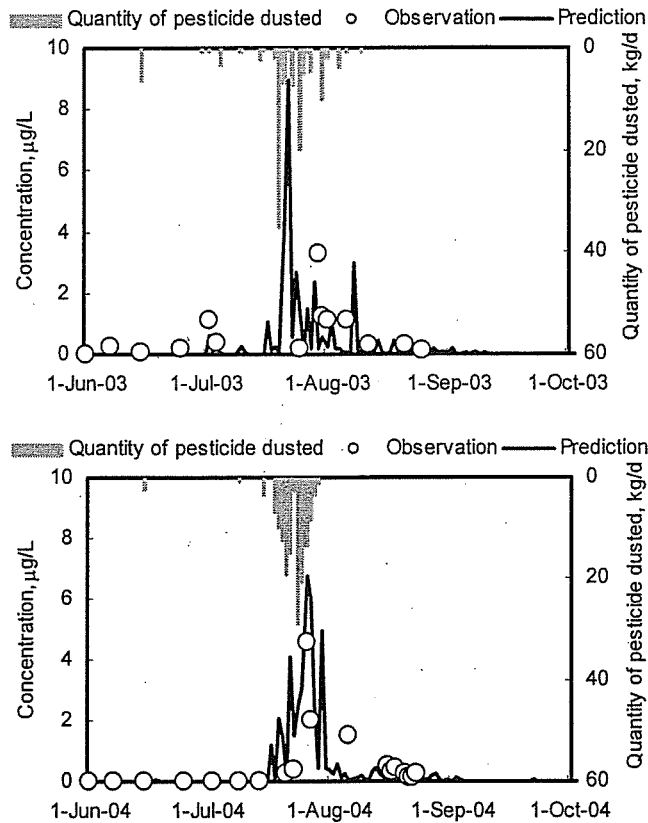


Figure 4 Comparison of observed time-series isoprotiolane concentrations with those predicted by the model.

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 shifted 11 days ahead when the input date was shifted ahead by 1 week, whereas it shifted behind by 1 week when the input date was shifted 1 week behind. 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 behind or ahead. 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 ahead or behind by 1 week, suggesting that pesticide runoff was

not caused primarily by spill-over of rice-paddy water during or after rainfall but was probably related to artificial drainage of rice-paddy water.

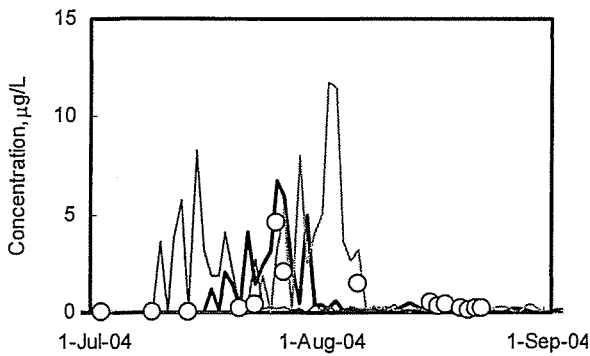


Figure 5 Effect of the accuracy of agricultural practice data on model prediction. Black line, prediction with accurate input data; blue line, prediction with agricultural schedule inputs moved forward by 1 week; red line, prediction with inputs moved back by 1 week.

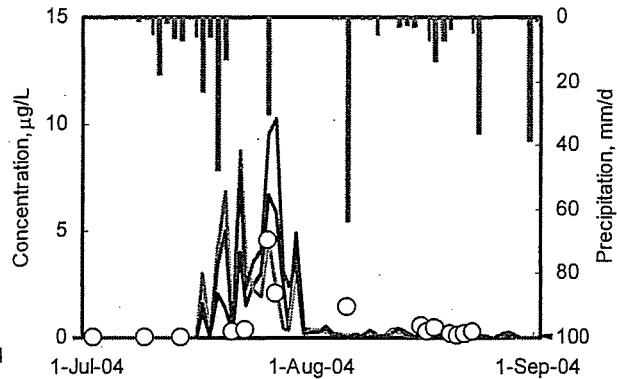


Figure 6 Effect of precipitation dates on model prediction. Green bars, actual precipitation; black line, prediction with actual precipitation data; blue line, prediction with precipitation input moved forward 1 week; red line, prediction with precipitation input moved back 1 week.

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 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.

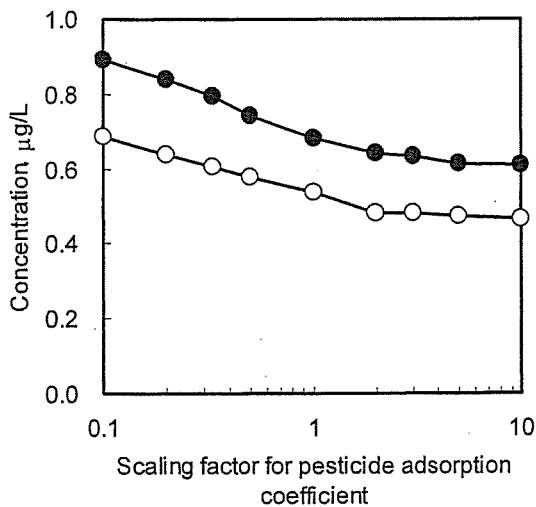


Figure 7 Effect of the pesticide adsorption coefficient (K_{oc}) on average and peak concentrations in July and August.

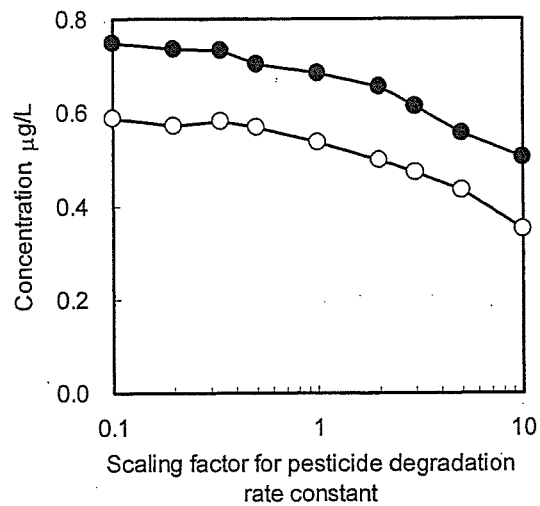


Figure 8 Effect of the pesticide degradation rate constant on average and peak concentrations in July and August.

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, 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

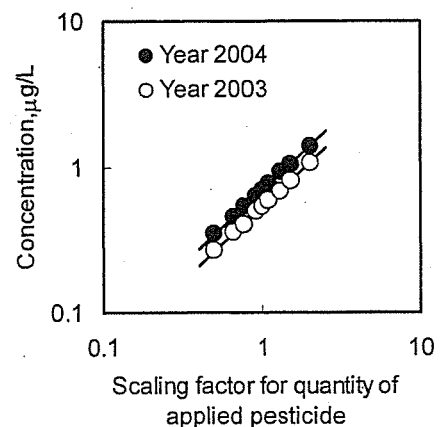


Figure 9 Effect of quantity of pesticide applied on average river water concentrations in July and August.