Development and validation of a simulation method, PeCHREM, for evaluating spatio-temporal concentration changes of paddy herbicides in rivers

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Electronic Supplementary Information

1. Application records of pesticide formulations

The application records submitted by farmers, written in Japanese, were previously published on webpages of Agricultural Cooperatives. However, these websites no longer publish the application records. Therefore, we provide one example record here. Names of materials including pesticides were Japanese

FY2007 Application record about paddy fields

Name: xxx Address: xxx

Breed of rice plants: xxx Area of paddy fields: 145 are

Date of seeding: 19 May Date of transplanting: 17, 18 June

Date of heading: 12 Aug. Date of harvesting: 18, 19 Sep.

Item	**Material (pesticide)**	**Use date**	**Concentration, amount, or dilution rate**
Seed disinfection	Sumichion emulsion	12 May	1000 times
	Tekuri-do flowable	12 May	200 times
Soil disinfection for seedbeds	Dakore-to wettable powder	19 May	500 ml/box
Pesticides for nursery box	Bi-mu Adomaiya- Supino box granule	16 June	50 g/box
Soil improvement materials	Toretaro	25 May	40 kg/10 a
Basal fertilizer	Kyu-kyokunoippatsu	10 June	45 kg/10 a
Additional fertilizer	-		
Herbicides (initial stage)	Teraga-do granule	17 June	1 kg/10 a
Herbicides (late stage)	Kurinntya-basu ME liquid	30 July	1000 ml/10 a
Core pest control	-		
Additional pest control	-		
Pest control using a helicopter	Yoshitake union of helicopter pest control[a)]	5 Aug. 21 Aug.	

a) A name of union applying pesticide formulations by helicopter.

2. Values used for other PADDY model parameters

We used following values from the literature[1].

Parameter	Value
Area (m^2)	828
Depth of water in the field (m)	0.032
Depth of surface soil (m)	0.005
Thickness of each sub-surface layer (m)	0.005
Water volume (m^3)	
Field water	26.5
Pore water in each sub-surface layer[a)] (0–2 cm)	2.3
Pore water in each sub-surface layer[a)] (2–4 cm)	1.9
Weight of soil (kg)	
Surface soil	2500
Sub-surface soil in each layer[a)] (0.5–2 cm)	2500
Sub-surface soil in each layer[a)] (2–4 cm)	2900
Runoff rate of water (m^3 day^{-1})	14.7
Penetration rate (to >4 cm) of water (m^3 day^{-1})	7.9

a) Value of each 0.005-m-thick sub-surface layer.

3. Explanation of equation 4

Equation 4 was derived from empirical equations published in a report written in Japanese[2]. Here, we summarize the results and related data, mostly from that report but partly from another report[3], below. The author investigated runoff percentages, measured with lysimeters, of 21 pesticides from a paddy. They found a significant relationship between runoff percentages and the water solubility of the pesticides (r = 0.872, n = 20; one pesticide, ethofenprox, was not used because its water solubility is unknown). Furthermore, he showed that the runoff percentages of pesticides measured with lysimeters and the runoff percentages from actual paddy fields to rivers, measured in the field, were also related significantly (r = 0.870, n = 8). These relationships are described by equations S1 and S2.

$$\mathrm{Log}_{10}(Y_1) = 0.531 + 0.327\ \mathrm{Log}_{10}(X) \qquad \text{S1}$$

$$\mathrm{Log}_{10}(Y_R) = -0.546 + 0.874\ \mathrm{Log}_{10}(Y_1) \qquad \text{S2}$$

where Y_1 denotes the average runoff percentage measured with lysimeters, X denotes the water solubility of a pesticide, and Y_R denotes the runoff percentage from actual paddy fields measured in Chiba Prefecture. The original data are listed in Table S1. From equations S1 and S2 we derived equation 4 as follows, by assuming that water solubility of pesticides expressed as ppm is equivalent to that expressed as mg L^{-1}.

$$\mathrm{Log}_{10}(Y_R) = -0.546 + 0.874\ \{0.531 + 0.327\ \mathrm{Log}_{10}(X)\} \qquad \text{S3}$$

$$\mathrm{Log}_{10}(Y_R) = -0.0819 + 0.286\ \mathrm{Log}_{10}(X) \qquad \text{S4}$$

Table S1 Runoff percentages used for deriving equation 4.

Pesticide	**Solubility[2] (ppm)**	**Runoff percentages measured with lysimeters[2] (%)**	**Runoff percentages from actual paddy fields[3] (%)**	**Target herbicide in this article?**
Chlornitrofen	0.25	1.58	0.109	
Dymron (Daimuron)	1.7	16.7	3.01	Yes
Chlomethoxyfen (Chlomethoxynil)	0.3	2.03	1.49	
Bifenox	0.35	1.75		
Butachlor	23	6.29	2.32	Yes
Pyrazolate	0.05	0.96	0.31	Yes
Bensulfuron methyl	12-120	23.0		Yes
Dimepiperate	20	12.3		
Mefenacet	4	9.10		Yes
Symetryn	450	44.4	5.65	Yes
Molinate	900	24.7	5.96	
Thiobencarb	30	7.07	1.44	
Cycloprothrin	0.091	1.68		
Fenthion	2	2.17		
Fenitrothion	14	3.14		
Fenobucarb	660	17.1		

Propoxur	2000	50.9	
Isoprothiolane	50	22.0	
Tricyclazole	700	13.8	
Mepronil	12.7	13.0	

4. Sources of physico-chemical data

We collected physico-chemical data from "reliable" sources consisting of lists of pesticides and their properties. Because the aim of our research was to develop a model that would be applicable to many paddy herbicides and to validate the reliability of the model, it is important to use a dataset that has been used for actual decision-making. Reference 4, "Noyaku Handobukku" (Agricultural Chemical Handbook), was compiled by the Japan Plant Protection Association, which collected the physico-chemical properties of pesticides from the pesticide manufacturers. This handbook is also used as a reliable data source for risk assessment under the Japanese Agricultural Chemicals Regulation Law. Reference 6, Risk Assessment Reports of Pesticides, was published by the Food Safety Commission of Japan, which performs risk assessments and publishes an assessment report for all pesticides that affect human foods. These risk assessments are published in Japanese, but some include summaries in English (http://www.fsc.go.jp/english/evaluationreports/agrichemicalsl_e1.html). Reference 7, "Noyaku no Kankyotokusei to Dokuseidetashu" (Data on environmental properties and toxicities of pesticides) has been used as a reliable source for the Initial Environmental Risk Assessment of Chemicals, which was carried out by the Japanese Ministry of the Environment. This document is also in Japanese, but summaries of some results are available in English (https://www.env.go.jp/en/chemi/chemicals/profile_erac/index.html). We believe, therefore, that these data sources are considered reliable for use in Japanese decision-making.

5. Supplemental tables and figure

Table S2 Chemical properties of the target herbicides.

Name	MW	Solubility (mg L^{-1})	Vapor pressure (Pa)	K_{oc} a) (L kg^{-1})	K_{ow} b)	Degradation rate in water (day^{-1})	Degradation rate in sediment (day^{-1})
Azimsulfuron	424.4	−47.6 c)	4.0×10^{-9} d)	278 c) *	0.043 c)	0.13 e) *‡	0.13 e) *‡
Bensulfuron methyl	410.4	6.65 c)	2.8×10^{-9} d)	2278 c) *	6.2 c)	0.014 f) *	0.017 f) *
Bentazon	240.3	570 c)	1.7×10^{-4} c)	20 c) *	31 c)	0.33 c)	0.035 f)
Benzobicyclon	447.0	0.052 c)	5.6×10^{-5} c)	10000 c)	1260 c)	0.97 e) *	0.17 e) *
Benzofenap	431.3	0.12 c)	3.2×10^{-6} c)	2113 f)	49000 c)	0.018 f) ‡	0.018 f)
Bromobutide	312.3	3.54 c)	5.9×10^{-5} c)	223 c) *	2880 c)	0.019 e) *†	0.019 e) *†
Butachlor	311.9	16 c)	2.5×10^{-4} c)	740 f)	26300 c)	0.28 f) *	0.013 f) *
Butamifos	332.4	6.19 c)	5.1×10^{-5} c)	2085 c) *	41700 c)	0.0062 f) *‡	0.0062 f) *
Cafenstrole	350.4	2.5 c)	5.3×10^{-5} c)	1641 e) *	1620 c)	0.050 e) †	0.050 e) †
Clomeprop	324.2	0.035 c)	4.3×10^{-5} c)	3483 f)	63100 c)	0.28 e) *‡	0.28 e) *
Cumyluron	302.8	0.879 c)	8.0×10^{-5} c)	852 c)	407 c)	0.0082 e) *†	0.0082 e) *†
Cyclosulfamuron	421.4	0.34 c)	2.2×10^{-5} c)	996 c) *	38 c)	0.41 d) †	0.41 d) †
Daimuron	268.4	0.79 c)	4.5×10^{-7} c)	847 f)	501 c)	0.014 f) ‡	0.014 f)
Dimethametryn	255.4	20.2 c)	1.1×10^{-4} c)	254 f)	1580 c)	0.025 f)	0.0050 f)
Esprocarb	265.4	4.92 c)	1.0×10^{-2} c)	2800 e) *	41700 c)	0.018 e) *†	0.018 e) *†
Halosulfuron methyl	434.8	10.2 c)	1.3×10^{-5} c)	89 c) *	6.7 c) *	0.35 e) †	0.35 e) †
Imazosulfuron	412.8	155.6 c)	6.3×10^{-4} c)	133 f)	39 c)	0.026 d) †	0.026 d) †
MCPA	200.6	825 c)	2.3×10^{-4} c)	98 f)	0.87 d) *	0.070 f) *	0.099 f)
Mefenacet	298.4	5 c)	4.5×10^{-7} c)	893 c) *	1700 c)	0.0097 f) *‡	0.0097 f) *
Oxaziclomefone	376.3	0.15 c)	1.6×10^{-8} c)	10000 c)	5010 c)	0.49 d) *†	0.49 e) *†
Pretilachlor	311.9	74 c)	6.5×10^{-4} c)	1146 c) *	7940 c)	0.036 e) †	0.036 e) †
Pyrazolate	439.3	0.056 c)	1.3×10^{-5} c)	2855 f)	380 c)	0.049 f) *‡	0.049 f) *
Pyrazosulfuron ethyl	414.4	9.67 c)	4.2×10^{-8} c)	209 f)	1450 c)	0.15 f) *‡	0.15 f) *
Pyriftalid	318.4	1.8 c)	2.2×10^{-8} c)	812 c) *	398 c)	0.11 e) *‡	0.11 e) *
Simetryn	213.3	428 c)	5.0×10^{-5} c)	8743 c)	138 c)	0.0072 f) *‡	0.0072 f) *

a) Soil organic carbon–water partition coefficient.

b) Octanol–water partition coefficient. c) Reference 4, d) Reference 5, e) Reference 6, f) Reference 7. If values of a property were obtained from several references, the value from the reference with the lowest number was used.

* Geometric average of multiple values.

† The half-life in aerobic soil was used.

‡ The degradation rate in sediment was used.

Table S3 LC/MS/MS conditions for the target herbicides.

Name	CAS RN®	ESI a) (positive or negative)	SRM b) ion (*m/z*)	Collision energy (eV)
Azimsulfuron	120162-55-2	positive	425 > 139	45
Bensulfuron methyl	83055-99-6	positive	411 > 182	17
Bentazon	25057-89-0	negative	239 > 197	13
Benzobicyclon	156963-66-5	positive	447 > 229	41
Benzofenap	82692-44-2	positive	431 > 119	17
Bromobutide	74712-19-9	positive	312 > 194	13
Butachlor	23184-66-9	positive	312 > 238	17
Butamifos	36335-67-8	positive	333 > 152	13
Cafenstrole	125306-83-4	positive	351 > 72	25
Clomeprop	84496-56-0	positive	324 > 203	9
Cumyluron	99485-76-4	positive	303 > 125	41
Cyclosulfamuron	136849-15-5	positive	422 > 218	25
Daimuron	22936-75-0	positive	269 > 91	45
Dimethametryn	42609-52-9	positive	256 > 96	29
Esprocarb	85785-20-2	positive	266 > 91	17
Halosulfuron methyl	100784-20-1	negative	433 > 154	29
Imazosulfuron	122548-33-8	positive	413 > 156	13
MCPA	94-74-6	negative	199 > 141	9
Mefenacet	73250-68-7	positive	299 > 120	25
Oxaziclomefone	153197-14-9	positive	376 > 190	9
Pretilachlor	51218-49-6	positive	312 > 132	49
Pyrazolate	58011-68-0	positive	439 > 173	13
Pyrazosulfuron ethyl	93697-74-6	positive	415 > 83	55
Pyriftalid	135186-78-6	positive	319 > 179	29
Simetryn	1014-70-6	positive	214 > 124	17

a) Electrospray ionization. b) Selected Reaction Monitoring.

Table S4 Sampling site information.

River name	Prefecture	Latitude	Longitude	Basin area [a] (km^2)
Yoshida	Miyagi	N 38°26' 40''	E 141°01' 32''	348.5
Usui	Gunma	N 36°19' 58''	E 138°57' 15''	284.6
Kokai	Tochigi	N 36°25' 33''	E 140°03' 32''	167.9
Koise	Ibaraki	N 36°11' 03''	E 140°15' 35''	153.1
Hanamuro [b]	Ibaraki	N 36°07' 19'' N 36°05' 32''	E 140°06' 01'' E 140°07' 23''	31.9
Asahina	Shizuoka	N 34°53' 24''	E 138°18' 01''	98.8
Koutsuki	Kagoshima	N 31°38' 30''	E 130°30' 52''	63.4

a) Basin areas were calculated from the basin segment area information included in the G-CIEMS model.[8]

b) The Hanamuro River was sampled at an upstream (upper row) and a downstream (lower row) site.

Table S5 Categorization of herbicide formulations based on Property A (the first day of the suggested usage period after transplanting) and calculated properties of each category.

Category	Property A	Average relative date of herbicide application (day)	Standard deviation of use date (day)
A0	On the transplanting day	2.5	7.7
A1	1 to 5 days after transplanting	6.8	5.2
A2	7 to 20 days after transplanting	30.4	17.1

Table S6 Comparison of RMSEs[a] and RMSLEs[b] among target herbicides.

Name	RMSE	RMSLE
Azimsulfuron	114	7.10
Bensulfuron methyl	146	1.49
Bentazon	182	2.72
Benzobicyclon	151	0.97
Benzofenap	145	0.57
Bromobutide	171	1.42
Butachlor	255	1.50
Butamifos	220	9.03
Cafenstrole	166	1.86
Clomeprop	182	2.55
Cumyluron	202	1.00
Cyclosulfamuron	301	3.04
Daimuron	192	1.50
Dimethametryn	108	1.79
Esprocarb	399	1.16
Halosulfuron methyl	174	5.39
Imazosulfuron	145	1.62
MCPA	248	1.59
Mefenacet	179	2.02
Oxaziclomefone	160	5.58
Pretilachlor	194	1.39
Pyrazolate	947	1.12
Pyrazosulfuron ethyl	143	3.17
Pyriftalid	170	1.30
Simetryn	202	1.39

a) Root mean square error. b) Root mean square logarithmic error.

Table S7 Summary of the field survey results at each site.

River name	Number of samples	Number of different herbicides detected	Total number of herbicides detected [a)]	Site detection ratio [b)]	Highest concentration herbicide	Highest detected concentration ($\mu g\ L^{-1}$)
Yoshida	7	24	116	0.66	bromobutide	12
Usui	8	21	74	0.37	bromobutide	0.70
Kokai	8	25	148	0.74	bentazon	11
Koise	13	25	252	0.78	bromobutide	13
Hanamuro	32	24	693	0.87	bromobutide	14
Asahina	6	25	101	0.67	bromobutide	17
Koutsuki	5	22	66	0.53	mefenacet	3.6

a) Determined by summing the number of herbicides detected in the samples collected at the site.

b) The ratio of the total number of detected herbicides to the product of the number of samples and the total number of target herbicides (25).

Table S8 Recovery rates for the target herbicides.

Name	Recovery rate (%)
Azimsulfuron	106.9
Bensulfuron methyl	106.4
Bentazon	234.1
Benzobicyclon	99.2
Benzofenap	92.2
Bromobutide	112.7
Butachlor	80.4
Butamifos	78.5
Cafenstrole	95.8
Clomeprop	95.4
Cumyluron	94.6
Cyclosulfamuron	103.8
Daimuron	100.8
Dimethametryn	89.7
Esprocarb	47.7
Halosulfuron methyl	102.9
Imazosulfuron	101.4
MCPA	90.7
Mefenacet	94.1
Oxaziclomefone	89.5
Pretilachlor	85.7
Pyrazolate	92.9
Pyrazosulfuron ethyl	107.2
Pyriftalid	95.7
Simetryn	113.7

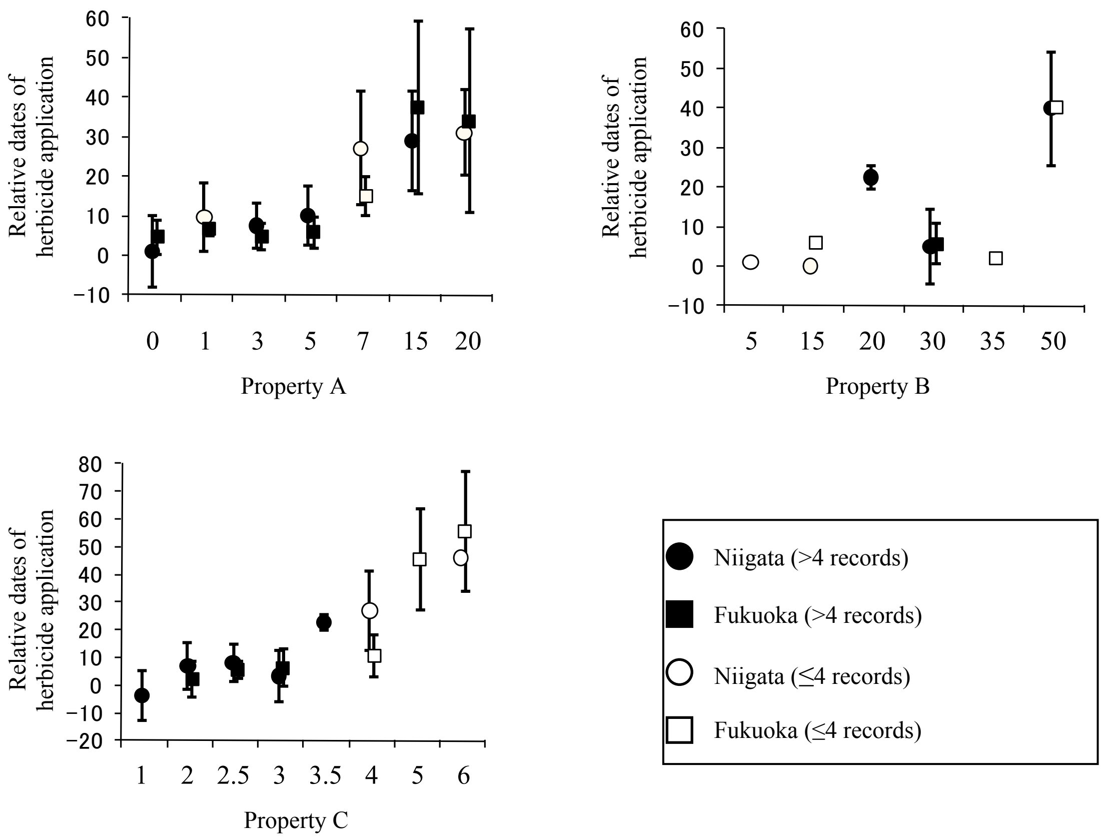

Fig. S1 Comparisons of dates of herbicide application relative to the transplanting date with values of Property A (first day of the suggested usage period after transplanting), B (last day of the suggested usage period after transplanting), and C (highest leaf-growth stage of barnyard grass in the suggested usage period). Symbols indicate average values, and error bars indicate standard deviations.

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