Chemosphere 75 (2009) 969–978

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Multimedia transport and risk assessment of organophosphate pesticides and a case study in the northern San Joaquin Valley of California

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ARTICLE INFO

Article history:
Received 6 May 2008
Received in revised form 19 December 2008
Accepted 2 January 2009
Available online 10 February 2009

Keywords:
Acetylcholinesterase inhibition
Human exposure
Multimedia modeling approach
Organophosphate pesticide
Risk assessment

ABSTRACT

This paper presents a framework for cumulative risk characterization of human exposure to pesticides through multiple exposure pathways. This framework is illustrated through a case study of selected organophosphate (OP) pesticides in the northern San Joaquin Valley of California. Chemical concentrations in environmental media were simulated using a multimedia environmental fate model, and converted to contamination levels in exposure media. The risk characterization in this study was based on a residential-scale exposure to residues of multiple pesticides through everyday activities. Doses from a mixture of OP pesticides that share a common mechanism of toxicity were estimated following US Environmental Protection Agency guidelines for cumulative risk analysis. Uncertainty in the human exposure parameters was included in the Monte Carlo simulation in order to perform stochastic calculations for intakes and corresponding risks of OP pesticides. Risk of brain acetylcholinesterase inhibition was reported as margins of exposure (MOEs) of the 99.9th population percentile for two age groups living in the northern San Joaquin Valley during 1992–2005. Diet was identified as the dominant exposure pathway in cumulative exposure and risk, while the temporal trend and spatial variation in total MOE levels were associated with exposures to contaminated drinking water and ambient air. Uniformly higher risks were observed for children because of their greater inhalation and ingestion rates per body weight, relative to adults. The results indicated that exposures for children were about twice of those estimated for adults. Concerns over children's exposure to OP pesticide through food and water ingestion were suggested based on the spatiotemporal variations predicted for the subchronic MOEs at the 99.9th percentile of exposure in the study area.

1. Introduction

Organophosphate (OP) pesticides, such as chlorpyrifos, diazinon, and methidathion from agricultural sources may have negative environmental impacts and are identified as a probable source of human exposure. Substantial toxicological evidence suggests that exposure of humans and animals to OP pesticides could lead to acute cholinergic poisoning and cause chronic and subchronic neurological, neurobehavioral, and psychiatric syndromes (Jamal, 1997). As a critical and common effect, the inhibition of acetylcholinesterase (AChE) is caused by most OP pesticides (USEPA, 2006b). A broad range of adverse effects can result from AChE inhibition, including smooth muscle contractions (*e.g.*, abdominal cramps), glandular secretions, skeletal muscle twitching, and flaccid paralysis (USEPA, 2000). OP pesticides can reach humans through the ambient air, through the food chain and drinking water, or by direct contact. Therefore, evaluations of cumulative doses from multiple pathways are required in human risk assessments for pesticides. A cumulative assessment of OP pesticide has been suggested by the US Environmental Protection Agency (USEPA), by combining the pesticide intakes from food, residential, and water pathways. An estimation of chemical concentration in the environment, based on modeling, is usually the starting point in a general human risk assessment. Regional mass balance models, such as fugacity-based multimedia environmental fate models, have been introduced in the assessments of human exposure to various organic compounds including pesticides (Bennett et al., 1999; Hertwich et al., 1999; Dunn, 2004; Morra et al., 2006; Strang, 2006; McKone et al., 2007). Those models, which have fewer parameters and are not as analytically complex as spatially distributed models, provide explicit and reliable predictions of chemical distributions in various environmental media. However, most multimedia environmental fate models are designed to evaluate the steady-state response of human health to chemical applications, and consider the entire simulation domain as a unit environment. Both temporal

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doi:10.1016/j.chemosphere.2009.01.005

Table 1
Physiochemical properties and reaction half-lives for selected OP pesticides.

Chemical	MW	K_{OW}	VP	H	K_{OC}	D_{air}	D_{water}	BCF
(a) Physiochemical properties								
Acephate	183.2	0.1	2.26E−4	5.07E−5	2.0	0.599	6.63E−5	1.1
Azinphos-methyl	317.3	501.2	2.13E−4	0.002	716.1	0.599	6.63E−5	81.3
Chlorpyrifos	350.6	83176	0.002	0.001	6025.6	0.491	4.41E−5	752
Diazinon	304.4	2238.7	0.012	0.011	1431.0	0.599	6.63E−5	173
Dimethoate	229.3	6.0	0.001	0.010	15.0	0.500	5.00E−5	173
Disulfoton	274.4	10471	0.020	2.20E−4	1531.1	0.512	4.19E−5	208
Malathion	330.4	724	0.001	4.95E−4	1180.0	0.480	4.20E−5	64
Methamidophos	141.1	0.16	0.005	8.82E−5	5.0	0.750	7.85E−5	3.1
Methidathion	302.3	158	4.49E−4	7.30E−4	30.0	0.461	4.92E−5	2.5
Methyl parathion	263.2	794.3	0.024	0.010	1479.1	0.520	4.57E−5	71
Naled	381.0	24	0.026	6.600	157.0	0.501	5.44E−5	8.5
Oxydemeton-methyl	246.3	0.18	0.005	1.51E−6	15.0	0.500	5.00E−5	0.0086
Phosmet	317.3	1000	6.50E−5	0.001	668.0	0.447	4.73E−5	88

	HLa	HLp	HLs	HLw	HLd
(b) Reaction half-lives					
Acephate	2.00	2.5	2.2	52.4	5.5
Azinphos-methyl	0.06	2.0	45.0	3.0	112.7
Chlorpyrifos	0.26	3.3	21.0	53.0	52.5
Diazinon	4.59	4.0	32.0	84.0	17.0
Dimethoate	0.21	3.0	3.0	10.0	20.0
Disulfoton	0.12	3.0	7.9	7.9	19.8
Malathion	0.23	1.0	5.0	28.0	70.0
Methamidophos	1.0	4.0	4.0	27.7	7.5
Methidathion	1.50	3.0	3.0	26.0	10.0
Methyl parathion	0.24	3.0	11.0	70.8	7.5
Naled	2.40	5.0	4.0	1.0	1.5
Oxydemeton-methyl	2.00	3.0	5.0	5.0	46.0
Phosmet	1.50	3.0	7.0	0.5	27.0

Notes – MW: molecular weight (g mol^{-1}); K_{OW}: octanol–water partition coefficient (–); VP: vapor pressure (Pa); H: Henry's Law constant (Pa m^3 mol^{-1}); K_{OC}: organic carbon partition coefficient (L kg^{-1}); D_{air}: diffusivity in pure air (m^2 d^{-1}); D_{water}: diffusivity in pure water (m^2 d^{-1}); BCF: bioconcentration factor (–); HLa: half life in air (d); HLa: half life in foliage (d); HLs: half life in soil (d); HLw: half life in surface water (d); HLd: half life in bed sediment (d).

trends and spatial variability are critical in the risk assessment of OP pesticides, especially when the assessment results are used as guidance for future pesticide management practices. To properly describe the relationship between the use and resultant risks of OP pesticides, a risk assessment framework is required to account for spatiotemporal variations in pesticide distribution and potential risk to human health.

The San Joaquin Valley of California is one of the most productive agricultural regions in the world. In the Valley, agricultural use of OP pesticides is widespread, and high levels of pesticide exposure incidents have been reported for the enclosed counties by California Environmental Protection Agency (CEPA, 2007b). Pesticides have the potential to wash off target areas and migrate with surface runoff and agricultural drainage to the San Joaquin River and its tributaries. The San Joaquin River was placed on the 2002 Clean Water Act Section 303(d) list for aquatic toxicity due to diazinon and chlorpyrifos (CEPA, 2002). Since 1988 the California Central Valley Water Quality Control Board has conducted aquatic toxicity surveys in the San Joaquin Valley. The observed toxicity has been primarily attributed to the presence of OP pesticides, and violations have been detected (Foe, 1995). Another source of potential human exposure is the volatilization of OP pesticides from agricultural fields. Based on the pesticide air-monitoring program conducted by the CEPA, some widely used OP pesticides rank high in acute inhalation toxicity (Harnly et al., 2005). Lee et al. (2002) estimated the hazard quotients for the median of children's acute exposures within agricultural communities as 4.0 and 0.8 for chlorpyrifos and diazinon, respectively. These findings suggest a potential public health concern for residents of the San Joaquin Valley.

In this paper, we present a cumulative risk assessment of human exposure to OP pesticides, with a case study in the northern San Joaquin Valley of California. Thirteen widely used OP pesticides, including three diethyls and ten dimethyls, were simulated and assumed to represent the total OP usage in the study area (Table 1). The specific objectives of this paper are as follows: (1) utilization of a multimedia environmental fate model developed in our previous studies (Luo and Yang, 2007; Luo et al., 2007a,b) to investigate the dynamic transport and fate of OP pesticides over the simulation domain; (2) estimation of exposure media concentrations and multi-pathway pesticide intakes; and (3) determination of the temporal trends and spatial variability in the cumulative risk characterizations.

2. Approach

2.1. Multimedia environmental fate model

Transport and fate of OP pesticides were simulated by a multimedia environmental fate model developed in our previous study (Luo et al., 2007a). The model was designed for analyzing unsteady-state dispersion and distribution of chemicals in multimedia environmental systems at watershed scale. Chemical transport and fate processes were considered within environmental compartments of air, canopy, soil layers, surface water, and sediment. By assuming environmental compartments were completely mixed and chemical equilibrium was established instantaneously between the phases within each compartment, a fugacity approach was utilized to formulate the mechanisms of diffusion, advection, and transformation reactions. Mass exchange across compartmental boundaries was represented mathematically by first order equations as follows:

$$Q_{ij} = M_{ij} \cdot N_{ij} = \left(\frac{D_{ij}}{V_i Z_i}\right) \cdot N_i \quad (1)$$

where Q_{ij} (mol d^{-1}) is the unidirectional chemical flux from compartment i to j, M_{ij} (d^{-1}) is the transfer rate constant from i to j,

N_i (mol) and Z_i (mol Pa^{-1} m^{-3}) are the inventory and fugacity capacity of the chemical in *i*, respectively, D_{ij} (mol Pa^{-1} d^{-1}) is the overall transport coefficient (Mackay-type *D* value) from *i* to *j*, and V_i (m^3) is the compartment volume. The transport coefficients were obtained from hydrometeorological simulation results or estimated based upon empirical and semi-theoretical methods. Mass balance of the chemical could be described by a set of differential equations developed for environmental compartments connected in an Eulerian system

$$\frac{dN_i}{dt} = S_i + \sum_j (M_{ji}N_j) - M_{Oi}N_i \quad (2)$$

where *j* is a running index for all compartments connected to compartment *i*, S_i (mol d^{-1}) is a source term of chemical application or emission in *i*, and M_{Oi} (d^{-1}) is the total loss rate constant of the chemical in *i*. The model has been successfully applied in the field conditions of the Connecticut River Basin and the Great Lakes region, using organic compounds with various physiochemical properties as test agents (Luo and Yang, 2007; Luo et al., 2007b). The model performance was evaluated in both dynamic and steady-state simulation scenarios, and the model yielded reasonable agreement with measured data.

In this study, the multimedia environmental fate model was applied in the field conditions of the northern San Joaquin Valley watershed. Monthly OP pesticide application was converted into effective environmental release levels to plant, surface soil, and air, where the release fraction was determined by pesticide products and suggested ratios in the literature (Strang, 2006; McKone et al., 2007). Pesticide transport was driven by the hydrologic flows and climate data described in the previous section. The predicted concentrations in the environmental media were compared to available measured data for evaluation. Due to the lack of accurate and complete data including simultaneous measurements for chemical application, concentration, and cross-media fluxes, a comprehensive validation of the multimedia environmental fate model was impractical for the entire simulation period and region. Based on data availability, pesticide loads and concentrations in the surface water, in the air, and in precipitation were targeted as the primary elements in the model evaluation. Predicted dissolved loads were compared to observed data at the watershed outlet by the US Geological Survey (USGS gauge #11303500, San Joaquin River at Vernalis). This site receives stream flow from upstream portions of the study area and thus characterizes the water quality in general. According to the CEPA and USGS monitoring results of OP dissolved concentration (CEPA, 2008; USGS, 2008), only four pesticides, i.e., chlorpyrifos, diazinon, dimethoate, and methidathion, were detected with >10% frequency over the northern San Joaquin Valley watershed during 1992–2005. Diazinon and methidathion were mainly detected in early years of 1992–1990 with relatively high use rates. Due to the low detection frequency, simulation results were compared to the measurements by percentiles at 50%, 75% and 95%. The comparison results were expected to provide a general evaluation of the model's performance in predicting the concentrations distribution and capturing the spatio-temporal variation. A similar method has been used in other studies in evaluating model prediction with limited observation data (USEPA, 2006b). In addition, predicted pesticide concentrations in the air and in rainfall samples were compared to measured data to investigate the model capability in simulating pesticide transport and fate in the air and cross the air-ground interface.

2.2. Multimedia and multi-pathway risk assessment

Human exposure to OP pesticides could be estimated from the mass exchange between humans and contaminated exposure media via inhalation, ingestion, and dermal contact. According to the USEPA Office of Pesticide Programs, the steady state for OP pesticides is reached after approximately 21–28 d of exposure (USEPA, 2006b). Therefore, this study focused on subchronic exposure at monthly intervals of a residential population exposed to OP pesticides via everyday activities – breathing, dining, drinking, etc. Human exposures through occupational and occasional activities, such as pesticide application, harvesting, and incidental intake, were not considered. For an individual exposure pathway, the generic equation for a specific OP pesticide intake (*I*, g kg^{-1}[body weight] d^{-1}) is calculated as

$$I = \frac{C^E \cdot CR \cdot EF}{BW} \quad (3)$$

where C^E is concentration of the specific chemical in exposure media (g kg^{-1}[water]), *CR* is the daily consumption rate (kg[drinking water] d^{-1}), *EF* is the exposure frequency which is set to one for inhalation and ingestion exposures, and *BW* is the average body weight (kg). All parameters in Eq. (3) were calculated as time-averaged values over one month, which was the evaluation period of subchronic human exposure to OP pesticide in this study. The intake calculations were performed for all potential exposure pathways and summed up as total intake of the chemical for a receptor. The highest monthly total intake during a year was used to estimate subchronic exposure for that year in this study.

2.2.1. Concentration in exposure media

Exposure pathways related to residential inhalation and dietary ingestion were considered in this study. Dermal exposure to water, soil, or air was not included. The contribution of dermal exposure to soils to overall risk is typically small (USEPA, 2005). Results of risk assessments in the Salinas Valley of California indicated that human exposure by dermal contact accounted for less than 5 percent of total exposure to the major organophosphate pesticides via everyday activities (McKone et al., 2007). In addition, the comparative effect levels for dermal endpoints are not determined for common OP pesticides such as chlorpyrifos and diazinon. Consequently, exposure media in this study included ambient and indoor air, tap water, produce, animal products, and soil particles. Pesticide concentrations in the exposure media were calculated based on the simulation results of the multimedia environmental fate model described above. Following the procedures extracted from USEPA (2005), concentration of pesticides in exposure media could be converted from those in environmental media by applying transfer factors (TF's),

$$C^E = \sum_i TF \cdot C_i \quad (4)$$

where C_i (g m^{-3}) is the concentration of a chemical in environmental medium *i*, with *i* as a running index for all involved environmental media. The gram unit was chosen for chemical concentration in order to simplify the conversion from chemical inventory (mol) and fugacity (Pa) used in multimedia simulation results as in Eq. (2). Pesticide concentration in tap water was assumed to be the same as that in surface water. Both the model simulation and the groundwater sampling program (Burow et al., 1998) indicated that OP pesticide concentrations in groundwater were significantly lower than those in surface water in the study area. Therefore, excluding groundwater as drinking water sources might overestimate the exposure, but it might be helpful in establishing an upper limit of risk through water ingestion. Pesticide concentrations in aboveground products were directly calculated with the multimedia environmental simulation, while pesticides in the root crops were assumed to be in equilibrium with the concentration in the root zone.

Pesticide concentration in fish was calculated as the product of the concentration in contaminated water and a bioconcentration

factor (BCF, Table 1). Pesticide residues in animal products were estimated based on an evaluation of the animal's ingestion and accumulation rate in tissues. USEPA (2005) recommended a simplified calculation for chemical concentration in animal products (C^E_{Animal}) from plant (forage, silage, and/or grain) and surface soil ingestion,

$$C^E_{Animal} = \mathrm{BTF} \cdot (C_p \cdot CR_p + C_g \cdot CR_g) \quad (5)$$

where C_p and C_g (g m^{-3}) are chemical concentrations in plants and ground soil, respectively, CR_p and CR_g (kg[dry weight] d^{-1}) are the corresponding consumption rates, and BTF (d kg^{-1}[tissue]) is the biotransfer factor for the animal. The BTF was estimated based on a regression equation developed by the Research Triangle Institute (2005):

$$\log\left(\frac{\mathrm{BTF}}{FC}\right) = -0.099(\log K_{OW})^2 + 1.07\log K_{OW} - 3.56 \quad (6)$$

where K_{OW} is the octanol–water partition coefficient (Table 1), and FC is the average fat content of the animal product, *e.g.*, 0.19 for beef, 0.04 for milk, 0.23 for pork, 0.14 for chicken, and 0.08 for egg, as suggested by USEPA (2005). The above equation is developed for organic chemicals having a log(K_{OW}) between −0.67 and 8.20. In this study, the equation was also applied to chemicals of acephate, methamidophos, and oxydemeton-methyl with log(K_{OW}) values slightly lower than −0.67.

2.2.2. Human activity and consumption rate

Table 3 shows the distribution of daily consumption rate per body weight for the individual exposure pathway. The mean values were taken from the USEPA Exposure Factor Handbook and Human Health Risk Assessment Protocol (USEPA, 1997, 2005), in which the consumption rates were usually derived from the 1987–1988 National Food Consumption Survey by US Department of Agriculture (USDA). The mean individual food consumption rates were weighted by age group (0–14 years old as child, and 20+ years old as adult, respectively), and adjusted for cooking and preparation loss as recommended by the USEPA (1997). The coefficients of variation for the consumption rate per body weight were adapted from Bennett et al. (1999). Those CV values were primarily derived by fitting survey data for the US population into a lognormal distribution for each age group. It was assumed that the mean and CV values listed in Table 3 represented average levels of inhalation and dietary ingestion rates, with associated uncertainty for the residential and non-occupational intake levels of the northern San Joaquin Valley.

The fractions of food locally produced were required in calculating chemical intake through daily dietary consumption. The chemical concentrations in local products were calculated as described before, while the concentrations in imported products were usually set as prescribed values or assumed to be free of chemicals. Based on a local product fraction of unit, i.e., assuming 100% of food was obtained from local sources, a conservative risk analysis was conducted in this study to evaluate the maximum potential intake of OP pesticides by local food supplies in the study area.

2.2.3. Risk characterization

A margin of exposure (MOE) approach was used to characterize human health risk from OP exposure. For a specific exposure pathway, the MOE is calculated as the ratio between the toxicologically relevant benchmark dose of the index chemical, and the cumulative observed intake of all evaluated chemicals. The MOE for an individual exposure pathway and the total MOE could be expressed as (Sielken, 2000)

$$\mathrm{MOE}_T = \left(\sum_k \mathrm{MOE}_k^{-1}\right)^{-1}$$
$$\mathrm{MOE}_k = \frac{\mathrm{BMD10}_{index,k}}{I_{CUM,k}} \quad (7)$$

where MOE_T is the total MOE for all exposure pathway, MOE_k is the MOE for an individual exposure pathway (k = inhalation or ingestion in this study), $\mathrm{BMD10}_{index}$ (mg kg^{-1} d^{-1}) is the benchmark dose of an index chemical where cholinesterase activity is reduced by 10% compared to background activity, and I_{CUM} (mg kg^{-1} d^{-1}) is cumulative intake of OP pesticides through the relevant exposure pathway k. Cumulative intake was calculated as the toxicity-weighted average of doses from individual OP pesticides.

$$I_{CUM,k} = \sum_h (I_{h,k} \cdot \mathrm{RPF}_{h,k} \cdot \mathrm{SF}_{h,k}) \quad (8)$$

where $I_{h,k}$ (mg kg^{-1} d^{-1}) is the exposure dose from OP chemical h through exposure pathway k, and RPF and SF are the associated relative potency factor and safety factor. The RPF value reflects the relative potency of a pesticide compound compared to the index chemical of methamidophos (USEPA, 2006b). USEPA provides ingestion RPFs for all selected OPs in this study, while inhalation RPFs are only available for acephate, disulfoton, malathion, methamidophos, and naled. Inhalation RPFs for other OPs were estimated based on

Table 2
OP pesticide usage in the northern San Joaquin Valley.

Chemical	Chem code[a]	1992–1999 Annual use[b]			2000–2005 Annual use[b]		
		kg		%	kg		%
Chlorpyrifos	253	116681	(0.15)	66.8	92408	(0.22)	82.5
Diazinon	198	56322	(0.47)	32.3	18851	(0.39)	16.8
Disulfoton	230	1602	(0.52)	0.9	788	(0.64)	0.7
Total diethyls		174605	(0.19)	100.0	112050	(0.18)	100.0
Acephate	1685	21173	(0.20)	11.4	7612	(0.54)	9.3
Azinphos-methyl	314	33912	(0.54)	18.2	5562	(0.54)	6.8
Dimethoate	216	24269	(0.23)	13.1	17411	(0.15)	21.2
Malathion	367	18954	(0.37)	10.2	13986	(0.21)	17.0
Methamidophos	1697	7441	(0.33)	4.0	1266	(0.68)	1.5
Methidathion	1689	13320	(0.38)	7.2	3479	(0.46)	4.2
Methyl parathion	394	3083	(0.56)	1.7	5675	(0.14)	6.9
Naled	418	19944	(0.78)	10.7	7664	(0.40)	9.3
Oxydemeton-methyl	382	1562	(0.90)	0.8	518	(0.50)	0.6
Phosmet	335	42224	(0.30)	22.7	18995	(0.32)	23.1
Total dimethyls		185882	(0.14)	100.0	82168	(0.13)	100.0

[a] Chem code is a unique chemical code number assigned to a particular pesticide's active ingredient by the California Department of Pesticide Regulation.
[b] The coefficients of variance are listed in parentheses.

Table 3
Consumption rates for two age groups of children and adults.

Exposure media/pathway	Consumption rate for adults[a]		Consumption rate for children[a]	
	Mean[b]	CV[c]	Mean[b]	CV[c]
Inhalation rate[d]	12.85	0.30	7.76	0.51
Ingestion rates				
Ground soil	1.43E−6	2.15	7.58E−6	2.75
Aboveground produce (dry weight)	9.30E−4	0.25	2.27E−3	0.54
Belowground produce (dry weight)	1.40E−4	0.30	2.30E−4	0.49
Milk, meat, and egg	1.68E−2	0.22–0.47	2.48E−2	0.12–0.48
Fish[e]	2.87E−4	0.89	5.34E−4	2.52
Drinking water[d]	1.40	0.60	0.67	0.64

[a] The unit for inhalation rate is $m^3\ d^{-1}$, and the unit for ingestion rate is $kg\ kg^{-1}$[body weight] d^{-1}. Body weight is set as 26.4 kg for children and 70.0 kg for adults.
[b] Mean values of consumption rates are taken from USEPA (2005) unless otherwise noted.
[c] Coefficient of variation (CV) is taken from risk assessments of a pesticide in the literature (Bennett et al., 1999; Lee et al., 2002).
[d] Inhalation rates and fluid consumption rates are derived using time-weighted averages for age groups from the survey results (USEPA, 1997).
[e] Adult intake of fish is set as 20.1 $g\ d^{-1}$, and child intake is estimated as 14.1 $g\ d^{-1}$ (70% of adult intake) both as recommended by USEPA (1997).

their No-Observed-Adverse-Effect-Levels (NOAEL) relative to the NOAEL of the index chemical of methamidophos. Safety factors are required by the US Food Quality Protection Act (FQPA) for the portion of population which is deemed more sensitive to a given pesticide than the average. In this study, the safety factors for inhalation route of exposure are applied to children. The ingestion safety factors are determined based on sensitivity of infants, children, and females between 15 and 50 (USEPA, 2007), and applied to both age groups of children and adults in this study, in order to produce a conservative risk assessment. Relative potency factors and safety factors for the selected OPs are summarized in Table 4.

2.2.4. Probabilistic risk assessment

Probabilistic risk assessment was performed in this study to determine a population's distribution of risk from OP exposure based on probabilistic distribution of the population-related parameters. Compared to a point value, distributions of risk provide more informative exposure characterization, along with appropriate data about toxicity and human activity. In this study uncertainty and variability were evaluated by stochastic simulations of risk. At least 1000 discrete Monte Carlo events were included in each simulation run. The random input datasets were generated by Latin Hypercube Sampling, based on the 95% cumulative frequency of parameter distribution defined in Table 3. To simplify the analysis, all input parameters were assumed to follow lognormal distributions (Slob, 1994; McKone, 1996a,b; Liu et al., 1999; MacLeod et al., 2002; Luo and Yang, 2007), except for those with zero coefficients of variation, which were assumed to be fixed values in the model simulation.

Based on stochastic simulation results of OP exposures, MOE at the 99.9th percentile was estimated and compared to the target MOE. USEPA guidelines for OP cumulative risk assessment consider any MOE of 100 or greater to be acceptable. Therefore, if at the 99.9th percentile of exposure the MOE is 100 or greater, 99.9% of the population is exposed to a dose 100 times less than the dose causing significant cholinesterase inhibition.

Table 4
Relative potency factors and safety factors for the inhalation and ingestion routes of exposure.

Pesticide	Inhalation			Ingestion[a]	
	NOAEL[b]	RPF[c]	SF[b]	RPF	SF
Acephate	1.49	0.208	3	0.081	3
Azinphos-methyl	0.22	1.366	3	0.091	3
Chlorpyrifos	0.10	3.000	10	0.054	1
Diazinon	0.03	11.538	3	0.013	3
Dimethoate	0.39	0.789	1	0.320	1
Disulfoton	0.05	6.596	10	1.143	3
Malathion	121.00	0.003	10	0.0003	3
Methamidophos (the index chemical)	0.30	1.000	1	1.000	1
Methidathion	0.20	1.500	10	0.320	3
Methyl-parathion	0.11	2.727	3	0.119	3
Naled	0.38	0.820	3	0.080	3
Oxydemeton-methyl	17.00	0.018	3	0.889	3
Phosmet	1.50	0.200	3	0.022	3

Notes – NOAEL: no observed adverse effect level ($mg\ kg^{-1}\ d^{-1}$); RPF: relative potency factor; SF: safety factor.
[a] OP cumulative risk assessment (USEPA, 2006b).
[b] Subchronic or intermediate NOAELs are taken from the re-registration eligibility decision (RED) for the corresponding chemicals (USEPA, 2007).
[c] Inhalation RPFs for disulfoton, malathion, and naled are from OP cumulative risk assessment (USEPA, 2006b), while inhalation RPFs for other chemicals are calculated based on their NOAELs.

2.3. Simulation design

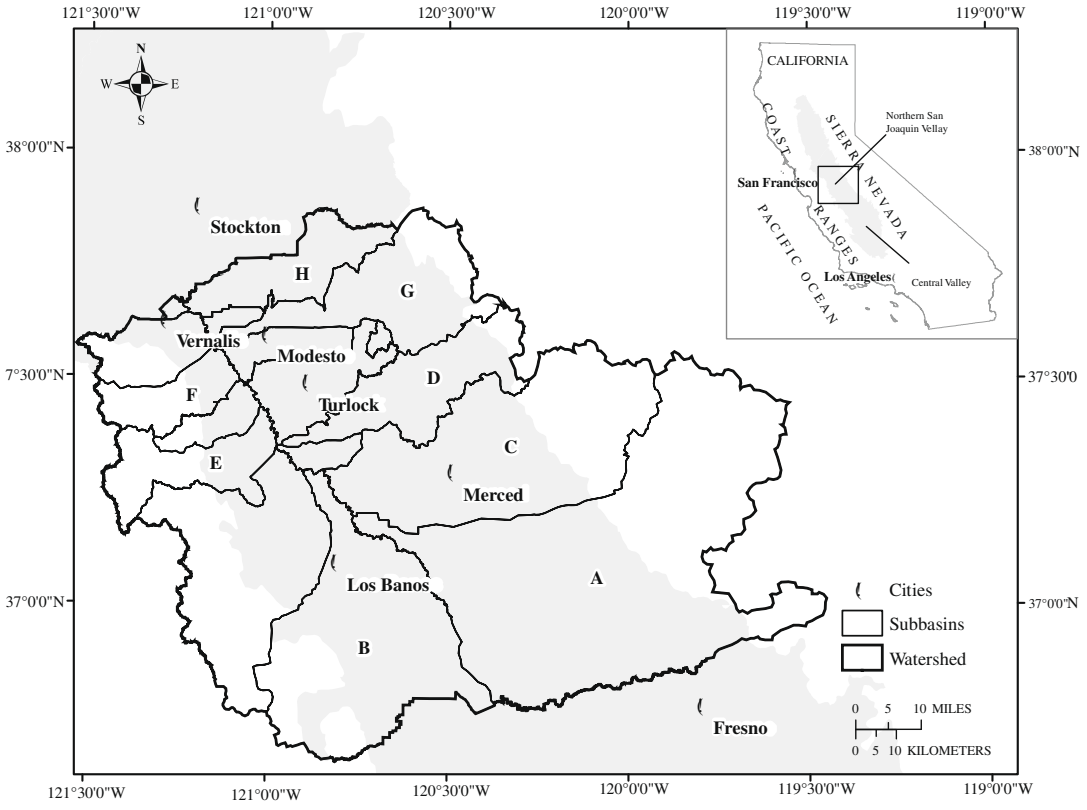
2.3.1. Site description

The area of study is the northern San Joaquin Valley of California, which experiences intensive agricultural land use and pesticide applications (Fig. 1). This valley is drained by the middle San Joaquin River and its tributaries, including the majority of agricultural areas in the counties of Stanislaus, Merced, and Madera, and portion of San Joaquin and Fresno Counties. The river test site was at Vernalis, CA (USGS gauge #11303500), the lowest station on the San Joaquin River not subject to tidal influence, which is usually set as the outlet of the watershed (Quinn and Tulloch, 2002). Inlets of the major upstream rivers, *i.e.*, the upper San Joaquin River, the upper Merced River, the upper Tuolumne River, and the upper Stanislaus River, were chosen as USGS gauges near the eastern boundary of the San Joaquin Valley. To simplify the hydrologic simulation, headwater drainage areas of small streams outside of the San Joaquin Valley were also included in the study area. The total area of the studied watershed is 14983 km^2, 66% of which is located in the San Joaquin Valley.

The watershed was delineated into 15 sub-basins. The sub-basin boundaries were derived following the watershed delineations in CEPA (2005), taking both the natural stream network and irrigation water diversion into account. Landscape characterization for the sub-basin was based on public databases available from various agencies. Land-use categorization was obtained from the GIRAS database maintained by USGS as well as land use surveys conducted by the California Department of Water Resources. Soil physical properties were extracted from the SSURGO database and aggregated to soil layers for each sub-basin.

2.3.2. Climate and hydrology conditions

Metrological data was extracted from the California Integrated Irrigation Management Information System (CDWR, 2007). Input



A: Chowchilla-Fresno Rivers subbasin, B: Salt Slough subbasin, C: Bear Creek subbasin, D: Merced River Subbasin, E: Orestimba Creek subbasin, F: Del Puerto Creek subbasin, G: Tuolumne River subbasin, and H: Stanislaus River subbasin

Fig. 1. Study area of the northern San Joaquin Valley watershed, with major sub-basins marked.

weather data used in this study included precipitation, solar radiation, temperature, relative humidity, and wind. Data were obtained from four weather stations positioned within the study area and applied to their respective sub-basins.

Hydrologic simulations were performed based on the Soil and Water Assessment Tool (SWAT), which was calibrated for the study area in our previous study (Luo et al., 2008). The model's predictions matched measured stream flows and sediment loads reasonably well, in terms of temporal trends and spatial variation within the watershed during the simulation period of 1992–2005. Therefore, it could be argued that the calibrated SWAT simulations were practical for predicting hydrologic conditions in the northern San Joaquin Valley watershed. This hydrologic simulation results were rearranged as monthly averages and used in the multimedia environmental fate model. The required elements included stream flow, surface runoff, evapotranspiration, lateral flow, percolation, groundwater recharge, sediment concentration, soil erosion, leaf area index, and biomass production.

2.3.3. Pesticide data

Thirteen OP pesticides are included in the risk assessment. Those pesticides are widely used in the study area and are detected in human urine samples (Castorina et al., 2003). Annual average use of those pesticides in the study area was about 305 ton during 1990–2005, accounting for 95.5% of the application amount of the OP pesticides causing AChE inhibition as listed by USEPA (2006b). The selection of pesticides was also consistent with those in other studies involving OP risk assessments in California and in the San Joaquin Valley (USEPA, 2006b; McKone et al., 2007). Table 1 lists the specific chemical properties applied in the transport and fate simulations. Most of those properties were obtained from published databases such as the chemical property database for the CalTOX model, the pesticide properties database maintained by USDA, and the Hazardous Substances Data Bank maintained by the US Institutes of Health (USDA, 2001; McKone et al., 2003, 2007; Neitsch et al., 2005; NIH, 2007). Diffusivity values in the air and water were estimated according to the method developed in Tucker and Nelken (1982). This method is also recommended by the USEPA for site assessment calculation (USEPA, 2006a). The bioconcentration factor (BCF), when its value was not available in the literature, was calculated from the octanol–water coefficient (K_{OW}) based on the following equation (Bintein et al., 1993),

$$\log \mathrm{BCF} = 0.91 \cdot \log K_{OW} - 1.975 \cdot \log(6.8 \times 10^{-7} \cdot K_{OW} + 1.0) - 0.786 \quad (9)$$

Since 1990, California has required 100% reporting of pesticide quantities applied in agriculture, construction and landscaping. Pesticide use reporting (PUR) data were obtained electronically for 1990–2005, the most recent year available at the time of this study (CEPA, 2007a). PUR data are organized by township, range, and section, with minimal resolution set at approximately 1 mi^2. In this study, pesticide use amount was averaged on a monthly basis, and spatially aggregated for each sub-basin. PUR data sets for 1992–2005 for the selected pesticides in the study area are summarized in Table 2. In the San Joaquin River watershed, almost all agricultural pesticide application is in the San Joaquin Valley. Therefore, pesticides were assumed to be uniformly applied to the in-valley

portion of a sub-basin (Fig. 1) during a given month. This assumption is also supported by the fact that OP pesticide applications, especially of those in granular forms, would be incorporated into the soil for slow release (McKone et al., 2007). Therefore, use of a pulse input might overestimate the chemical residues during the period of application.

Air monitoring was conducted by CEPA for the pesticides under evaluation as possible toxic air contaminant. Air samples were usually taken in the locations and months with the highest reported use of each pesticide in recent years. Details in the air monitoring have been discussed by Baker et al. (1996). Nondetectable analytic results were included in the statistical process to avoid underestimation of the concentration mean values (Lee et al., 2002). For pesticides with detection frequency less than 10%, mean concentration was estimated by including nondetectable samples as zero-value. For other pesticides, the nondetectable samples were replaced by 50% of the minimum quantity limit (MQL) in the calculation of means. Pesticide concentration in rainfall was measured in the San Joaquin Valley for 41 pesticides and 23 transformation products during 2002–2004 (Majewski et al., 2006). The sampling results were reported as mean, maximum, and detection frequency over all the stations. Dissolved concentrations of OP pesticides in surface water were monitored by the CEPA and USGS at multiple sites on the main stem and tributaries of the San Joaquin River (CEPA, 2008; USGS, 2008).

3. Results and discussion

3.1. Concentrations in environmental media

Simulation results showed that the majority (>60%) of OP pesticides residues in the study area were stored in the soil, although some of those pesticides had short half-lives in soils. Therefore, the transport and fate processes in soil compartments were important in determining the overall distribution pattern of OP pesticides in the multimedia environment. Taking chlorpyrifos as an example, the total use of chlorpyrifos in the study area was 1490 ton during 1992–2005 (Table 2), and the average chlorpyrifos inventory in the simulation domain was predicted as 6253 kg, with higher values during growing season than domain season. Compartmental distribution showed that chlorpyrifos inventory in soil accounted for about 98% of the total residues. Therefore, about 0.41% of applied chlorpyrifos was expected to be stored in soils in the northern San Joaquin Valley watershed during 1992–2005. This finding was consistent with the results of a daily PRZM model simulation for OP application to nut trees in the San Joaquin Valley, in which soil storage of chlorpyrifos was estimated as 0.56% of total use (USEPA, 2006b).

The OP compounds with large organic carbon partition coefficients (KOC), such as chlorpyrifos, diazinon, disulfoton, malathion, and methyl parathion, had moderate-to-low mobility in the soils, and more than 90% of their soil inventories were predicted to be adsorbed onto soil particles. The field experiments conducted by Detmer and Purpus (2007) showed that OP pesticide concentrations in solid phase were higher than soluble concentrations by up to 3 orders. For those pesticides, leaching into shallow aquifers was not expected to be an important fate process. For some dimethyl OP pesticides with low KOC values, very high mobility in soil was predicted in the model simulation. According to the modeling results of dimethoate transport and fate in the soils, for example, less than 10% of dimethoate would be adsorbed onto soil particles and a loss of about 36% would be attributed to leaching of soil layers. Due to the small values of their vapor pressures (Table 1), the selected OP pesticides are not expected to volatilize from dry soil surfaces. For some pesticides, such as chlorpyrifos, disulfoton, and naled, however, volatilizations from moist soil surfaces and water surface are expected to be an important fate process (based upon their Henry's Law constants). Once exposed to air, OP pesticides in this study are predicted to exist in both vapor and particulate phases in the ambient atmosphere. Since most of those pesticides have airborne half-lives of less than 5 d, vapor-phase pesticides will be degraded quickly in the atmosphere by reaction with photochemically produced hydroxyl radicals. Pesticides in particulate phase are primarily removed by rain scavenging and dry deposition.

Surface and subsurface runoff and soil erosion were important transport mechanisms for pesticide migration to surface waters. The simulation results indicated that 70–80% of losses of OP pesticides in surface waters were originated from ground and root-zone soils. For those pesticides with moderate-to-low mobility in the soils, soil erosion was expected to contribute a significant portion (*e.g.*, 5–30% for chlorpyrifos through the sub-basins) of the total mass transport from ground soil to surface water.

Simulation results of dissolved pesticide loads in surface water at the watershed outlet (USGS gauge #11303500, San Joaquin River at Vernalis) were compared to observations for the most frequently detected OP pesticides of chlorpyrifos and diazinon. The annual trends of dissolved pesticide loads simulated by the multimedia environmental fate model in this study matched the USGS observations during the simulation period of 1992–2005, with Nash-Sutcliffe coefficients of 0.53 and 0.90 for chlorpyrifos and diazinon, respectively. Compared to the performance of the pesticide transport component of the SWAT model in the same watershed in our previous study (Luo et al., 2008), the multimedia environmental fate model showed great success in predicting the temporal trend of OP pesticides in surface water at watershed scale. Predicted concentrations at the 50th, 75th, and 95th percentiles were compared to the corresponding concentrations measured by the USGS and CDPR in the northern San Joaquin Valley watershed. The predicted percentile concentrations were in general agreement with the actual measurements, indicating that the multimedia environmental model had the capability to capture the general spatiotemporal variability in dispersion and distribution of the selected OP pesticides in this study.

Predicted pesticide concentrations in the air for the sub-basins of Salt Slough and Chowchilla-Fresno Rivers were compared to air-monitoring data. These measurements were taken from sampling projects conducted by CEPA at multiple sites in Fresno County. The simulation results showed reasonable agreement with measurements (within an order of magnitude). For example, Stein and White (1993) reported mean concentrations of 0.31 and 7.51 ng m^{-3}, for chlorpyrifos and diazinon, respectively, in Fresno County during August to October 1991. For the same period, the corresponding model prediction in the sub-basins of Salt Slough and Chowchilla-Fresno Rivers was in the range of 0.54–2.18 ng m^{-3} for chlorpyrifos and 0.70–9.08 ng m^{-3} for diazinon. During January and February 1998, the average diazinon concentration in the air was reported as 9.8–49.3 ng m^{-3} over five sites in the Fresno county (CEPA, 1998), while the model in this study predicted an reasonable range between 1.74 and 20.73 ng m^{-3}.

In addition, model performance in predicting pesticide partitioning between gaseous and particulate phases was evaluated by tests of rainfall chemistry. OP pesticide concentrations in rainfall, as predicted in this study, fell into the range of the observed data measured by the USGS (Majewski et al., 2006).

3.2. Human exposures

Summarized in Table 5 are predicted exposure doses of individual OP pesticides, as watershed-wide averages during 2000–2005. A distribution was estimated for each exposure pathway by

Table 5
Watershed-wide average intakes ($\mu g\ kg^{-1}\ d^{-1}$) for (a) children and (b) adults in the northern San Joaquin Valley watershed during 2000–2005.

Chemical	Inhalation	Ingestion			
		Food	Water	Other	Total
(a)					
Acephate	9.38E−10	1.28E−3	4.46E−4	4.44E−6	1.73E−3
Azinphos-methyl	2.29E−5	1.60E−2	3.29E−4	8.12E−4	1.71E−2
Chlorpyrifos	8.81E−4	2.76E−2	2.02E−3	1.80E−2	4.77E−2
Diazinon	8.66E−4	3.63E−3	1.33E−3	1.14E−2	1.63E−2
Dimethoate	8.72E−5	5.62E−2	6.29E−4	1.00E−3	5.78E−2
Disulfoton	4.94E−6	1.18E−4	3.61E−5	9.42E−5	2.48E−4
Malathion	5.05E−5	1.66E−2	4.85E−4	1.01E−3	1.81E−2
Methamidophos	4.18E−7	5.29E−4	2.27E−4	1.22E−5	7.68E−4
Methidathion	1.78E−6	1.34E−3	1.03E−4	4.29E−5	1.49E−3
Methyl-parathion	6.42E−5	4.90E−3	7.21E−5	8.52E−4	5.82E−3
Naled	6.06E−4	5.96E−3	1.35E−5	9.04E−5	6.07E−3
Oxydemeton-methyl	1.52E−9	9.91E−5	2.68E−5	3.96E−6	1.30E−4
Phosmet	2.71E−5	2.43E−2	3.80E−4	1.17E−3	2.58E−2
Cumulative intake	5.89E−2	3.20E−2	1.15E−3	2.81E−3	3.60E−2
(b)					
Acephate	5.86E−10	8.11E−4	3.52E−4	3.93E−8	1.16E−3
Azinphos-methyl	1.43E−5	1.10E−2	2.60E−4	1.67E−4	1.14E−2
Chlorpyrifos	5.50E−4	1.92E−2	1.59E−3	4.52E−3	2.53E−2
Diazinon	5.41E−4	2.64E−3	1.05E−3	3.77E−3	7.46E−3
Dimethoate	5.45E−5	4.01E−2	4.95E−4	3.60E−4	4.10E−2
Disulfoton	3.09E−6	8.58E−5	2.84E−5	2.66E−5	1.41E−4
Malathion	3.15E−5	1.19E−2	3.82E−4	2.75E−4	1.25E−2
Methamidophos	2.61E−7	3.66E−4	1.79E−4	3.33E−6	5.48E−4
Methidathion	1.11E−6	5.98E−4	8.09E−5	1.03E−5	6.90E−4
Methyl-parathion	4.01E−5	2.92E−3	5.68E−5	2.66E−4	3.24E−3
Naled	3.78E−4	2.47E−3	1.06E−5	1.47E−5	2.49E−3
Oxydemeton-methyl	9.51E−10	6.01E−5	2.11E−5	3.63E−8	8.13E−5
Phosmet	1.70E−5	1.56E−2	3.00E−4	2.30E−4	1.62E−2
Cumulative intake	3.68E−2	1.68E−2	5.91E−4	5.19E−4	1.79E−2

Note: The additional Food Quality Protection Act (FQPA) safety factor is included as an adjustment to the chemical-specific relative potency factors in calculating cumulative intakes.

incorporating uncertainty into human consumption rates (Table 3). The coefficients of variation (not presented in the table) were about 0.30 for inhalation, and 0.16–0.51 for ingestion pathways throughout the watershed, respectively. The predicted exposures for children were about 2 times those of adults, and the ratios varied among chemicals and exposure pathways. This might be attributed to children's relatively larger rate of consumption per body weight. The result of this study was similar to that reported by Bennett et al. (1999), in which children exposure to atrazine was 1.6X of average lifetime exposure in the mid-western region of the United States.

The relative contribution of a pesticide to the cumulative intake of all OP pesticides in this study (as methamidophos equivalents) was determined by its individual intake values, relative potency factor and safety factor. Intakes from inhalation were significantly lower than those from ingestion (by two orders or more). However, the cumulative inhalation intakes were generally double the ingestion intakes. More than 90% of the cumulative inhalation intakes were contributed by chlorpyrifos and diazinon, which showed high values in relative potency factors and safety factors. Public health concerns about non-cancer risks to children from airborne chlorpyrifos and diazinon have been addressed in other studies (Lee et al., 2002; Harnly et al., 2005). For the inhalation pathway, OP pesticides could be ranked by the ratio of exposure to the annual use of each chemical. This ratio reflected a direct relationship between pesticide applications and the consequent potential risks to human health. It's interesting to note the statistically significant correlation ($p = 0.013$) between exposure/use ratio and the vapor pressure of OP pesticides. Vapor pressure has been correlated with pesticide air concentration in other studies (Woodrow et al., 1997; Lee et al., 2002). By incorporating actual pesticide use, the correlation revealed in this study reflected the actual exposure risks and provided guidance for further pesticide management practices.

For the ingestion route of exposure, cumulative intake was dominated by dimethoate, with a high relative potency factor of 0.32, followed by azinphos-methyl and chlorpyrifos. Due to the lack of biomonitoring data for OP pesticides in the study area, the human exposure simulation was evaluated by comparing the predicted dietary ingestion dose and the intakes estimated from pesticide residues in separated food items and the method for intake estimation was documented by McKone et al. (2007). The pesticide residues were taken from the Total Diet Survey conducted by US Food and Drug Administration. Watershed-wide averages of dietary ingestion dose estimates for adults ranged from 1.14E−4 to 0.021 $\mu g\ kg^{-1}\ d^{-1}$ for diethyl OP pesticides, and from 8.12E−5 to 0.041 $\mu g\ kg^{-1}\ d^{-1}$ for dimethyl OP pesticides. The dietary intakes for individual pesticides predicted in this study were comparable to the intakes estimated from pesticide residues in food items. This proved the capability of the multimedia environmental model in this study to predict OP pesticide concentrations in both environmental media and exposure media.

The information in Table 5 suggests that multiple pathways have to be considered in evaluating the human intakes of OP pesticides. Dietary intake, as the sum of intakes from fresh produce, animal produce, and fish, was a significant contributor to the total ingestion dose for all OP pesticides in this study. Since dietary exposures are likely to show significantly less regional variability, they are assumed to be nationally uniform in most studies (USEPA, 2006b; McKone et al., 2007). In the intensively farmed area of the San Joaquin Valley, however, it is reasonable to assume a relatively high representation of local foods in a dietary intake analysis, especially for fresh produce, animal and dairy products. Therefore, an estimate of dietary doses based on local pesticide concentrations in the exposure media might prove helpful in establishing a direct linkage between pesticide use and human health risk. This study identified soil as a critical environmental compartment for human exposure of OP pesticides. Root-zone soil contamination was directly related to the pesticide residues in both aboveground and belowground plants. Humans are exposed to those plant-bound residues by direct ingestion, or else through animal products which have accumulated chemicals in contaminated forages, silages, or grains. In addition, both humans and animals are subject to incidental ingestion of contaminated surface soils.

The OP pesticide dose from drinking water was another important pathway of ingestive exposure. Due to the large amount of pesticide usage and relatively high runoff potential (compared to the southern part of the Valley), the northern San Joaquin is one of the areas which are most prone to pesticide runoff in the US (Kellogg et al., 1999). Surface water is the main source of drinking water in the study area, especially in the counties of San Joaquin, Stanislaus, and Merced (USEPA, 2006b). In this study, intake through drinking water was estimated directly from the average dissolved pesticide concentration in the surface water throughout the watershed. This approach might overestimate the pesticide dose through drinking water. The results could be applied as a conservative surrogate for the portion of the population deriving its drinking water from groundwater or other sources outside of the study area.

3.3. Risk characterization

Shown in Table 6 are the cumulative MOE values of OP at the 99.9th population percentile, calculated from watershed-wide average subchronic exposures for two age groups during 1992–2005. USEPA guidelines for OP cumulative risk assessment con-

Table 6
Margins of exposure (MOEs) at the 99.9th percentile of subchronic exposures, averaged over the northern San Joaquin Valley during 1992–2005.

Year	MOEs for children			MOEs for adults		
	Ingestion	Inhalation	Total	Ingestion	Inhalation	Total
1992	104	134	58	245	299	135
1993	147	357	104	340	794	238
1994	99	156	61	180	347	118
1995	79	289	62	128	643	107
1996	153	428	113	379	952	271
1997	151	536	118	376	1191	286
1998	164	445	120	391	990	280
1999	165	336	111	393	747	257
2000	171	479	126	407	1065	295
2001	142	589	115	326	1310	261
2002	177	479	129	417	1064	299
2003	168	556	129	404	1237	305
2004	171	417	121	408	927	284
2005	169	669	135	390	1488	309

sider any MOE of 100 or greater to be acceptable. The simulation results indicated that MOEs at the 99.9th percentile for individual exposure pathways were above 100, except for the food ingestion MOE values in 1994 and 1995 for children (MOE = 99 and 79, respectively). Total MOEs for children were lower than 100 during the simulation years of 1992, 1994 and 1995, associated with lower MOE values for inhalation and ingestion routes in those years.

The average MOEs for food exposure at the 99.9th percentile were 196 and 457 for children and adults, respectively, in the northern San Joaquin Valley during the study period. Risks of food exposure were calculated in this study as annual averages, and expected to reflect a chronic or subchronic human health risk due to OP pesticides entering through food ingestion. Compared to the MOE values for other exposure pathways in Table 6, food exposure to OP pesticides was the major contributor to the ingestion MOE, as well as to the total MOE. Risks of food exposure might be related to uncertainty and variability in the diet structures of local residents. The USEPA has conducted stochastic calculations of cumulative OP intake through food for various periods up to 21 d (USEPA, 2006b). The results indicated that, at the 99.9th percentile, dietary MOEs for a single day analysis may be 2–4 times less than those averaged for multiple days. When this result was applied in our study to convert the average food exposures into acute risks, substantial violations could be observed at the 99.9th percentile of exposure, especially for children. This raised concerns over children's health risks from OP pesticides, although the MOE surpassing 100 at the 99.9th percentile only represented an extreme exposure potential for subchronic risk assessment in this study.

There were general decreasing trends for subchronic MOE values from 1992 through 2005, as shown by the analyses for individual and aggregated exposure pathways (Table 6). Total MOEs were significantly correlated to both individual MOEs for inhalation and water ingestion ($p < 0.001$). Therefore, the ambient air and surface water were identified as primary determinants of the temporal trend of overall risk of human exposure to OP pesticides. Spatial variations in human risk from OP pesticides were evaluated in sub-basins of the northern San Joaquin Valley during 2000–2005. No obvious spatial patterns were observed, but some "hot spots" were identified, with high risk potential from OP pesticides. Significantly high risks of ingestion exposure were found in the Valley regions west of the San Joaquin River, such as the Orestimba Creek sub-basin. The high ingestion risk in those sub-basins might be attributed to the high levels of OP pesticide contamination in their surface waters. Due to higher clay content in soil and steeper slopes, the western sub-basins were more vulnerable to surface runoff (Luo et al., 2008). On the other hand, high inhalation risks were associated with the eastern sub-basins of the Chowchilla and Fresno Rivers, Merced River, and Tuolumne River. This spatial pattern might be related to pesticide use and prevailing wind direction.

This study provides insight on risk assessments and pesticide management practices. The simulation results showed that dietary intake, associated with pesticide concentrations in the soils, was the major contributor to ingestion dose and thus to the total MOE (see Table 5). However, annual trend and spatial variation in total risk were primarily related to the OP pesticide levels in the air and surface water. These results suggested that the dynamic simulation were required for a better understanding of human health risks through multiple exposure pathways. For pesticide management, the cropping areas with high pesticide runoff potentials would be candidates for further evaluation to minimize the pesticide contamination and associated risk. In the northern San Joaquin Valley, preventive and mitigative management practices for OP pesticides should be first focused on surface water quality control for the western sub-basins, and on air quality control for the eastern sub-basins, respectively.

4. Conclusion

This paper presents a computational framework for the assessment of human health risks due to OP pesticide through multimedia and multi-pathway exposures. Pesticide distribution through environmental media in the field conditions of the northern San Joaquin Valley was simulated by a multimedia environmental model developed in our previous study. Noncancer risk of brain acetylcholinesterase inhibition caused by exposure to OP pesticides was evaluated in the study area based on the two primary pathways of inhalation and ingestion. In order to evaluate the model's performance in simulating OP pesticide distribution through the study area, the predicted pesticide concentrations were compared to the reported monitoring data. Due to data availability, the evaluation was focused on pesticide residues in the air and in surface water. Generally, the predicted concentrations fell within the observed ranges, and showed reasonable matches with the temporal trends, spatial variability, and chemical species in the measured data. These compared results suggested that the multimedia environmental model used in this study was appropriate in performing a dynamic simulation of chemical fate and transport at watershed scale.

The assessment approach and modeling results of this study may serve many purposes in environmental public health and provide helpful information in minimizing and preventing any adverse health impact via OP pesticide exposure. In this study, food exposure, through ingestion of fresh produce, animal products and fish, was evaluated according to both local contamination levels and food pesticide residues in the US market. This comprehensive analysis showed promise in estimating the actual dietary exposure in the study area more accurately, as opposed to other studies in which only local simulations or national data were used (Bennett et al., 1999; McKone et al., 2007). It's likely that food exposure involves significantly less spatial and temporal variability than do drinking water and non-dietary residential exposures. However, the assumption of national uniformity in food exposure may not necessarily hold in all regions, especially in agriculturally intensive areas such as the San Joaquin Valley.

Results of this study indicated that multimedia fate modeling and multi-pathway exposure analysis are necessary to generate a comprehensive understanding of human health risk to OP pesticide exposure. Contamination of soil compartments was considered to be critical in OP pesticide distribution and in the resulting residues in local produce and animal products. In addition, the risk assessment in this study indicated that food ingestion was the dominant pathway of human exposure to OP pesticides, and that it made a

substantially larger contribution to the total MOE value than did any other exposure pathway. However, soil contamination and food exposure, applied as annual averages in this study, only contributed moderately to the temporal trend and spatial variation of total MOEs. Based on further correlative analysis, the primary contributors to the variability in total MOE were identified as inhalation and water ingestion. This finding reinforced public concerns over risk from pesticide residues in ambient air and surface water.

Acknowledgements

The authors would like to acknowledge funding support from the Coalition for Urban/Rural Environmental Stewardship and California State Water Quality Control Board. This research received partial financial support from the Wenzhou Medical College (award number XNK07035) and Wenzhou Science and Technology Bureau (award number S20070033). We are also grateful to the editor and reviewers who have helped improve the present article with their most appropriate suggestions.

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