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Single Toxicity and QSAR-Assistant Toxic Mechanisms of Pesticides (Dimethoate, Malathion, Atrazine, Prometryn and Acetochlor) to *Photobacterium phosphoreum* in the Sediment Lixivium

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To investigate the toxicity of diverse pesticides in the lixivium of sediments, 5 kinds of typical pesticides (dimethoate, malathion, atrazine, prometryn and acetochlor were selected as target objects to explore their single toxicity and toxic mechanisms to *Photobacterium phosphoreum* through the quantitative structure-activity relationship (QSAR) model, respectively. The dose-response curves of pesticides were fitted through Weibull and Logit models based on the single toxicity experiments, which indicated the toxic order of the pesticides to *Photobacterium phosphoreum* as follows: prometryn > dimethoate > malathion > atrazine > acetochlor. To reveal the mechanism of single toxicity, the DFT-B3LYP method with the basis set 6-31G (d) was employed to calculate 29 quantum chemical parameters of the typical pesticides as theoretical descriptors, thus a QSAR model was established using multiple linear regression method. It was found that both the first-order hyperpolarizabilities β_{yyz} and β_{xyz} have significant influence on the single toxicity of 5 pesticides and they are in proportion to the single toxicity of 5 pesticides to *Photobacterium phosphoreum*, where β_{yyz} plays a dominant role in controlling pesticide toxicity.

Keywords: Sediment, Single toxicity, Pesticides, *Photobacterium phosphoreum*, QSAR.

INTRODUCTION

China is an agricultural country, with a large consumption of pesticides applied widely. As the biggest production country of pesticides, China produced 3.549 million tons of pesticides nationwide in 2012 (according to the effective component)[1]. With the ever-increasing application types, range and dosage, only 0.1 % of the pesticides act on target disease and pest, while 99.9 % enter the ecosystem[2]. Pesticides have large extent of toxic effects; many of them have endocrine disruption effects, some of them even lead to carcinogenesis, teratogenesis and mutagenesis or likely[3]. Surface sediment (hereinafter "sediment") is a major carrier of migration and transformation, as well as a main fate for numerous pollutants in water body. Due to the characters of high toxicity, high environmental release rate and broad scope of influence, numerous pesticides enter the water body and remain in sediments, which generate low-level combined pollution and toxicity to aquatic microbial communities, resulting in an impact on environment and human health. Therefore, it is necessary to study on the toxic effect of pesticides on aquatic sediments, providing theoretical basis for pollution prevention.

The methods used to study on the toxicity of pesticides and their mixtures are various. At concentration level, the dose-response curves (DRC) for pollutants can be fitted by nonlinear sigmoid functions, especially Weibull and Logit regression models[4,5]. Zhu *et al.*[6] applied Weibull, Logit and Box-Cox-Weibull models to conducting the nonlinear fitting of short-term and long-term dose-response of 6 triazine herbicides on vibrio qinghaiensis sp.-Q67 and founded a parabolic relationship between the pEC_{50} and $logK_{ow}$. Liu *et al.*[7] analyzed the toxicity of five pesticides and one herbicide to Vibrio qinghaiensis sp.-Q67. using microplate toxicity testing method. The concentration of pesticides and inhibition rate of luminous intensity corresponded with non-linear Weibull model and according to the dose-response curves, the toxicity order is simetryn > bromacil > dichlorvos > prometon > velpar > diquat. At molecular level, there are studies on quantitative structure-activity relationship (QSAR) model for pollutants. Xu *et al.*[8] applied Broyden-Flether-Goldfarb-Shanno (BFGS) method to calculate quantum chemical parameters of 14 heterocyclic nitrogen compounds, which were used to establish a QSAR model along with the K_{ow} and toxicity data for *Photobacterium phosphoreum*. The result agreed with the target theory, which revealed the bioactivity in both chemical

transport process and interaction process successfully. Zhu *et al*.[9] applied density functional theory (DFT) method at B3LYP/6-31G level and calculated the quantum chemistry descriptors of 11 quaternary ammonium compounds (QAC) and partial least squares (PLS) analysis was employed to obtain the QSAR model for the toxicity of quaternary ammonium compounds on *C. vulgaris*, which could be used for predicting the toxicity of quaternary ammonium compounds presented in the study.

Weedicides, insecticides and bactericides always exist in the form of mixtures in the wild[10]. To meet practical situations, this work selected 5 kinds of typical pesticides: dimethoate (DI), malathion (MA), atrazine (AT), prometryn (PR) and acetochlor (AC) as target pesticides, which vary in biotoxicity, pesticide category and chemical classification, to investigate their toxicity to *Photobacterium phosphoreum* in the lixivium of sediments. Their main physical and chemical properties and parameters are listed in Table-1.

The dose-response curves between concentrations of 5 pesticides and inhibition rates of luminous intensity of *Photobacterium phosphoreum* were established by *Photobacterium phosphoreum* toxicity testing method and the response relationship is fitted by Weibull and Logit models, which can predict single toxicity of pesticide to *Photobacterium phosphoreum*. On this basis, integrating with the physical and chemical properties of pesticides themselves, a QSAR model for single toxicity of 5 pesticides to *Photobacterium phosphoreum* was established through quantum chemistry methods, which analyzed the toxic mechanism of pesticides at molecular level. This study also provides basic data for biological toxicity research of the target pesticides.

EXPERIMENTAL

Main apparatus employed include DXY-2 toxicity analyzer (made by Institute of Soil Science, Chinese Academy of Sciences Nanjing, P.R. China), magnetic stirring apparatus, whirlpool oscillators, sterilizing installation and conventional glass apparatus.

Atrazine (purity 97 %) was purchased from Songbei pesticide plant of Jilin Chemical Industry Co., Ltd.; malathion (purity 91.3 %) was purchased from Huludao Lingyun Group Pesticide & Chemicals Co., Ltd; dimethoate (purity 98.9 %), prometryn (purity 96.1 %) and acetochlor (95.1 %) were purchased from the National Pesticide products quality supervision and Inspection Centre.

Photobacterium phosphoreum (T3 mutation), freeze-dried powder, was purchased from Institute of Soil Science, Chinese Academy of Sciences, Nanjing, P.R. China.

Toxicity determination of pesticides to *Photobacterium phosphoreum:* To simulate the form of pesticides in actual water environment, pass the sediment samples through 0.9 mm sieve, place them in Erlenmeyer flasks, add deionized water by the solid-to-liquid ratio of 1 g: 10 mL and then vibrate 2 h at the speed of 200 rpm, with indoor temperature of 18-25 °C. Take the supernate after 24 h of standing through membrane filter of water-phase and the filtrate is the sediment lixivium, which acts as background solution during the toxicity experiment for *Photobacterium phosphoreum* to investigate the toxicity of pesticides under the background environment of sediments.

The determination method refers to GB/T 15441-1995 "Water quality-Determination of the acute toxicity-Luminescent bacteria test". Take the sediment lixivium as background solution, use DXY-2 toxicity analyzer to determine the 15 min luminous inhibitory toxicity of 5 pesticides (dimethoate, malathion, atrazine, prometryn and acetochlor) individually.

Toxic data representation and processing method

Toxic data representation: Use relative luminous intensity or relative luminous inhibition rate to represent, the computational formula is as follows:

$$\text{Relative luminous intensity} = \frac{\text{sample}}{\text{control}} \frac{\text{luminous intensity}}{\text{luminous intensity}} \times 100\ \% \quad (1)$$

$$\text{Relative inhibition rate of luminous intensity (\%)} = 1 - \text{Relative luminous intensity}$$

$$= \frac{\text{control luminous intensity-sample luminous intensity}}{\text{control luminous intensity}} \times 100\ \% \quad (2)$$

The higher is the relative luminous intensity, the less toxicity the sample has, whereas the higher is the relative inhibition rate of luminous intensity, the more toxicity the sample has. In addition, the toxicity to *Photobacterium phosphoreum* can also be expressed by the half effect concentration (EC_{50}). As the value of EC_{50} is relatively low, its negative logarithm to base 10 (-log EC_{50}) is usually applied in literatures.

Toxic data processing: As the dose-response curves of toxicity of pesticides to *Photobacterium phosphoreum* often appear in an "S" shape and because Weibull and Logit models present asymmetric curves with strong applicability, this article applies nonlinear least square method, using Weibull and Logit models to fit the dose-response curve between pesticide concentration and relative inhibition rate of luminous intensity. Specifically, make the curve with the concentration of pesticide (c) as abscissa and the relative inhibition rate of luminous intensity (E) as ordinate, then use the "self-defining function

TABLE-1
MAIN PHYSICAL AND CHEMICAL PROPERTIES AND PARAMETERS OF 5 TYPICAL PESTICIDES

Name	m.f.	m.w.	Vapor pressure (Pa)	Solubility (mg/L)	log K_{ow}	pKa	Pesticide category	Chemical classification	CAS
Dimethoate	$C_5H_{12}NO_3PS_2$	229.2	0.001	39800	0.7	2.0	Insecticide/miticide	Organophosphorus	60-51-5
Malathion	$C_{10}H_{19}O_6PS_2$	330.4	0.00004	145	2.89	-	Insecticide	Organophosphorus	121-75-5
Atrazine	$C_8H_{14}CN_5$	215.7	0.00004	33	2.61	1.7	Herbicide	Triazine	1912-24-9
Prometryn	$C_{10}H_{19}N_5S$	241.4	0.169	33	3.1	-	Herbicide	Triazine	7287-19-6
Acetochlor	$C_{14}H_2ONO_2Cl$	269.8	4.53	223	4.14	Neutral	Herbicide	Amide	34256-82-1

module" in Origin 8.0 to programmable realize the nonlinear least square fitting of the dose-response between pesticide and *Photobacterium phosphoreum*, thus deriving the dose-response curve parameters and fitting model, from which yields the EC_x of each pesticide.

Toxic experimental level selection and calculating method of quantum chemical parameters for pesticides

Experimental factors and level design of single toxicity to *Photobacterium phosphoreum* by 5 pesticides: Select 5 types of pesticides (dimethoate, atrazine, malathion, prometryn and acetochlor) as target objects, using sediment lixiviums to prepare pesticide solutions at different levels. As the solubility of different pesticides varies, the concentration gradients in the preparation procedure differ accordingly. The experimental concentration gradients of each pesticide are shown in Table-2.

Theoretical basis and method of calculating quantum chemical parameters for pesticides: Quantum chemistry is a subject based on quantum mechanics, which utilizes quantum mechanical fundamentals and methods to study on chemical issues and it's an effective mean of researching molecular microscopic properties[11]. Among it, the DFT has achieved great success in theoretical calculation and prediction for thermodynamic properties of environmental pollutants[12-15]. This article employed DFT-B3LYP method with the basis set 6-31G (d) to conduct the structure optimization of 5 pesticide molecules. On the basis of optimum structure, 29 quantum chemical parameters were calculated using Gaussian 09W as descriptors: the total energy (E_{Total} in a.u.), the energy of the lowest unoccupied molecular orbital (E_{lumo} in eV), the energy of the highest occupied molecular orbital (E_{homo} in eV), the frontier molecular orbital energy gap (ΔE in eV), the dipole moment (μ in Debye), the quadrupole moments (Q_{xx}, Q_{yy}, Q_{zz}, Q_{xy}, Q_{xz} and Q_{yz} in Debye-Ang), the polarizabilities (α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz} and α_{zz} in a.u.), the average polarizab ility ($\overline{\alpha}$ in a.u.), the anisotropy of polarizability ($\Delta\alpha$ in a.u.) and the first-order hyperpolarizabilities (β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz} and β_{zzz} in a.u.). The quantum chemical parameters are listed in Table-3.

QSAR model applies the combination of theoretical calculation and statistical analysis to the description of the relationship between molecular structure and biological activity of compounds[16,17]. The QSAR model in this article is established by multiple linear regression, with quantum chemical parameters (X_i) as independent variables and toxicity of pesticides to *Photobacterium phosphoreum* (-log EC_x) as dependent variable. α_i is the coefficient of independent variable, reflecting the load of quantum chemical parameter. Thus, the QSAR model of toxicity of pesticides to *Photobacterium phosphoreum* is as follows:

$$-\log EC_x = \alpha_0 + \alpha_1 \times X_1 + \alpha_2 \times X_2 + \ldots + \alpha_i \times X_i$$

Table-3 shows the correlation analysis between quantum chemical parameters and -log EC_{30} of pesticides.

RESULTS AND DISCUSSION

Toxic characteristics of 5 pesticides to *Photobacterium phosphoreum*

Determination and analysis of single toxicity of 5 pesticides to *Photobacterium phosphoreum*: Take the inhibition rate of luminous intensity of *Photobacterium phosphoreum* by single pesticide for 15 min as toxic effect index; use Weibull and Logit models to fit the dose-response curves between pesticide concentrations and inhibition rate of luminous intensity to *Photobacterium phosphoreum*. The dose-response curves and parameters are shown in Fig. 1 and Table-4, respectively.

The determination coefficient squares (R^2) between the fitting value and experimental value of toxicity of 5 pesticides are no less than 0.9483, which possess remarkable statistical significance. The α-values are within -0.4722 to 0.6494 and their difference shows the toxic diversity of pesticides. The β values are within 0.8038 to 1.4938, indicating the gradient difference of dose-response curves of pesticides, namely the inhibition rate of luminous intensity to *Photobacterium phosphoreum* varies differently as the pesticide concentration increases. Particularly the toxicity of prometryn increases the slowest while the toxicity of malathion increases the fastest. The dose-response curves of 5 pesticides are all in "S" shape, but none of them show a smooth area where the inhibition rate varies slowly, which, could be the result of inappropriate pesticide concentration range selection. Within the selected concentration range, the dose-response curve embody the phase in which the toxicity of pesticide increases rapidly along with the increase of concentration. There is also a "platform" where the inhibition rate of luminous intensity to *Photobacterium phosphoreum* increases slowly as the concentration increases continuously.

It is always the -log EC_{50} value that measures the toxic order of different toxic substances. Therefore, using the curvilinear equation, the EC_{50}s of pesticides are obtained. The -log EC_{50} value is in proportion to the toxicity of pesticides. However, in this article, the toxicity of some pesticides couldn't reach EC_{50} through Weibull and Logit fittings. Thus the value of -log EC_{30} is used as comparative index and the toxic order of 5 pesticides to *Photobacterium phosphoreum* is prometryn > dimethoate > malathion > atrazine > acetochlor.

Substitute all fitting parameters into Weibull and Logit models and the prediction models of single toxicity of 5

TABLE-2
EXPERIMENTAL CONCENTRATION GRADIENTS OF 5 PESTICIDES

Pesticides	Levels (mmol/L)									
	1	2	3	4	5	6	7	8	9	10
Dimethoate	5×10^{-4}	5×10^{-3}	0.01	0.05	0.10	0.20	0.40	0.60	0.80	1.00
Malathion	1×10^{-4}	1×10^{-3}	5×10^{-3}	0.01	0.05	0.10	0.15	0.20	0.30	0.40
Atrazine	1×10^{-5}	5×10^{-5}	1×10^{-4}	1×10^{-3}	0.01	0.02	0.05	0.10	0.12	0.15
Prometryn	1×10^{-4}	5×10^{-4}	1×10^{-3}	0.01	0.02	0.05	0.08	0.10	0.12	0.15
Acetochlor	1×10^{-3}	5×10^{-3}	0.01	0.05	0.10	0.15	0.30	0.45	0.60	0.75

TABLE-3
CORRELATION BETWEEN QUANTUM CHEMICAL PARAMETERS AND –log EC_{30} OF PESTICIDES TO *Photobacterium phosphoreum*

Quantum chemical parameters	Pesticides					r	p
	Dimethoate	Malathion	Atrazine	Prometryn	Acetochlor		
E_{Total}	-1615.97	-1981.64	-1047.28	-1064.51	-1210.93	-0.033	0.958
E_{lumo}	-0.02	-0.02	-0.02	0.00	-0.01	0.220	0.723
E_{homo}	-0.25	-0.23	-0.24	-0.22	-0.24	0.462	0.433
ΔE	0.23	0.22	0.22	0.22	0.23	-0.558	0.328
μ	4.10	6.47	4.06	2.76	6.02	-0.712	0.178
Q_{xx}	-88.79	-145.23	-74.44	-89.86	-115.62	0.309	0.613
Q_{yy}	-89.12	-130.26	-88.83	-96.79	-118.02	0.434	0.465
Q_{zz}	-97.83	-121.81	-91.05	-106.06	-108.21	0.084	0.894
Q_{xy}	14.39	2.23	-0.76	6.18	-11.37	0.806	0.100
Q_{xz}	4.98	4.36	-0.75	-0.41	-1.84	0.366	0.545
Q_{yz}	-7.59	3.51	0.33	-0.57	-0.47	-0.139	0.823
$\bar{\alpha}$	189.23	200.01	147.88	163.98	189.38	-0.311	0.611
$\Delta\alpha$	128.54	110.86	89.86	94.58	121.02	-0.419	0.483
α_{xx}	308.57	239.45	221.23	201.86	224.02	0.031	0.960
α_{xy}	15.27	10.90	14.38	-1.57	9.32	-0.404	0.500
α_{yy}	174.49	225.34	139.48	179.80	239.15	-0.547	0.340
α_{xz}	6.56	-3.90	-7.02	-0.28	6.03	-0.314	0.607
α_{yz}	-9.34	0.11	-2.41	-2.75	-13.96	0.671	0.215
α_{zz}	84.62	135.23	82.94	110.28	104.96	0.039	0.950
β_{xxx}	-4450.27	40.45	-636.59	151.30	-852.40	0.000	1.000
β_{xxy}	696.19	107.32	228.71	429.86	612.11	-0.215	0.728
β_{xyy}	-542.58	407.81	-43.04	-133.54	175.06	-0.407	0.496
β_{yyy}	-223.18	286.53	-235.46	357.11	586.60	-0.366	0.544
β_{xxz}	-696.20	-59.21	-186.48	63.45	-235.22	0.178	0.775
β_{xyz}	289.55	-20.73	-75.65	-10.62	-31.10	0.238	0.700
β_{yyz}	-80.06	-41.93	-36.42	3.32	-133.22	0.889	0.044
β_{xzz}	-289.54	42.73	-13.87	-3.72	4.09	-0.199	0.748
β_{yzz}	35.85	76.78	-31.15	7.11	-38.27	0.472	0.422
β_{zzz}	-98.64	18.78	13.32	82.49	9.40	0.188	0.762

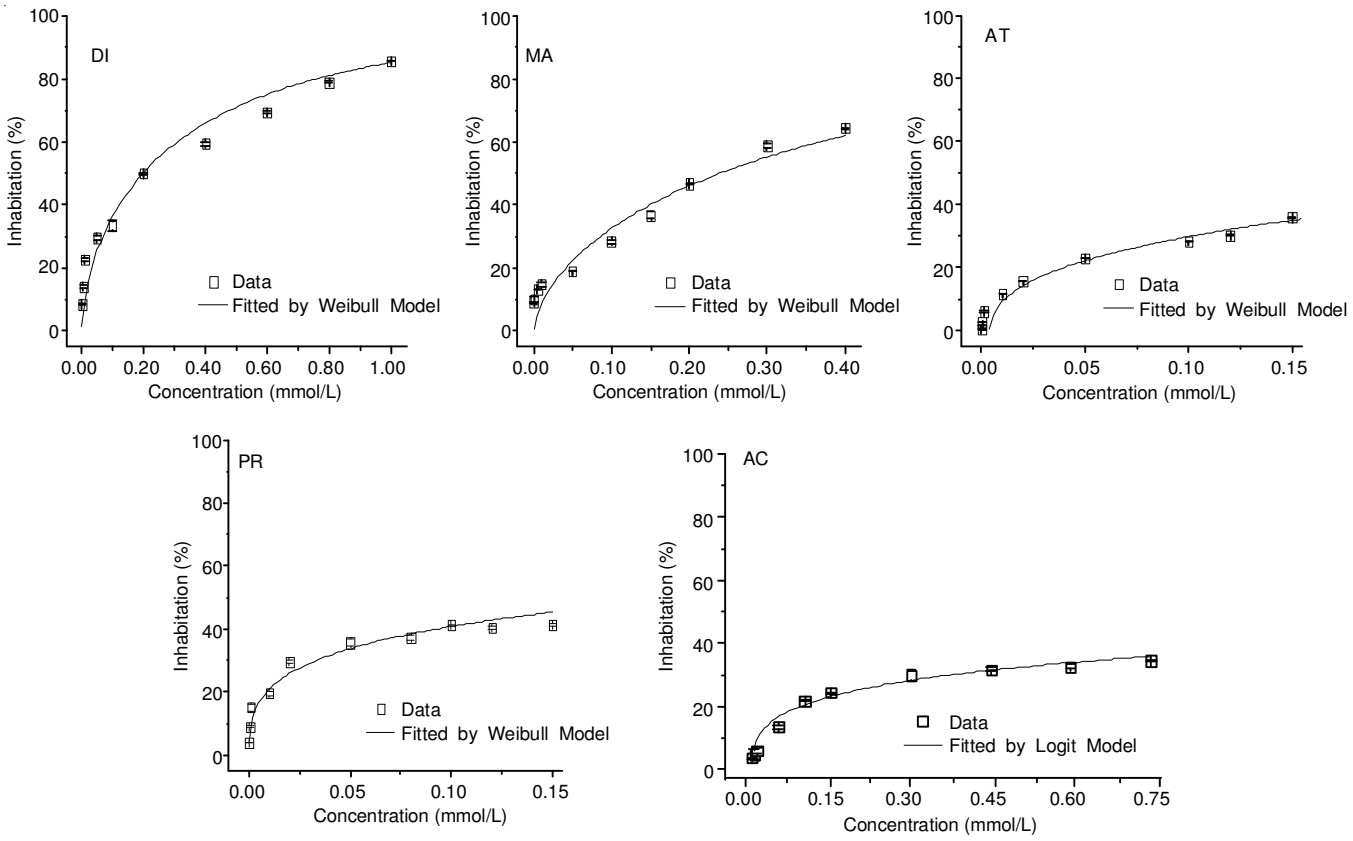

Fig. 1. Dose-response curves (DRCs) of pesticide concentration and relative inhibition rate of luminous intensity to Photobacteriumphosphoreum

TABLE-4
PARAMETERS OF WEIBULL AND LOGIT MODELS FOR SINGLE TOXICITY OF 5 PESTICIDES

Pesticides	Reacting time (min)	Fitting function	α	β	n	R^2
Dimethoate	15	Weibull	0.6494	1.4444	10	0.9918
Malathion	15	Weibull	0.5629	1.4938	10	0.9483
Atrazine	15	Weibull	0.0577	1.0797	10	0.9982
Prometryn	15	Weibull	0.1596	0.8038	10	0.9904
Acetochlor	15	Logit	-0.4722	0.8795	10	0.9812

pesticides to *Photobacterium phosphoreum* are obtained, which have certain toxicity prediction effect for the pesticides in the experimental concentration range.

Dimethoate: $E = 1\text{-}\exp(-\exp(0.6494 + 1.4444 \times \log c))$ (3)

Malathion: $E = 1\text{-}\exp(-\exp(0.5629 + 1.4938 \times \log c))$ (4)

Atrazine: $E = 1\text{-}\exp(-\exp(0.0577 + 1.0797 \times \log c))$ (5)

Prometryn: $E = 1\text{-}\exp(-\exp(0.1596 + 0.8038 \times \log c))$ (6)

Acetochlor: $E = 1/(1 + \exp(-0.4722\text{-}0.8795 \times \log c))$ (7)

QSAR model between the single toxicity of 5 pesticides to *Photobacterium phosphoreum* and their quantum chemical parameters

Establishment of the QSAR model: Conduct a multiple linear regression by SPSS 20.0, with 29 quantum chemical parameters calculated by Gaussian09 W as independent variables and -log EC_{30} values of 5 pesticides as dependent variable, using the stepwise method. The QSAR model achieved is as follows:

$$-\log EC_{30} = 1.417 + 0.007\beta_{yyz} + 0.001\beta_{xyz} \quad (8)$$

Model test: The sample number of model (8) is 5. Table-5 shows R = 0.995, $R^2 = 0.989$, $R_{adj}^2 = 0.978$, SE = 0.0559, that this model has a good correlation.

TABLE-5
GOODNESS OF FIT TEST FOR THE ESTABLISHED QSAR MODEL

R	R^2	R_{adj}^2	SE
0.995	0.989	0.978	0.0559

Table-6 shows the degree of freedom of F-distribution is (2, 2). Given the significance level $\alpha = 0.05$, $f_{0.95}(2, 2) = 19.000$, $F = 91.99 > f_{0.95}(2, 2)$ and $p = 0.011 < 0.05$, so this regression equation is considered to pass the test of significance.

TABLE-6
F–TEST FOR THE ESTABLISHED QSAR MODEL

Model	Sum of squares	df	Mean square	F	p
Regression	0.575	2	0.288	91.999	0.011
Residual error	0.006	2	0.003	-	-
Total	0.581	4	-	-	-

Table-7 shows the significant correlation between the -log EC_{30} and the first-order hyperpolarizabilities β_{yyz} and β_{xyz}, while β_{yyz} plays the leading role according to their standard coefficients. The single toxicity of 5 pesticides to *Photobacterium phosphoreum* increases along with β_{yyz} and β_{xyz}.

The variance inflation factor (VIF) evaluates the degree of correlation between independent variables of an equation and it's defined as $VIF = 1/(1\text{-}R^2)$. VIF = 1 means there is no autocorrelation between independent variables, VIF = 1-5 means the autocorrelation between independent variables is small and the regression equation is acceptable. VIF > 10 means the regression equation is unstable and unacceptable[18]. The VIFs of the regression equation in this article are both 1.052, which means there is no autocorrelation between independent variables and the regression equation is acceptable.

The leave-one-out (LOO) cross-validation coefficient R_{cv}^2 represents the robustness and predictive ability of a model. It is usually think that $R_{cv}^2 > 0.5$ then the model has strong robustness and predictive ability[19]. The R_{cv}^2 of the regression equation in this article is 0.547 and the regression equation is acceptable.

In conclusion, the QSAR model established in this article reveals how the structural factors of pesticide affects the single toxicity to *Photobacterium phosphoreum*.

Conclusion

The single toxicity of 5 typical pesticides in sediment lixivium to *Photobacterium phosphoreum* could be well expressed by Weibull and Logit models and the determination coefficient squares (R^2) are no less than 0.9483. The toxicity order is follows: prometryn > dimethoate > malathion > atrazine > acetochlor, which shows different growth trends of pesticides toxicity to *Photobacterium phosphoreum* as the pesticide concentration increases.

To reveal the toxic mechanism of single pesticide at molecular level, 29 quantum chemical parameters of 5 pesticide molecules was calculated by DFT-B3LYP method with the basis set 6-31G (d), which acted as theoretical descriptors. The QSAR model for inhibition rate of luminous intensity by single pesticide was established by multiple linear regression, with the R = 0.995, $R^2 = 0.989$, $R_{adj}^2 = 0.978$, SE = 0.0559. The F-test and *t*-test afterwards indicated that the first-order

TABLE-7
t–TEST FOR THE ESTABLISHED QSAR MODEL

Model	Unstandardized coefficients		Standard coefficients	t	p
	Γ_i	Standard deviation			
Constant	1.417	0.040		35.385	0.001
β_{yyz}	0.007	0.001	0.992	13.188	0.006
β_{xyz}	0.001	0.000	0.452	6.018	0.027

hyperpolarizabilities β_{yyz} and β_{xyz} have significant influence on the single toxicity of 5 pesticides and they are in positive correlation with the inhibition rate of luminous intensity for *Photobacterium phosphoreum*. Specifically, β_{yyz} plays a dominant role in controlling pesticide toxicity.

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