Investigation of Combined Pollution between Malathion and a Variety of Pollutants Based on the Fractional Factorial Design (Resolution IV)

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Abstract

In order to reveal the combined pollution characteristics of malathion adsorption onto the surficial sediments with pesticides (dimethoate, metalaxyl, atrazine, malathion, prometryn) and heavy metals (Cu, Zn, Pb, Cd, Ni) present, a 2^{10-5} fractional factorial design of resolution IV was employed to identify non-interactive effects and two-way interactions of the chosen factors on malathion adsorption. The missing values of malathion adsorption in the experiment were approximated using the algorithm of back propagation neural network. It was found that Zn (13.69%), atrazine (8.76%), and metalaxyl (5.99%) have significant positive effect (α=0.05) on the malathion adsorption; 44.92% of the total contribution to malathion adsorption came from the non-interactive effects, while 55.08% was from the two-way interactions (Cu×metalaxyl, Zn×atrazine, Cu×prometryn, Pb×Cu, Cu×atrazine, and Cu×Ni). Notably in the two-way interactions, Zn×atrazine (12.93%) and Cu×prometryn (5.97%) have a strong synergistic effect on malathion adsorption, while Pb×Cu (15.80%), Cu×atrazine (7.82%), Cu×metalaxyl (6.63%), and Cu×Ni (5.93%) present intense antagonisms to malathion adsorption. The whole philosophy could be used as a new methodology in accessing the degree of combined pollution and the effect of multiple pollutants on the selected pollutants.

Keywords: malathion, surficial sediments, combined pollution, fractional factorial design, interactive effect

Introduction

With the rapid development of industry and agriculture, pollution problems have become increasingly prominent [1]. Pesticides and heavy metals discharged into the environment are cumulative [2, 3], which has caused serious pollution to the atmosphere [4], water [5], and soil [6], and threatens the health of animals, plants, and humans [7, 8]. We rarely find only one pollutant or sole pollution in our environment, and combined pollution is most likely in every case [9]. Combined pollution would further pollute the environment because the co-existence of pollutants has changed their environmental behavior and eco-toxicity by the interaction effect [10]. Along with the change of environment, pollutants in the environment migrate in a certain environmental medium or between different environmental

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media [11]. Combined pollution could change the pollutants' migration pathways and their biological effect [12], with Pbs to the combined pollution among pesticides [13], heavy metals, and other pollutants being a key issue of concern to researchers for a long time [14].

Surficial sediment as an important carrier in migration of many pollutants in natural water is also a main destination of pollutants in the water [15]. It can gather a variety of heavy metals, pesticides, and other pollutants from the water environment [16]. Therefore, scholars from various countries have made a lot of research to study the adsorption behavior of heavy metals and pesticides in the water-sediment environment [17], including the content study on pesticides and heavy metals in different regional sediments [18], the mechanism analysis of pollutants' adsorption onto sediments [19], and adsorption mechanism analysis of pollutants onto the sediments under combined pollution cases. David et al. studied the interacting effects of pH, phosphate, and time on the release of arsenic from As-rich riverbed sediments. Arsenic release edges and kinetic release experiments, in the absence and presence of phosphate, coupled with sequential extraction procedures, SEM/EDX analyses, and geochemical calculations, were carried out to evaluate and to elucidate the mechanisms involved [20]. Guo et al. measured the effects of Cr (VI) and As (V) on lindane sorption. Results show that more lindane is adsorbed by biofilms than by suspended particles and sediments on a total mass basis, whereas the sediments had a higher lindane sorption capacity per unit mass organic carbon than suspended particles and biofilms. Co-occuring Cr (VI) or As (V) decreased lindane sorption on the biofilms by about 48% [21].

Organophosphorus pesticides have the advantages of being economic, effective, and convenient, and they are widely used in prevention and control of plant diseases and pests of agriculture [22, 23]. Some kinds of the non-durable organophosphorus pesticides also have a longer survival period in certain environmental conditions and would accumulate in the animal body [24]. Malathion is an organophosphorus pesticide with highly selective features [25]. It is a highly toxic pesticide for aquatic organisms and the human immune system [26], and it is an important monitoring project in the water environment. A study shows that its residue has been detected in water bodies [27].

At this point, the biggest challenge is how to reveal the combined pollution mechanism from their adsorption process onto the surficial sediments. Wang et al. used a fractional factorial design of resolution III method to explore the combined pollution rules of Zn and atrazine onto surficial sediments [28]. But it didn't show a clear effect from the non-interactive pollutant and the two-way interactions among different pollutants.

In this study, we used a 2^{10-5} fractional factorial design of resolution IV method and a multiple linear regression adsorption model to reveal the composite contaminations characteristic of malathion adsorption onto the surficial sediments in a contamination system composed by pesticides (dimethoate, metalaxyl, atrazine, marathon, and prometryn) and heavy metals (Cu, Zn, Pb, Cd, and Ni).

It would provide a theoretical support for revealing the combined pollution mechanism between pesticides and heavy metals. In addition, the back propagation (BP) neural network was applied for predicting the missing values of malathion adsorption in the experiment [29].

Experiments and Methods

Reagents and Apparatus

The malathion used was 99.5% pure in the experiments and it was supplied by the Agro-environmental Protection Institute of China's Ministry of Agriculture. Methanol with HPLC (SHIMADZU, model: LC20A) grade was purchased from Fisher Co. USA. All other chemicals were of analytical grade. Deionized water was used for all experiments.

The Collection and Pre-Treatment of Sediment Samples

Wang et al. (one member of our research group) already revealed the combined pollution characteristic of zinc adsorption onto the surficial sediments [30]. Considering the continuity of the study, we selected the same sediment sampling site: the Songhua River in Jilin, China. Samples were dug by a type sampler, and the sampling depth was sediment surface layer (0-5 cm). Every sample was made by mixing four samples taken from 20 cm around the sampling point. Then all samples were mixed and combined uniformly as a sample. After the sample dried, and plant and animal residues (i.e. gravel, wood chips, weeds, and other debris) removed, the sediment samples were packed in plastic bags. Then the samples would be transferred into the laboratory as soon as possible, dried at room temperature, and ground with a mortar pestle. The final step was letting the sample dry in a cool ventilated place, refrigerated or lyophilized at 4ºC.

Experimental Methods and Design

The module (Design of Experimental) in Minitab software package was adopted in experimental design and statistical analysis. In this experiment, representative heavy metals (Pb, Cu, Zn, Cd, and Ni) and pesticides (dimethoate, metalaxyl, atrazine, marathon, and prometryn) were selected as study factors, and malathion was chosen as the target pollutant factor. This study used a 2^{10-5} fractional factorial design of resolution IV with low order confounding. Concentrations for the pollution factor must reach the detection limit, and must be under the solubility of solution. Therefore, the pollution factor levels were determined through the preliminary experiment. Factor levels are shown in Table 1. Thirty-two experiments were taken as a unit, and the parallel sample experiment was set up. Through the statistical analysis software (Minitab), a 2^{10-5} fractional factorial design table (Table 2) was summarized. Based on the principles of fractional factorial design in

Table 1. The high and low levels of five heavy metals and five pesticides (µmol/L).

Select level (µmol/L)	Dimethoate	Metalaxyl	Atrazine	Malathion	Prometryn
Low level (-)	10	10	10	10	10
High level (+)	25	25	25	25	25
Select level (µmol/L)	Cu	Zn	Pb	Cd	Ni
Low level (-)	60	60	60	60	60
High level (+)	150	150	150	150	150

Table 2. The 2^{10-5} fractional factorial design of ten pollutants adsorbed onto the sediments.

	Cu	Zn	Pb	Cd	Ni	Atrazine	Malathion	Prometryn	Dimethoate	Metalaxyl
1	1	1	1	1	1	1	1	1	1	1
2	-1	-1	1	-1	-1	-1	-1	1	-1	-1
3	1	1	-1	1	-1	-1	1	-1	1	1
4	1	1	-1	-1	-1	1	1	1	-1	-1
5	1	-1	1	-1	-1	1	1	-1	1	-1
6	-1	1	1	1	-1	-1	1	1	1	-1
7	1	1	-1	1	1	-1	-1	1	-1	-1
8	1	-1	1	1	1	-1	-1	-1	1	-1
9	-1	-1	1	1	-1	1	-1	-1	1	1
10	-1	1	-1	1	-1	1	-1	1	-1	1
11	1	1	-1	-1	1	1	-1	-1	1	1
12	-1	1	-1	-1	-1	-1	-1	-1	1	-1
13	1	-1	1	-1	1	1	-1	1	-1	1
14	1	-1	1	1	-1	-1	1	1	-1	1
15	1	-1	-1	1	-1	1	-1	1	1	-1
16	-1	-1	1	-1	1	-1	1	-1	1	1
17	-1	1	1	-1	-1	1	1	-1	-1	1
18	-1	-1	-1	1	-1	-1	1	-1	-1	-1
19	-1	1	-1	-1	1	-1	1	1	-1	1
20	-1	1	-1	1	1	1	1	-1	1	-1
21	-1	1	1	-1	1	1	-1	1	1	-1
22	-1	-1	-1	-1	-1	1	1	1	1	1
23	1	1	1	-1	-1	-1	-1	1	1	1
24	-1	1	1	1	1	-1	-1	-1	-1	1
25	1	-1	-1	-1	1	-1	1	1	1	-1
26	-1	-1	1	1	1	1	1	1	-1	-1
27	1	1	1	-1	1	-1	1	-1	-1	-1
28	1	-1	-1	-1	-1	-1	-1	-1	-1	1
29	-1	-1	-1	-1	1	1	-1	-1	-1	-1
30	1	1	1	1	-1	1	-1	-1	-1	-1
31	1	-1	-1	1	1	1	1	-1	-1	1
32	-1	-1	-1	1	1	-1	-1	1	1	1

Minitab software and through the interactions of Pb, Cu, Zn, prometryn, and marathon, and the form of generating element, the concentration levels of Cd, Ni, atrazine, metalaxyl, and dimethoate were listed as follows (we used "×" to express the two-way interaction in the equation):

Cd = Pb×Cu×Zn×prometryn
Ni = Pb×Cu×Zn×malathion
atrazine = Pb×Cu×prometryn×malathion
metalaxyl = Pb×Zn×prometryn×malathion
dimethoate = Cu×Zn×prometryn×malathion

The concentrations of 10 different kinds of pollutant solution were mixed according to the corresponding requirements of randomized trial in Table 2. Twenty ml solutions were extracted from mixed solutions of 64 groups and were separately fitted to 64 conical flasks containing 0.5000±0.0001 g sediment samples. After oscillation for 48 h, mixed solutions were filtered with 0.22 μm filter paper. Levels of malathion in the solution before and after adsorption were measured by HPLC, and the adsorption amount of malathion was calculated by subtraction, i.e., the adsorption amount of malathion calculated by the subtraction including the soil background values, and the effects of soil background values on the experimental results were avoided.

It can be seen from *Design and Analysis of Experiments* written by Douglas C. Montgomery, that the priority is to investigate the interaction effect of low order, a principle of statistics [31]. When the factor is too much, interactions more than two-way could be ignored. This premise can reduce the number of experimental groups and improve efficiency and accuracy. Without considering the interactions more than two-way, there is no alias for the non-interaction effects in the fractional design of resolution IV. But the two-way interactions had an alias as follows:

Pb×Cu = metalaxyl×dimethoate
Pb×Zn = atrazine×dimethoate
Pb×prometryn = Ni×dimethoate
Pb×malathion = Cd×dimethoate
Pb×Cd = malathion×dimethoate
Pb×Ni = prometryn×dimethoate
Pb×atrazine = Zn×dimethoate
Pb×metalaxyl = Cu×dimethoate
Pb×dimethoate = Cu×metalaxyl = Zn×atrazine =
      prometryn ×Ni = malathion×Cd
Cu×Zn = atrazine×metalaxyl
Cu×prometryn = Ni×metalaxyl
Cu×malathion = Cd×metalaxyl
Cu×Cd = malathion×metalaxyl
Cu×Ni = prometryn×metalaxyl
Cu×atrazine = Zn×metalaxyl
Zn×prometryn = Ni×atrazine
Zn×malathion = Cd×atrazine
Zn×Cd = malathion×atrazine
Zn×Ni= prometryn×atrazine
prometryn×malathion = Cd×Ni
prometryn×Cd = malathion×Ni

It could be seen from the above alias structure of interactions that two-way interactions of fractional factorial design of resolution IV were fewer and more conducive to

estimate than that of resolution III, which includes supplementary experiments (completely folded experiments and block experiments).

The Prediction of Missing Data about Malathion Concentration

Models of BP neural network have been used to approximate the missing value of marathon concentration in solution. The results of the experiment were divided into two groups: 55 samples (80%) were used for neural network model training and the remaining 12 samples (20%) were used as a verification sample to test the results of the model prediction. The number of hidden layer nodes was determined to be 50 by the dynamically constructed method. The minimum target error of 0.01 was selected through several preliminary experiments. The LM Bayesian regularization algorithm was adopted to train the model after normalizing data [32, 33]. The model achieved target error after 16 steps of training.

The remaining 12 groups of data were chosen as the verification sample to test the model. The correlation coefficient r between the simulated value (from BP neural network) and measured values was 0.821 (> 0.80) and the bias was 0.37, indicating that the result of neural network model simulations had high accuracy and the model simulation result was reliable. As is shown in Table 3, the predicted missing data font was bolded.

Results and Analysis

Selection and Fit-Tested for Fixed Effect Model

Because the levels of all experimental factors (fixed factors) were controllable, the fixed effects model of Minitab was adopted to do variance analysis on the non-interactive effects and two-way interactions of pollutant factors [34]. Firstly, the residual analysis module in Minitab software package was selected to fit the model. Then, variance analysis was used on the non-interactive effects and two-way interactions. Finally, the results of variance analysis would demonstrate whether they have a significant effect on the adsorption of malathion in sediment (significance level α = 0.05). Structure of the fixed effect model was chosen as follows:

$$y_{ijk}=\mu+\tau_i+\beta_j+(\tau\beta)_{ij}+\delta_k+\varepsilon_{ijk} \qquad (1)$$

...where τ_i and β_j denote main effects of two different pollutants, respectively; $(\tau\beta)_{ij}$ was the two-way interactions effect; i and j represented the levels of two different pollutants, respectively; δ_k denoted the effect of the k block; ε_{ijk} was the random error component of the model, which merged the other sources of variation in the experiment; y_{ijk} was experimental testing value of the target pollutant.

Before using a fixed effects model, a fit test (i.e. normal assumption, independence assumption of residuals, and

Table 3. The measured and predicted data for initial and equilibrium concentration of malathion in adsorption.

Class number	Equilibrium concentration I	Equilibrium concentration II	Initial concentration
1	3.174	3.397	4.101
2	1.535	1.445	1.536
3	3.065	2.726	3.913
4	2.653	3.197	4.422
5	2.769	3.115	3.410
6	3.382	3.793	4.109
7	1.955	**1.170**	**2.272**
8	**3.797**	**3.864**	**3.962**
9	**1.168**	**1.208**	1.863
10	**1.708**	1.484	2.681
11	**2.057**	**2.307**	**2.909**
12	**2.378**	**2.415**	**2.515**
13	1.115	**1.128**	1.172
14	1.802	1.863	2.915
15	1.048	1.232	**1.665**
16	2.730	3.473	4.134
17	1.864	1.973	3.422
18	2.139	2.370	2.684
19	3.294	3.142	3.800
20	2.436	3.063	3.643
21	1.661	1.875	2.726
22	2.602	2.519	2.884
23	0.743	0.790	0.896
24	0.497	**0.502**	1.220
25	1.873	2.355	2.884
26	2.509	3.011	3.522
27	**1.728**	**1.527**	**2.181**
28	**0.401**	0.591	1.168
29	**0.504**	0.469	0.603
30	**2.140**	**2.102**	**2.665**
31	**2.084**	**1.902**	**2.589**
32	**0.824**	**0.810**	**0.878**

The bold text is the predicted data for initial and equilibrium concentration of malathion in adsorption.

homogeneity assumption of the variance) was carried out [35]. Only if the model meets the above conditions would it be suitable. The residual was the difference between the values from experiment and model estimation. The residual testing module in the Minitab software was used in inspection and the test results are shown in Fig. 1.

Table 4. Analysis of variance of non-interactive effects and two-way interactions of the pollutant facts concentrations affecting malathion in the sorption of heavy metals and pesticide system.

Source	DOF	Seq SS	Adj MS	F	P
Non-interactive effects	10	1.6346	0.1634	8.87	0.000
Two-way interactions	21	1.8379	0.0875	4.75	0.000
Residual error	32	0.5895	0.0184	-	-
Pure error	32	0.5895	0.0184	-	-
Total	63	4.0620	-	-	-

In normal probability plot and histogram of residual, there is no abnormal point that deviated from the normal distribution, which satisfied the normality assumption of the model. Meanwhile, there was no positive or negative residual in the sequence of the residuals diagram, indicating that there was no violation in the assumption of independence in the model. It was also found that residuals and fitted values had no obvious pattern in fitted values of the residuals plot, which met homogeneity assumption of the variance. The residuals analysis showed that the fixed effects model could be used to make proper variance analysis for non-interactive effects and two-way interactions.

Simulation Analysis and Conclusion

Screening and Analysis for Significant Impact Pollutants

Effect estimation and variance analysis of the concentration level for each pollutant (heavy metals and pesticides in the system) on malathion adsorption onto the sediment was made. The factors that had significant influence were filtrated under significance level $\alpha=0.05$. Analyses of variances are shown in Table 4, and effect estimates are presented in Table 5.

The result of variance analysis in Table 4 showed that P value of the non-interactive effects and two-way interactions was much lower than the significance level of 0.05. Thus the non-interactive effects and two-way interactions of 10 pollutants had a significant influence on malathion adsorption onto the sediment as a whole. As can be seen in Table 5, non-interactive effects of the pollutants that had a significant influence were malathion=0.2111, Zn=0.1753, atrazine=0.1121, and metalaxyl=0.1767. They all will promote malathion adsorption onto the sediment. Obviously, the most striking impact on malathion adsorption was Zn. Gao's study about competitive adsorption of organic pesticides onto the sediment showed that the adsorption of non-polar organic pesticides onto the sediment was inversely proportional to its solubility [36]. It is very likely that the presence of Zn could affect the solubility of malathion in water.

It also can be seen from Table 5 that the two-way interactions had a significant impact on malathion adsorption onto the sediments. The related data are listed in detail below:

Cu×Pb = -0.2023
Zn×atrazine = 0.1656
Cu×atrazine = -0.1001
Cu×prometryne = 0.0764
Cu×metalaxyl = -0.0849
Cu×Ni = -0.0759

There are four two-way interactions (Cu×Pb, Cu×atrazine, Cu×metalaxyl, and Cu×Ni) which showed antagonistic effects on malathion adsorption onto the sediment. On the contrary, the others showed synergistic effects.

The Contribution Rate of Non-Interactive Effects and Two-Way Interactions on Malathion Adsorption

The pollutants that have significant non-interactive effects and two-way interaction effects were extracted. The degree of the effects and contribution rates for malathion adsorption are estimated and listed in Table 6. The formula used for calculating the contribution rate was as follows:

$$C \text{ (contribution rate)} = [E \text{ (effect estimated)} \div (\textstyle\sum E)] \times 100\% \quad (2)$$

From Table 6, the total contribution rate of synergy effects from non-interactive effects and two-way interactions on malathion adsorption was 63.82%; while the total antagonisms contribution rate was 36.18%. The contribution rate of Zn's synergy was 13.69%, which has the largest contribution rate except for malathion among all pollutants. In addition, the antagonism contribution rate of Cu×Pb for two-way interaction on malathion adsorption onto the sediment was 15.80%, which could provide guidance in controlling malathion adsorption onto the sediments.

Conclusions

The fractional factorial design of resolution IV could effectively distinguish the mixed phenomenon of non-interactive effects and two-way interactions, and it largely reduced the complexity fractional factorial design of resolution III (completely folded), and eliminated the interference from block effects. The missing values of malathion adsorption in the experiment were solved through the
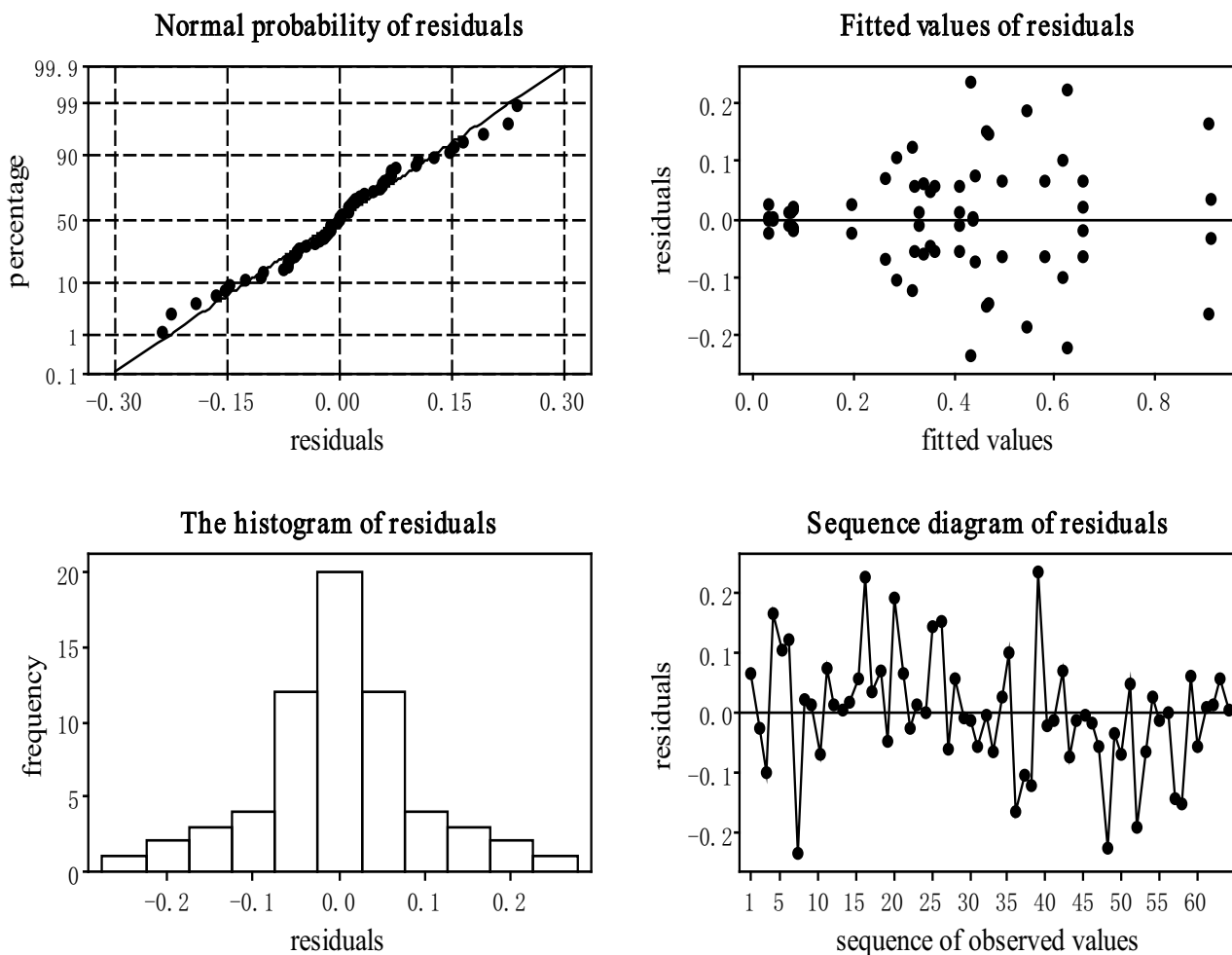

Fig. 1. The fit test of the model of ten pollutants adsorbed onto the sediments.

Table 5. The estimates of non-interactive effects and two-way interactions of the pollutant facts concentrations affecting malathion in the sorption of heavy metals and pesticide system.

Item	Effect estimates	Coefficient	Standard error of coefficient	P
Constant	0.3805	0.01697	22.43	-
Cu	0.0174	0.0087	0.01697	0.611
Zn	0.1753	0.0877	0.01697	**0.000**
Pb	-0.0049	-0.0024	0.01697	0.887
Cd	0.0386	0.0193	0.01697	0.263
Ni	-0.0437	-0.0219	0.01697	0.207
Atrazine	0.1121	0.0560	0.01697	**0.002**
Malathion	0.2111	0.1056	0.01697	**0.000**
Prometryn	-0.0106	-0.0053	0.01697	0.756
Dimethoate	-0.0674	-0.0337	0.01697	0.056
Metalaxyl	0.0767	0.0384	0.01697	**0.031**
Cu×Zn	-0.0469	-0.0235	0.01697	0.176
Cu×Pb	-0.2023	-0.1012	0.01697	**0.000**
Cu×Cd	0.0032	0.0016	0.01697	0.925
Cu×Ni	-0.0759	-0.0379	0.01697	**0.032**
Cu×Atrazine	-0.1001	-0.0500	0.01697	**0.006**
Cu×Malathion	0.0397	0.0198	0.01697	0.251
Cu×Prometryn	0.0764	0.0382	0.01697	**0.031**
Cu×Dimethoate	-0.0175	-0.0087	0.01697	0.610
Cu×Metalaxyl	-0.0849	-0.0424	0.01697	**0.018**
Zn×Pb	-0.0621	-0.0310	0.01697	0.077
Zn×Cd	-0.0206	-0.0103	0.01697	0.547
Zn×Ni	0.0093	0.0047	0.01697	0.785
Zn×Atrazine	0.1656	0.0828	0.01697	**0.000**
Zn×Malathion	-0.0299	-0.0150	0.01697	0.384
Zn×Prometryn	0.0273	0.0136	0.01697	0.427
Pb×Cd	0.0001	0.0001	0.01697	0.997
Pb×Ni	0.0479	0.0239	0.01697	0.168
Pb×Atrazine	0.0057	0.0028	0.01697	0.869
Pb×Malathion	0.0524	0.0262	0.01697	0.132
Cd×Ni	-0.0462	-0.0231	0.01697	0.183
Cd×Atrazine	-0.0197	-0.0098	0.01697	0.566

The bold text is the pollution factor which has a significant impact on malathion adsorption onto the sediments.

method of the BP neural network. Based on this experimental design and combined with the fixed effects model, we screened the pollutants with significant non-interaction effects and two-way interactions on the target contaminants (malathion). According to the result, the total synergy contribution rate of non-interactive effects and two-way interactions on malathion adsorption onto the sediment was 63.82%. The contribution rate of Zn's synergy was 14.7%, which was the highest contribution rate except malathion among all pollutant factors. The total negative contribution rate was 36.18%, and the highest antagonism contribution rate among all two-way interactions was Cu×Pb 16.9%.

Table 6. The contribution rates of the facts with a significant impact to malathion adsorption onto the sediments.

Factor	Effect estimates	Rate of contribution	
		synergy	antagonism
Malathion	0.2111	16.49%	-
Zn	0.1753	13.69%	-
Atrazine	0.1121	8.76%	-
Metalaxyl	0.0767	5.99%	-
Cu×Pb	-0.2023	-	15.80%
Cu×Metalaxyl	-0.0849	-	6.63%
Zn×Atrazine	0.1656	12.93%	-
Cu×Atrazine	-0.1001	-	7.82%
Cu×Prometryn	0.0764	5.97%	-
Cu×Ni	-0.0759	-	5.93%
Total	-	63.82%	36.18%

Acknowledgements

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