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Occurrence Characteristics and Ecological Risk Assessment of Organophosphorus Compounds in a Wastewater Treatment Plant and Upstream Enterprises

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Abstract: Organophosphorus compounds have toxic effects on organisms and the ecosystem. Therefore, it is vital to monitor and control the effluent organophosphorus levels of wastewater treatment plants (WWTPs). This study analyzed the composition and concentration of organophosphorus compounds from the upstream enterprises of a WWTP and conducted ecological risk and toxicity assessments using ECOSAR (ecological structure activity relationship model), T.E.S.T (Toxicity Estimation Software Tool), and risk quotient (RQ) methods. A total of 14 organic phosphorus pollutants were detected in the effluent of the upstream enterprises and WWTP. The concentration of influent total organic phosphorus from the WWTP was 39.5 mg/L, and the effluent total organic phosphorus was merely 0.301 mg/L, indicating that good phosphorus removal was achieved in the WWTP. According to the acute and chronic toxicity analysis, the ECOSAR ecotoxicity assessment showed that 11 kinds of organophosphorus compounds were hazardous to fish, daphnia, and algae in different degrees. Among them, triphenyl phosphine (TPP) had a 96 hr LC50 of 1.00 mg/L for fish and is a substance with high acute toxicity. T.E.S.T evaluates the acute toxicity of each organophosphorus component and the bioconcentration factor (BCF). The evaluation results showed that the LC50 of TPP and octicizer were 0.39 and 0.098 mg/L, respectively, and the concentrations of these two organophosphorus compounds from the effluent of an environmental protection enterprise were as high as 30.4 mg/L and 0.735 mg/L, which exceeded the acute toxicity values and has led to serious hazards to aquatic organisms. The BCF values of each organophosphorus component in the upstream enterprises and the effluent of the WWTP were less than 2000, implying that there was no bioaccumulation effect on aquatic organisms. The developmental toxicity assessment demonstrated that there were nine types of organophosphorus compounds belonging to developmental toxicants, that the presence of developmental toxicants was found in the effluent of each upstream enterprise, and that triethyl phosphate (TEP) was the most common organophosphorus compound. Comparing the RQ of the effluent from various enterprises, it was found that the effluent from the environmental protection enterprise presented the highest degree of environmental hazard, mainly due to the higher toxicity of TEP and octicizer.

Keywords: organophosphorus; ecological risk; bioconcentration factor (BCF); developmental toxicity; risk quotient (RQ); upstream enterprises

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1. Introduction

With rapid social development, water bodies are subjected to increasingly serious phosphorous pollution [1]. Phosphorous is widely used as a raw production material in food, pesticides, fertilizers, and fire retardants, and it enters the phosphorus cycle of human society in the form of phosphorite mining [2]. Meanwhile, the phosphorous content in water bodies increases due to the excessive application of pesticides and fertilizers, the afflux of domestic sewage, and the discharge of industrial wastewater [3]. Studies showed that when the total phosphorous concentration in a water body exceeds 0.02 mg/L, eutrophication can be triggered, thereby posing potential threats to the aquatic ecosystem [4]. Therefore, controlling the concentration of organophosphorus compounds in water bodies is important for the safety of aquatic ecosystems. Organophosphorus compounds are an important constituent part of total phosphorous in the environment. In recent years, more organophosphorus compounds have entered human society because of the rapid development of the phosphorous chemical industry. Organophosphorus flame retardants (OPFRs) are used to produce foams, coatings, and textiles, and organophosphorus pesticides (OPPs) have been adopted to ensure disease resistance and increase crop yield. OPFRs are a family of chemicals that have become a re-emerging environmental issue. Tris-b-chloroethyl phosphate (TCEP), phosphoric acid tris (2-chloro-1-methylethyl) ester (TCPP), tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP), and triphenyl phosphate are used in flexible and rigid polyurethane foams, plastics, and textiles [5,6]. Municipal landfill leachate is an important source of contamination of OPFRs in the aquatic environment. The range of total OPFR concentrations across China was measured as 29.0–437 and 0.652–32.4 mg/μL in raw and final leachates, respectively, and the annual emissions of OPFRs discharged were estimated to be between 170 and 7094 g [7,8]. Studies have revealed that OPFRs can: (1) transfer among soil–atmosphere–water through volatilization, leaching, and deposition during production and use; (2) accumulate in living organisms via skin exposure, ingestion, and inhalation; and (3) induce all kinds of diseases [9,10]. The P=S or P=O groups in most OPPs can generate neurotoxicity by repressing acetylcholine esterase, thereby harming animals and the human body considerably [11]. Hence, the concentration of organophosphorus compounds in the effluent of WWTPs should be stringently monitored and controlled.

Owing to the phosphorus removal technique centering on biological–chemical synergy in WWTPs, the phosphate content in the total phosphorus of the effluent is relatively low; however, it is difficult for traditional activated sludge systems to effectively remove most organophosphorus compounds. The absorption capacity of powdered activated carbon, which has shallow pores and many exposed active sites, for triphenyl phosphate (TPP) can reach as high as 467.6 mg·g^{-1}, which is double that of granular activated carbon [12]. Under alkaline conditions, many $OH-$ can enhance the hydroxylation effect of the photocatalyst surface, promoting the generation of more ·OH to improve the photochemical reaction rate and facilitate the decomposition effect of organophosphorus compounds [13]. Compared with the removal effect of activated carbon catalysts solely loaded with ozone and those loaded with both ozone and ferrihydrite on the organophosphorus pesticide omethoate, it was found that ferrihydrite nanoparticles can serve as the main active sites of ozonolysis to promote the transformation of ozone in the aqueous phase into ·OH, thereby accelerating the degradation of omethoate [14]. The electrochemical oxidation method [15–17] can effectively realize the transformation of organophosphorus compounds; however, owing to the diversity and complexity of upstream enterprises of WWTPs, there are a wide variety of organophosphorus compounds in the effluent in high concentrations. Therefore, controlling and removing organophosphorus compounds is complicated for WWTPs, and monitoring the varieties and concentrations of organophosphorus compounds in the wastewater discharged by upstream enterprises is of great significance to the practical operation of WWTPs.

After inorganic phosphorus is lowered to the limiting level through advanced treatment, the residual organophosphorus components constitute another important problem harming aquatic organisms and algae [18]. The organophosphorus compounds in sewage influences algae and other organisms differently because of the differences in the morphology and category of organophosphorus components [19]. Studies have shown that organophosphorus insecticides generate a toxic effect on aquatic phytoplankton; pyridaphenthione can significantly inhibit the cell growth, chlorophyll content, and the activity of photosynthesis-related enzymes in two blue-green algae Anabaena laxa and Nostoc muscorum [20]; and acephate can evidently destruct the antioxidant system of freshwater diatom Nitzschia palea [21]. Therefore, the ecological risks and toxicity of organophosphorus components in the effluent of WWTPs need to be evaluated. Many methods have been employed to evaluate the ecological risks and toxicity caused by pollutants or soil, mainly including the risk quotient (RQ) [22], cluster analysis method [23], and Nemerow ecological pollution index [24]. RQ is used to evaluate the ecological risks of organophosphorus compounds; specifically, it acquires the risk coefficient by comparing the actually measured maximum environmental concentration (MEC) and the predicted no-effect concentration (PNEC) [22]. At present, most studies regarding the environmental risks of pollutants have focused on single chemical compounds, lacking an investigation on their combined ecological effect, and simple supervision models have been used in most studies to calculate the joint toxicity risk entropy of various pollutants. ECOSAR, a computerized prediction system [25], can be adopted to evaluate the toxicity of pollutants to water ecology. To be specific, SARs in ECOSAR are used to predict the aquatic toxicity of chemicals based on similar structures and the previously measured aquatic toxicity of chemicals to obtain the acute and chronic toxicity of chemical substances to fish (including freshwater and saltwater), daphnia, and green algae. According to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), fish, daphnia, and algae represent the response effect of most aquatic organisms to toxicity [26]. T.E.S.T software, which is developed by the Environmental Protection Agency, can evaluate the models of toxic and physiochemical endpoints, process and statistically identify toxic groups in target structures based on mass data, predict the toxicity of chemical compounds, and rapidly analyze the toxicity of chemical compounds related to the structure of test objects.

To sum up, the organophosphorus components in the wastewater discharged by an upstream enterprise of a WWTP and the effluent in this sewage treatment plant were analyzed. In addition, the organophosphorus concentration along the path of the WWTP was determined. Three methods—ECOSAR, T.E.S.T., and RQ—were used to evaluate the ecological risks and toxicity of organophosphorus compounds in the effluent of the WWTP, which can provide theoretical guidance for monitoring and controlling organophosphorus compounds in the practical operation of WWTPs.

2. Materials and Methods

2.1. Sample Collection and Organophosphorus Determination

The WWTP was located in Jiangsu, China, with a treatment scale of 40,000 t/d; a treatment process of grid-cyclic activated sludge technology (CAST), coagulation–sedimentation, rotary disc filtration, and UV disinfection; and a sludge treatment process of belt pressure filtration dehydration. The upstream enterprises of the WWTP included a pharmaceutical enterprise, two pump stations (I and II), an electronic material enterprise, a carbon black material enterprise, a tire material enterprise, an environmental protection enterprise (a pollution control enterprise), and a food company. The wastewater discharged by the upstream enterprises and the effluent from the WWTP were collected and preserved at 4 °C. The water samples were extracted through the solid-phase extraction method via 0.45 μm membranes, and the pretreated concentrated solution was subjected to a solid-phase extraction (Supplementary Table S1). Moreover, peak materials in the chromatogram were qualitatively analyzed through the automatic retrieval function of the gas chromatograph–mass spectrometer (GC-MS) (Pegasus BT, LECO, America). The sample pretreatment method was solid-phase extraction. The water sample was filtered with a 0.45 μm membrane, and then the pH value was adjusted to 4 using hydrochloric acid or sodium hydroxide.

SPE extraction column (Cleanert PEP-2) was washed with 10 mL methanol and then with 10 mL deionized water. After the extraction was finished, the ultrafints were washed to increase the filtration capacity and drain the extraction column. The extraction column was eluted twice with 4 mL methanol, and the eluent was dried with nitrogen gas. Finally, the eluent was filled to 0.5 mL with methanol containing 0.025% formic acid. Additionally, the categories of the main soluble organic compounds in the effluent sample and their proportions in total organic compounds were further detected. All samples were analyzed for quality assurance; a 9-point calibration standard with concentrations ranging from 0.5 to 200 μg/L for the 10 targeted OPFRs was used for the calculation of concentrations in the samples. The linear regression coefficients of the calibration curves were >0.997. Internal standards were spiked into each calibration standard and sample at 20 μg/L.

2.2. Evaluation of the Ecotoxicity

2.2.1. ECOSAR

SMILES of organophosphorus compounds to be evaluated were input into ECOSAR application 2.2, and the toxicity prediction result of each substance was calculated by clicking "Submit". The SMILES symbol, the abbreviation of the simplified molecular linear input system [27], consisted of atoms, bonds, round brackets, and numbers, which could be searched by inputting the names or chemical formulas of organophosphorus compounds into the webpage of https://chem.nlm.nih.gov/chemidplus/ (accessed on 1 July 2022).

2.2.2. T.E.S.T.

T.E.S.T (Version 5.1.1) was used; the chemical compound to be predicted was input into the search bar of the main interface, and the compound was imported via CAS number. Subsequently, the endpoint needing prediction was selected in "Endpoint". This study only aimed to explore the acute toxicity of fish, bioconcentration factors (BCF), and developmental toxicity (DevTox). Therefore, "Fathead minnow LC50 (96 h)", "Bioconcentration factor", and "Developmental Toxicity" were selected, respectively. The integration method in the QSAR method required was chosen in "Method", which could take the mean value of toxicity predicted through the above methods and improve the deficiencies of single-method prediction. The green button "Calculate" was finally clicked to obtain the prediction result and a detailed description in a new window of the browser.

2.2.3. RQ

The calculation formula for RQ is as follows [28]:

$$\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \tag{1}$$

$$\mathrm{PNEC} = \frac{\mathrm{LC_{50}\ OR\ EC_{50}}}{\mathrm{AF}} \tag{2}$$

$$\mathrm{RQ_{SUM}} = \sum_{i=1}^{n} \mathrm{RQ_i} \tag{3}$$

PNEC is the maximum concentration which has not been found to generate any adverse effect on the ecosystem among the existing studies. LC50 denotes the semi-lethal concentration, and EC50 represents the half-maximal effective concentration. PNEC is usually calculated through evaluation factors, whose values depend on the type of toxicity experiment, the number of trophic levels included in the detected species, and uncertainties generated by the prediction of ecological risks [29]. Specifically, the influencing factor is taken as 1000 for the acute toxicity experiment of a single trophic level, 100 for the chronic toxicity experiment with a single trophic level, 50 for the long-term toxicity experiment with two trophic levels, and 10 for the long-term toxicity experiment with three trophic levels. In this study, EC50 and LC50 were acute toxicities of a single trophic level (Af = 1000). The values of LC50 and EC50 were provided by ECOSAR. According to the technical guide of risk evaluation prepared by the European Commission, RQ > 1 indicates high ecological risk, 0.1 < RQ < 1 an intermediate ecological risk, and RQ < 0.1 a relatively low ecological risk.

3. Results and Discussion

3.1. Detection Levels and Concentrations of Organophosphorus Compounds

The upstream enterprises of the WWTP included a pharmaceutical enterprise, two pump stations (I and II), an electronic material enterprise, a carbon black material enterprise, a tire material enterprise, an environmental protection enterprise (a pollution control enterprise), and a food company. The organophosphorus compounds in the effluent from the upstream enterprises and the WWTP were subjected to a component analysis (Table 1). Organophosphorus compounds in the wastewater of the pharmaceutical enterprise included triethyl phosphate (TEP), (MethoxyMethyl) diphenyl phosphine oxide (MDPO), triphenyl phosphine oxide (TPPO), and triphenyl phosphine sulfide (TPPS), with a relative abundance of 0.049%, 0.022%, 0.049%, and 0.01%, respectively. TEP is a high-boiling-point solvent extensively applied to rubber and plastic production as a plasticizer and one of the main raw materials for pesticide preparation as an additive [30]. MDPO is an important organic synthesis intermediate extensively used for the synthesis of various pesticides and chiral phosphine ligands [31]. TPPO has been widely applied in the pharmaceutical industry and organic synthesis analysis, and it can also be used as a sensitizer of fuel technology [32]. Organophosphorus compounds in the effluent from pump station I included TEP, dichloro [1,7,7-trimethylbicyclo [2.2.1]heptan-2-yl]phosphine (DCPP), tris-b-chloroethyl phosphate (TCEP), TPPO, and TPPS, among which TEP and TPPO presented high relative abundance at 0.047% and 0.061%, respectively. Only one type of organophosphorus compound—TEP—was contained in the wastewater from the electronic material enterprise, carbon black material enterprise, and tire material enterprise, with a relative abundance of 0.051%, 0.067%, and 0.074%, respectively. Triphenyl phosphate (TPP) and octicizer were the organophosphorus components in the wastewater from the environmental protection enterprise in addition to TEP, where the relative abundance of TPP was 0.124%. TPP, a commonly used additive flame retardant, has been widely used as the fire retardant for polymers, such as vinylite, and natural and synthetic rubbers. It can also serve as the additive of gasoline and lubricating oil [33]. The organophosphorus compounds in the effluent from the food company were mainly TEP and TCEP, with a relative abundance of 0.016% and 0.002%, respectively. There were many types of organophosphorus components in the effluent from pump station II, including trimmethyl phosphate (TMP), dimethyl methane phosphonate (DMMP), diethyl methyl phosphonite (DEMP), TEP, dibutyl phosphate (DBP), TCEP, phosphoric acid tris(2-chloro-1-methylethyl) ester (TCPP), and N-Dimethylaminomethyl-tert-butyl-isopropylphosphine (NDTPI). DMMP, DEMP, TEP, and DBP reached a high relative abundance of 0.07%, 0.084%, 0.088%, and 0.018%, respectively. DMMP is a type of cheap high-performance organic phosphine fire retardant that does not contain formaldehyde or halogen, and it can also be used as the intermediate in organic synthesis and as an agent to extract rare metals [34]. DEMP is an important organic chemical intermediate in pesticides, medicines, and synthetic materials and has been widely adopted to synthesize organophosphorus-type pesticides. DBP is the by-product during the production process of the metal ionic extraction agent tributyl phosphate [35]. The wastewater discharged by the above upstream enterprises was collected and treated in a WWTP and discharged into the lake. The organophosphorus components in the effluent from the WWTP included DMMP, DEMP, TEP, DCPP, and TECP, with a relative abundance of 0.027%, 0.073%, 0.199%, 0.148%, and 0.013%, respectively.

Table 1. Organic phosphine components from upstream enterprises and WWTP.

Water Samples	Organic Phosphonic	Abbreviation	Chemical Formula	Relative Abundance (%)	CAS
Pharmaceutical company	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.049	78-40-0
	(MethoxyMethyl) diphenyl phosphine oxide	MDPO	$C_{14}H_{15}O_2P$	0.022	4455-77-0
	Triphenyl phosphine oxide	TPPO	$C_{18}H_{15}OP$	0.049	791-28-6
	Triphenyl phosphine sulfide	TPPS	$C_{18}H_{15}PS$	0.01	3878-45-3
Pump stationxuxuan (I)	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.047	78-40-0
	Dichloro [1,7,7-trimethylbicyclo [2.2.1]heptan-2-yl]phosphine	DCPP	$C_{10}H_{17}Cl_2P$	0.008	74630-16-3
	Tris-b-chloroethyl phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	0.008	115-96-8
	Triphenyl phosphine oxide	TPPO	$C_{18}H_{15}OP$	0.061	791-28-6
	Triphenyl phosphine sulfide	TPPS	$C_{18}H_{15}PS$	0.009	3878-45-3
Electronic material enterprise	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.051	78-40-0
Carbon black material enterprise	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.067	78-40-0
Tire material enterprise	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.074	78-40-0
Environmental protection enterprise	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.004	78-40-0
	Triphenyl phosphate	TPP	$C_{18}H_{15}O_4P$	0.124	115-86-6
	Octicizer	—	$C_{20}H_{27}O_4P$	0.003	1241-94-7
Food company	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.016	78-40-0
	Tris-b-chloroethyl phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	0.002	115-96-8
Pump stationxuxuan (II)	Trimmethyl phosphate	TMP	$C_3H_9O_4P$	0.008	512-56-1
	Dimethyl methane phosphonate	DMMP	$C_4H_{11}O_4P$	0.07	813-78-5
	Diethyl methyl phosphonite	DEMP	$C_5H_{13}O_4P$	0.084	867-17-4
	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.088	78-40-0
	Dibutyl phosphate	DBP	$C_8H_{19}O_4P$	0.018	107-66-4
	Tris-b-chloroethyl phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	0.001	115-96-8
	Phosphoric acid tris(2-chloro-1-methylethyl) ester	TCPP	$C_9H_{18}Cl_3O_4P$	0.017	13674-84-5
	N-Dimethylaminomethyl-tert-butyl-isopropylphosphine	NDTPI	$C_{10}H_{24}NP$	0.013	83718-54-1
WWTP	Dimethyl methane phosphonate	DMMP	$C_4H_{11}O_4P$	0.027	10463-05-5
	Diethyl methyl phosphonite	DEMP	$C_5H_{13}O_4P$	0.073	598-02-7
	Triethyl phosphate	TEP	$C_6H_{15}O_4P$	0.199	78-40-0
	Dichloro [1,7,7-trimethylbicyclo [2.2.1]heptan-2-yl]phosphine	DCPP	$C_{10}H_{17}C_{12}P$	0.148	74630-16-3
	Tris-b-chloroethyl phosphate	TCEP	$C_6H_{12}C_{13}O_4P$	0.013	115-96-8

Table 2 presents the categories and concentrations of the organophosphorus compounds in the wastewater from the upstream enterprises. A total of 14 organophosphorus pollutants appeared in the effluent samples from the upstream enterprises and the WWTP. According to the component analysis, there were eight organophosphorus components in the water sample from pump station II, namely, TMP, DMMP, DEMP, TEP, DBP, TCEP, TCPP, and NDTPI. Among them, there were high concentrations of TEP, DBP, DEMP, and DMMP (0.292, 0.192, 0.383, and 0.320 mg/L, respectively). Five types of organophosphorus compounds were found in the effluent from pump station I, namely, TEP, DCPP, TECP, TPPO, and TPPS. Among them, TEP and TPPO were in high concentrations (0.164 and 0.213 mg/L, respectively). Notably, only TEP, TPP, and octicizer were in the effluent from the environmental protection enterprise, with the concentrations reaching 0.981, 30.4, and 0.735 mg/L, respectively. Among the 11 water samples, therefore, the total concentration of organophosphorus compounds in the effluent from this enterprise was the highest, at 32.1 mg/L. In the effluent from the food and pharmaceutical companies, there were few types of organophosphorus compounds with low concentrations. Only one organophosphorus component—TEP—was contained in the effluent from the electronic material enterprise, carbon black material enterprise, and tire material enterprise, and their concentration was low at 0.075, 0.035, and 0.465 mg/L, respectively. The organophosphorus components in the effluent from the WWTP were TEP, TCEP, DEMP, DMMP, and TECP, and the total organophosphorus concentration was 0.301 mg/L. As TEP was detected from upstream water samples, its concentration was the highest, at 0.130 mg/L. The concentration of TCEP (organophosphorus flame retardant) was 0.008 mg/L, which was significantly higher than the values in most of the WWTPs [7]. The organophosphorus concentration from the upstream enterprises was summed to obtain a total organophosphorus concentration in the influent from the WWTP of 39.5 mg/L. The influent concentration was compared with the effluent concentration, and the result showed that the WWTP achieved a good phosphorous removal effect. After being treated in the wastewater treatment system, most organophosphorus components experienced good levels of degradation, transfer, or conversion.

3.2. Evaluation of ECOSAR Ecotoxicity

The ECOSAR program is an important tool of computational toxicology extensively applied to environmental risk prediction. Specifically, it groups structurally similar organic chemicals and applies experimental effect levels to organic matters with related physiochemical properties to predict the toxicity of new or untested industrial chemicals [36]. In this study, the ECOSAR model was used to evaluate the acute and chronic toxicity of organophosphorus components in the effluent from the WWTP and its upstream enterprises to fish, daphnia, and green algae. Moreover, this model was used to fully understand their environmental chemical behaviors and provide guidance for the WWTP to remove organophosphorus compounds (Supplementary Table S2).

Table 2. Organophosphorus concentration at each sampling point.

Organic Phosphonic (Abbreviated Name)	**Organophosphorus Concentration (mg/L)**								
	Pharmaceutical Company	**Pump Station I**	**Electronic Material Enterprise**	**Carbon Black Material Enterprise**	**Tire Material Enterprise**	**Environmental Protection Enterprise**	**Food Company**	**Pump Station II**	**WWTP**
TEP	0.172	0.164	0.075	0.035	0.465	0.981	1.2	0.292	0.13
TCEP	0	0.028	0	0	0	0	0.149	0.005	0.008
TMP	0	0	0	0	0	0	0	0.037	0
TPP	0	0	0	0		30.4	0	0	0
TCPP	0	0	0	0	0	0	0	0.078	0
DBP	0	0	0	0	0	0	0	0.192	0
TPPO	0.172	0.213	0	0	0	0	0	0	0
TPPS	0.035	0.031	0	0	0	0	0	0	0
MDPO	0.077	0	0	0	0	0	0	0	0
DEMP	0	0	0	0	0	0	0	0.383	0.048
DMMP	0	0	0	0	0	0	0	0.32	0.018
NDTPI	0	0	0	0	0	0	0	0.059	0
Octicizer	0	0	0	0	0	0.735	0	0	0
DCPP	0	0.028	0	0	0	0	0	0	0.097

The classification method for the predicted toxicity value in GHS is shown in Supplementary Table S2, according to which the toxicity of organophosphorus compounds was evaluated. Figure 1 describes the relationships of logarithmic functions of LC50, EC50, and ChV with the organophosphorus compounds. As shown in Figure 1, five types of organophosphorus components showed no acute toxicity or harm to fish, daphnia, or algae, and three types presented no chronic toxicity or harm. Among them, TMP, DEMP, and DMMP were all harmless in the acute and chronic toxicity evaluations. TMP was only detected in the pump station II, and two types of organophosphorus components were not detected in the upstream enterprises but were detected out in the WWTP. A possible reason for this is that the WWTP receives other wastewater, or some organophosphorus components are degraded and converted after the treatment. In the acute and chronic toxicity evaluations, the other 11 kinds of organophosphorus components had different degrees of harm to fish, daphnia, and algae. Notably, in the toxic and highly toxic zones, daphnia showed a minimum toxicity resistance, followed by fish and green algae. In the acute toxicity evaluation, octicizer and DCPP were classified as drugs with high toxic levels to fish, daphnia, and algae were. In the chronic toxicity evaluation, TPPS and NDTPI were additionally classified as two organophosphorus components with high toxic levels, which showed slightly lower acute toxicity than chronic toxicity. The accumulative chronic toxicity of TPPS, which was applied to the pharmaceutical company, may be higher. Thus, higher attention should be paid to its toxicity to aquatic organisms owing to its long-term existence in water bodies. According to the evaluation results, organophosphorus components in the effluent from the upstream enterprises and the WWTP posed ecological risks to aquatic organisms to different degrees. Moreover, attention should be paid to the possible additive/synergistic effect of different drugs in the aquatic environment [37,38].

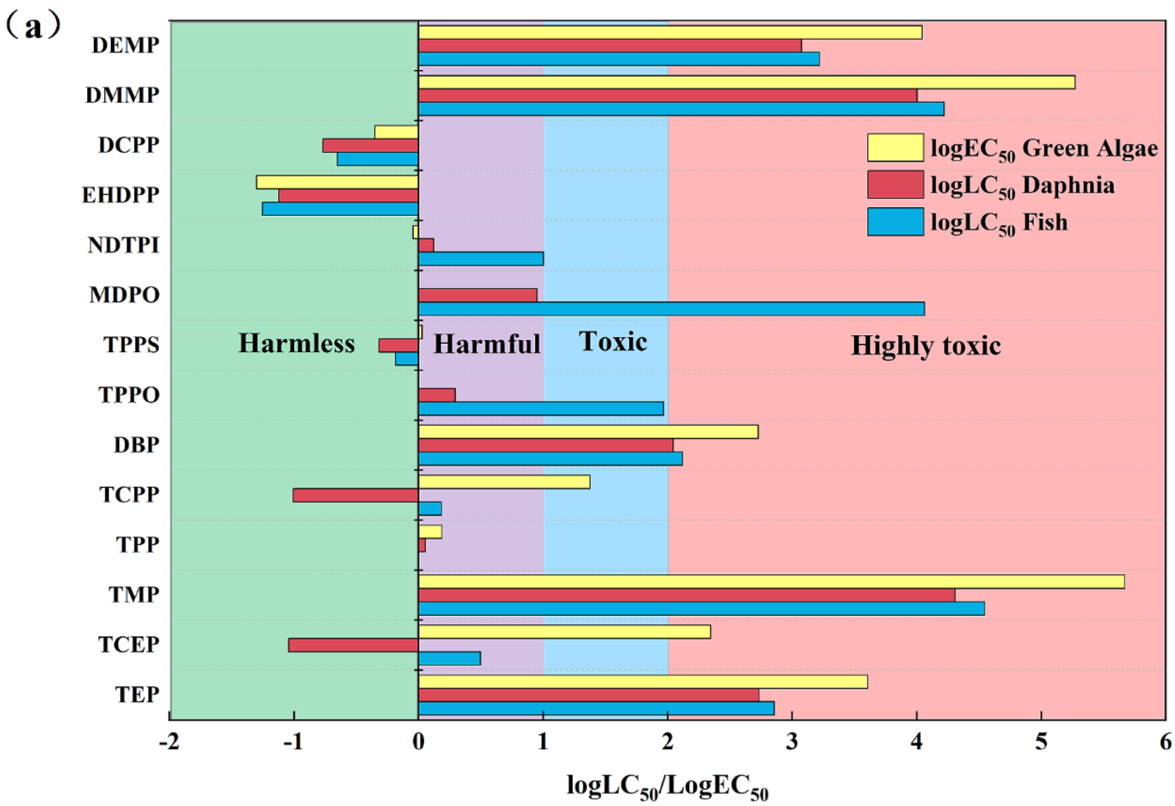


Figure 1. *Cont.*

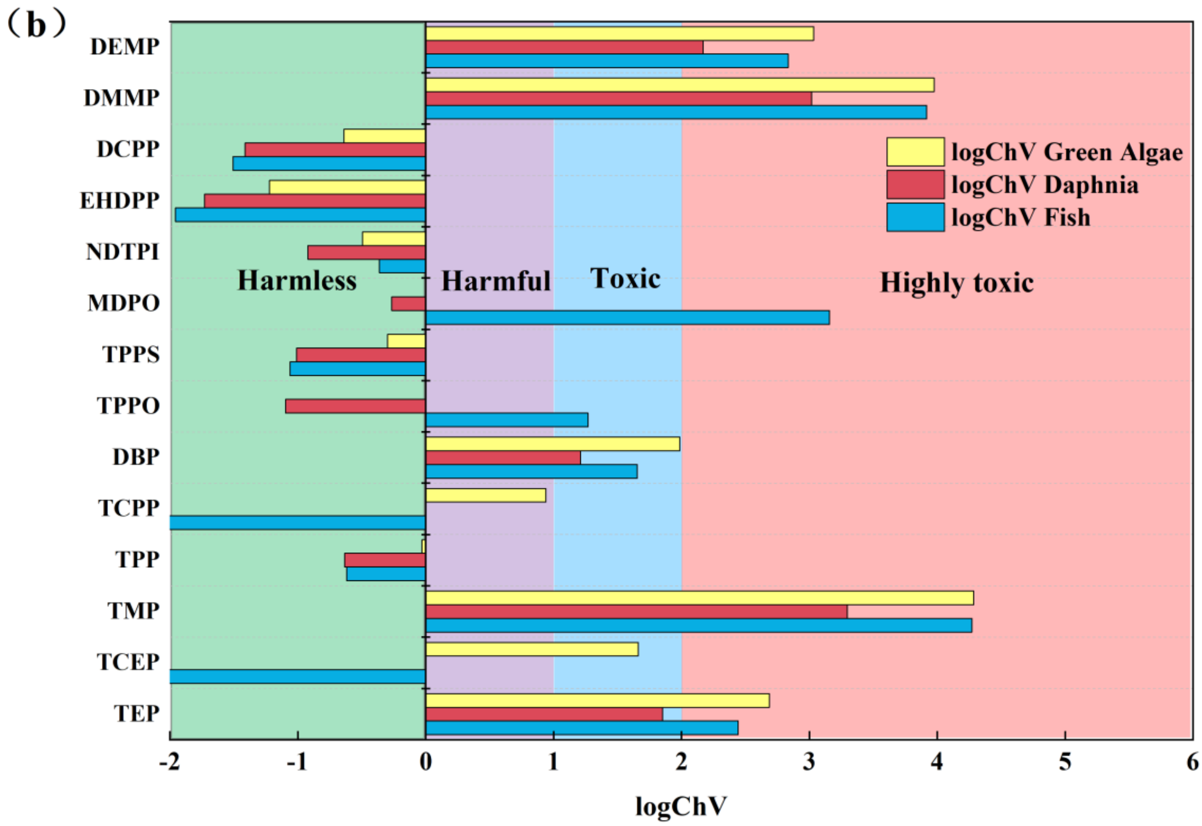


Figure 1. Acute toxicity (**a**) and chronic toxicity (**b**) of various organophosphorus compounds.

The toxicity evaluation results and the organophosphorus components and concentrations in the effluent from each enterprise and the WWTP were combined for further analysis of their ecological risks. TEP has been extensively used in industries; however, it can be completely mixed with ethanol and water, making it difficult to treat, which may lead to its presence in the effluent from both the upstream enterprises and WWTP. The LC50 of TEP to fish was 716.9 mg/L and that to daphnia was 542.3 mg/L. Its ChV to algae was 4041.4 mg/L, and all the toxic levels were harmless, with only its chronic toxicity to daphnia considered to be harmful. Moreover, its maximum concentration in the effluent from the food company was 1.191 mg/L, which was much lower than the concentration constituting a harmful level. TPP can be used as hydraulic oil and fire retardant [39], and its 96 h LC50 to fish was 1.00 mg/L. Thus, TPP is considered a substance with high acute toxicity according to the aquatic toxicity standard (Supplementary Table S3). Meanwhile, its chronic toxicity to fish, daphnia, and green algae was 0.24, 0.23, and 0.94 mg/L, respectively, indicating that its chronic toxicity was also toxic to aquatic organisms. TPP was only detected in the effluent from the environmental protection enterprise, with the concentration reaching 30.4 mg/L. This value far exceeded the medial lethal concentration, which might be related to the main business undertaken by this plant. Therefore, high attention should be paid to TPP with high toxicity in the effluent as it may generate direct adverse impacts on aquatic organisms and pose threats to human beings by polluting drinking water. After the wastewater from the environmental protection enterprise was collected in the WWTP, this organophosphorus component was not detected in the effluent. This result indicates that TPP was well treated by the wastewater treatment process; however, it might generate a toxic action on microorganisms through the biochemical treatment stage.

The effluent evaluation of the WWTP was of vital importance; the effluent can certainly pollute the receiving water and even finally endanger human health if the toxicity is high after the treatment process. The organophosphorus components detected in the effluent from the WWTP were TEP, TCEP, DCPP, DMMP, and DEMP. As for acute toxicity, TEP, DMMP, and DEMP were all harmless. TCEP showed different toxic levels to three aquatic organisms, and its LC50 and EC50 to fish, daphnia, and green algae were 3.14, 0.09, and 221.8 mg/L, respectively. These values were considered to pose a toxic level to fish, a highly toxic level to daphnia, and a harmless level to green algae according to aquatic toxicity standards. The effluent concentration of the WWTP was 0.008 mg/L, which was sufficiently low to reach the harmful concentration. As for chronic toxicity, TEP was harmful to daphnia, and TCEP was harmful to green algae. What should attract high attention in the effluent from the WWTP is DCPP, which was classified as a highly toxic organophosphorus compound in both the acute and chronic toxicity evaluations. In addition, its concentration in the effluent from the WWTP was 0.097 mg/L, which already exceeded the ChV value for fish (0.03 mg/L) and daphnia (0.04 mg/L). If the effluent is directly discharged into the water body, then it might generate chronic toxicity to fish and algae; consequently, it should be further removed through a wastewater treatment process, and it is crucial to evaluate the ecotoxicity of organophosphorus components in the water body.

3.3. Acute Toxicity Evaluation

LC50—the toxic concentration leading to the death of half of the animals subjected to an acute toxicity experiment—is an important parameter measuring the toxicity of toxicants in water to aquatic animals and that of toxicants in the air to mammals and even human beings. BCF denotes the ratio of the concentration of some elements or nondegradable compounds in living organisms to the concentration of such substances in the living environment, which can be used to indicate the degree of bioconcentration. This index is of practical significance for evaluating the environmental impacts of chemical substances and the fishery water quality standards of chemicals. DevTox means that a deleterious effect appears before offspring become adults because of contact with exogenous physiochemical factors via the male parent and (or) female parent before birth, including structural abnormality, growth retardation, dysfunction, and death. Whether each organophosphorus component is a developmental toxicant can be judged via T.E.S.T.

The acute toxicity of organophosphorus components in the effluent samples from the WWTP and its upstream enterprises was predicted using T.E.S.T, with results listed in Supplementary Table S4. TPP and octicizer were highly toxic to aquatic organisms and both belonged to acute toxicity Category 1, with LC50 values of 0.39 and 0.098 mg/L, respectively. This result indicates that these two organophosphorus components can result in a death rate of 50% among 96 h fathead minnows at the two concentrations. Both components were only present in the water sample from the environmental protection enterprise at concentrations of 30.4 and 0.735 mg/L, respectively. Both far exceeded the acute toxicity value, reflecting their severe harm to aquatic organisms. As a type of OPFR with high production and detection frequency, TPP has been widely applied to polyvinyl chloride materials, printed circuit boards, and commercial mixed fire retardants (FM550 and AC073 fire retardants) [40]. Studies showed that the exposure of TPP at a certain dose will generate an ecotoxic effect on aquatic organisms; a lethal effect on crustacean shellfish [41], fish, and insects; and present reproductive toxicity [42] and neurotoxicity to fish. In addition, TPP will influence the growth of algae and fish [43], and octicizer, an aryl organophosphorus fire retardant, is mainly used as a fire retardant and plasticizer [44]. As a physical additive, octicizer can easily enter the environment; the detection rate of octicizer was 88% and 100%, and its average concentration was 1.9 and 2.8 ng/L, respectively [45].

TPPO, TPPS, and TCPP detected in the water belonged to acute toxicity Category 2, with LC50 values of 4.98, 2.46, and 7.24 mg/L, respectively, indicating their certain toxicity to aquatic organisms. Such organophosphorus components mainly came from medicines, dyestuffs and sensitizers, macromolecular polymers, antioxidants of color film developing, plasticizers of rubbers and plastics, and raw materials of pesticides and insecticides, which were detected from pharmaceutical enterprise wastewater, pump station I, and pump station II. However, their concentration in the water sample was low, only 1/100 of the acute toxicity value, with minor harm. TMP, DEMP, and DMMP detected in the effluent from pump station II and the WWTP did not belong to the category of acute toxicity, with 96 h LC50 values (to fish) of >100 mg/L, at 133.6, 120.8, and 143.3 mg/L, respectively. However, their concentration in the water sample was <1 mg/L. In addition, all other organophosphorus components belonged to acute toxicity Category 3, with 96 h LC50 values (to fish) falling in the range of 10–100 mg/L, whereas their concentration in the effluent from each enterprise and the WWTP was always below 2 mg/L, indicating relatively low toxicity. To sum up, for the effluent from each enterprise and the WWTP, high attention should be paid to the removal of TPP and octicizer.

A total of 14 organophosphorus components were contained in the influent from the WWTP, among which the content of TPP was the highest (30.4 mg/L), which belonged to acute toxicity Category 1 with an LC50 of 0.39 mg/L. The influent concentration far exceeded the LC50, indicating enormous harm to aquatic organisms. However, after being effectively treated through the wastewater treatment process, this component was not contained in the effluent. This could be due to the transportation, degradation, and conversion of organophosphorus components along with the wastewater treatment process [38]. Octicizer, which also belonged to acute toxicity Category 1, reached the concentration of 0.735 mg/L in the influent, which far exceeded the LC50. Conversely, its concentration declined to 0 mg/L in the effluent after being treated in the WWTP, showing that the wastewater treatment process could effectively reduce the potential ecological risks of octicizer. In addition, most organophosphorus components were removed, and only two components had a higher content after the wastewater treatment process, namely, DMMP and DEMP. This may be attributed to their being generated after the degradation, transfer, or conversion of other organophosphorus components.

3.4. BCF and DevTox Evaluation

Supplementary Table S5 shows the BCF and DevTox prediction results in the effluent samples from the WWTP and its upstream enterprises via T.E.S.T. In the effluent from the upstream enterprises and the WWTP, the BCF value of each organophosphorus component was smaller than 2000, indicating their minor accumulative effect on aquatic organisms. Regarding the organophosphorus components in the water sample from each upstream enterprise, the BCF in the influent from the WWTP was also smaller than 2000, implying no bioconcentration in aquatic organisms.

DevTox means that some chemical compounds influence individual growth and development as they can interfere with nucleic acid translation and expression functions. Based on the prediction of DevTox, the T.E.S.T. software can only qualitatively divide organophosphorus components into developmental and non-developmental toxicants. Supplementary Table S5 shows that seven types of organophosphorus components existed in the effluent from each upstream enterprise as developmental toxicants, namely, TEP, TPP, octicizer, TMP, DEMP, DBP, TCPP, DMMP, and DEMP. Among them, the content of TEP with reproductive toxicity, neurotoxicity, carcinogenicity, and endocrine-disrupting effects [46–49] was the highest, and it was present in the effluent from each enterprise and the WWTP. TPP may be neurotoxic, and TCEP and TCPP are carcinogenic to animals. Hence, for the developmental toxicant TEP in the effluent from the WWTP, as well as for TCPP, DMMP, and DEMP, an additional treatment process should be established to ensure the safe use of reclaimed water.

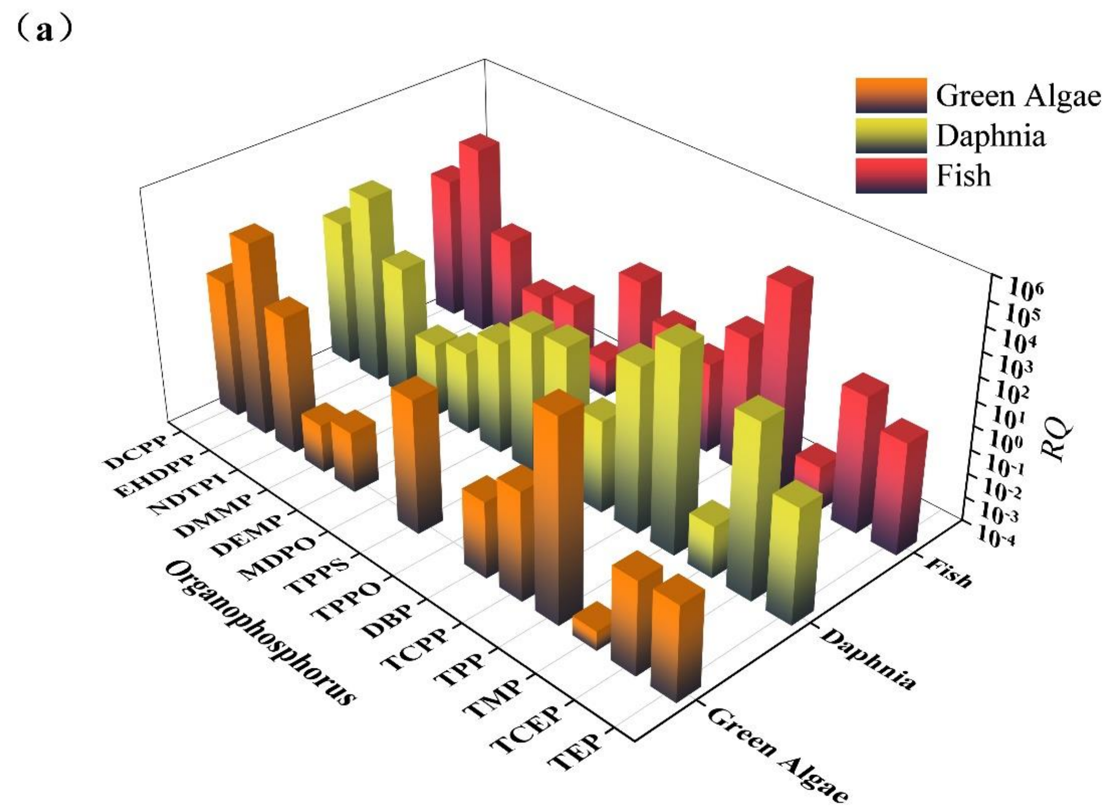
3.5. Risk Entropy Evaluation

Table 3 shows that a certain amount of TEP was contained in the effluent from the eight enterprises. Notably, the environmental risk value of TEP in the water sample from the environmental protection enterprise and food company was high and exceeded the standard. TPP, TCPP, TPPO, TPPS, NDTPI, octicizer, and TCEP reached RQ values much greater than 1 in the effluent from the enterprises, all of which belonged to highly toxic organophosphorus compounds. Although the above substances were not detected after being treated in the WWTP, they were highly toxic; therefore, the potential environmental risks triggered by leakage through municipal pipe networks should be strictly prevented [50]. The risk entropies of the effluent from each enterprise were compared according to Table 3. The effluent from the environmental protection enterprise posed the greatest harm to the environment, which was mainly attributed to the strong toxicity of TPP and octicizer. Octicizer harms the human body mainly by influencing the energy metabolic balance of human hepatic cells, endoplasmic reticulum stress, apoptosis, cell cycle, and inflammatory response [51]; thus, attention should still be paid to octicizer.

Figure 2 shows that after the conventional treatment with phosphorus removal in the WWTP, most organophosphorus components were effectively removed. Among the detected organophosphorus components in the effluent, the RQ value of DMMP and DEMP was smaller than 0.1, which can be considered as a low environmental risk to the natural water body. In the effluent from the WWTP, the RQ value of TCEP and DCPP was greater than 1, indicating great impacts on the natural water body. According to the LC50 and EC50, TCEP showed significant toxic action on daphnia and fish whereas little toxicity to algae. Zhao et al. [52] discovered that when the TCEP content exceeds 100 μg/L, it will exert negative impacts on the survival rate, specific growth rate, and body weight of yellowhead catfish juveniles, mainly through the oxidation resistance of the liver and gills. Given that there was a certain bioconcentration of TCEP in the food chain, it will trigger relatively high environmental risks after entering the natural water body [53]. Table 3 shows that TCEP was mainly discharged from the environmental protection enterprise, and it could not be effectively removed by the conventional phosphorus removal process, while Liang and Liu [54] found that TCEP content was higher after the biochemical and physiochemical treatment in the WWTP. TCEP usually comes from the plasticizers of rubbers and plastics and the raw materials of pesticides and insecticides [52]; therefore, if industrial wastewater was discharged from the rubber enterprise and pesticide enterprise into the municipal pipe network and the WWTP, then close attention should be paid to TCEP to prevent it from causing environmental harm to the natural water body. In addition, DCPP did not show a major content change after the wastewater treatment process, indicating that the chemical phosphorus removal is not conducive to DCPP removal. Moreover, the LC50 and EC50 of DCPP, a highly toxic organophosphorus compound, were relatively low. In general, DCPP comes from plasticizers, fire retardants, pesticide intermediates, and oil paint batch materials. Therefore, upstream chemical enterprises and farmlands should be checked when DCPP is detected. Further, DCPP was probably introduced from pump station I (Table 3).

Table 3. Organophosphorus RQ of upstream enterprises and WWTP.

Organophosphorus Compound	Creature	Pharmaceutical Company	Pump Station I	Electronic Material Enterprise	Carbon Black Material Enterprise	Tire Material Enterprise	Environmental Protection Enterprise	Food Company	Pump Station II	WWTP
TEP	Fish	0.068	0.228	0.104	0.048	0.648	1.368	1.661	0.407	0.1813
	Daphnia	0.090	0.302	0.138	0.064	0.857	1.809	2.196	0.538	0.2397
	Green Algae	0.012	0.040	0.018	0.008	0.115	0.242	0.294	0.072	0.0322
TCEP	Fish		0.039					47.39	1.59	2.5447
	Daphnia		0.051					1643	55.16	88.263
	Green Algae		0.006					0.671	0.022	0.0361
TMP	Fish								0.008	
	Daphnia								0.014	
	Green Algae								0	
TPP	Fish						30484			
	Daphnia						26794			
	Green Algae						19780			
TCPP	Fish								51.24	
	Daphnia								791.3	
	Green Algae								3.275	
DBP	Fish								0.622	
	Daphnia								0.740	
	Green Algae								0.153	
TPPO	Fish	0.528	2.296							
	Daphnia	24.81	107.8							
	Green Algae									
TPPS	Fish	15.38	47.70							
	Daphnia	20.80	64.49							
	Green Algae	9.365	29.03							
MDPO	Fish	0.002								
	Daphnia	2.463								
	Green Algae									
DEMP	Fish								0.231	0.0290
	Daphnia								0.321	0.0403
	Green Algae								0.034	0.0043
DMMP	Fish								0.084	0.0011
	Daphnia								0.123	0.0018
	Green Algae								0.01	0.0001
NDTPI	Fish								5.852	
	Daphnia								44.48	
	Green Algae								65.52	
Octicizer	Fish						13147			
	Daphnia						9746.9			
	Green Algae						14651			
DCPP	Fish		125.9							436.27
	Daphnia		163.8							567.56
	Green Algae		62.86							217.77



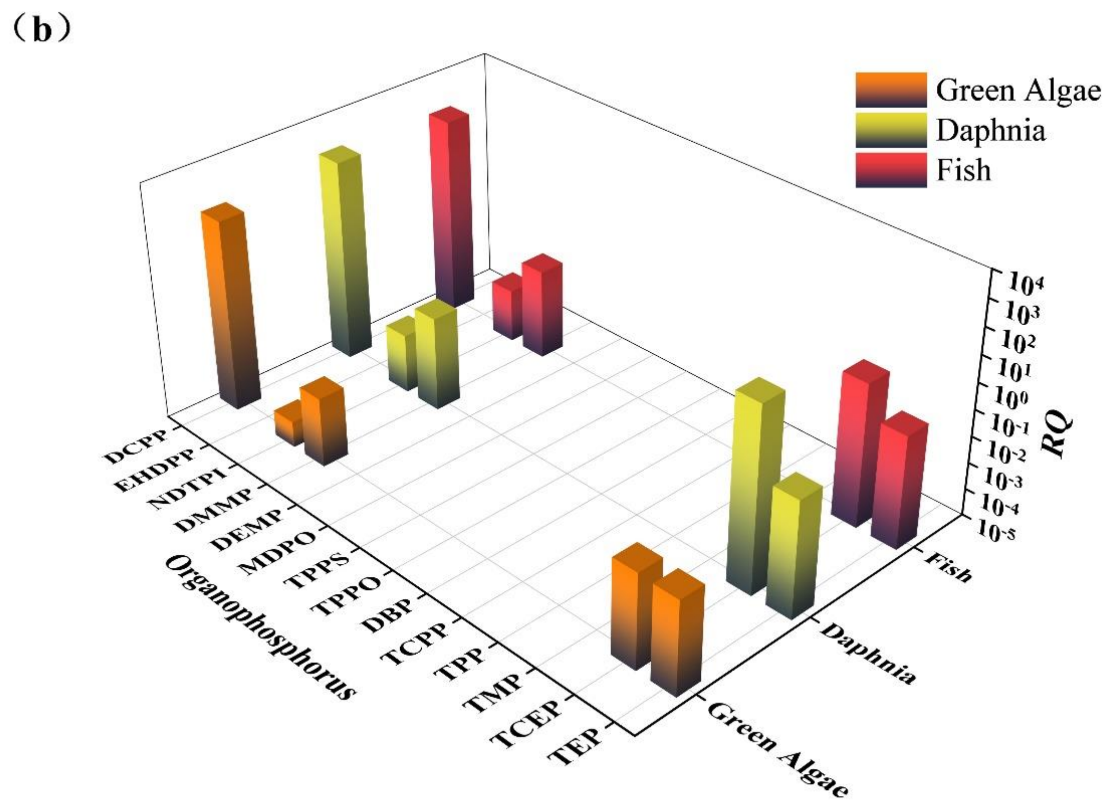


Figure 2. RQ value of organophosphorus compounds in influent (**a**) and effluent (**b**) from WWTP.

4. Conclusions

Monitoring and controlling the concentrations of organophosphorus compounds in wastewater discharged from upstream enterprises and WWTPs and conducting ecological risk and toxicity assessments are of great importance to ensure ecological security. The operation strategy of WWTPs can be adjusted in time to prevent the organic phosphorus in the effluent from exceeding the standard and subsequently prevent adverse effects on the ecological environment and provide basic data for ecological risk and toxicity assessments. A total of 14 organophosphorus pollutants were present in the upstream enterprises and the WWTP, and the influent and effluent total organophosphorus concentrations were 39.5 and 0.301 mg/L, respectively. The tolerance toxicity of daphnia was the lowest, followed by fish and green algae, and there were 11 kinds of organic phosphorus that will harm fish, daphnia, and algae in acute or chronic toxicity. TPP belongs to acute toxicity Category 1 with an LC50 of 0.39 mg/L, and the influent TPP was much higher than the LC50, causing great harm to aquatic organisms. Nine kinds of organic phosphorus with developmental toxicity were found in the effluent of the upstream enterprises. Additional treatment facilities are required for the higher removal of organophosphorus substances. The environmental risk value of TEP was high and exceeded the standard. The RQ values of TPP, TCPP, TPPO, TPPS, NDTPI, octicizer, and TCEP in the effluent of the enterprises were much greater than 1, these organophosphorus compounds being highly toxic; however, the RQ values of DMMP and DEMP were less than 0.1, indicating a low risk of environmental harm.

Supplementary Materials: E-supplementary data of this work can be found in the online version of the paper: https://www.mdpi.com/article/10.3390/w14233942/s1. Table S1: Solid phase extraction of water samples. Table S2: ECOSAR alculation results (mg/L). Table S3: Concentration dependent toxic classification (mg/L). Table S4: Prediction of acute toxicity of organophosphorus components. Table S5: Prediction of bioconcentration factor and developmental toxicity of organophosphorus components.

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Abbreviations

1	Bioconcentration factor	BCF
2	Cyclic activated sludge technology	CAST
3	Developmental toxicity	DevTox
4	Dibutyl phosphate	DBP
5	Dichloro [1,7,7-trimethylbicyclo [2.2.1]heptan-2-yl]phosphine	DCPP
6	Diethyl methyl phosphonite	DEMP
7	Dimethyl methane phosphonate	DMMP
8	Ecological structure activity relationships	ECOSAR
9	Gas chromatograph–mass spectrometer	GC-MS
10	Half-maximal effect concentration	EC50
11	Maximum environmental concentration	MEC
12	(MethoxyMethyl) diphenyl phosphine oxide	MDPO
13	N-Dimethylaminomethyl-tert-butyl-isopropylphosphine	NDTPI
14	Organophosphorus flame retardants	OPFRs
15	Organophosphorus pesticides	OPPs
16	Phosphoric acid tris(2-chloro-1-methylethyl) ester	TCPP
17	Predicted no-effect concentration	PNEC
18	Risk quotient	RQ
19	Semi-lethal concentration	LC50
20	Toxicity Estimation Software Tool	T.E.S.T.
21	Triethyl phosphate	TEP
22	Trimmethyl phosphate	TMP
23	Triphenyl phosphate	TPP
24	Triphenyl phosphine oxide	TPPO
25	Triphenyl phosphine sulfide	TPPS
26	Tris[2- chloro-1-(chloromethyl)ethyl] phosphate	TDCP
27	Tris-b-chloroethyl phosphate	TCEP
28	Wastewater treatment plants	WWTPs

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