A New Method for Environmental Risk Assessment of Pollutants Based on Multi-dimensional Risk Factors

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Abstract

Deterioration of watershed environment and pollutant discharge had seriously threatened human health and ecosystem function. The importance of improving risk warning system is becoming more and more prominent. Traditional chemical risk assessment methods focused on toxicity and exposure of pollutants without considering the impact of persistent pollutants in different environmental media. So there are cases which pollutants that have been assessed as safe using these methods end up being classified as persistent organic pollutants. In this study we proposed a synthetical risk factor (SRF) analysis with multi-dimensional evaluation of pollutants. The new method integrated toxicity endpoint values, environmental exposure level, persistent properties and compartment features from various dimensions. Selected pesticides, perfluorinated compounds, organophosphate and endocrine disruptors were analyzed with both SRF and risk quotient (RQ) methods. The results showed, a higher risk outcome using SRF analysis for PFOS, imazalil, testosterone, androstenedione and bisphenol A, which were different from those obtained with RQ method but were consistent with existing risk management. The study demonstrated that SRF method improved risk assessment of various pollutants in surface water in a more robust fashion, and also provided a more accurate decision basis for ecological environment protection.

Introduction

With the development of industry and agriculture more chemicals have been used as medicines, agricultural fertilizers, herbicides and pesticides (Meng et al. 2021). Many potential hazard substances are released into water and cause water pollution (Zeng et al. 2018). Although toxic pollutants in environmental water are present at relatively low level, they can be accumulated in the human body and cause adverse effects (Qi 2021). Therefore, it is necessary to assess direct and indirect, short-term and long-term risk in detail (Virendra et al. 1994). Environmental risk assessment can help define the possibility of a certain compound to cause severe effect to the environment before these effects are noticed (Bureš et al 2021). At present, the most widely used method for environmental risk assessment of organic pollutants is the risk quotient (RQ) method, which is suitable for assessment for a single compound (Andrew et al. 2009). However, increased attention has been paid to a class of chemical substances, namely, new pollutants. Evidence has shown that these pollutants exhibit adverse effects at typical ambient concentrations and have not been done for risk management. These pollutants are often produced from urban, agricultural and wastewater sources. Therefore, risk assessments for individual chemicals may underestimate the risks of contaminants in the actual environment. By introducing the environmental persistence coefficient of chemical compounds, multi-dimensional risk assessment of pollutants can be carried out, and the exposure level of pollutants can be accurately estimated, and corresponding measures can be taken to control the potential risk in time.

Methods of environmental risk assessment are evolving to meet the need for global awareness. The research on environmental risk was originated from the understanding, evaluation and prevention of natural disasters in the 1930s. With rapid development of industrialization and urban construction in Europe and America, environmental and health problems began to draw attention. At that time, environmental risk studies focused on describing the adverse health effects of human exposure to environmental hazards. In the 1940s, toxicological identification system was mainly used to analyze the health effects. Quantitative methods have increasingly being used to study the health of population exposed to different concentrations of pollutants (Mao and Liu 2003). Since 1970s, health risk assessment studies have been gradually standardized, a well-known “four-step” method of risk assessment started in the United States, that is, hazard identification, dose-response relationship assessment, exposure assessment and risk characterization (Liu et al. 2020). The method was later adopted by France, Netherland, Japan and other countries as well some international organizations. In the early 1990s, Glenn and Suter proposed a more applicable and comprehensive framework for environmental risk assessment based on the three-step method of ecological risk assessment by combining human health and ecological risk studies. In the mid-1990s, Canada, Britain, Australia and other countries launched environmental risk research work successively, forming a complete environmental risk assessment process. Nowadays, the environmental risk assessment mainly focuses on the development of risk management and control in the application domain.

Traditional environmental risk assessment is mainly focused on a single substance rather than chemical mixtures (Mu et al. 2021). Even though many pollutants are found in the environment at very low concentrations, nature living organisms are predominantly exposed to chemical mixtures of the pollutants (Bagnis et al. 2018). Hence, for a more accurate evaluation of risk potential, we adopted a synthetical risk factor approach by introducing compound environmental persistence coefficients. This method allowed for the timely identification of potential environmental risk compounds and adverse ecological impacts. Because it took into account the measurement uncertainty as well as the variability of the environmental concentrations and toxicity data (Giuliana et al. 2016). It provided a more accurate decision-making basis for ecological and environmental protection and risk management.

Materials And Methods

Data source

The study aimed to conduct risk assessment of pesticide residues, perfluorinated compounds, organophosphate esters and endocrine disruptors detected in the Ebro River in Spain, Tianjin and Xiang Jiang surface water in China. The half-life ($T_{1/2}$) data of pollutants were obtained from Chemical Book (HTTP://www.chemicalbook.com/) and other chemical search engines. In the absence of chronic toxicity data, short-term EC or LC_{50} data were used. Toxicity data were mainly obtained from the United States EPA ECOTOX database (https://cfpub.epa.gov/ecotox/quick_query.htm). The basic data of residual pesticides, perfluorinated compounds, organophosphates and endocrine disruptors shown in Tables 1, 2, and 3 were derived from the publications (Wu et al. 2021; Qi et al. 2021; Ccanccapa et al. 2016; Luo et al. 2019).

Environmental Persistence Coefficient Of The Compound(C)

The measured half-life of a pollutant was associated with the persistence limit value to form the environmental persistence coefficient of the compound:

$$C = T_{CV} / T_{1/2} \quad (1)$$

Where, $T_{1/2}$ is the half-life (days) of the pollutant to be measured; T_{CV} is the half-life limit value (days). Half-life refers to the time required for pollutants to disappear 50% in the environment. According to the requirements of the Stockholm Convention on the half-life of persistent pollutants, the critical value of half-life in water here was determined to be 60 (d).

Risk quotient (RQ)

According to EU regulations, in order to assess the risk of pollutants in the aquatic environment, environmental risk assessment calculations for pollutants must be performed. This risk assessment is usually expressed as a risk quotient (RQ) (Hafsa et al. 2020). The calculation formula of risk quotient is as follows:

RQ = MEC/PNEC (2)

Where, MEC is the measured environmental concentration (ng L^{-1}); PNEC is the predicted no effect concentration of pollutants (ng L^{-1}).

Synthetical risk factor (SRF)

The current RQ approach as described above characterizes the toxicity of pollutants under the conditions of measured environmental concentrations without consideration of the possibility of aquatic organisms exposed to potentially unsafe levels. Certain pollutants with a long-term presence in water may have a greater impact on non-target organisms than those pollutants with a short-term presence. In addition, risk of pollutants that are frequently detected may be different from those that are occasionally detected. Therefore, by introducing environmental persistence coefficient in performing multi-dimensional risk assessment of pollutants, results of priority detection for potential risk substances may change greatly. The synthetical risk factor (SRF) based on the mean RQ value and the frequency of exceeding PNEC was used to evaluate the potential risks due to detected substances. This was close to the natural scenario and favored the selection of priority pollutants. The SRF value was calculated according to the following equation:

F (R) = MEC/PNEC*C (3)

Risk factor was calculated with 3 parameters: 1) the measured environmental concentration of pollutants in environmental media, 2) the predicted no effect concentrations and 3) the persistence coefficient of pollutants in the environment.

Scope of environmental risk assessment

The risk ranking criteria were adopted from the literature:
RQ or SRF < 0.01: adverse effects are unlikely to occur and thus can be considered to have negligible hazard; $0.01 < RQ < 0.1$:the minimum risk to the organisms; $0.1 < RQ < 1$: medium risk; and $RQ \geq 1$: high risk.

Procedures

The steps and flow chart for risk assessment using the multi-dimensional evaluation factor are shown in Fig. 1 below:

i. Review and collect relevant literature on environmental risk assessment methods; determine the factors affecting environmental risk, and their limitations.

ii. Establish comprehensive risk factor function by applying persistence coefficient.

iii. Apply the function to a multi-dimensional risk assessment of new pollutants in selected surface waters and validate accordingly based on the scope of risk.

Validation Analysis

Four types of target pollutants were selected for the risk assessment, and measured environmental concentrations, predicted no-effect concentration and persistence coefficient were then calculated. The comprehensive risk factors were determined and compared with RQ method to verify the accuracy of the comprehensive risk factor method according to the environmental risk assessment grade.

Results And Discussion

Application domain for pesticide residues based on SRFs

Pesticides have been widely used since the mid-twentieth century for pest control. They are present in a wide range of physicochemical diversity and can be persistent in water, accumulated in sediments, and bio-accumulated in biota, which could cause potential environmental and health issue due to their potential toxicity to non-target organisms (Ccanccapa et al. 2016). The residual pesticide compounds were sampled from the water of the Ebro River Basin as the target pollutant, followed by a multi-dimensional assessment and analysis of the environmental risks of the pollutants. Basic data of pollutants in river water are shown in Table 1. The comparison of risk levels of pollutants in river basins using both methods are shown in Fig. 2.

Table 1
The half-life data of target pollutants in Ebro River and PNEC data table

Name of contaminant	CAS	Chemical formula	Half-life(d)	Half-life threshold(d)	C	MEC (ng L^{-1})	PNEC (ng L^{-1})
Carbendazim	10605-21-7	$C_9H_9N_3O_2$	8	60	7.5	2.78	1.5
Fenitrothion	122-14-5	$C_9H_{12}NO_5PS$	86.1	60	0.70	0.11	0.09
Hexythiazox	78587-05-0	$C_{17}H_{21}ClN_2O_2S$	24.6	60	2.44	7.41	6.1
Imazalil	35554-44-0	$C_{14}H_{14}Cl_2N_2O$	151	60	0.40	61.01	92
Metolachlor	51218-45-2	$C_{15}H_{22}ClNO_2$	39	60	1.54	0.55	1
Prochloraz	67747-09-5	$C_{15}H_{16}Cl_3N_3O_2$	60	60	1	15.59	18
Propazine	139-40-2	$C_9H_{16}ClN_5$	90	60	0.67	0.14	40
Tebuconazole	107534-96-3	$C_{16}H_{22}ClN_3O$	62	60	0.97	2.36	100

The results indicated that the risk levels for carbendazim (CARB), hexthiazole (HTZ) and imazalil in the pollutants were changed significantly. CARB is a broad-spectrum fungicide and used for foliar spraying, seed treatment and soil treatment (Mrinmay et al. 2019). After use, residues may subsequently appear in food, water, soil, or other media, and can also be absorbed by crops and passed along the food chain to humans. Exposure to CARB can lead to downregulation of humoral immune function and failure of spermatogenesis (Fang et al. 2010; Xiao et al. 2013). The risk of CTAB is reduced from high to medium by calculating and comparing the two methods, which can appropriately reduce the risk assessment of carbendazim. HTZ is an efficient and environmentally friendly acaricide. HTZ is also a widely used to control pests of a variety of food crops. According to the European Food Safety Authority (EFSA), EFSA recently proposed to increase the maximum residue limit of hexythiazox in tea from 0.05 mg/kg to 4 mg/kg, which to a certain extent can reflect the doubts about its environmental risk, and the risk should be appropriately reduced.

For all water samples obtained, SRF values were calculated to be below 0.1, indicating the presence of pesticides may cause a low risk to aquatic organisms with the exception for imazalil where an SRF value of 1.66 was observed, indicating that its presence may pose a high risk to aquatic organisms. These fungicides like imazalil have been used in some agribusinesses at concentrations up to 0.6-2 g L^{-1} to control fungal infections during fruit and seed storage (Lozowicka et al. 2016). As a result, high amounts of imazalil residues were released during the washing step, producing high volume of contaminated wastewater (Carra et al. 2015; Karas et al. 2016; Ponce-Robles et al. 2017). Imazalil is also recommended for use as a fungicide by the Ministry of Agriculture in China. Although its toxicity is low, due to the high emission strongerenvironmental sustainability, the monitoring of its environmental emission should be further strengthened. In addition, the European Union's Food Safety Authority (EFSA) recommend that the potential environmental risk of azole drugs should be under close vigilance after reviewing the maximum Residue Limits (MRLS) for imazole in certain foods in On 30 October 2018.

As expected, after evaluating the worst-case scenario imazalil exhibited a high risk to aquatic organisms while the presence of carbendazim and hexythiazox posed a moderate risk to aquatic organisms. The presence of pesticide residues in the aquatic environment, particularly at high concentrations, may cause detrimental effects on aquatic organisms and eventually human beings.

Application Domain For Pfoas Based On Srfs

In this study, the surface water of Tianjin city was sampled for the risk assessment, and target pollutants included perfluorinated compounds and organophosphate. Basic data such as chemical formula and half-life of pollutants are shown in Table 2. The evaluation results are shown in Fig. 3.

Table 2
Perfluorinated compounds and organophosphate in Tianjin surface water

Compound	Abbr.	CAS	Chemical formula	Half-life(d)	Half-life threshold (d)	C	MEC (ng L^{-1})	PNEC (ng L^{-1})
Perfluorrooctane sulphonate	PFOS	1763-23-1	$C_8HF_{17}O_3S$	1.48E + 04	60	0.0041	1.61	1000
Perfluorooctanoic acid	FFOA	335-67-1	$C_8HO_2F_{15}$	1.58E + 03	60	0.038	15.1	100000
Triethyl phosphate	TEP	78-40-0	$C_6H_{15}O_4P$	4.90	60	12.24	1.683	9.0E + 05
Tri(2-ethylhexyl) phosphate	TEHP	78-42-2	$C_{24}H_{51}O_4P$	4.23	60	14.18	47.4	5.0E + 05
Tri(2-chloroethyl) phosphate	TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$	3.68	60	16.30	473.79	5.1E + 04
Tris(1-chloro-2-propyl) phosphate	TCPP	13674-84-5	$C_9H_{18}Cl_3O_4P$	3.68	60	16.30	6.3	4.5E + 04
Tris(1,3-dichloro-2-propyl) phosphate	TDCP	13674-87-8	$C_{12}H_{15}Cl_6O_4P$	4.08	60	14.71	3.249	3.9E + 04

Perfluorinated compounds (PFCs) have been recognized as emerging global pollutants and have attracted scientific and political attention worldwide (He et al. 2018). To date, PFCs have been found to be released into the environment and biological matrices through the use of PFC-containing products or through the degradation of their precursors. Due to their bioaccumulation and multiple toxicities, PFCs are persistent in the environment and widely present in wildlife and humans (Coperchini et al. 2015). Their presence in the environment poses a risk to ecosystems. Using both RQ and SRF methods of, the risk values of PFOS were found to be less than 1, and its risk level were changed from low to medium. The rise of PFOS levels in surface water may therefore affect aquatic ecosystems. The PFOA risk level was not changed. But the risk of PFCs contamination in surface water to ecosystem should draw more attention because of their bioaccumulation (Lu et al. 2019).

Organophosphate esters (OPEs) are widely used in plastics, textiles, building materials, lubricants, electronics and coatings due to their excellent physicochemical properties and high cost performance (Li et al. 2016). Although incidents of environmental contamination from OPE are rarely reported, they are ubiquitous in the environment as re-emerging contaminants considered to be potential health concerns, and research on the toxic effects of these chemicals is increasing. Bioaccumulation data and risk assessments of OPEs in aquatic organisms such as fish, algae and snails have been reported (Xing et al. 2019; Zha et al. 2018). The SRF values of TEP, TEHP, TCEP, TCPP, and TDCP in the organophosphate in the figure were all less than 1, indicating that there was no risk for aquatic organisms in the watershed.

Application domain for endocrine disruptors based on SRFs

Endocrine disruptors (EDs) are compounds that cause great environmental problems. EDs are a large group of substances of natural or anthropogenic origin that interfere with an organism's endocrine system. They interact with estrogen receptors to enhance or inhibit the normal function of the hormone, potentially leading to adverse effects such as sterility and species extinction in aquatic organisms (Filipkowska and Lubecki 2016; Tijani et al. 2016). Although such pollutants are usually present in the environment in low concentrations, some of them are toxic per liter concentrations (Teixeira et al. 2021). Their adverse effects leading to certain cancers and other non-communicable diseases such as diabetes and adverse effects on aquatic life populations have been reported (Olaniyan and Okoh 2020). In this study, endocrine disruptors in surface water of Xiang Jiang River were used as target pollutants to evaluate their environmental risks. Related pollutant data are shown in Table 3. RQ and SRF methods were used to calculate the risk value of each pollutant of endocrine disruptors in Xiang Jiang River. The comparison results are shown in Fig. 4.

Table 3
Endocrine disruptors in surface water of Xiang Jiang River, China

Name of contaminant	CAS	Chemical formula	Half-life(d)	Half-life threshold(d)	C	MEC (ng L^{-1})	PNEC (ng L^{-1})
Progesterone	57-83-0	$C_{21}H_{30}O_2$	666.66	60	0.09	8.1	415
Testosterone	58-22-0	$C_{19}H_{28}O_2$	1.17E + 04	60	5.1E-03	6.5	100
Androstenedione	1963-5-8	$C_{19}H_{26}O_2$	1.12E + 03	60	5.4E-02	4.4	14
Estrone	53-16-7	$C_{18}H_{22}O_2$	1.06E + 05	60	5.7E-04	51.33	6
Bisphenol A	1980-5-7	$C_{15}H_{16}O_2$	4.02E + 06	60	1.5E-05	30.9	2000

The lack of regulated monitoring has resulted in increasing concentrations of micropollutants in the environment and increased public concern about the presence of endocrine disrupting compounds in surface waters. In order to remove these compounds, appropriate identification and evaluation methods need to be employed. The risk values were significantly changed for progesterone, testosterone, androstenedione and bisphenol A from low to high risk using the SRF method. Chronic exposure to testosterone at lower concentrations can cause endocrine disruption in aquatic animals (Appa et al. 2018). In addition, environmental pollutant levels of estrogen may contribute to breast cancer in women, prostate cancer in men, and reproductive system abnormalities in men (Sutaswiriya et al. 2021). Androstenedione belongs to steroidal androgens. It mainly comes from the excrement and urine of livestock and poultry as well as the discharge of wastewater from paper mills and urban sewage treatment plants. The continuous discharge of pollution sources leads to the male phenomenon of fish in some areas, which has a strong negative impact on species richness and ecological balance, and raises the environmental risk.

Bisphenol A (BPA) is a well-known endocrine disrupting compound commonly found in industrial wastewater and wastewater treatment plants (Godiya and Park 2022). The widespread use of BPA in the plastics industry has led to its widespread distribution in the environment and to inevitable human exposure to the substance through dietary and non-dietary sources (Geens et al. 2012; Usman and Ahmed 2016). Previous studies have shown that BPA can be detected in dust, surface water, industrial sewage, sediment and soil. BPA can interact with estrogen and nuclear receptors to varying degrees, interfering with their natural expression, thereby acting as endocrine disruptors. There is good evidence that BPA at 1–10 $\mu g\ ml^{-1}$ is acutely toxic to freshwater and marine species, and this disturbance can adversely affect reproductive and metabolic functions. This has prompted strict EU regulations on the use of BPA in some industrial products, leading to the widespread use of its structural and functional analogs in manufacturing, such as bisphenol AF (BPAF) (Artham and Doble, 2012; Mouneimne et al. 2017; Chen et al. 2021). Combining the persistence level and the exposure effect, the risk assessment level is high, so the release of BPA in the water environment and its further identification are still worthy of attention.

Conclusions

As risks are gradually recognized by people, risk assessment theories are constantly enriched and developed, and we should pay close attention to pollutants with potential environmental risks. Existing chemical risk assessment methods are mostly based on the short-term exposure effects of pollutants, aiming at the environmental pollution that has occurred. The accuracy of environmental risk prediction for some new pollutants that are not included in routine environmental monitoring but may enter the environment and cause known or potential negative ecological or health effects needs to be improved.

In this study, a multi-dimensional environmental risk assessment method combining with pollutant stabilization period was proposed. The diagnostic results indicated that the assessment method is more accurate to determine the environmental risk level of unknown risk pollutants, and data were consistent with those from existing control measures. Comparing with the existing methods based on the theoretical basis, the SRF method is superior in the identification of toxic substances. The SRF method can be more comprehensively applied to discover new environmental pollutants from different dimensions, improve the risk prediction performance of new pollutants, and provide better environmental early warning references. It helped protect human health, biology and other environmental components. Therefore, the application of persistence coefficient in environmental risk assessment method improved the risk assessment. Since samples were collected from a few selected areas in this study, for future research, the sampling sites can be appropriately expanded to study the risks of different new pollutants, which have broad application prospects.

Declarations

Availability of data and materials The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Authors contributions L. Li: The integrity of the entire thesis work, from creation, design to the completion of the final version; Y. Dong: The integrity of the entire research work, including innovative ideas, procedures, implement and revision; Y. Chen: Data collation and paper editing; J. Jiao: Data collection and analysis; X. Zou: Formal analysis and modification.

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Figures

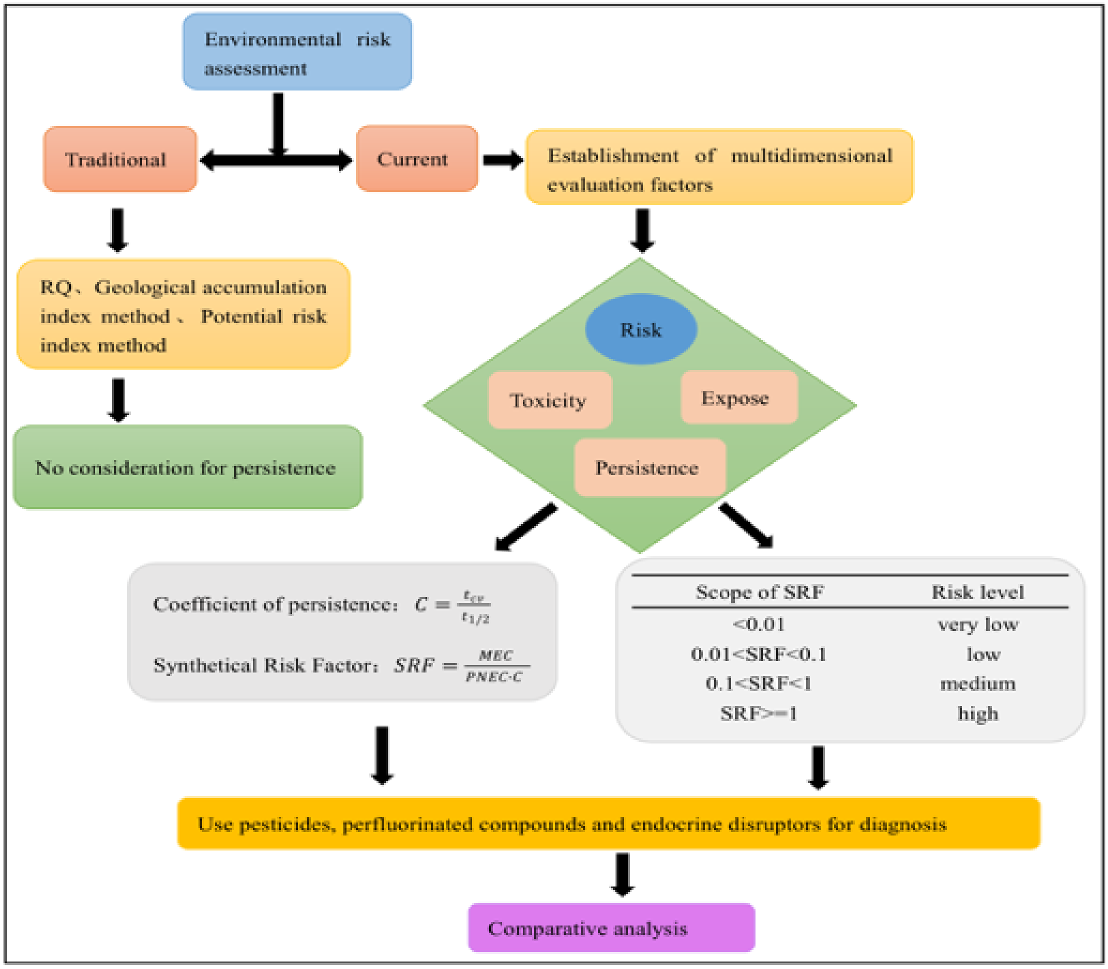

Figure 1

Flow chart of multi-dimensional assessment factor environmental risk method. It can visually display the difference between the traditional evaluation method and the new method in a graphic way, which can better reflect the logic and hierarchy of the article.

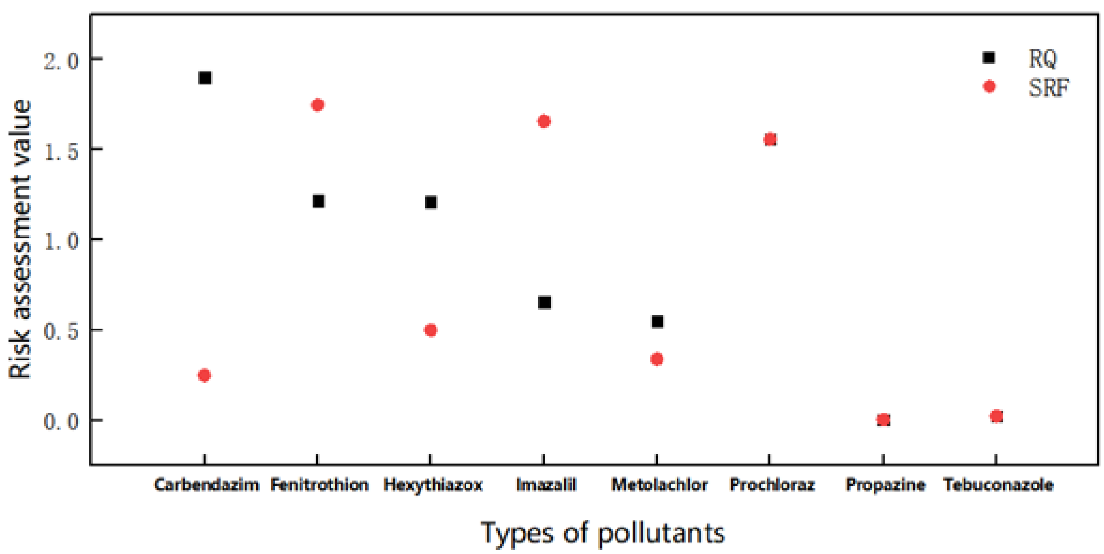

Figure 2

Evaluation chart of environmental risk grade of pesticide residues. The potential ecotoxicology risk from the presence of pesticides to aquatic organisms was assessed with RQ and SRF methods. The RQ value or SRF value is greater than 1 indicate that the water may be risky to aquatic ecosystem.

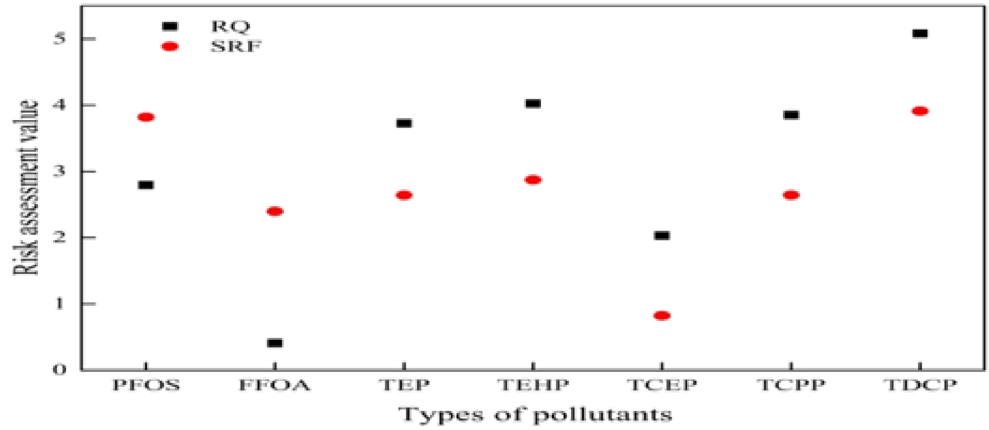

Figure 3

Evaluation chart of environmental risk grade of perfluorinated compounds and organophosphates. The risk assessment values on the y-axis in the above graph are logarithmic. The risk of exposure to perfluorinated compounds and organophosphates in the aquatic environment was assessed according to the RQ and SRF methods by comparing the detected concentrations of the target individuals with the advisory guideline values.

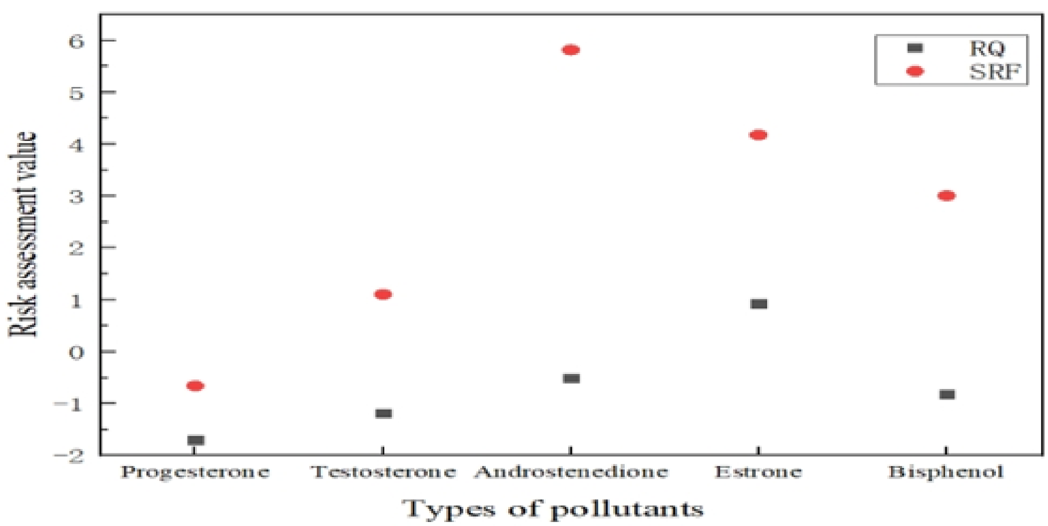

Figure 4

Evaluation chart of environmental risk grade of pesticide residues. The above values are logarithmic. According to the risk assessment grade, the degree of changes in pollutant risk of the two assessment methods was compared.