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Revealing the Extent of Pesticide Runoff to the Surface Water in Agricultural Watersheds

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Abstract: Pesticides are beneficial in protecting crops from pests and improving agricultural productivity; however, concerns on pesticide pollution in water have increased due to their indiscriminate use and lack of adequate regulations. Many studies have focused on the risks of pesticides considering the limited number and types of pesticide residues in crops and soils, and duration, and very few have focused on surface water throughout the year. Therefore, this study comprehensively identified 308 pesticides in surface water samples collected monthly over one year in the Saemangeum Basin, Korea. Both targeted and non-targeted analyses were used to identify 171 and 24 pesticides, respectively. Results highlight the extensive extent of pesticide contamination. Among the quantified pesticides, bromobutide and pretilachlor consistently exhibited high concentrations and risk levels, as indicated by their elevated risk quotient (RQ) values. Seasonal variations in pesticide concentrations revealed distinct patterns with intensified herbicide use during summer and increased insecticide concentrations during autumn. This study highlights the presence, distribution, and associated ecological risks of pesticides in surface waters, emphasizing the necessity of comprehensive monitoring and regulatory measures to protect aquatic ecosystems. The high RQ values identified for specific pesticides underscore the urgent need to implement effective strategies to mitigate these environmental risks.

Keywords: pesticide; non-targeted analysis; predicted no effect concentration; risk quotient; surface water

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1. Introduction

Historically, pesticide management has primarily focused on residual concentrations in agricultural products, primarily from the consumer's perspective [1]. However, in addition to their role in increasing production [2–4], it is important to recognize that these chemicals can have adverse effects not only on consumers but also on agricultural workers [5] and the environment. Pesticides are initially registered with the establishment of safe usage standards based on environmental biotoxicity tests and assessments of environmental persistence [6]. However, often, there is a lack of institutional oversight or monitoring systems during pesticide application in terms of their excessive or inappropriate use, potentially violating the established safe usage standards [7]. In many countries, the established environmental standards and monitoring programs for pesticides focus exclusively on organophosphorus compounds, and even for these, the scope is limited only to some of them. Approximately 47 types of organophosphorus pesticides have been reported [8], 42 of which are distributed in Korea. Notably, the environmental standards in Korea include only five types of organophosphorus pesticides such as diazinon, phenthoate, parathion, ethoprophos (EPN), and demethon-S-methyl. Furthermore, parathion, EPN, and demethon-S-methyl were classified as banned pesticides approximately a decade ago, leaving diazinon and phenthoate as the only organophosphorus pesticides in active use. Consequently, of the 47 types of organophosphorus pesticides, only two are subject to regulations.

Among the pesticides with a significant market share, the major categories are organophosphates, neonicotinoids, organochlorine, carbamates, triazoles, and amides [9,10]. Organophosphates offer a significant advantage over highly persistent organochlorines because of their rapid decomposition and extensive use in pest control [11,12]. Within this group, organophosphorus pesticides are estimated to account for nearly 40% of the global pesticide market [13,14]. Organochlorine pesticides have been banned globally through the Stockholm Convention, and organophosphorus pesticides are emerging as replacements [11–14]. However, there is limited enthusiasm in the environmental sector to monitor and establish environmental standards for organophosphorus pesticides. To enhance agricultural productivity, approximately 500 types of pesticides, totaling approximately 2 million tons, are applied globally each year [15,16]. In Korea, 520 types of pesticides are used, amounting to approximately 20,000 t per year [17]. However, the extent to which these pesticides are released into the environment and their impact on aquatic ecosystems remains largely unknown. According to 2020 data from the Food and Agriculture Organization of the United Nations (FAO) [17], pesticide usage in South Korea is 10.0 kg per hectare (ha). This usage was approximately 10 times higher than that of countries with larger land areas, including Brazil (0.2 kg/ha), China (0.5 kg/ha), the United States (1.0 kg/ha), and Canada (1.4 kg/ha). On the contrary, South Korea's pesticide consumption was on par with countries known for intensive rice-based agriculture and smaller land areas, such as Hong Kong (13.8 kg/ha), Taiwan (13.4 kg/ha), and Japan (11.1 kg/ha).

Surface water is an important water supply system [18]. Surface water is susceptible to pesticide contamination via surface runoff, leaching, and rainfall from agricultural fields [19,20]. Furthermore, drainage can transport pesticides from the soil and groundwater to surface water [21]. Surface water contamination is typically linked to the farming season, and its effect may be more temporary than that of ground water [22]. Every year, many research papers on pesticide distribution in surface waters are published. However, the majority of these studies focus on a limited selection of pesticides, typically numbering just a few dozen at most [21,23–26]. Li et al. [27] investigated the spatiotemporal distribution of 106 pesticides in 16 major estuaries in China for representative months during the wet, dry, and normal seasons but only for three months. Sun et al. [28] conducted a study during the annual cycle, but only identified 25 pesticides (of 164 targeted) in surface water in Poland. Therefore, it remains unclear whether the studied pesticides represent the entirety or only a fraction of those that have been released into the environment. From this perspective, we recognized the urgency of assessing the extent to which pesticides applied to farmland run off into nearby rivers. Additionally, continuous monitoring is required to estimate the residues of various pesticides in environmental waters, regardless of the farming season. Therefore, in this study, we aimed to quantify the presence of all pesticides without limitations on the availability of standard materials, as opposed to focusing solely on a select few pesticides of interest. Through the exclusive analysis of pre-targeted substances, it is possible to mistakenly assume that compounds beyond the considered scope do not exist. To address this issue, our study employed a comprehensive approach, that combined targeted analysis with a non-targeted analysis technique to identify all the pesticides present in the samples. Although non-targeted analysis methods do not provide precise quantification of chemicals in a sample, they are primarily utilized as a qualitative approach to identify the chemicals present, and hence are widely applied in metabolomic research.

In this study, we developed a comprehensive method for the quantitative determination of 308 pesticides in surface water samples by combining online solid phase extraction (SPE) and liquid chromatography-mass spectrometry (LC-MS/MS) [29,30]. We also developed a qualitative pesticide determination method using a metabolite research technique [31]. From March 2021 to February 2022, we collected 14 water samples monthly, for a total of 167 samples. Our study focused on assessing the runoff and distribution of pesticides in Saemangeum Basin, Korea. We also introduced an ecological toxicity risk assessment approach to evaluate the impact of pesticides on aquatic ecosystems [32].

2. Materials and Methods

2.1. Study Area

The Saemangeum Basin, which is recognized as the largest artificially reclaimed land area worldwide, was chosen as the study site. The construction of the Saemangeum embankment, achieved by blocking the estuaries of the Mangyeong and Dongjin Rivers, commenced in November 1991. Water barrier construction was completed in 2006, followed by reclamation work and site preparation in 2020. Despite the implementation of various water quality improvement measures, the Saemangeum Basin has not yet attained a satisfactory water quality level. As a result, it only marginally meets water quality standards through seawater distribution. With a catchment basin covering 3319 km^2 on the eastern side, the Saemangeum Reservoir exhibits diverse land uses, including agricultural, forested, and urban or built-up areas accounting for 49.8, 34.6, and 8.8%, respectively. Although pastureland comprises only 1.7% of the basin's total area, livestock breeding activities contribute to 24% (based on the standard for biochemical oxygen demand) of the contamination within the Saemangeum Basin. The Saemangeum Basin consists of the Mangyeong and Dongjin Rivers. The Mangyeong River is connected to the Jeonju Stream, which serves a population of 650,000, and the Iksan Stream, which traverses vast expanses of densely populated pasturelands. On the other hand, the Dongjin River runs through an agricultural area that yields approximately 234,000 tons of rice per year.

2.2. Sample Collection and Preservation

Surface water samples were collected from seven sampling sites, each in the Mangyeong and Dongjin River Basins. The sampling was conducted monthly from March 2021 to February 2022. The geographical locations of the sampling points are shown in Figure 1. The sampling points are denoted as M for the Mangyeong River and D for the Dongjin River. Starting with Gosan (M1), which represents the uppermost point of the Mangyeong River, the following points include the middle stream (M2) and Jeonju Stream (M2-1), which run through Jeonju, a small city with a population of 650,000; the Samrye branch (M3) representing the middle part of the Mangyeong River; and Iksan Stream (M3-1). The downstream point of the Mangyeong River is designated as M4, whereas the upstream junction is marked as M4-1. In the case of the Dongjin River, the uppermost point is labeled as D1, followed by the middle stream (D2) and the junction of the Jeongeup Stream (D2-1). The downstream point of the Dongjin River is designated as D3, and the junctions of the Gobu (D3-1), Wonpyeong (D3-2), and Sinpyeong (D3-3) streams are also included. The sample from the Sinpyeong Stream (D3-3) could not be collected in July 2022 due to river flooding, resulting in a total of 167 samples (14 points $\times$ 12 months—1 point).

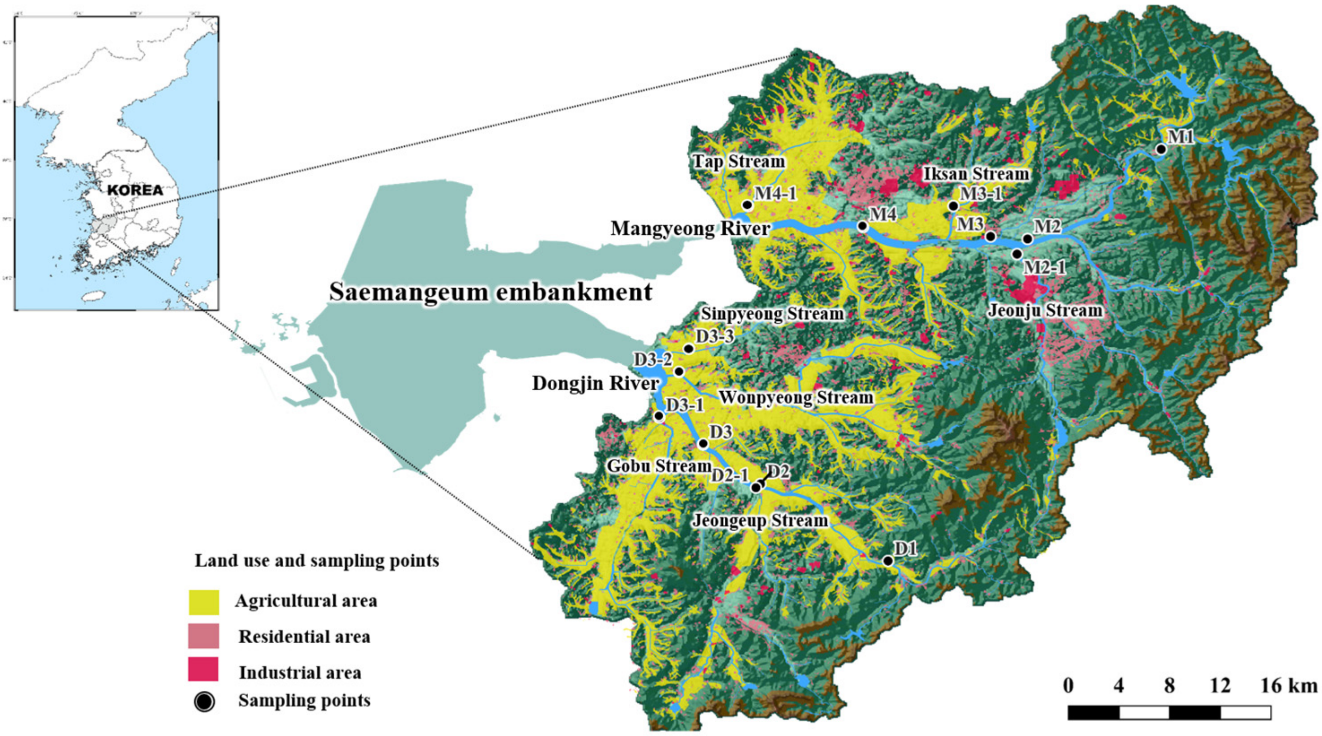

Figure 1. Map showing water sampling points.

2.3. Sample Analysis

The sample preparation and LC-ESI-Orbitrap-MS analysis were modified from Jeon et al. [33] as follows. The collected samples were filtered onsite using a 0.2-µm pore size filter. They were then transported to the laboratory while maintaining a low temperature using an ice box and stored in a freezer at −20 °C until analysis. Formic acid and deionized purified water were obtained from Fisher Scientific (Loughborough, UK), whereas high performance liquid chromatography grade or higher acetonitrile, acetone, and methanol were obtained from Honeywell Burdick & Jackson (Charlotte, NC, USA). Ammonium formate was obtained from Sigma-Aldrich (St. Louis, MO, USA). A total of 308 standard materials were used in this study, including products from AccuStandard (New Haven, CT, USA), Dr. Ehrenstorfer GmBH (Augsburg, Germany), Sigma-Aldrich (St. Louis, MO, USA), HPC Standards GmbH (Cunnersdorf, Germany), CHIRON (Trondheim, Norway), TRC (Toronto, ON, Canada), AK Scientific (Union City, CA, USA), and Carbosynth (Compton, UK). Standard stock solutions were prepared by mixing 308 standard substances at a concentration of 100 µg/L. These solutions were further diluted with acetonitrile to obtain concentrations of 2.5, 5, 10, 20, 25, 50, and 100 µg/L. Sample pretreatment was conducted using the Equan MAX online SPE system from Thermo Fisher Scientific (Waltham, MA, USA), employing Hypersil GOLD aQ (20 × 2.1 mm, 12 µm) as the trap column. Prior to sample injection, the system was washed with 2% methanol, and then 1000 µL of the sample was injected. During sample injection, nonpolar organic substances are adsorbed onto the trap column, whereas highly polar ions and water are discarded. The mobile phase, with the same composition as the LC analysis, was subsequently passed through the trap column in the reverse direction using a pipeline switch, allowing for the elution and separation of nonpolar organic compounds as they passed through the LC analysis column. The Dionex Ultimate 3000-Q LC system from Thermo Fisher Scientific (Waltham, MA, USA), coupled with the CORTECS T3 column (100 × 2.1 mm, 1.6 µm) from Waters (Milford, CT, USA) was used. The column oven was maintained at a temperature of 40 °C. The mobile phases consisted of degassed deionized water (mobile phase 1) and methanol (mobile phase 2) containing 0.1% formic acid and 5 mM ammonium formate. The mixing ratio of mobile phases 1 and 2 varied over time, while the flow rate was maintained at 200 µL/min. The

Orbitrap Q Exactive Plus model from Thermo Fisher Scientific (Waltham, MA, USA) was used for mass spectrometry analysis. Ions were generated in heated electrospray ionization positive-ion mode with a spray voltage of 3800 V. The mass accuracy was set to 5 ppm or less with a resolution of 70,000 in the full-scan mode and 13,000 in the $ddMS^2$ mode. The mass range varied from 150 to 1500 m/z. The MS/MS method was based on a previous report [34] with some modifications. Specific details regarding the ionization source and mass spectrometer operating conditions are provided in Table S1.

2.4. Quality Assurance and Control

The standards of 308 target compounds were prepared at a concentration of 100 ng/L and seven replicate samples prepared at a concentration of 500 ng/L were analyzed. The standard deviation of the result values of the seven replicates was obtained, which was multiplied by 10 to obtain the LOQ. The accuracy and precision of the results were obtained using the recovery rate and relative standard deviation. Details of the resulting values are presented in Table S1.

2.5. Environmental Risk Assessment of a Mixture of Pesticides

Environmental Risk Assessment (ERA) can be employed to evaluate the potential risks associated with the use of pharmaceutical and chemical substances intended for human use. The risk quotient (RQ) is used to estimate the potential risk. This value is calculated by dividing the predicted environmental concentration (PEC) by the predicted no effect concentration (PNEC) [35]. The PNEC is defined as the environmental concentration at which no harmful effects on non-human ecosystems are predicted to occur. When the measured environmental concentration (MEC) is available instead of the PEC, the RQ is determined by dividing the MEC by the PNEC value. The PNEC value was calculated by selecting the lowest value among the half-lethal dose (LC_{50}) or toxic effect dose (EC_{50}) of birds, *Daphnia*, and fish and dividing it by the assessment factor (AF). When all three toxicity values were present, the AF was entered as 100, and when two or fewer toxicity values were present, the AF was entered as 1000. Toxicity data were obtained from ECOSAR (Version 2.0) for algae and the toxicity estimation software tool (Version 5.1.1) for *Daphnia* and fish. The consensus method option was used for obtaining the LC_{50} values for *Daphnia magna* (48 h) and fathead minnow (*Pimephales promela*) (96 h).

$$\begin{aligned} RQ_{single} &= \max\left(\frac{MEC}{PNEC_{algae}}, \frac{MEC}{PNEC_{daphnia}}, \frac{MEC}{PNEC_{fish}}\right) \\ &= \max\left(\frac{MEC \times AF_{algae}}{LC_{50,algae}}, \frac{MEC \times AF_{daphnia}}{LC_{50,daphnia}}, \frac{MEC \times AF_{fish}}{LC_{50,fish}}\right) \end{aligned} \quad (1)$$

The ERA of mixtures is based on the whole-mixture and component-based approaches. In the component-based approach [36], the concentration addition (CA) and independent action methods are commonly employed. In this study, the CA method, which is widely recommended in guidelines and research, was utilized to determine the PNEC of the mixture. If the individual PNEC calculation method is directly applied to the CA method, it results in varying species and AFs for each substance, contradicting the principles of the same biological endpoints and organisms.

3. Results and Discussion

3.1. Occurrence of Pesticides

Among the 308 pesticides analyzed, 171 were above the LOQ. The non-targeted analysis revealed 24 additional pesticide types, further expanding the scope of the study. The pesticides detected are listed in Table S2. Because non-targeted analysis does not provide concentration data, only peak areas are presented. Bromobutide exhibited the highest mean concentration of 1.18 μg/L followed by pretilachlor at 0.49 μg/L. In the 167 samples analyzed, bromobutide and pretilachlor were detected 72 and 68 times, respectively. The most frequently detected pesticides were carbendazim and dinotefuran at 156 and 128 times, with average concentrations of 0.20 and 0.09 μg/L, respectively. The substance with the highest concentration was bromobutide at 9.9 μg/L at point M3-1 in June. The next highest concentration was also attributed to bromobutide, at 7.9 μg/L in June at point M4-1. The 171 pesticides detected in this study, including 52 herbicides, 58 fungicides, and 61 insecticides, were evenly distributed according to their intended use. A total of 67 pesticides were used for rice farming, whereas 104 were employed in horticulture. The number of pesticides used in horticulture was approximately 1.5 times greater than that used in rice farming. The distinction between the pesticides used in rice farming and horticulture is somewhat ambiguous. Therefore, when rice is included as a specific crop, it is categorized as rice farming.

Prioritization of pesticides is essential when dealing with substances characterized by low and high detection frequencies and average concentrations. Although no detection of a particular substance in a sample can be considered as "zero," this approach is generally avoided as it distorts the mean values. Therefore, in this study, we assigned priorities by multiplying the mean concentration without "zero" by the detection frequency (%), and these rankings are represented in Figure 2, which includes a quartile graph and frequency distribution. Based on the simultaneous consideration of the average concentration and detection frequency (from top left to bottom right of Figure 2), herbicides were found to occupy top positions, particularly those used in rice were predominant. In the study area, the extent of rice cultivation (66,611 ha) was 2.7 times larger than that of fields of other crops (24,329 ha), implying a significantly greater use of pesticides in rice farming. Additionally, because rice farming uses more water than other crops, there are frequent cases of the direct discharge of water from paddy fields into nearby rivers due to deliberate discharge or rainfall-induced flooding. This may have contributed to the high detection levels of pesticides used in paddy fields.

However, this inference is not confirmed in Figure 3. This figure presents a chart that aggregates all the detected pesticides by location and month. While pesticide quantities increased sharply in October across the entire region, no distinct variation was observed from May, when rice cultivation begins with water confinement, to September, during the period of rice growth, when the rice is cultivated by submerging. Figure 3 shows a decrease in both the number and total concentration of detected pesticides in July and August, which aligns with the characteristics of the monsoon season. During this period, pesticides are often washed away from the crops because of heavy rainfall [37–40]. This could also be due to cost considerations, as people refrain from using pesticides during rainy seasons. Alternatively, the decrease in the number and total concentration of the detected pesticides may result from an increase in water flow in rivers leading to a dilution effect. The sharp increase in both the quantity and variety of pesticides in October can be attributed to a significant surge in pesticide usage to reflect preparations for the upcoming harvest season, followed by a gradual decrease in the following months. Notably, even during winter, which is considered a non-growing season for crops, pesticides are continuously detected. The Sinpyeong Stream exhibited the highest pesticide concentration even in December (Figure 3b). Conversely, other locations exhibited a different pattern, with a decline in December and a subsequent increase in January of the following year. When pesticides enter environmental water, processes such as transformation and degradation occur, which are influenced not only by the pesticide's chemical properties but also by environmental conditions such as humidity and temperature [41,42]. For instance, Bloomfield et al. [43] reported that higher relative humidity induces faster degradation of pesticides. Indeed, climate factors lead to changes in the type and amount of pesticide application, which results in seasonal occurrence patterns [44]. Previous studies have mentioned the seasonal variations of pesticides [12,21,27], but the reasons for these patterns are not fully understood. Although it seems that the rainfall event is a major factor for seasonal variation, further research is needed to assess its extent.

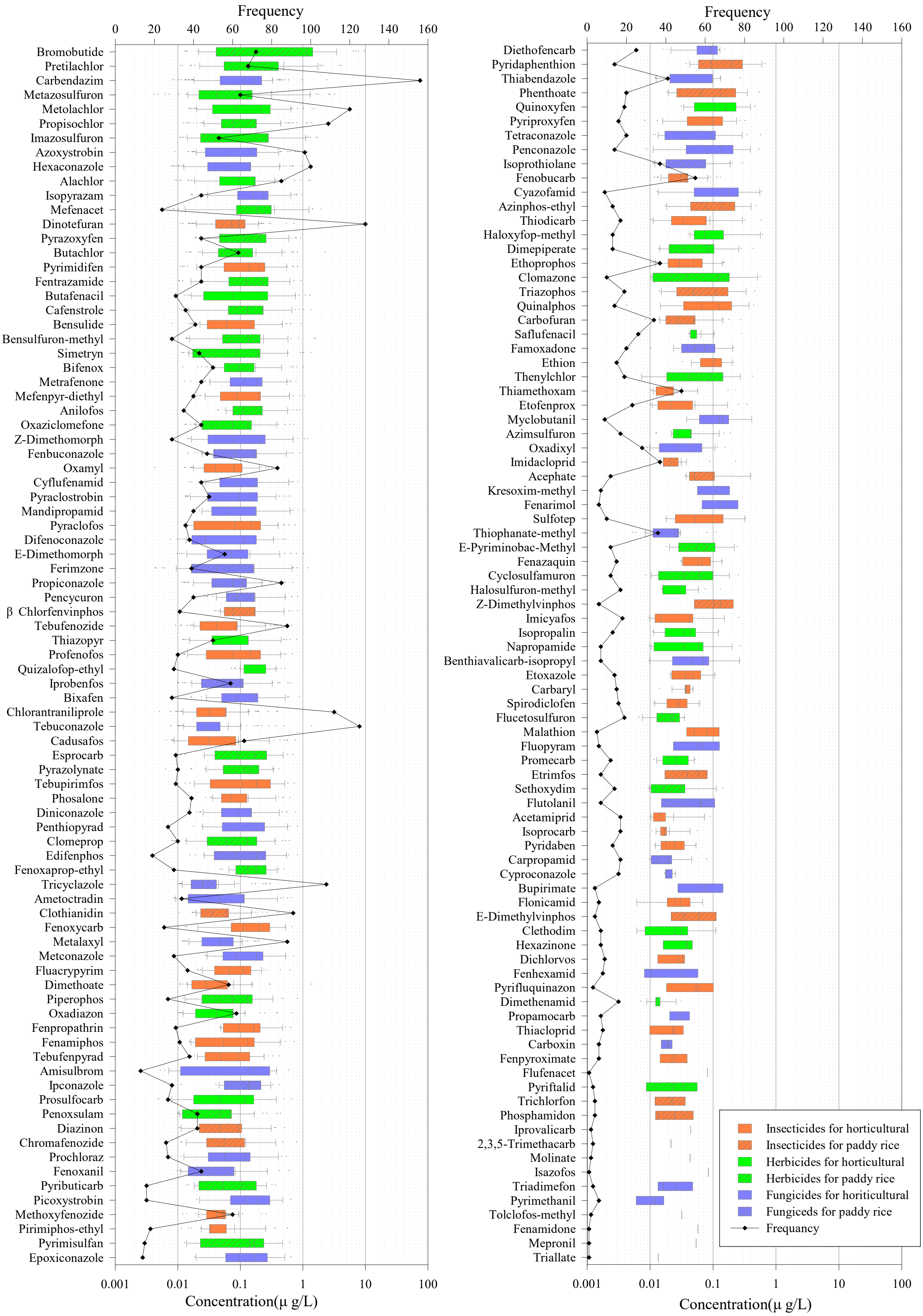

Figure 2. Concentration range and frequency of 171 targeted pesticides.

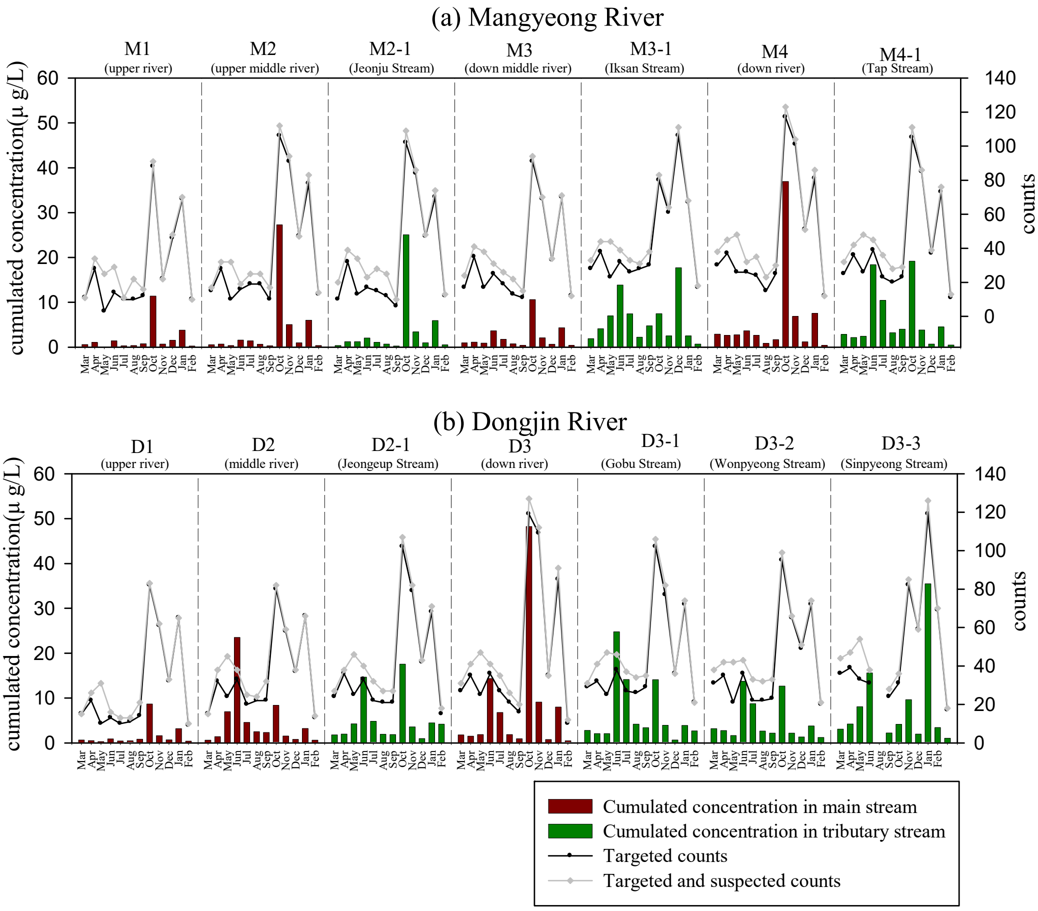

Figure 3. Cumulative concentrations and counts of pesticides.

Obtaining representative water samples that accurately reflect complex and dynamic aquatic environments is challenging. Factors, such as fluctuations in water flow due to precipitation or upstream weir (dam) discharge, as well as the timing of sampling, such as sampling upstream later than in the downstream, can disrupt trends and increase the complexity of interpretation. It is firmly established that pesticides are consistently detected even in winter; however, it is challenging to provide a clear explanation for this phenomenon. Based on location, the overall total concentrations of pesticides in both the Mangyeong and Dongjin Rivers increased after their confluence with the Iksan and Jeongeup Streams, respectively. In contrast, a different pattern emerged midstream in the Mangyeong River, where the total concentrations were consistently lower than those upstream. Unlike the trends observed downstream, this phenomenon was regarded as a result of dilution due to an increase in the volume of water, despite its lower pesticide impact. This trend corresponds to the phenomenon observed in the Jeonju Stream, located between the upstream and midstream, which consistently showed lower total concentrations compared to other tributaries (except for October). The Jeonju Stream passes through a medium-sized urban area with a population of 650,000, distinguishing it from other tributaries that are significantly affected by agriculture. Consequently, it experiences less of an agricultural impact.

Nevertheless, the sharp increase in total concentrations in October suggests some influence of crop farming, and this inference becomes clearer, as shown in Figure 4. Before passing through the urban area, the upper reaches of the Jeonju Stream are adjacent to mountainous regions, making it difficult to engage in rice farming in this area. Additionally, it is evident that the proportion of pesticide usage for rice farming is lower in this area than in other areas. Notably, an increase in the proportion of pesticides used in rice farming during summer, regardless of the absolute quantities of pesticides used across all locations, can be observed (Figure 4). During seasons other than summer, pesticides used for horticultural farming account for approximately two-thirds of the total pesticide usage. However, during summer, there was a significant increase in the share of pesticides used for rice, accounting for approximately 80% of the total usage. Considering all these aspects, pesticides are continuously released into the aquatic environment irrespective of the season, and significant variations in both the quantity and types of pesticides are observed depending on the types of cultivated crops and their growth stages.

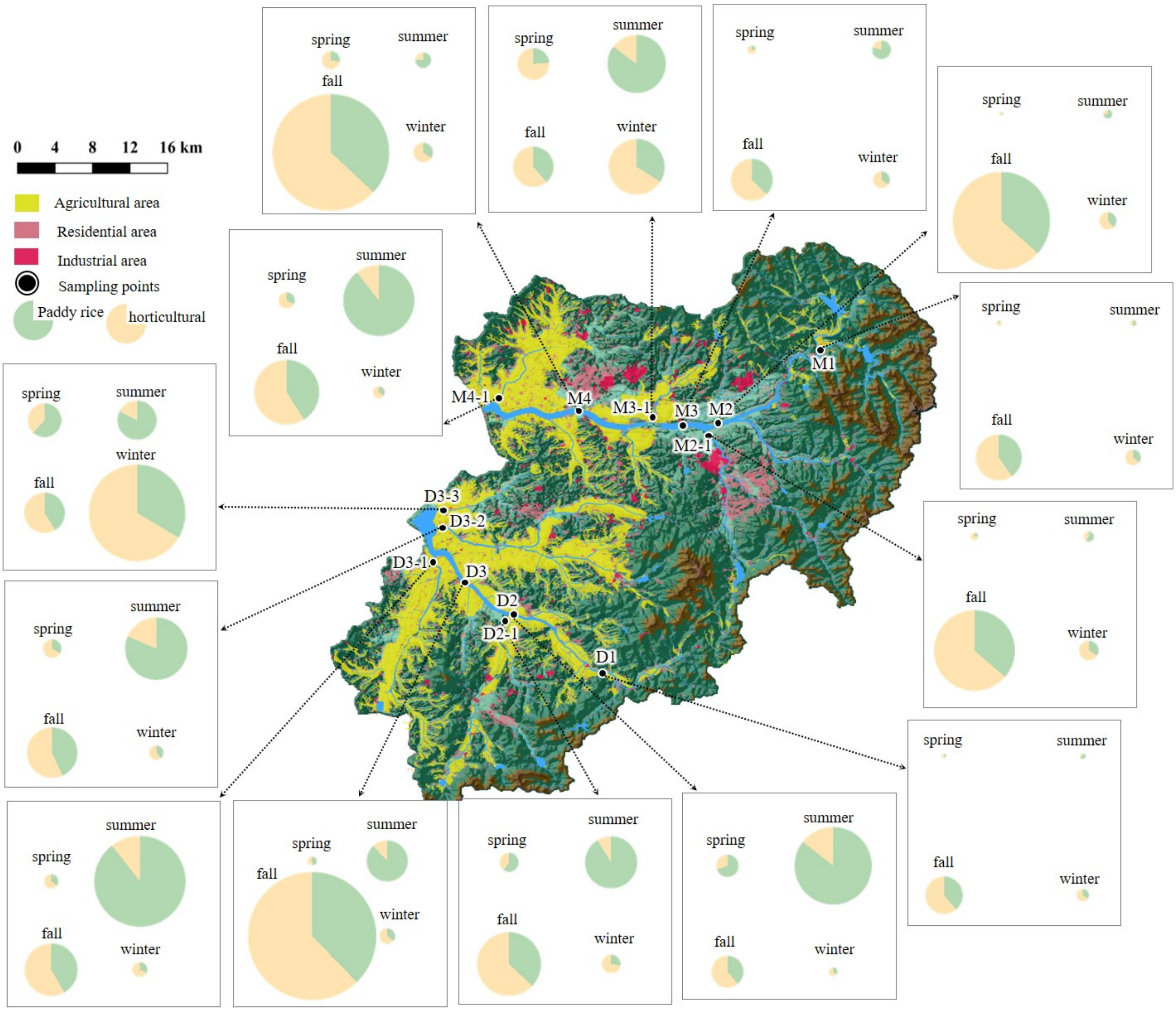

Figure 4. Distribution of pesticides for rice paddy farming and horticulture by seasonal sampling point.

3.2. Tracking Pesticide Sources

A volcano plot was constructed to assess the differences in pesticide concentrations between the Mangyeong River watershed, which is impacted by a complex interplay of agricultural, industrial, and urban influences, and the Dongjin River watershed, which is primarily influenced by rural agricultural activities (Figure 5). A volcano plot is commonly employed in biology and genetics. It visualizes the relationship between statistical significance (e.g., p values) and effect size (e.g., fold change), enabling the identification of statistically significant features and their magnitude of change within a dataset. A volcano plot was constructed by dividing the concentrations detected in Dongjin River by those in Mangyeong River. In cases with missing data, the gap was filled using a minimum value of one-fifth of that available. Among the 12 substances exhibiting more than a 2-fold higher concentration in the Dongjin River compared to the Mangyeong River (within the range of statistical significance; $p \geq 0.1$), eight were associated with rice farming (right panel of Figure 5. As approximately 61% of all detected pesticides were used in horticulture, this suggests a stronger influence of rice farming on the Dongjin River region than on the Mangyeong River region. In contrast, only two horticultural herbicides, napropamide and alachlor, were detected in the Mangyeong River. This suggests that the Mangyeong River is less affected by rice farming than the Dongjin River. However, this volcano plot combines the results from 84 samples for each river (seven locations × 12 months), without distinguishing between months, upstream and downstream, or tributary locations. Consequently, it does not adequately account for spatiotemporal variations.

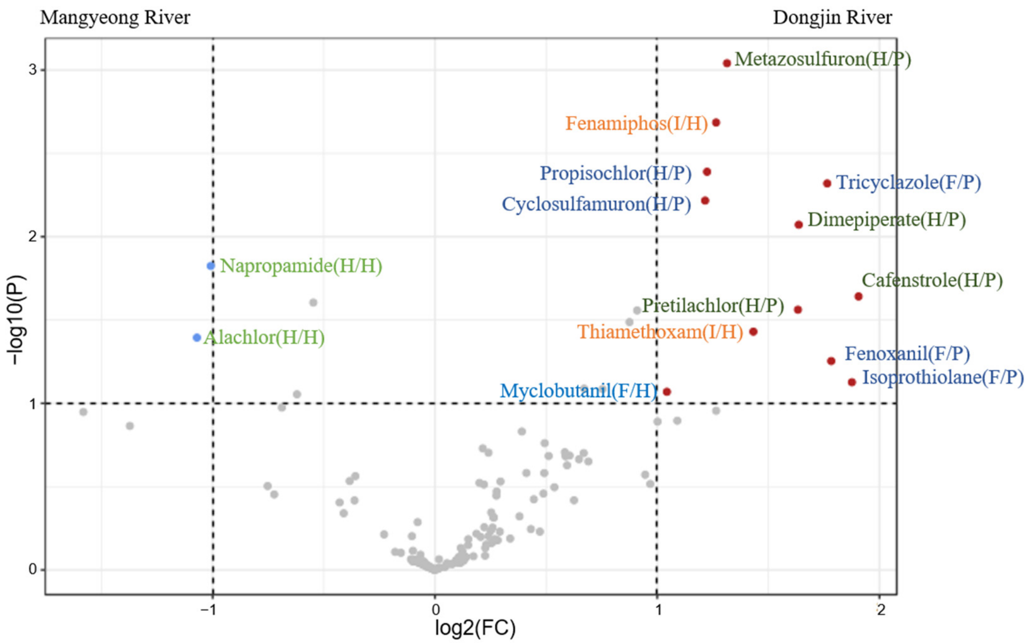

Figure 5. Volcano plot of Dongjin River/Mangyeong River.

Therefore, we conducted a hierarchical cluster analysis between the detected pesticides and each sample using Euclidean distance measurements and Ward's clustering method. The sample rows were normalized and the pesticide columns were standardized using the autoscaling method. However, because the 167 samples included both temporal and spatial elements and acted in a complex manner, the results of the cluster analysis heat map were not clear. To understand the spatiotemporal variations more clearly, we divided the samples into spatial (Figure 6a) and temporal groups (Figure 6b). The pesticides clustered differently based on their spatial and temporal distributions. Notably, the pesticides influencing points D3, D3-3, M4, M2, and M2-1 formed one cluster, whereas those affecting points M3-1 and D2-1, which were expected to cluster similarly, diverged. These findings indicate that the primary contributors to downstream contamination of the Mangyeong River (M4) are the midstream Mangyeong River (M2) and Jeonju Stream (M2-1). In contrast, the Iksan Stream (M3-1) exerted a relatively lower influence on the pesticide levels in the Mangyeong River. Most pesticides that significantly affect the Iksan Stream are intended for horticultural use, differentiating it from other regions. Downstream of the Dongjin River (D3), we were also unable to find a connection with the Jeongeup Stream (D2-1), which is expected to have a significant impact. Contrary to our expectations, the downstream of the Dongjin River (D3) also exhibited no apparent connection to the Jeongeup Stream (D2-1). These findings suggest that the downstream Dongjin River probably receives pesticide inflow through agricultural waterways, small streams, or groundwater percolation through the soil. The division based on temporal distribution was more distinct, making it easier to differentiate the substances that had the greatest impact in October. Among the 100 pesticide types that demonstrated a significant effect in October, 63 were associated with horticulture and 37 were related to rice farming. These included 26 and 24 types of horticultural fungicides and pesticides, respectively. Furthermore, winter and spring exhibited comparable patterns, and autumn and summer exhibited similar trends.

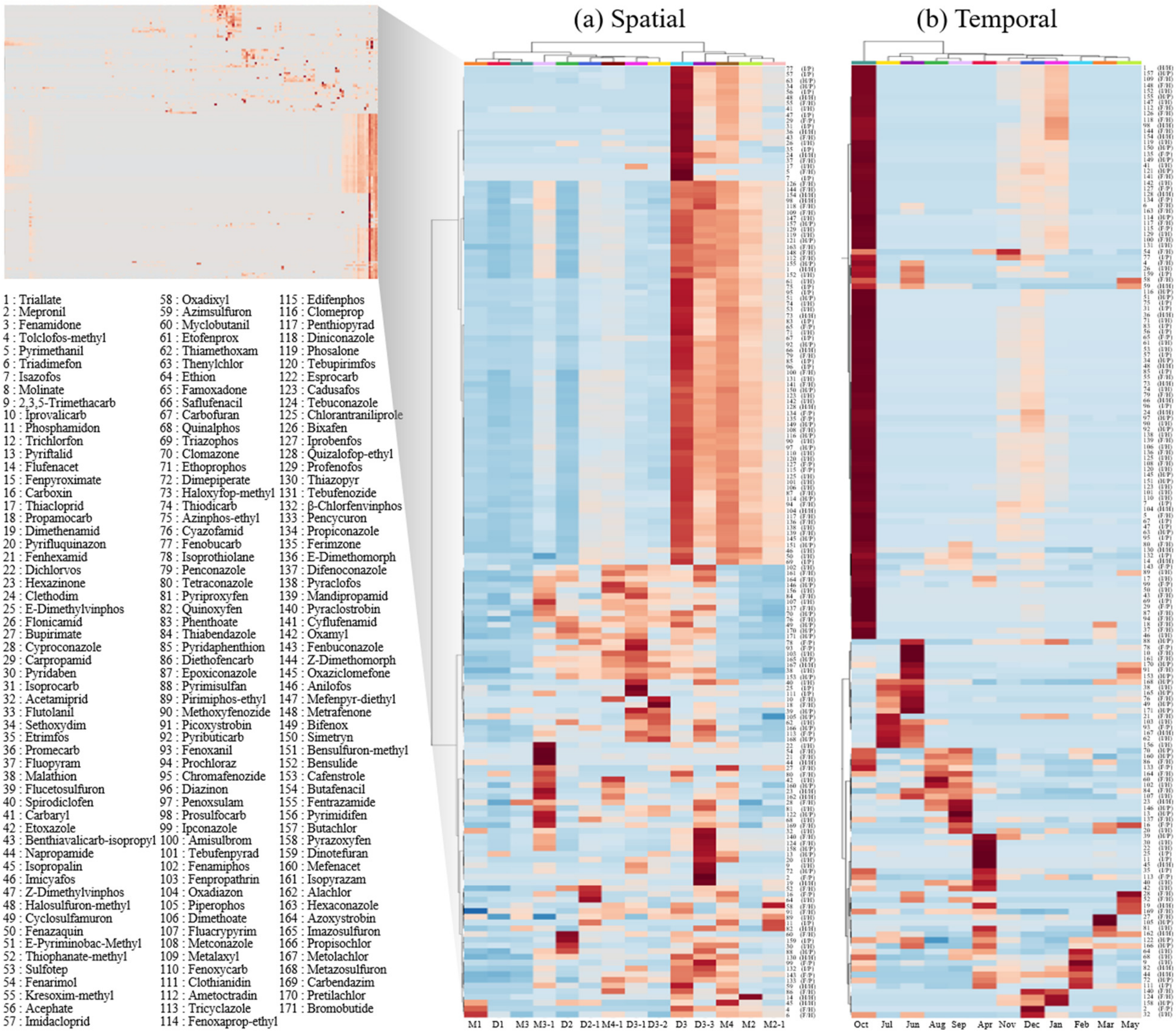

Figure 6. Hierarchical cluster analysis with (**a**) spatial and (**b**) temporal groupings.

3.3. Environmental Risk Assessment

Pesticides can contaminate surface water via several routes such as surface runoff, draining, drift, and leaching [19,20]. Contaminated water can directly or indirectly affect human health and aquatic ecosystems [45,46]. Indiscriminate and excessive usage of pesticides and runoff cause aquatic plants to die, oxygen levels in water to decrease, and fish to suffocate [47]. Relyea et al. [48] reported that glyphosate, one of the most ubiquitous herbicides, causes extremely high mortality in tadpoles and amphibians. Although humans are not directly affected by pesticides, indirect but continuous exposure can cause cancer, diabetes, respiratory disorders, and neurological dysfunction [49,50]. Therefore, the residues and ecological risks of pesticides in environmental waters should be investigated.

We employed an ERA for the 171 detected pesticides to evaluate their potential risks to aquatic environments.

Typically, when calculating RQ values, the PEC values representing the maximum concentration or those derived from Monte Carlo simulations are used [51,52]. However, when using MEC values, average concentrations may be employed. Although the maximum value is generally used, it is important to exercise caution when selecting contaminants of emerging concern. Relying solely on the maximum values may lead to an inappropriate regulatory approach and potentially exacerbate environmental issues. As an example, tolclofos-methyl (31st from the left in Figure 7) has an RQ_{max} value of 1.1, indicating a level of concern; however, its RQ_{mean} value is 0.8, which is below the threshold of concern, and, furthermore, its $RQ_{mean \times frequency}$ value is 0.01, indicating a nonhazardous level. This dramatic variation in values is because this substance was detected only twice in the 167 samples.

According to the criteria set by the European Commission [53], RQ > 1 represents a high-risk level, indicating that action should be taken to reduce risk. Then, $0.1 \leq RQ \leq 1$ signifies a medium risk level, suggesting the need for attention to environmental concerns and further observation. RQ < 0.1 indicates minimum risk to organisms, and no additional risk reduction measures were required. Substances with an RQ value greater than 1, based on fish toxicity criteria, included 26 substances, starting from bromobutide at the top left of Figure 7 and ending at pyrazoxyfen. Based on the *Daphnia* toxicity criteria (bottom right of Figure 7), nine substances, ranging from fenamiphos to prosulfocarb, had RQ_{mean} values >1. For the algae-based criteria, there were seven substances, starting with imazosulfuron and ending with metazosulfuron.

However, when the MEC values representing the mean concentrations and their frequencies were considered, the number of substances exceeding the threshold decreased. Based on fish toxicity criteria, substances with RQ_{mean} values exceeding 1 were bromobutide, pretilachlor, butachlor, propisochlor, ethion, phosalone, metolachlor, diazinon, sulfotep, alachlor, fenpropathrin, and anilofos. In the case of the *Daphnia* toxicity criteria, substances with RQ_{mean} values exceeding 1 included fenamiphos, chlorfenvinphos, flufenamid, fentrazamide, and pyraclostrobin. Finally, when assessed based on algal toxicity, only imazosulfuron and penoxsulam exceeded an RQ of 1.

As is evident from these findings, it appears more reasonable to use $RQ_{mean \times frequency}$ values than RQ_{max} or RQ_{mean} values. Nevertheless, this method has limitations in comprehensively assessing the ecological impact of pesticides on a sample unit basis and according to site and season. To gain a more detailed understanding of the ecological impact of pesticide runoff in surrounding rivers, it is essential to evaluate it separately for each sampling site and season, rather than calculating MEC values using average or maximum concentrations. Conversely, from the toxicity perspective, it is necessary to consolidate the effects of pesticides. The levels of detected pesticides in this study are relatively low compared to those reported in other literature [21,54–57]. Bromobutide, the pesticide with highest mean concentration in this study, has been previously reported to be detected at 5.77 μg/L in Japan [21], particularly during the farming season (April–August) in lake water. Another study analyzing water sources for six years reported concentrations of up to 10 μg/L [54]. Morohashi et al. [55] also reported a range of 1640–2230 μg/L in water in paddy fields in three rice-producing areas in Japan. In Korea, water samples from 50 major rivers and nearby agricultural areas revealed concentrations of butachlor of 0.212–8.78 μg/L [56]. Another study conducted in the same study area in Korea during the peak farming season (May–June) reported concentrations of butachlor, carbendazim, pretilachlor, and diazinon of 0.1–0.9, 0.5–7.7, 0.4–1.1, and 0.01–0.33 μg/L, respectively [57]. Considering these factors and recognizing the scarcity of research that quantifies a wide range of pesticides, including 171 different substances in surface water, the utilization of the $RQ_{mean \times frequency}$ value may be deemed reasonable.

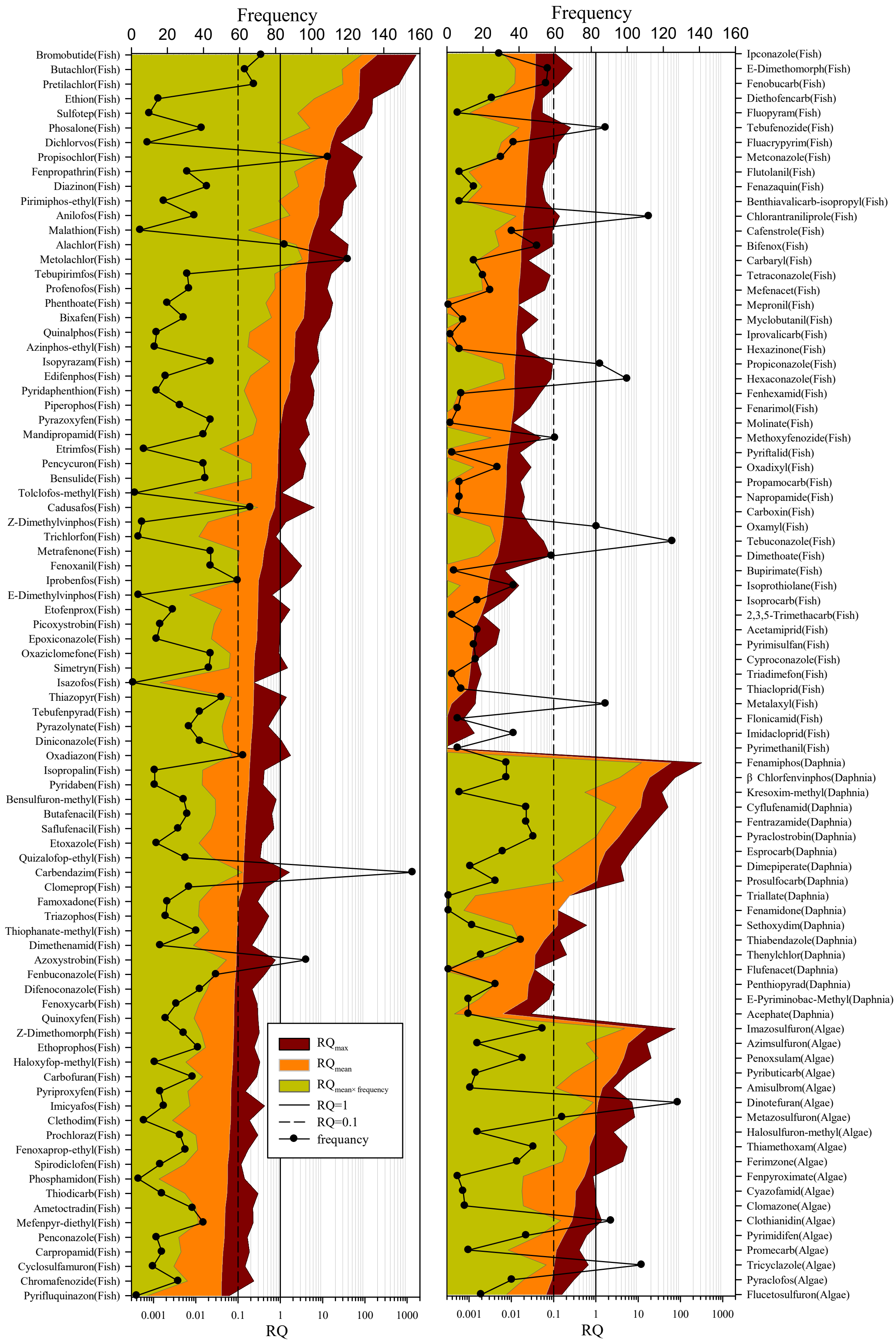

Figure 7. Risk quotients of individual pesticides.

4. Conclusions

This study comprehensively utilized targeted and nontargeted analytical techniques to identify pesticide runoff from surface water. Through the targeted and non-targeted analyses, 171 and 24 pesticides were identified, respectively. This study underscores the extensive nature of pesticide contamination, in terms of both quantity and diversity. Furthermore, the majority of the evaluated pesticides surpassed safe levels, indicating potential environmental threats.

Substantial seasonal and crop-specific variations in pesticide contamination levels were observed. Herbicides were predominantly used during summer, whereas insecticides were used more frequently in autumn. These results suggest that pesticide usage patterns can vary seasonally and depend on crop type, emphasizing the need for tailored approaches to water quality monitoring and pesticide regulation. In addition, a comprehensive ERA that considers both mean concentrations and detection frequencies are valuable for a more accurate understanding of the overall impacts of pesticide contamination. This approach enables the evaluation and management of environmental risks associated with specific pesticides and regions.

In conclusion, this study contributes significantly to the understanding of the complexity of pesticide contamination by considering substance diversity and seasonal variations. Future research must consider a wider range of pesticide types and diverse regions to enhance pesticide management and environmental preservation.

Supplementary Materials: The following supporting information can be downloaded from https://www.mdpi.com/article/10.3390/w15223984/s1. Table S1: QA/QC results for 308 targeted compounds; Table S2: Concentration and risk quotients of 171 target compounds; Table S3: Peak areas of non-target compounds.

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