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Fish Tissue Contamination with Organic Pollutants and Heavy Metals: Link between Land Use and Ecological Health

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Abstract: Under pressure from existing and emerging contaminants, lotic ecosystems are becoming increasingly susceptible to ecological deterioration. Therefore, investigations of the impacts of persistent organic pollutants (POPs) and heavy metals on riverine fish health, water quality, and biotic integrity are critical. We examined the effects of 52 POPs and heavy metals on ecological health and land use, based on the monitoring of fish assemblages and river water quality from 2007 to 2014. Among the 52 chemical species, 35 were present in water and fish tissues, including eight heavy metals. The concentrations of these POPs and heavy metals in 12 fish species are presented. Most POPs were either undetected or present at negligible levels in fish tissues, although a few polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs; dichlorodiphenyltrichloroethanes and heptachlor epoxide) were detected above the screening values (SVs). Hg, As, and Cd were detected in most water samples and fish species at concentrations above their SVs. Among the fish species in the investigated trophic guild, heavy metal contents were in the order of Zn < Cr < Cu < Pb < Se, while trophic levels were in the order of insectivorous < omnivorous < carnivorous. Agricultural cover showed an association with endosulfan II (R^2 = 0.50, r = 0.70), followed by alachlor (R^2 = 0.43, r = 0.66). For PAHs, all detected substances showed significant relationships with forest cover. Ecological health assessment revealed that most river sites are in poor condition, indicating the direct impacts of pollutants. In conclusion, of the 28 POPs detected, 16 PAHs and 3 OCPs (hexachlorobenzene, lindane, and heptachlor epoxide) were of significant concern, such that action is needed to curb their inflow to the riverine environment. The studied river basin is under substantial threat from harmful POPs that endanger ecological health and fish biodiversity.

Keywords: heavy metals; pesticides; ecological health; POPs; river; land use; fish tissues

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1. Introduction

Inland aquatic ecosystems are becoming increasingly vulnerable to various emerging pollutants with multifaceted anthropogenic impacts [1–3]. Conventional analyses of healthy and sustainable freshwater systems are primarily based on physicochemical and biotic integrity [4,5]. Traditional and simple methods of estimating physical and chemical parameters have been replaced by more accurate techniques for investigating the type and extent of disturbance events occurring in freshwater ecosystems over time [6,7]. Notably, most pesticide residues in aquatic ecosystems go undetected due to their diffusion and transient nature, with low concentrations below the detection limit (BDL). Nevertheless, low concentrations of contaminants can still lead to physiological impairment, which is subsequently detected at the population level [8–10]. Biological monitoring has emerged as the most reliable technique, providing a snapshot of the transient impacts of various contaminants present at both detectable and undetectable concentrations.

Ecological degradation has intensified in recent years due to massive increases in economic activity, rapid expansion of urban populations, and the implementation of progressive and intensive farming practices in riverine watersheds worldwide [11–14]. Environmental contaminants include a variety of harmful substances that enter the environment through anthropogenic and natural processes [15,16]. In general, these contaminants encompass heavy metals [17,18] and a variety of pesticides [19,20], which severely threaten the entire ecosystem by hindering its sustainable functions, biological diversity, and ecological health [21,22]. However, the relationship between environmental health assessment results and the impacts of various pollutants remains elusive in most parts of the world. Therefore, research studies targeting the relationships among ecological health, watershed-scale factors, and the occurrence of hazardous contaminants from the perspective of land use are essential for elucidating the harmful impacts of existing and emerging contaminants.

Ecological health assessment based on fish assemblages has recently become the most common method for evaluating river health. This method comprehensively assesses the functional relationships, species abundance, fish population density, and diverse functions and structures of fish communities that are affected by ecological disturbances in aquatic ecosystems [23,24]. Land-use patterns have multiple impacts, including heavy metal pollution and agricultural intensification, which promote the accumulation of harmful substances, such as pesticides, in riverine ecosystems [22,25–30]. Therefore, evaluation of the major links among ecological health assessment, land-use patterns, and various contaminants is necessary to elucidate how fish assemblages are impacted by anthropogenic threats.

Despite sophisticated rules governing agricultural and industrial contaminants, several field investigations have found associations of their incidence, persistence, and toxicological effects in ecosystems, such as rivers, with adverse ecological impacts [9,15,31]. Agricultural pollutant inputs have increased rapidly with the adoption of modern and intensive farming practices in advanced countries [32]. Due to this shift, modern agricultural activities have emerged as the leading cause of lentic and lotic system contamination worldwide [9,32]. Excessive application of various chemicals used in crop and livestock farming, including fertilizers, pesticides, herbicides, and hormones, contributes to the chemical contamination of recipient aquatic ecosystems [33–35]. Such contamination becomes a priority for treatment when immediate (acute) or delayed (chronic) toxic effects are observed in aquatic biota [8,36]. Such environmental disturbances manifest as changes in the number of individuals, biodiversity, and species composition in recipient ecosystems [37,38]. In addition, some contaminants, such as heavy metals, can be transported up the food chain through bioaccumulation, reaching high levels in edible aquatic species, especially fish, which can ultimately affect multiple non-target species, including humans [39,40].

South Korea is a highly industrialized country with an increasing tendency toward modern and intensive farming practices. In this study, we investigate the status of physiochemical water quality, and the relationships of agricultural, urban, and forest cover with relevant water quality factors, including the concentrations of organochlorine pesticides (OCPs), heavy metals, and polycyclic aromatic hydrocarbons (PAHs). Further, we investigated the loads of eight metals (Cr, Cu, Zn, As, Se, Cd, Hg, and Pb) in fish species categorized based on trophic and tolerance guilds. We also assessed chemical substances including OCPs, organic phosphorus pesticides (OPPs), chlorophenoxy herbicides (CPHs), endocrine-disrupting chemicals (EDCs), and PAHs in fish gill, gut, and muscle tissues. Furthermore, this study includes a biological health assessment of the study region based on the index of biotic integrity (IBI), as well as an evaluation of the empirical links among various fish assemblages and water quality factors.

2. Materials and Methods

2.1. Study Area

We sampled 20 sampling sites along tributaries of the third longest river in South Korea, the Geum River, over 7 years (2007–2014; Figure 1). The study and reference streams were selected according to the distribution of 170 study stations of the national fish biomonitoring network in the Geum River watershed. Three of the 20 sampling points were designated as reference sites. The remaining 17 sampled streams are the main channel of the Geum River, Gap Stream, Noseong Stream, Nonsan Stream, Daegyo Stream, Musim Stream, Miho Stream, Baekgok Stream, Bocheong Stream (2nd order), Bonghwang Stream, Sook Stream, Sucheol Stream, Oicheon Stream, Yudeung Stream, Jo Stream, Juwon Stream, and Chupungryeong Stream. The three reference stream sites are the Cho River (S07), Yeongdong (S01), and Mujuinamdae (S03). Except where noted, all streams are between 4th and 6th order, based on the classification of Strahler [41].

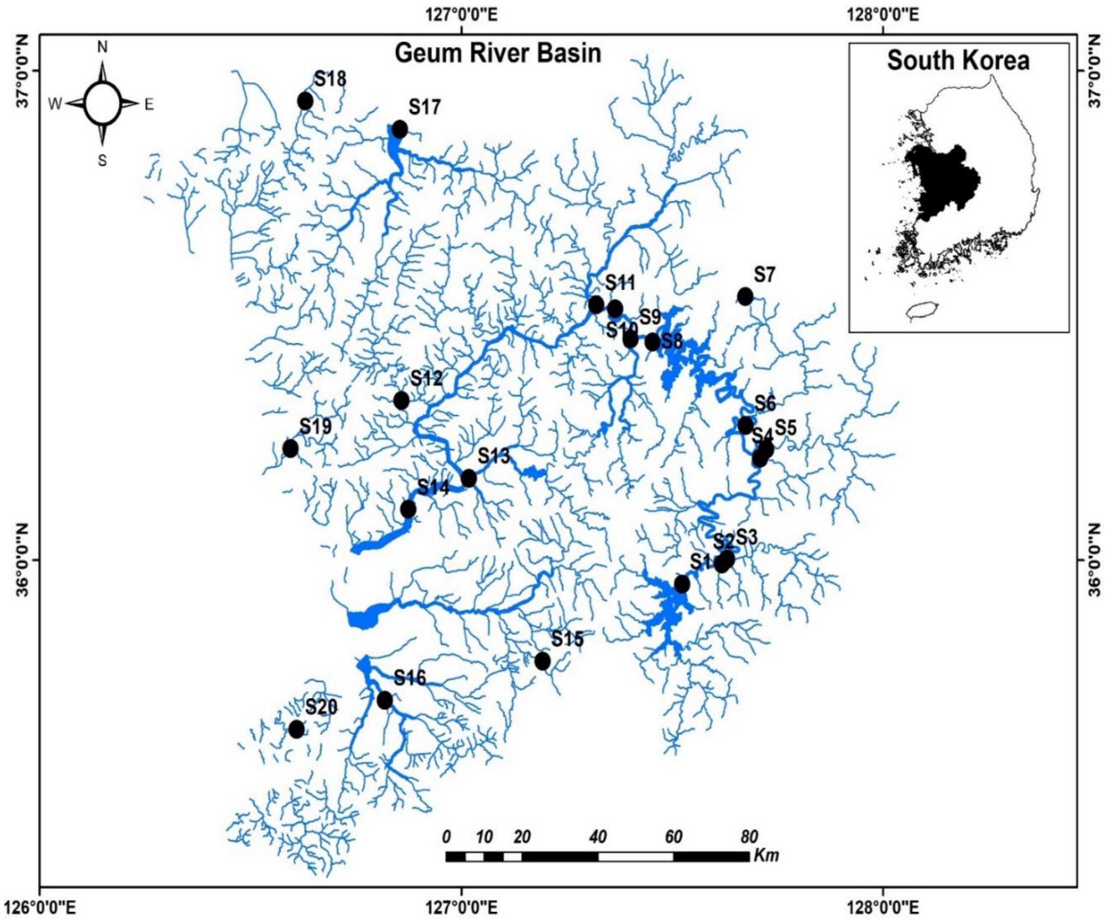

Figure 1. Map of the study area showing the sampling sites and boundaries of the watershed, i.e., the Geum River Basin.

2.2. Land Use and Cover

A preliminary field survey was performed to assess the predominant land use and cover types around the monitoring sites in the Geum River watershed. Factors that may affect the aquatic environment were also investigated using a 1:50,000 scale map. Further, land use and cover were classified as forest, agriculture, or urban depending on the ratios of forest area, agricultural area, and residential and commercial areas obtained from satellite images (1:20,000); data freely available from the United States Geological Survey website were also analyzed. The relative ratios of these areas were calculated for the estimated locations of each survey site. We used satellite images captured by the National Geographic Information Institute (NGII) to confirm land cover types. Forest cover dominated the upstream study sites, while agricultural areas were present in almost all study sites and became dominant in downstream areas. Urban cover was less than 20%, except at site nine, where it was 37% (Supplementary Figure S1).

2.3. Analysis of Water Chemistry

The monthly water chemistry dataset was procured from the Korean Water Environment Information System maintained by the Korean Ministry of Environment (MOE). The long-term water chemistry dataset covered the period from January 2007 to December 2014. Of 17 water quality parameters, we evaluated the 7 most crucial, including total phosphorous (TP, μg/L), total nitrogen (TN, mg/L), biological oxygen demand (BOD, mg/L), chemical oxygen demand (COD, mg/L), total suspended solids (TSS, mg/L), electrical conductivity (EC, mS/cm), and chlorophyll-a (CHL-a, μg/L). Water samples were collected in standard sampling water bottles from a depth of 50 cm (with exposure to sunlight being limited), followed by storage in an icebox. EC and CHL-a were assessed in the field using a multiprobe instrument (YSI 6600 Sonde; YSI, Yellow Springs, OH, USA).

The Eaton and Franson [42] method was used to estimate the TSS, COD, and BOD. TN was assessed chemically through the second derivative method following sample digestion in a persulfate solution [42,43], while TP was estimated through the ascorbic acid method following persulfate oxidation [42,44]. Based on standard procedures, nutrient-related parameters (TN, TP) were examined in triplicate, while BOD, COD, and TSS were evaluated in duplicate to ensure the reliability of the resulting data [45,46].

2.4. Assessment of Harmful Chemicals

We evaluated 52 harmful chemical substances, including 8 selected heavy metals of significant concern, in the river water and fish tissues (twice per year from 2007–2014). As mentioned, the chemical substances included 8 heavy metals (As, Cd, Cu, Zn, Pb, Cr, Se, and Hg), along with 6 OPPs (chlorpyrifos, diazinon, disulfoton, ethion, terbufos, and simazine), and 15 OCPs including chlordane (cis and trans), dichlorodiphenyltrichloroethane (DDT) compounds (2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT), dicofol, dieldrin, endosulfan (I,II), endrin, heptachlor epoxide, hexachlorobenzene, lindane, mirex, toxaphene, atrazine, alachlor, metolachlor, and carbofuran. In addition, 3 CPHs, including oxyfluorfen, 2,4-D, and MCPA (2-methyl-4-chlorophenoxyacetic acid), 17 PAHs, including acenaphthene, acenaphthylene, anthracene, bena(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(g,h,i)peryrene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, ineno{1,2,3-cd}pyrene, phenanthrene, and pyrene, 2 EDCs, bisphenol-A and nonylphenol and 1 polychlorinated biphenyl (PCB), i.e., arochlor, were investigated. The United States Environmental Protection Agency (USEPA; 1997) guidelines for assessing chemical contaminants were followed when estimating the levels of these harmful chemical substances and heavy metals in water and fish tissues. The concentrations of harmful chemicals were calculated based on values extracted from the water samples collected at each sampling site rather than from organisms. The latest instrumental methods were used for detection of these chemical substances, including high-performance liquid chromatography tandem mass spectrometry, gas chromatography tandem mass spectrometry, gas chromatography with an electron capture detector, and inductively coupled plasma mass spectrometry. We used the method detection limit (MDL) and limit of quantification (LOQ) to ensure the quality of the methods and instruments employed for detection under laboratory conditions, followed by an assessment of the precision and accuracy of each evaluation. Detailed information on the conditions for the GC analysis of organic phosphorous and organic chlorine pesticides, oxyfluorfen, and PAHs is given in Supplementary Table S1. Conditions for PCB GC-ECD analysis and ICP/MS specifications for metal analysis are provided in Supplementary Tables S2 and S3, respectively.

2.5. Fish Sampling and Allotment of Tolerance and Trophic Guilds

Fish data collection was conducted twice per year at all study sites during 2007–2014. The first annual sampling event took place during the pre-monsoon (May–June) period, while the second survey was conducted during the post-monsoon (September–October) season. The sampling times and locations were selected due to their relatively steady hydrological flow conditions to minimize sampling errors. Each fish sampling event was 50–60 min in duration and covered both upstream and downstream stretches of the sampling site. Each type of microhabitat, including riffles, pools, and runs, was explored to increase the fish sample size and to maximize the likelihood of capturing all fish species present. The fish sampling methods applied in this study include the wading method (modified from the USEPA method by Barbour et al. [47] and the MOE-approved method described by An and Kim [48]. Two fishing gear types, namely a cast net (mesh size 5 × 5 mm) and kick net (mesh size 4 × 4 mm), were used, and a fyke net was utilized at sites with greater depths in the main river channel. The fish species were identified using the Korean fish species identification key in Kim and Park's book (Freshwater Fish of Korea. Kyohak Publishing, Seoul, Republic of Korea, 2002).

Furthermore, Nelson's method was followed for scientific classification. Each individual fish was carefully observed for structural defects, such as deformities (D), erosions (E), lesions (L), and tumors (T), collectively known as DELT, to assess the physical health of each captured individual. Trophic and tolerance guilds provide valuable information about feeding niches and the ability to tolerate harmful chemical substances in the riverine ecosystem. Therefore, fish species were categorized on the basis of feeding type, i.e., omnivorous, carnivorous, herbivorous, or insectivorous, and assigned to tolerance guilds comprised of sensitive, tolerant, or intermediate species (Supplementary Table S4). The allotment of each species to trophic and tolerance guilds was performed following the methods of Karr [49] and An and Choi [21].

2.6. Multimetric Fish Model: Index of Biotic Integrity (IBI)

The interactions of fish assemblages, assessed based on habitat availability, number of individuals, and species diversity, reflect the biological integrity of a riverine environment, and can be examined using Karr's IBI. For the IBI evaluation of the sampling locations along the Geum River, we used a regionally developed and validated IBI [50]. The IBI comprises eight distinct metrics based on predominant fish assemblages. Categorization is based on three aspects, namely species richness and composition, trophic and tolerance guilds, and fish abundance, and provides insight into physical health. Further details about the IBI were provided by Atique et al. [51]. Scores of 5, 3, and 1 were assigned to each metric using the maximum species richness line (MSRL) concept based on stream order and fish abundance. The final scores were calculated by aggregating all scores for individual metrics to quantify each riverine site's overall biotic integrity. The final health status of the study sites was ranked based on the final IBI score as excellent (36–40), good (28–34), fair (20–26), poor (14–18), or very poor (8–13).

2.7. Statistical Analysis

The whole dataset was assessed for normality using the Kolmogorov–Smirnov normality test prior to log transformation for empirical modeling and other computations. All illustrations were prepared using SigmaPlot (ver. 14.5; Systat Software Inc., Chicago, IL, USA) and Microsoft Excel 2016 (Microsoft Corp., Redmond, WA, USA).

3. Results and Discussion

3.1. Presence of Harmful Chemical Substances in Fish Bodies

Of the 44 harmful chemical substances investigated, 28 were detected during this study. One targeted PCB was absent from the study. Of the 28 chemicals detected, 16 PAH species and 3 OCPs (hexachlorobenzene, lindane, and heptachlor epoxide) were of grave concern, such that future action is required to control their levels in the riverine ecosystem. The toxic inorganic substances tested herein include an extensive list derived via recently developed sophisticated detection methods. The flow of such harmful chemicals is generally unidirectional, and they persist after entering aquatic ecosystems [2]. However, the cycling of such toxic substances is relatively low in flowing waters compared to stagnant water bodies, with the exception of metals that can settle and then become resuspended on faster currents in downstream areas (thereby intensifying their impact on fish and other aquatic organisms) [18,52]. Among the metals, highly toxic Hg was associated with agricultural land cover, and Se showed relationships with both urban and agrarian areas. Mercury can accumulate rapidly in the bodies of fish and undergo conversion to the more toxic substance methylmercury. Moreover, it is excreted very slowly, making it problematic for both fish and their consumers. In contrast, Se is a typical example of a nutritional paradox, as it can function as a toxin or nutrient at similar levels in various fish species. Fish species show varying responses to heavy metal pollution, with salmonids being more sensitive than cyprinids [53]. Pesticides are generally more likely to be fatal, and are intrinsically biocidal and particularly important pollutants of flowing waters [54].

The presence of harmful chemicals in fish bodies is illustrated in Figure 2. These results indicate that among the OCPs, mirex and dicofol were present only at site 11 in *Zacco platypus*; however, their concentrations were below the level designated as harmful to fish.

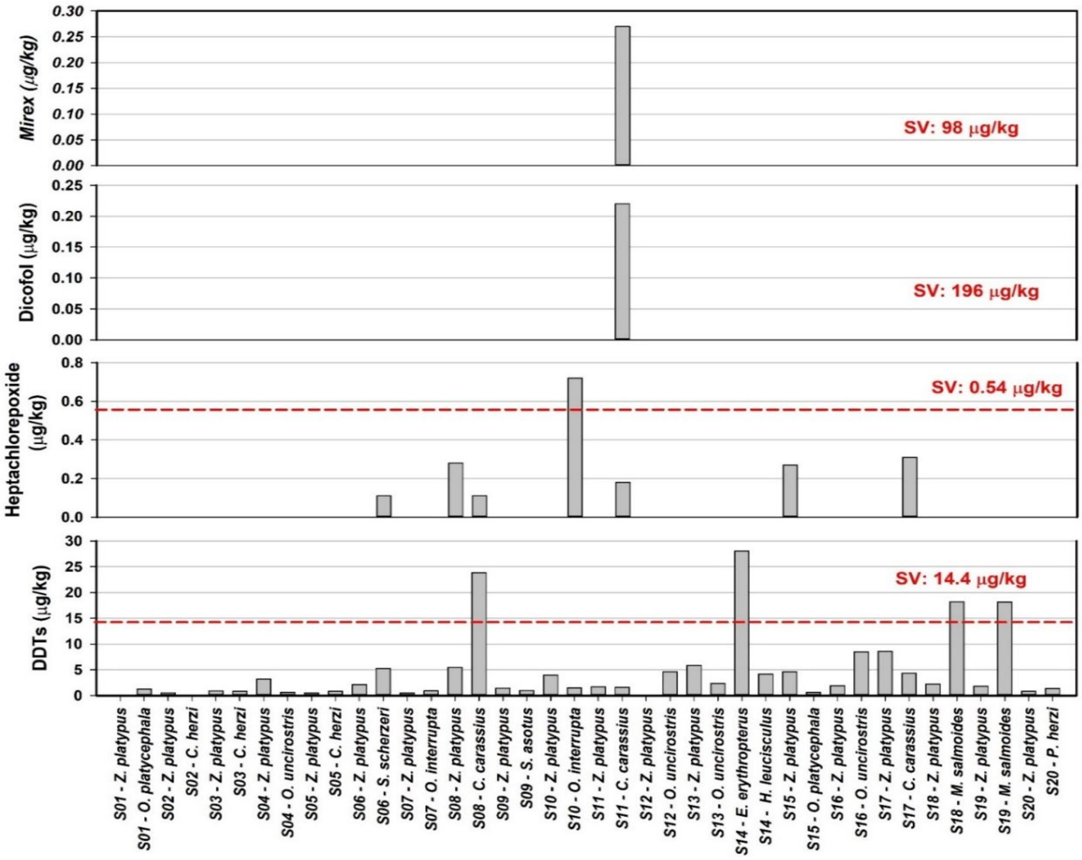

Figure 2. Organic chlorine pesticide (OCP) levels in various fish species at the sampling sites (SV: screening value, adapted from USEPA).

The screening value (SV) is used to determine whether a chemical substance is present above the concentration designated as safe. Heptachlor epoxide was detected at seven sites, with only one site exceeding the SV (0.54 µg/kg). Similarly, DDT was observed at high levels in four distinct locations and three fish species, namely *Carassius carassius, Erythroculter erythropterus*, and *Micropterus salmoides.* Similarly, among the tested OPPs, all three chemicals were present at levels below the critical SV; therefore, they appear to pose no serious threat to fish species (Supplementary Figure S2). Similarly, all tested PAHs were abundant at nearly all study sites and were regularly detected at high levels in most fish species (Figure 3). Furthermore, we investigated the presence of PAHs and BPA in the three organs of selected fish species. The results indicated that fish guts bioaccumulated the most harmful chemical substances, followed by fish muscles. In contrast, fish gills did not possess substantial loads of these chemicals (Figure 4).

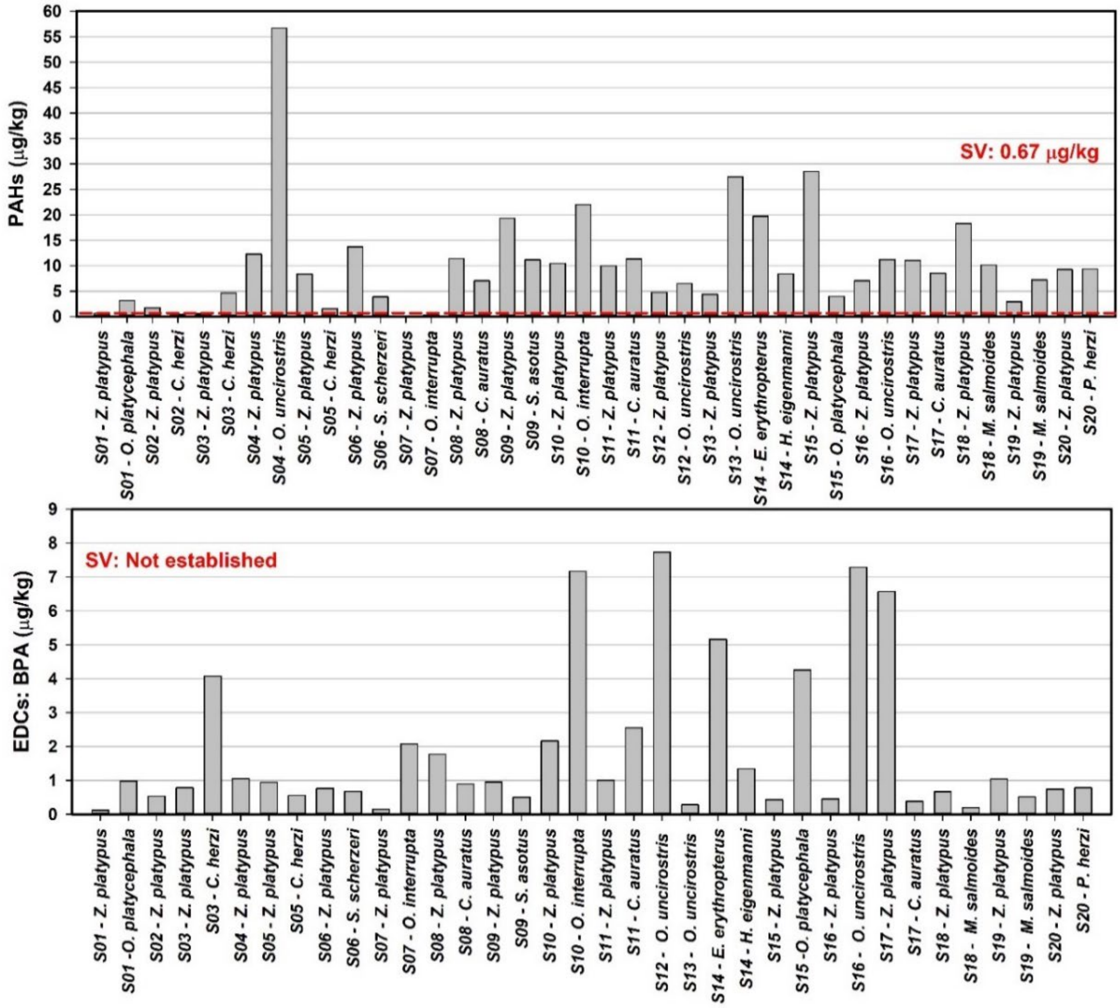

Figure 3. Polycyclic aromatic hydrocarbon (PAHs) and endocrine-disrupting chemicals (EDCs) represented by bisphenol-A (BPA) at the study sites in various fish species (SV: screening value, adapted from USEPA).

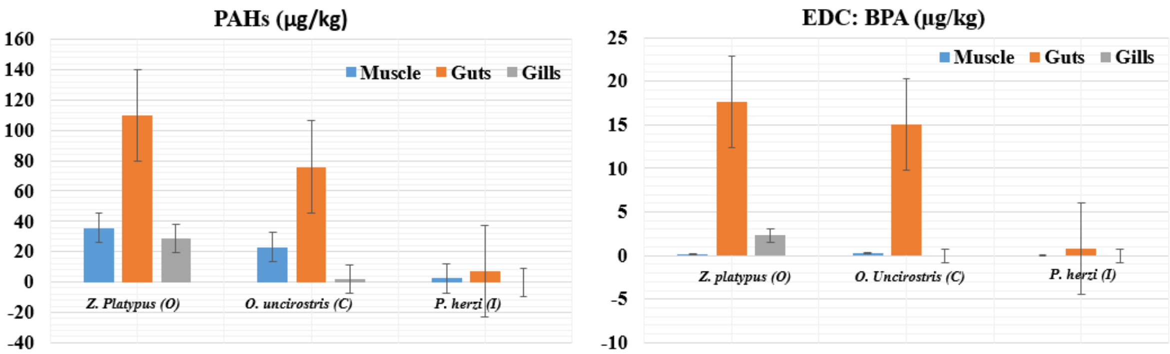

Figure 4. Polycyclic aromatic hydrocarbons (PAHs) and endocrine-disrupting chemicals (EDCs) represented by bisphenol-A (BPA) in various organs of selected fish collected in the Geum River (O: omnivore, C: carnivore, I: insectivore).

The spatial distributions of OCPs and OPPs in the surface water samples are shown in Supplementary Figure S4. The variations in EDCs and CPHs are shown in Supplementary Figure S5. Spatial biomonitoring revealed the concentrations of PAHs in surface water, which are presented in Supplementary Figure S6. The environmental impacts of these harmful chemicals are many fold, including rapid induction of death; moreover, they are persistent due to low solubility in water, and high solubility in lipids and fatty tissues (strong bioaccumulation), which can be extremely detrimental to the fish and their environment [36,55].

3.2. Metal and Pollutant Loads in Various Fish Species and Vital Organs

In the fish species investigated during this study, we identified a link between the mode of fish feeding (trophic guild) and tolerance to excessive levels of environmental pollutants (tolerance guild) based on the levels of targeted metals observed in the vital organs of selected fish species; the results are presented in Figure 5. The concentrations of harmful substances (excluding metals) in 12 fish species, namely *Micropterus salmoides, Carassius auratus, Coreoperca herzi, Erythroculter erythropterus, Hemiculter eigenmanni, Odontobutis platycephala, Odontobutis interrupta, Opsariichthys uncirostris amurensis, Pungtungia herzi, Silurus asotus, Siniperca scherzeri* and *Zacco platypus*, are presented. The trophic and tolerance guild assessment results indicated that insectivorous fish (*Pungtungia herzi*), followed by omnivorous fish (*Zacco platypus*), showed the highest levels of Zn in the gills, followed by the guts and edible muscle tissues. Among the species in these trophic guilds, the sequence of heavy metals was in the order of Zn < Cr < Cu < Pb < Se, while metal contents were in the order of insectivorous < omnivorous < carnivorous among trophic levels.

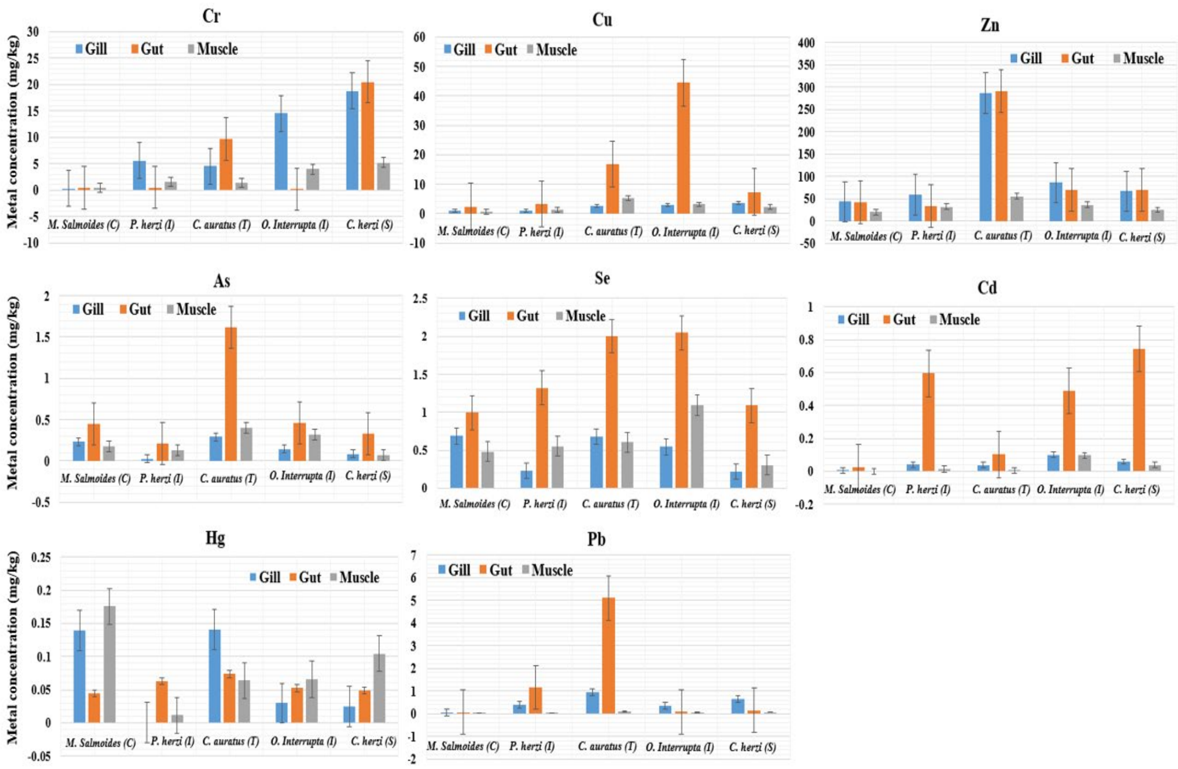

Figure 5. Metal concentrations in various organs of selected fish in the Geum River (Cr: chromium, Cu: copper, Zn: zinc, As: arsenic, Se: selenium, Cd: cadmium, Hg: mercury, Pb: lead).

The tolerance guilds (tolerant < intermediate < sensitive) and fish organs (gills < guts < muscles) showed similar sequences of metal concentrations. Strikingly, the order of heavy metals was identical to the loads of metals, as was also observed for trophic guilds. After Zn, the metal with the second highest level was Cr, followed by Cu and Pb, corroborating the impact of agricultural activities in the riverine watershed. The spatial variations of concentrations for the most significant metals in surface water (Cr, As, Se, and Hg) are presented in Supplementary Figure S3. Hg, As, and Cd were detected at most study sites and in most fish species with concentrations above their SVs (Figure 6). We also presented the concentrations of these eight metals in the whole fish body of the omnivorous fish

Zacco platypus, which was one of the most abundant fish species in this riverine watershed (Figure 7, Supplementary Table S5).

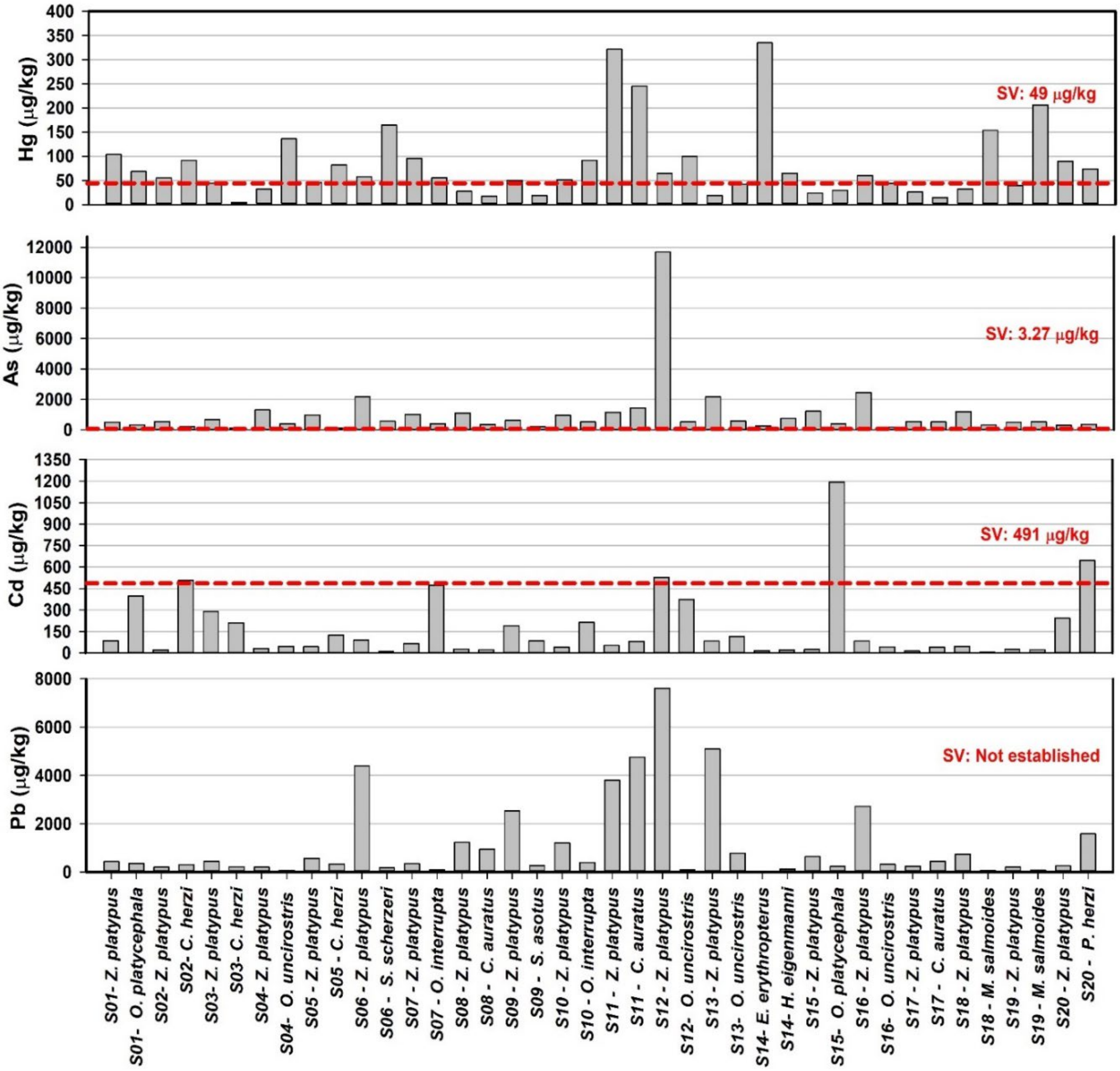

Figure 6. Heavy metal concentrations at the sampling sites in various fish species (SV: screening value).

The presence of heavy metals in the environment and fish may have beneficial or harmful effects, depending upon the form and concentration of metals and the type of organism [56]. Therefore, investigating the loads of metals in vital organs, and the relative levels among fish species and vital tissues, including edible parts, is an important research topic.

The persistence of heavy metals is always controversial, and they can remain after several decades due to sinking into the sediments before becoming available again after certain processes occur in the flowing water body [18,57]. Bio-enrichment was observed here; the concentrations of heavy metals followed the order of insectivorous < omnivorous < carnivorous, indicating stepwise transfer of heavy metals through the fish food chain of the riverine ecosystem [58]. With increasing trophic levels of fish species, loads of heavy metals exhibited a gradual increase that could have resulted from biogenic amplification [59].

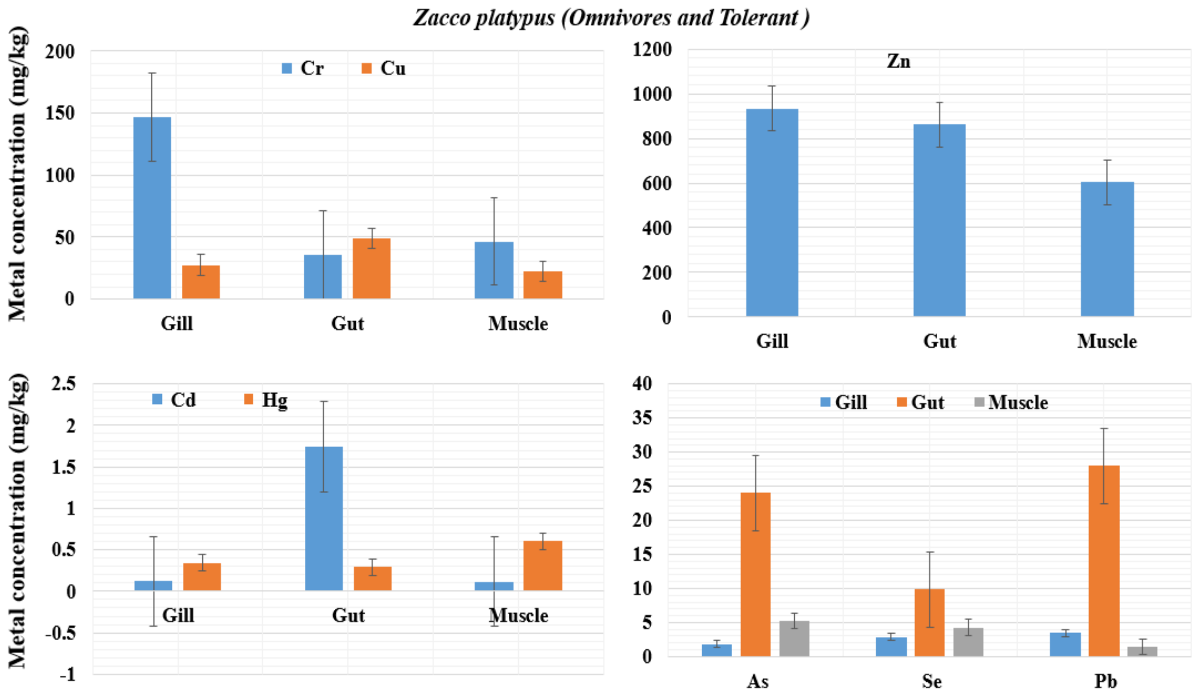

Figure 7. Metal concentrations in various organs of *Zacco platypus* (Cr: chromium, Cu: copper, Zn: zinc, As: arsenic, Se: selenium, Cd: cadmium, Hg: mercury, Pb: lead).

Heavy metals and other pollutants in freshwater ecosystems originate from natural sources (e.g., soil erosion, rock weathering) and a variety of harmful anthropogenic activities, including the release of untreated industrial wastes, wastewater inflow mixed with rainfall currents, mining, the usage of chemicals (pesticides and insecticides) in livestock and crop farming, fossil fuel combustion, transportation, and atmospheric deposition [60]. Most of these pollutants are persistent and complex, and thus can be detected several decades after their usage was banned (e.g., DDTs). Furthermore, investigation of their loads and changes in fish and water is essential to understanding their health risks, stability, origins, and bioaccumulative tendencies in aquatic organisms, especially fish [61].

Exceptionally high levels of Zn were observed, followed in magnitude by Cu; aquatic organisms, including fish and crustaceans, are notably more sensitive to these metals than humans [62]. Therefore, these metals may pose a large risk to fish species, and in-depth investigations into Zn and Cu in this river system may be needed for the conservation of endangered fish species. Furthermore, the results of this study suggest that investigations into the links between Zn, Cu, and agricultural practices in this riverine watershed are warranted.

3.3. Relationships of Trophic and Tolerance Guilds with Water Quality

The abundance of a trophic guild is closely related to the levels of nutrients, organic matter, and algal chlorophyll in the watershed (Figure 8). In this study, the highest abundance of omnivores was found with 433 μgL^{-1} TP; on the other hand, the lowest abundance of insectivores was observed with 433 μgL^{-1} TP. Notably, omnivore richness showed positive functional relationships with TP (R^2 = 0.32, r = 0.56) and TN (R^2 = 0.16, r = 0.40); thus, omnivores were abundant in the watershed. Similar patterns were observed for omnivores in relation to BOD (R^2 = 0.33, r = 0.57), COD (R^2 = 0.32, r = 0.57), and CHL-a (R^2 = 0.23, r = 0.48). Insectivores exhibited negative functional relationships with TP (R^2 = 0.35, r = −0.59), TN (R^2 = 0.12, r = −0.34), BOD (R^2 = 0.30, r =−0.55), COD (R^2 = 0.27, r = −0.51), and CHL-a (R^2 = 0.15, r = −0.38) in this watershed.

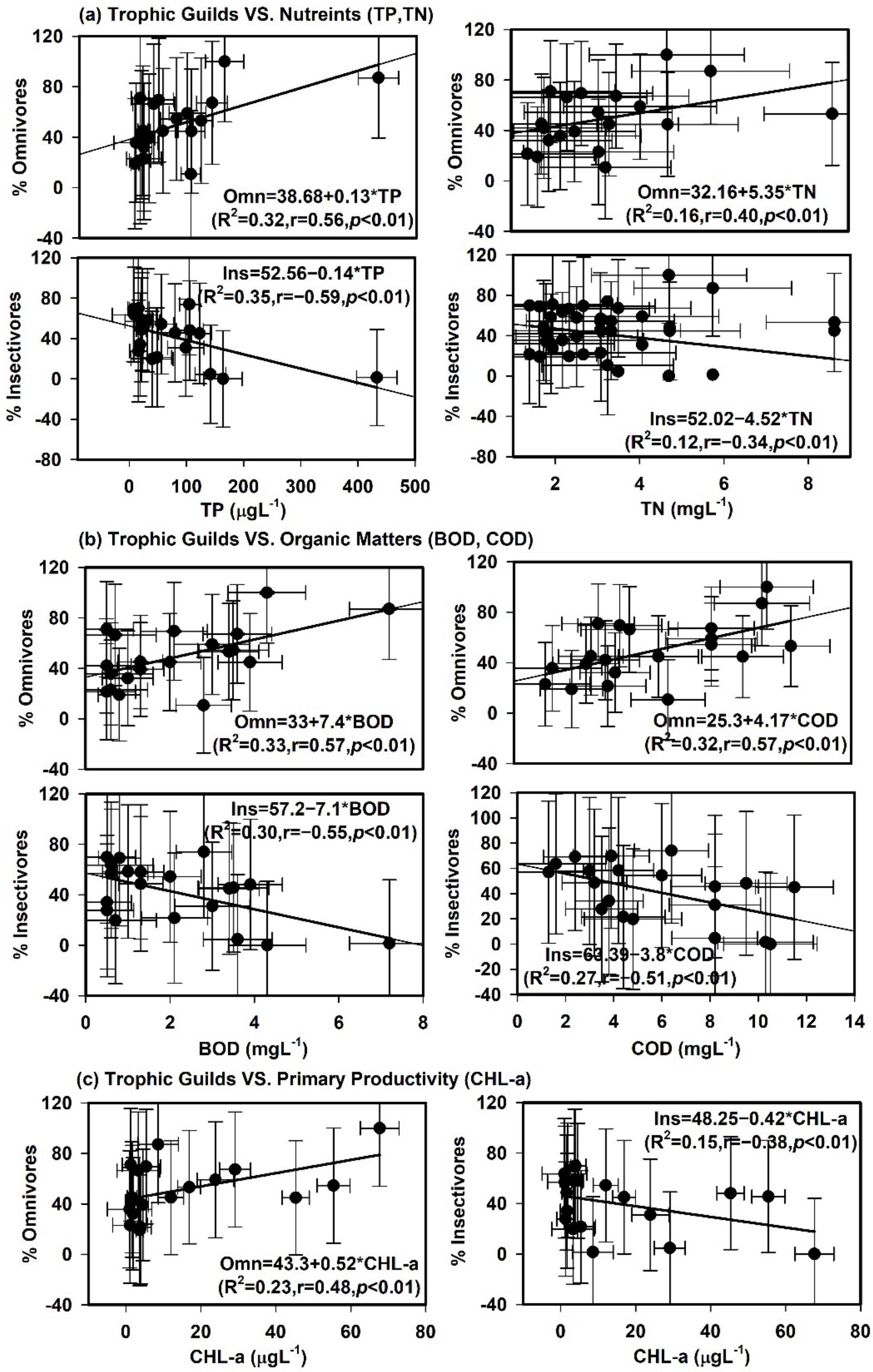

Figure 8. Influence of nutrients (TP: total phosphorus, TN: total nitrogen), organic matter (BOD: biological oxygen demand, COD: chemical oxygen demand), and primary productivity (CHL-a: chlorophyll-a) on trophic guilds (n = 20).

The tolerance guilds of the Geum River watershed are strongly influenced by nutrients (TN and TP), organic matter (BOD and COD), and chlorophyll (Figure 9). As a result, the abundance of sensitive species was low in the Geum River watershed, and they were associated with minimum concentrations of TP, TN, BOD, COD, and CHL-a. However, sensitive species respond strongly to increasing levels of nutrients, organic matter, and eutrophication in the watershed. As a result, sensitive species exhibited negative functional relationships with TP (R^2 = 0.17, r = −0.41), TN (R^2 = 0.18, r = −0.42), BOD (R^2 = 0.24, r = −0.50), COD (R^2 = 0.47, r = −0.69), and CHL-a (R^2 = 0.27, r = −0.52). In contrast, the abundance of tolerant species displayed positive linear functional relationships with TP (R^2 = 0.50, r = 0.70), TN (R^2 = 0.25, r = 0.50), COD (R^2 = 0.51, r = 0.72), BOD (R^2 = 0.50, r = 0.71), and CHL-a (R^2 = 0.33, r = 0.57).

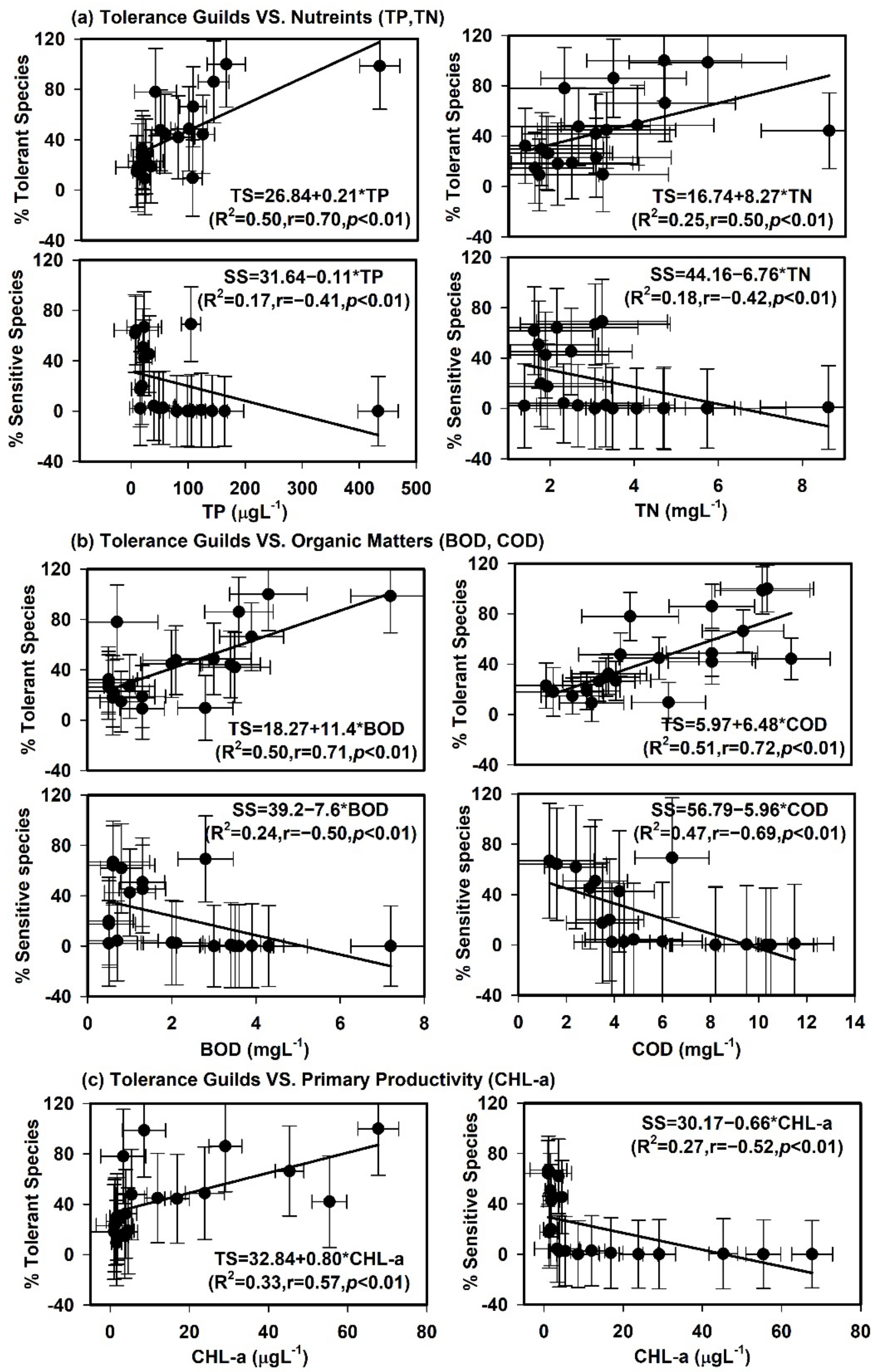

Figure 9. Influence of nutrients (TP: total phosphorus, TN: total nitrogen), organic matter (BOD: biological oxygen demand, COD: chemical oxygen demand), and primary productivity (CHL-a: chlorophyll-a) on tolerance guilds (n = 20).

Nutrients, organic matter, and algal chlorophyll can affect trophic and tolerance guilds in aquatic systems, especially streams and rivers [63–65]. Previous research into the relationships of trophic and tolerance guilds with nutrients, organic matter, and CHL-a has shown that the relative abundances of tolerant and omnivorous species are positively related to water quality factors, but these relationships are negative for sensitive and insectivorous species [63,66,67].

High proportions of tolerant and omnivorous species in streams or rivers indicate that nutrient enrichment and organic pollution severely affect the water body, leading to reduced abundance of sensitive and insectivorous species [68,69]. The present findings strongly support previous ecological health assessment results in the stream [66,70]. Due to the excessive loading of nutrients and organic matter from agricultural and urban sources, algal growth in streams and rivers is high, posing a severe threat to sensitive and insectivorous fish species [47,71]. Increasing CHL-a has a negative impact on sensitive and insectivorous species in streams.

3.4. Assessment of Integrity Based on IBI

The Korean index of biotic integrity (IBI_{KR}) model based on fish assemblages was used to assess the ecological health of the Geum River watershed (Table 1). The average IBI value in the watershed was 19.10, indicating that it was in poor condition. Among the 20 sites sampled, 15% were in good condition, 20% were in fair condition, 45% were in poor condition, and 20% were in very poor condition. The upstream part of the watershed was in good to fair condition but became degraded in the downstream direction due to the higher abundances of tolerant and omnivorous fish species, as well as lower amounts of sensitive and insectivorous species. The biological health of the watershed is closely related to water quality parameters (Figure 10). IBI showed linearly decreasing trends with increasing TP (R^2 = 0.21, r = −0.46), TN (R^2 = 0.16, r = −0.40), BOD (R^2 = 0.26, r = −0.51), COD (R^2 = 0.41, r = −0.64), and CHL-a (R^2 = 0.31, r = −0.56) concentrations. This result indicates that water quality parameters affect the biological health of this river.

Table 1. Site-based biological health assessment (BHA) based on the Korean multimetric index of biotic integrity (IBI_{KR}) using fish assemblages.

Sampling Site	Species Richness and Tolerance				Trophic Composition		Fish Abundance and Health		Overall IBI Score (Health Status)
	M_1: Total Number of Native Fish Species	M_2: Number of Riffle Benthic Species	M_3: Number of Sensitive Species	M_4: Proportion of Individuals Belonging to Tolerant Species	M_5: Proportion of Individuals Belonging to Omnivorous Species	M_6: Proportion of Individuals Belonging to Native Insectivorous Species	M_7: Total Number of Native Individuals	M_8: Percent of Individuals with Anomalies	
S_1	12(3)	3(3)	5(3)	14.8(3)	19.07(5)	69.02(5)	63(1)	0(5)	28 (good)
S_2	10(3)	2(1)	3(1)	9.17(3)	45.14(1)	48.63(5)	237(3)	0(5)	22 (fair)
S_3	15(5)	4(3)	7(5)	18.79(3)	39.19(3)	57.95(5)	84(1)	0(5)	30 (good)
S_4	14(3)	1(1)	3(1)	29.76(1)	42.06(3)	34.13(3)	76(1)	0(5)	18 (poor)
S_5	14(3)	3(3)	4(3)	26.80(1)	32.15(3)	58.33(5)	62(1)	0(5)	24 (fair)
S_6	11(3)	0(1)	5(3)	26.36(1)	70.97(1)	27.63(3)	51(1)	0(5)	18 (poor)
S_7	15(5)	3(3)	4(3)	9.64(3)	10.75(5)	73.98(5)	102(3)	0(5)	32 (good)
S_8	13(3)	1(1)	1(1)	32.34(1)	21.47(3)	69.84(5)	57(1)	0.05(3)	18 (poor)
S_9	10(3)	1(1)	1(1)	44.33(1)	53.22(1)	45.00(3)	45(1)	0(5)	16 (poor)
S_{10}	5(1)	1(1)	1(1)	44.82(1)	44.99(3)	54.32(5)	47(1)	0(5)	18 (poor)
S_{11}	5(1)	1(1)	1(1)	66.28(1)	44.82(3)	48.11(5)	45(1)	0(5)	18 (poor)
S_{12}	10(3)	2(1)	0(1)	47.61(1)	69.47(1)	21.44(3)	37(1)	0(5)	16 (poor)
S_{13}	10(3)	0(1)	0(1)	86.05(1)	67.27(1)	4.65(1)	130(1)	0.03(3)	12 (very poor)
S_{14}	8(3)	1(1)	0(1)	41.96(1)	54.46(1)	45.54(5)	44(1)	0(5)	18 (poor)
S_{15}	7(3)	1(1)	4(3)	22.96(1)	22.96(3)	56.91(5)	67(1)	0(5)	22 (Fair)
S_{16}	15(3)	2(1)	2(1)	48.71(1)	59.03(1)	30.97(3)	167(3)	0.001(3)	16 (poor)
S_{17}	9(3)	0(1)	0(1)	100.00(1)	100.00(1)	0.00(1)	46(1)	0.001(3)	12 (very poor)
S_{18}	5(1)	0(1)	0(1)	98.61(1)	87.13(1)	1.39(1)	44(1)	0(5)	12 (very poor)
S_{19}	5(1)	2(1)	0(1)	77.98(1)	66.44(1)	19.64(1)	17(1)	0(5)	12 (very poor)
S_{20}	7(3)	2(1)	3(1)	17.95(3)	35.63(3)	63.47(5)	85(1)	0(5)	20 (fair)

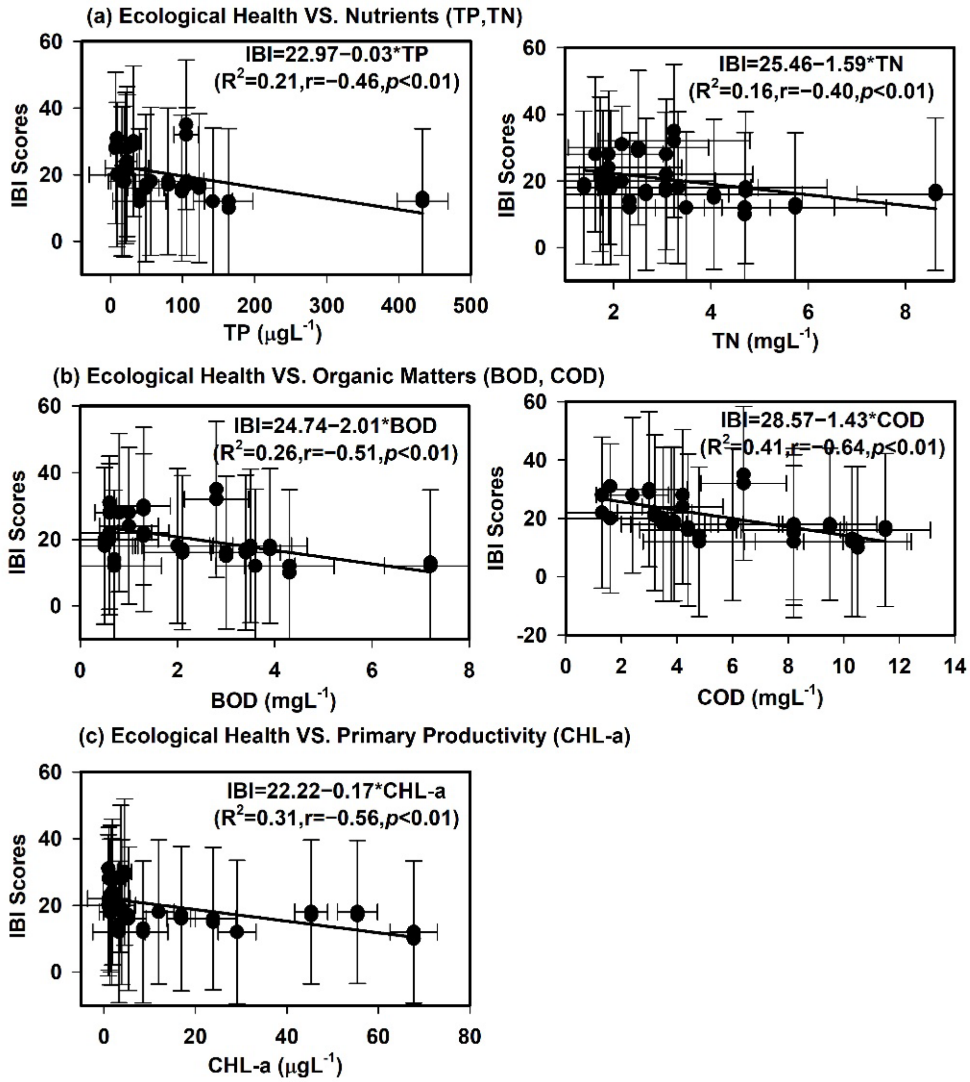

Figure 10. Effects of nutrients (TP: total phosphorus, TN: total nitrogen), organic matter (BOD: biological oxygen demand, COD: chemical oxygen demand), and primary productivity (CHL-a: chlorophyll-a) on the ecological health of the Geum River Basin (n = 20).

The IBI is flexible in its application and can be modified according to the species and size of the target water body. The IBI reflects the overall health status of an ecosystem based on standard values and cumulative scores. Ecological health assessment of rivers and streams using fish as a bioindicator species is a widely accepted method of estimating the impacts of various disturbances in aquatic ecosystems. As this investigation included the assessment of 52 harmful chemicals, including 8 heavy metals, in fish and water, determining the ecological health status of the study sites was essential. Previous research suggested that the abundances of native, riffle benthic, and sensitive fish species decreased with increasing levels of nutrients, organic matter, and non-algal turbidity [48,63]. The USEPA [65] reported higher abundances of omnivores, tolerant species, and carnivores in degraded systems. This accords with the poorer ecological health status seen at sites where harmful pollutants and metals are present at high concentrations, which may lead to the displacement of fish species due to unfavorable conditions for feeding and breeding in their natural ranges.

3.5. River Water Quality and Nutrients

We evaluated water quality at the river sites based on nutrients (TN, TP), organic matter (BOD, COD), volatile solids and ionic content (TSS, EC), and algal CHL-a productivity; the results are presented in Figure 11. Based on nutrients and CHL-a, heterogeneous sites showed tendencies toward nutrient enrichment. TP showed its highest concentration (433 μg/L) at S18, which is located near the estuarine area and is highly eutrophic, while the lowest TP values were observed at S1 (7 μg/L) near the Yeongdam dam, which exhibits ultra-oligotrophic conditions. In contrast, the same site (S18) showed an oligo-mesotrophic algal CHL-a level based on similar criteria. All except one of the river sites sampled showed mesotrophic to meso-eutrophic phosphorus loads.

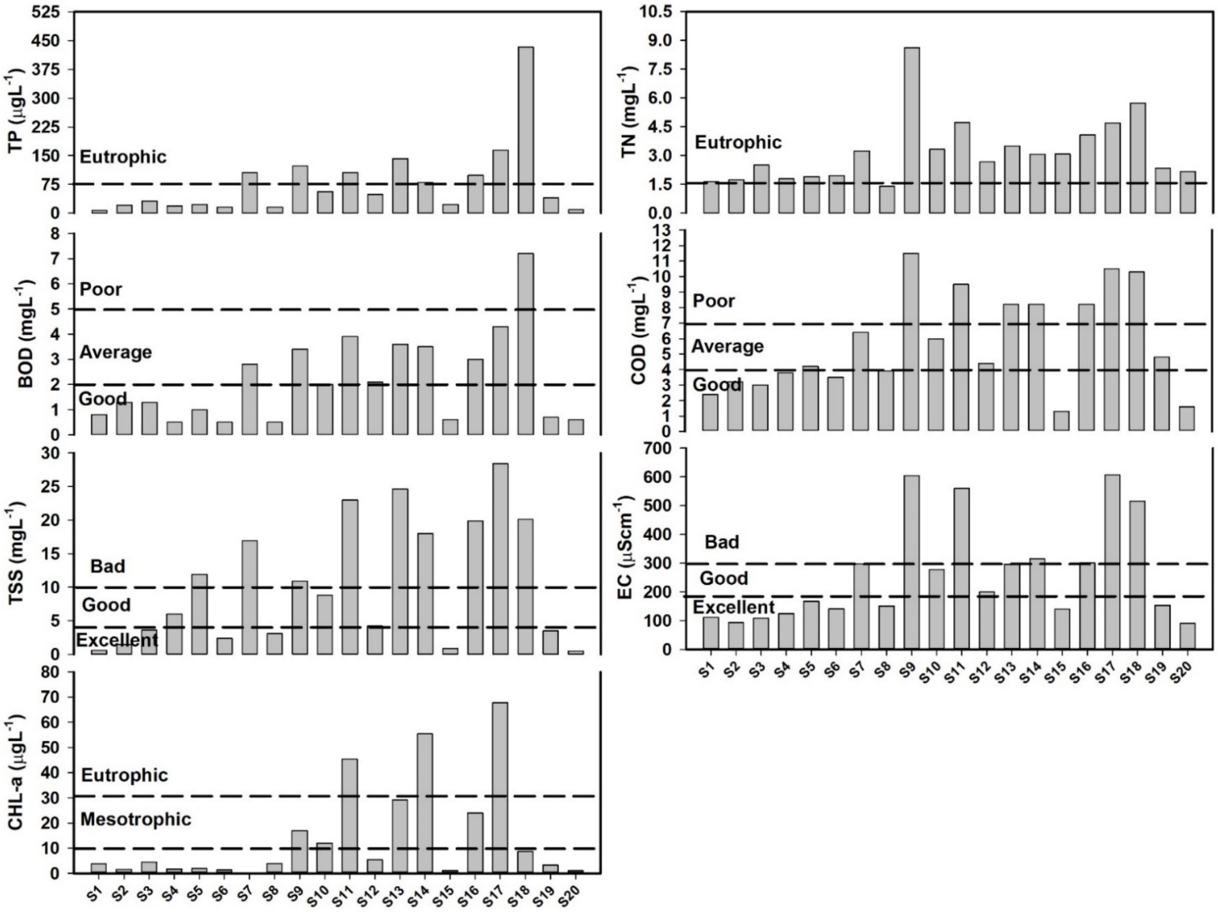

Figure 11. Variations in selected water quality parameters and classification of study sites along the Geum River based on individual parameters and nutrient enrichment status.

The general loads of TN indicated eutrophic conditions that steadily increased from upstream to downstream sites. For algal CHL-a, we observed a consistent increase after every two sites between Sites 11 and 17, with a steep decline observed near the estuarine area. According to the tested organic matter indicators (BOD, COD), most study sites had "average" water quality based on the criteria of the Korean Ministry of Environment. Most of the study sites showed "good" water quality based on BOD, and "average" quality based on COD.

Heterogeneous variations among the study sites were observed for TSS and EC. As most of the study sites are impacted by varying degrees of agricultural activities, as determined based on the predominance of agricultural land cover, the water quality status of downstream sites determined from TP, TN, and CHL-a reflected a tendency toward eutrophication. In addition, such high levels of nutrient enrichment indicate the increasing use of pesticides and other agricultural chemicals, worsening riverine water quality. Furthermore, the application of large amounts of mineral fertilizers for intensive crop production and municipal waste inputs is detrimental to river water quality [33,72,73]. Nutrient levels are relatively low in the upstream stretches of rivers, and increase continuously after the rivers pass through intensive crop and animal production zones, industrial areas, and urban settings [38,51,74].

3.6. Impact of Land Use Patterns on Riverine Water Quality

We performed linear regression analysis on three land-use types (agricultural, urban, and forest) and the most significant river water quality indicators (TP, TN, BOD, COD, TSS, and EC) in the Geum River, as presented in Figure 12. The maximum impact of land use was observed, with urban cover (%) as a contributing factor, which led to decreased river water quality, followed by agricultural zones. Forest cover, in contrast, showed negative associations, indicating a positive effect on river water quality. TP showed a weak positive relationship (R^2 = 0.33, r = 0.57) with agricultural land use. In contrast, a negative association was observed between TP and forest cover (R^2 = 0.38, r = −0.61). Agricultural cover (%) exhibited strong positive relationships (R^2 = 0.51, r = 0.71) with TSS and COD (R^2 = 0.40, r = 0.63), while the strongest links with urban cover were observed for TN (R^2 = 0.64, r = 0.80), EC (R^2 = 0.56, r = 0.74), and COD (R^2 = 0.51, r = 0.71). In contrast, we observed moderate to strong negative impacts of forest cover on COD (R^2 = 0.63, r = −0.80) and TS (R^2 = 0.54, r = −0.73) and a similar negative relationship between BOD and EC (R^2 = 0.45, r = −0.67).

Significant landscape changes, land surface cover, and land use patterns critically influence the hydrological regime and pollutant cycling of the recipient freshwater ecosystem [75]. Therefore, understanding water quality degradation factors and nonpoint sources (NPS), as well as the allocation of pollutant sources, is essential for the effective implementation of water resource management practices. Changes in landscape composition and land cover result in strong fluctuations in NPS loadings, which affect the nutrient regime, surface erosion, and sedimentation [76].

Runoff currents from urban and agricultural landscapes transport large amounts of nutrient pollutants, dissolved organic matter, and sediments, which may degrade downstream riverine water quality [77,78]. Therefore, unhealthy environments with major changes in land use and cover lead to water quality degradation, which is clearly evident in this study. Thus, the type, size, quantity, and land cover distribution of a riverine watershed are essential determinants of the ecosystem's habitat availability, ecological features, and species [79].

3.7. Empirical Links between Land Use and Riverine Pollutants

The observed empirical link between land cover and hazardous chemical substances (OCPs, metals, and PAHs) illustrated the dominant role of agricultural activities in the riverine watershed (Figure 13). For OCPs, agricultural land cover showed the strongest link with endosulfan II (R^2 = 0.50, r = 0.70), followed by alachlor (R^2 = 0.43, r = 0.66), and metolachlor (R^2 = 0.33, r = 0.57). With the exception of endosulfan I (R^2 = 0.30, r = 0.54), all pesticides displayed relationships with agricultural land cover, suggesting their utilization in agricultural activities. Other types of pesticides showed no significant links with land use in the riverine watershed. However, most metals showed very weak relationships (R^2 < 0.30) with all types of land cover; the exception was Se, which showed a weak relationship with urban cover (R^2 = 0.32, r = 0.57). In contrast, for PAHs, all measured substances showed significant relationships with forest cover.

For example, fluorene showed the strongest association with forest cover (R^2 = 0.40, r = 0.62), followed by fluoranthene (R^2 = 0.29, r = 0.54). One of the most important findings of this study is that agricultural cover is a major contributor of hazardous chemical substances to riverine ecosystems that endanger threatened fish species.

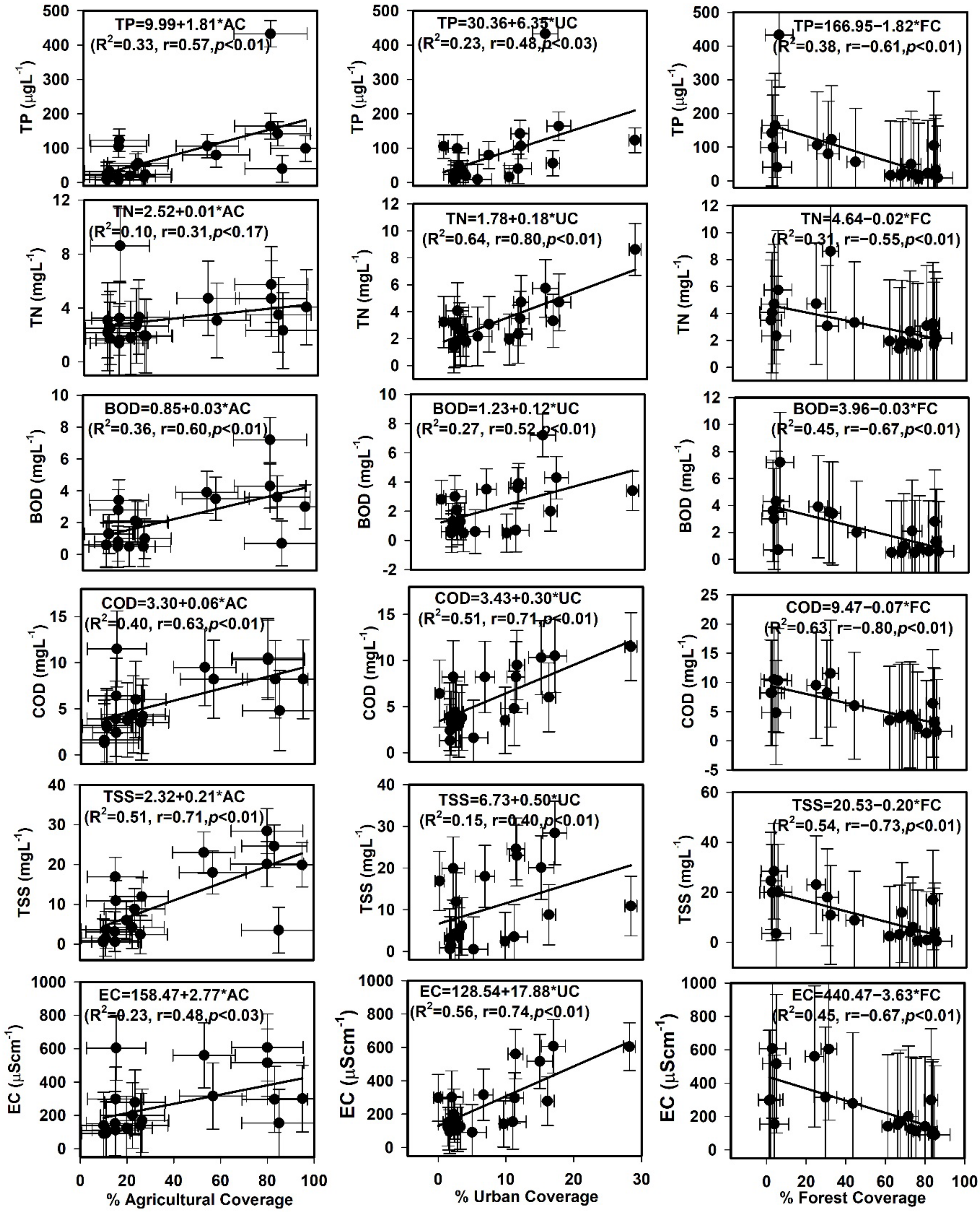

Figure 12. Effects of land use on water quality parameters. (TP: total phosphorus, TN: total nitrogen, BOD: biological oxygen demand, COD: chemical oxygen demand, TSS: total suspended solids, EC: electrical conductivity, n = 20).

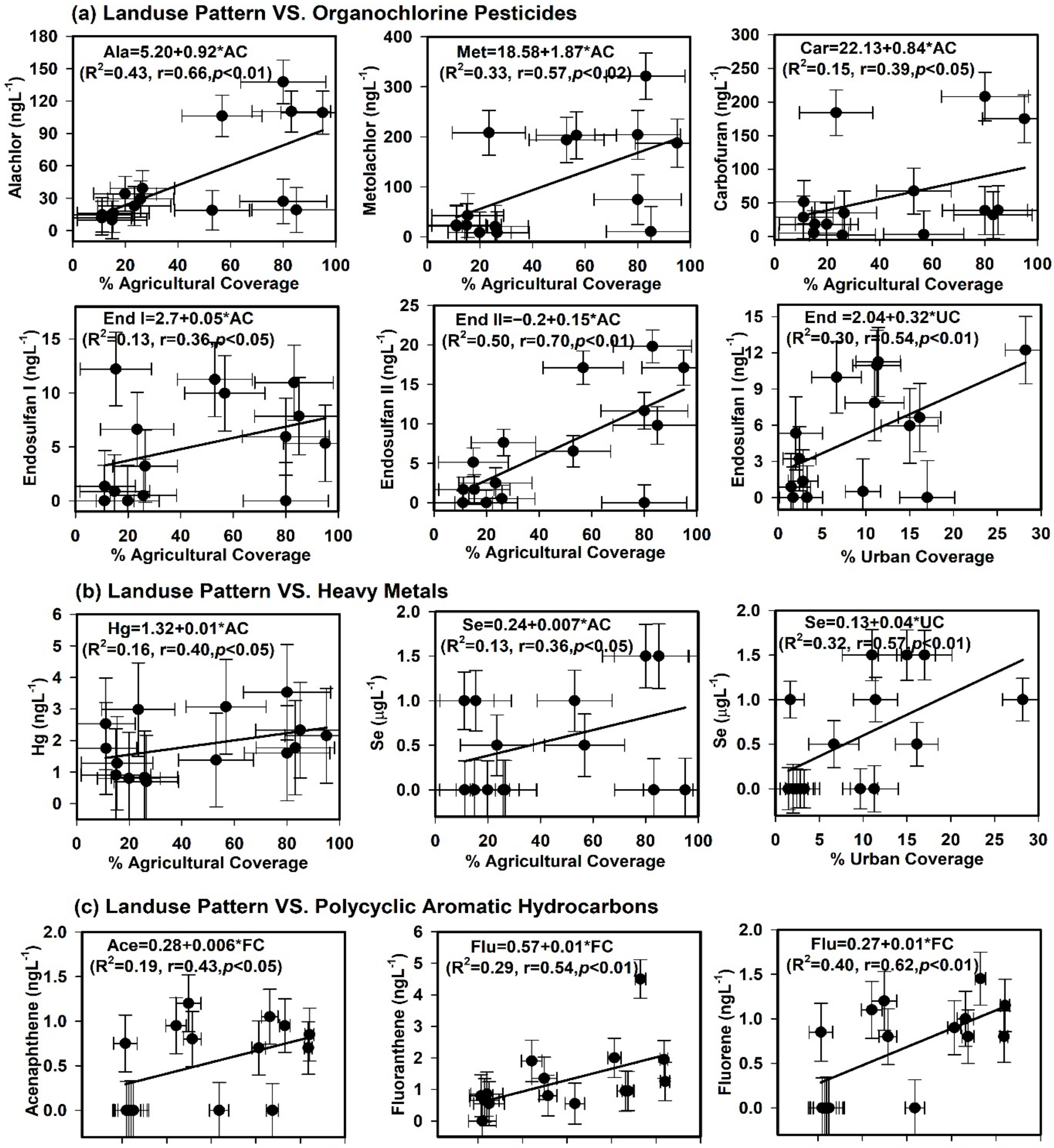

Figure 13. Effects of land use on chemical substances in surface water of the Geum River (n = 20).

Persistent organic pollutants (POPs) are widely used in agricultural and industrial activities and eventually reach rivers and streams. POPs are of global concern and may be produced intentionally or unintentionally. These hazardous chemicals can accumulate in the tissues of aquatic organisms (particularly fish) and various compartments of the biosphere. Moreover, they actively resist biochemical and photochemical breakdown, and may be transported long distances [80,81]. POPs have become pollutants of great concern due to their strong bioaccumulation tendencies, high toxicity, and exposure risks for humans and other organisms. These harmful chemicals are readily detected in the aquatic environments of countries that have undergone rapid industrial growth and have adopted modern high-yield agriculture technologies [81].

The major sources of POPs and heavy metals for surface waters, especially rivers and streams, include direct releases of waste and wastewater treatment plant effluent, agricultural runoff from adjacent farmlands subjected to modern agricultural practices, atmospheric deposition, and leaching of pollutants in snowmelt [82]. Intensive rainfall events during the monsoon season play a critical role in the inflow of pollutants from surface soils and riverine watersheds, providing direct inputs of harmful pollutants to rivers and streams [48,51]. Furthermore, the hydrological features of riverine watersheds, including seasonal modifications of water flow, water residence time, and the disruption of rivers through the construction of dams and weirs, can greatly impact the spatiotemporal patterns of POPs and other pollutants in riverine sediments and water [83].

3.8. Recommendations

This study suggests that the Geum River watershed has faced significant environmental challenges due to various anthropogenic activities, including agricultural practices, urbanization, and industrialization. To mitigate the environmental impacts of these activities, there is a need to implement effective measures that focus on prevention and remediation. Prevention measures could include stricter regulations and enforcement, public education, and promoting sustainable agricultural practices. Remediation measures could involve the use of innovative technologies, such as phytoremediation, bioremediation, and electrokinetic remediation, to reduce the levels of pollutants in water. Furthermore, developing green infrastructures, such as wetlands and buffer zones, can enhance the natural capacity of the watershed to absorb and filter pollutants. Life cycle impact assessment [84] and machine learning tools [85] can also help control aquatic systems' heavy metals and organic pollutants. Finally, collaborative efforts between various stakeholders, including government agencies, industries, and communities, are essential to achieving sustainable management of the Geum River watershed. In addition, the information obtained from this study could be helpful for environmental agencies in monitoring aquatic systems for managing human health practices and evaluating legacy environmental insurance claims. This study also recommends a continuous bio-monitoring program for organic pollutants and heavy metals in Korean freshwater systems, especially in the Geum River watershed.

4. Conclusions

The present study investigated water chemistry factors, their impacts on river water quality, links between land use and water quality, harmful chemical substances, and heavy metals. The results revealed that 35 toxic chemicals were present, including all investigated heavy metals, in both the water samples and fish tissues. The study sites displayed spatial heterogeneity in water quality factors, nutrient enrichment, and the persistence of harmful chemical substances. Agricultural land cover was the main determinant of river water quality and hazardous chemical substances (OCPs, metals, and PAHs), followed by urban cover. Most chemical substances were either not detected or present in negligible amounts, with the exception of a few PAHs and OCPs (DDTs and heptachlor epoxide) detected above the designated SVs. Similarly, Hg, As, and Cd were detected in most study sites and fish species at concentrations exceeding their SVs. In the trophic guild species, heavy metal contents were in the order of Zn < Cr < Cu < Pb < Se, while trophic levels were in the order of insectivorous < omnivorous < carnivorous. The fish organs showed a consistent sequence of metal levels, i.e., gills < guts < muscles. Overall, river health based on the IBI was poor due to the impacts of increasing levels of toxic pollutants and chemical substances.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15101845/s1, Figure S1: Variations in land use pattern in different sites of the Geum River during the study period; Figure S2. Organic phosphorus pesticides (OPPs) at different sites in different fish species (SV: screen value); Figure S3: Variations in metal concentration of surface water in different sites of the Geum River; Figure S4: Variations in organochlorine and organic phosphorus pesticides of surface water in different sites of the Geum River; Figure S5: Variations in endocrine disrupting chemicals and chlorine phenoxy herbicides of surface water in different sites of the Geum River; Figure S6: Variations in polycyclic aromatic hydrocarbons of surface water in different sites of the Geum River; Table S1: Conditions for the GC analysis of organic phosphorous and organic chlorine pesticides, oxyfluorfen, and PAHs; Table S2: Conditions for PCB GC-ECD analysis; Table S3: ICP/MS specifications for metal analysis; Table S4: Fish species name with tolerance and trophic guilds (TS: tolerant species, IS: intermediate species, SS: sensitive species, O: omnivores, I: insectivores, C: carnivores, and H: herbivores); Table S5: Metal Concentration at different sites of *Zacco platypus.* (Cr: Chromium, Cu: Copper, Zn: Zinc, As: Arsenic, Se: Selenium, Cd: Cadmium, Hg: Mercury, Pb: Lead).

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