

Article

Distribution of Silver (Ag) and Silver Nanoparticles (AgNPs) in Aquatic Environment

Zainab Mat Lazim ¹, Salmiati Salmiati ^{1,2,*}, Marpongahtun Marpongahtun ³, Nor Zaiha Arman ¹, Mohd Ridza Mohd Haniffah ^{1,2}, Shamila Azman ¹, Ee Ling Yong ^{1,2} and Mohd Razman Salim ⁴

¹ Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia, Skudai 81310, Malaysia; zaienab88@yahoo.com (Z.M.L.); n.zaiha@utm.my (N.Z.A.); mridza@utm.my (M.R.M.H.); shamila@utm.my (S.A.); eeling@utm.my (E.L.Y.)

² Department of Water and Environmental Engineering, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Skudai 81310, Malaysia

³ Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan 20155, Indonesia; marpongahtun@usu.ac.id

⁴ Civil Engineering Department, Faculty of Engineering, Technology and Built Environment, UCSI University, Cheras, Kuala Lumpur 56000, Malaysia; razman@ucsiuniversity.edu.my

* Correspondence: salmiati@utm.my

Abstract: Nanomaterials, classified as emerging pollutants that are toxic to the environment, are known to bioaccumulate across different trophic levels in the aquatic ecosystem. This study therefore investigates the distribution of silver and silver nanoparticles (AgNPs) in the aquatic environment of Skudai River, Johor, Malaysia. Water, sediment, plant, and fish samples were collected seasonally along four sites along Skudai River between May 2018 and April 2019. All samples were subjected to Ag analysis using an inductively coupled plasma mass spectrometer (ICP-MS). The analysis demonstrated that the concentration of Ag detected in water samples ranging from 0.001 to 0.505 mg/L was the lowest, whereas in the plants, 0.235 to 4.713 mg/kg of Ag was quantified. The upper sediments contained 0.036 to 28.115 mg/kg of Ag, whilst fish samples presented the highest accumulation of Ag, averaging between 9.144 and 53.784 mg/kg of Ag. Subsequently, the formation of silver nanoparticles was further proven by TEM-EDX analysis, where the detected size of AgNPs ranged from 20 nm to 35 nm. The overriding conclusion implied by bioaccumulation factor (BAF) and biota–sediment accumulation factor (BSAF) calculations suggested that Skudai River was indeed polluted by Ag and AgNPs. The values obtained stipulated that silver accumulation is occurring at an alarming rate and could therefore endanger fish consumers.

Keywords: emerging pollutants; distribution; silver; silver nanoparticles; aquatic environment



Citation: Mat Lazim, Z.; Salmiati, S.; Marpongahtun, M.; Arman, N.Z.; Mohd Haniffah, M.R.; Azman, S.; Yong, E.L.; Salim, M.R. Distribution of Silver (Ag) and Silver Nanoparticles (AgNPs) in Aquatic Environment. *Water* **2023**, *15*, 1349. <https://doi.org/10.3390/w15071349>

Academic Editor: Constantinos V. Chrysikopoulos

Received: 20 February 2023

Revised: 24 March 2023

Accepted: 24 March 2023

Published: 31 March 2023



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1. Introduction

Silver speciation is capable of interacting with various proteins. Thus, the mechanism of silver toxicity is the same as that of other heavy metals, persistent organic pollutants, polyaromatic hydrocarbons (PAHs), pesticides, and other emerging contaminants causing adverse effects on humans and living organisms [1–3]. Silver nanoparticles (AgNPs) are extensively used in a broad spectrum of consumer and industrial products due to their superior antibacterial, anticancer agents, optical, electrical, and catalytic properties [4–9]. Recently, concerns have been raised regarding the usage of silver products as they are shown to bear adverse effects on the environment and human health from repeated and prolonged applications [10–14].

Increased incidences of environmental pollution caused by AgNPs are expected as the substance is ubiquitously employed in personal care products without proper guidelines [15]. Wastewater treatment plants from both domestic and industrial are common sources of AgNPs in aquatic ecosystems, signifying the inadequacy of the current treatment process in removing AgNPs from wastewater before its release [16,17].

It was found that natural aquatic systems contain silver levels ranging from 0.03 to 500 mg/L [17], and this dissolved Ag can undergo a range of chemical and physical transformations [18]. In England and Wales, the highest dissolved Ag concentration in rivers was found to be 19.8 ng/L [19], while in the total Ag concentration in Rhine River in Germany, the lowest AgNP concentrations predicted could range from 40 to 320 ng/L [20]. Similarly, AgNP concentrations in the rivers Meuse and IJssel in the Netherlands were found to be between 0.3 and 2.5 ng/L [21]. River Isar in Germany found AgNP concentrations ranging from 2.0 to 8.6 ng/L [22]. Amongst them, the lowest concentration of AgNPs in surface water (freshwater), ranging between 0 and 44 pg/L, was found in Denmark [23]. Meanwhile, abnormally high AgNP counts (17.9×10^6 to 45.1×10^6 AgNPs/L) were detected in Besòs and Ebro Rivers in Barcelona [24].

Evidence has proven that AgNPs have significant effects on the ecosystem, especially when prolonging the release of Ag waste into the environment, leading to concentration alleviation [18,25,26]. The potential threats of AgNPs include bacteria, algae, fungi, invertebrates, plants, and fish [27–32]. Bioaccumulation and biomagnification in particular impose significant dangers to the environment and human health [19,33,34]. However, predicting AgNP-imposed risks remains difficult because they are differentially toxic to different organisms [20]. Furthermore, AgNPs are easily transferred to a diverse range of species in the aquatic ecosystem via the food web [35–37]. Therefore, studying their distribution in aquatic environments is crucial for determining potential human health risks and developing safety guidelines, as well as assessing and mitigating any potential environmental impacts. Additionally, understanding their distribution can help researchers develop strategies to manage and maintain water quality and inform the development of safe and effective nanotechnology applications.

Bioaccumulation factor (BAF) and biota–sediment accumulation factor (BSAF) were commonly employed to quantify the transfer of pollutants across the trophic level of a food web. BAF implies the ability of aquatic organisms to accumulate metal from the surrounding water environment. A BAF value of above 100 indicates that fish populations found in the aquatic ecosystem would exhibit a high potential of accumulating metal [36,38]. The corresponding BSAF value expresses the ability of aquatic organisms to absorb or accumulate metal from river sediments [39]. Previous studies stated that a BSAF value exceeding 2 would indicate that the bio-pollutant could be transferred and accumulated in the aquatic organisms living within the environment [40,41]. To the best of our knowledge, information on the trophic transfer efficiency of Ag via the food web was previously scarce.

This study therefore investigated the distribution of AgNPs in the aquatic ecosystem of Skudai River, Johor. The BAF and BSAF values were calculated to estimate Ag accumulation behavior in the water and sediment samples collected from the four sampling stations. Both parameters are vital in estimating the transfer efficiency of Ag from such samples into the aquatic biota. Results obtained here would therefore illustrate that the distribution of Ag and AgNPs in aquatic environments was an indication of the trophic transfer of Ag through the food chain in the Skudai River ecosystem.

2. Materials and Methods

2.1. Chemicals and Reagents

Nitric acid (HNO₃) 65% and perchloric acid (HClO₄) 65% were obtained from Thermo Fisher Scientific (Fisher Scientific UK), and hydrogen peroxide (H₂O₂) 30% was obtained from Merck (Darmstadt, Germany). All chemicals purchased were of analytical grade.

2.2. Sample Collection

Field sample collection was conducted once a month over a one-year period from May 2018 to April 2019. Four stations were chosen, namely Bandar Putra, Lee Rubber, Impian Emas, and Kampung Pengkalan Rinting, along the main Skudai River, Johor, Malaysia (Figure 1). These catchments are urban areas full of residential, commercial, industrial, and infrastructure, and utilities could be the high potential source of pollution

within the watershed area. The distance between these sampling stations ranged from 5.3 km to 7.5 km. Samples included river water (12 samples), sediments (12 samples), plants (5 samples), and fish (7 species). Three 250 mL polyethylene bottles of water samples were collected using a water grab sampler. Sediment samples were obtained using a grab sampler and kept in sealed plastic bags. While aquatic weeds were randomly collected at the river bank of Skudai River. Fish were purchased from local fishermen near each sampling station. All samples were kept in ice immediately after acquisition and stored in a 4–8 °C refrigerator until analysis.

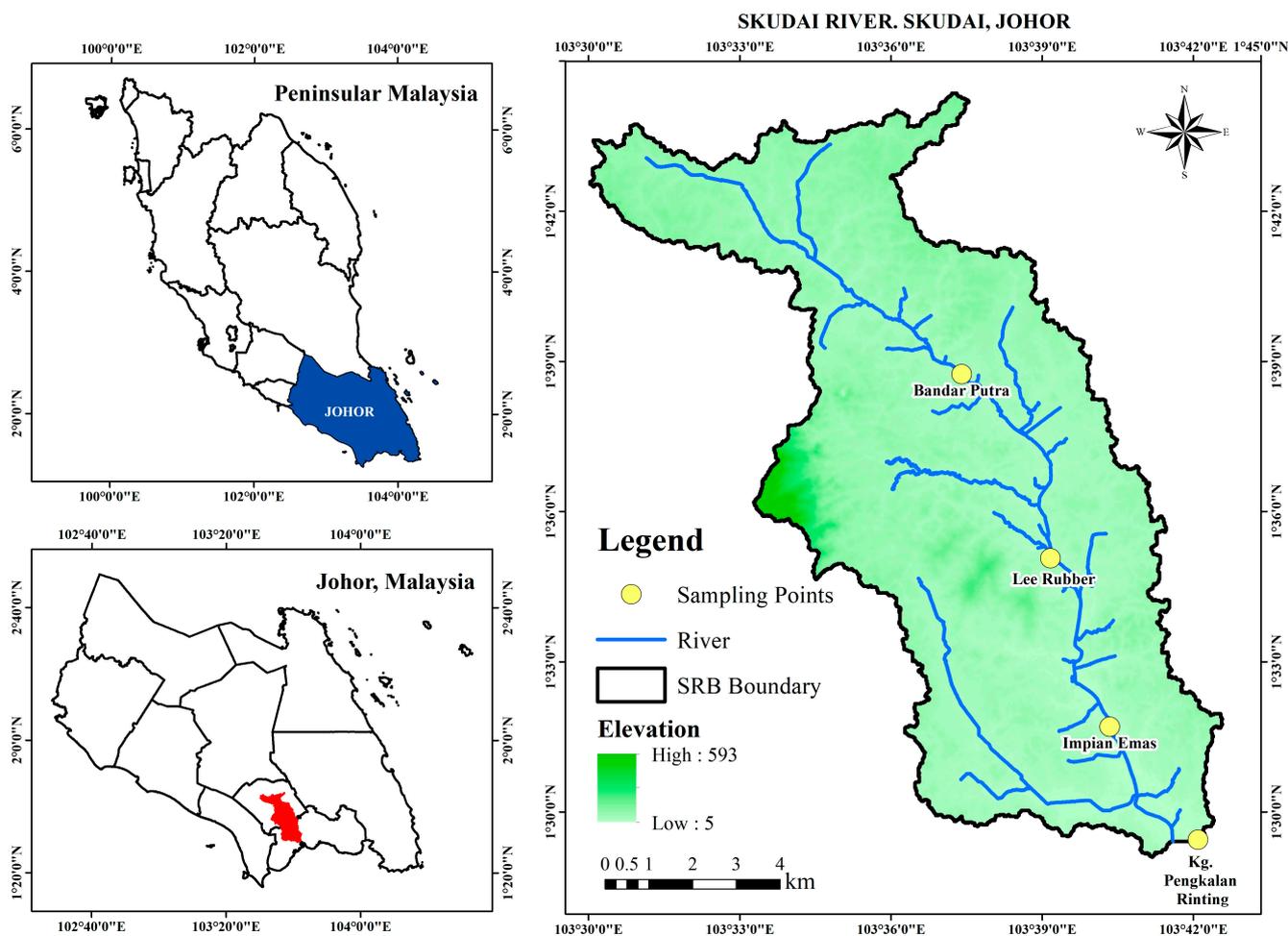


Figure 1. Location of sampling stations along Skudai River.

2.3. Preparation of Samples

Samples of river water and sediments were transferred into 50 mL centrifuge tubes wrapped with aluminum foil for protection from direct light. Samples of plants were washed repeatedly with tap water and distilled water to purify any impurities. Then, the samples were separated by the root and aerial part and fully dried at room temperature. The plant sample was then ground to powder and transferred into 50 mL centrifuge tubes. The exact species of collected fishes were determined and recorded in Table 1. Each fish was dissected for its muscle, liver, heart, kidney, and gills. The obtained tissues were separated into individual centrifuge tubes based on fish and organ type before being frozen immediately.

Table 1. The recorded examined fish species.

Sampling Station	Scientific Name	English Name
Bandar Putra	<i>Anabas testudineus</i>	Climbing Perch
	<i>Oreochromis niloticus</i>	Nile Tilapia
Lee Rubber	<i>Clarias macrocephalus</i>	Catfish
	<i>Oreochromis niloticus</i>	Nile Tilapia
	<i>Pangasianodon hypophthalmus</i>	Silver Catfish
	<i>Channa striata</i>	Snakehead Murrel
Impian Emas	<i>Barbus schwanenfeldii</i>	Tinfoil Barb
	<i>Clarias macrocephalus</i>	Catfish
Pengkalan Rinting	<i>Pangasianodon hypophthalmus</i>	Silver Catfish
	<i>Clarias macrocephalus</i>	Catfish
	<i>Oreochromis mossambicus</i>	Mozambique Tilapia
	<i>Pangasianodon hypophthalmus</i>	Silver Catfish

All sample tubes were stored in a cold box prior to transport to the laboratory for analysis, where they were first processed via microwave-assisted digestion (MILESTONE START D, MODEL: SK-10). The weight of the samples and designated composition of HNO₃ and H₂O₂ were added to the samples (Table 2) before introducing into the microwave oven digester. The settings of the microwave oven digester are listed in Table 3. After the digestion process was completed, the vessels were cooled to room temperature. The samples were then filtered into a 25 mL volumetric flask and marked up to the mark with deionized water.

Table 2. Analysis for acid digestion.

Sample	Sample Weight (g)	Acids Used
Water	5	7 mL HNO ₃ 65% 1 mL H ₂ O ₂ 30%
Sediment	0.25	6 mL HClO ₄ 65% 6 mL HNO ₃ 65% 1 mL H ₂ O ₂ 30%
Plants	0.5	7 mL HNO ₃ 65% 1 mL H ₂ O ₂ 30%
Fish	0.5	7 mL HNO ₃ 65% 1 mL H ₂ O ₂ 30%

Table 3. Setting for acid digestion for the microwave oven digester (Milestone START D, Model: SK-10).

Step	Time (min)	Temp. (T1)	Temp (T2)
1	15	200 °C	110 °C
2	15	200 °C	100 °C

2.4. Analytical Method

To identify elemental contents and determine the silver concentration, samples were then introduced into an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (PERKIN ELMER NEXION 350X). Water samples were further analyzed by using a high-resolution transmission electron microscope (HR-TEM 200KV) with an energy-dispersive X-ray spectrometer (EDX) (JEOL JEM-ARM 200F) to obtain the quantitative particle size and distribution and the shape and morphology of silver nanoparticles.

2.4.1. Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

Standards were prepared based on the concentration range needed. Samples were transferred into sample tubes and arranged on the sample rack. The sample information and the location of the samples were key to the software. Performance checks were performed to make sure that the instrument is in good condition. Blank and QC were analyzed before sample analysis was carried out (ICP-MS setting: Peristaltic pump speed, 20 rpm; Nebulizer gas flow, 1.06; Vacuum pressure, 7.45×10^{-6}). Sample tubing was rinsed using ultrapure water after each sample analysis.

2.4.2. High-Resolution Transmission Electron Microscope (HR-TEM 200KV) with Energy-Dispersive X-ray Spectrometer (EDX)

The physical properties of AgNPs were examined using a combination of analytical techniques. HRTEM-EDX was used to investigate the morphology, elemental composition, and purity of the nanoparticles. To perform the analysis, a small amount of the water sample was applied to a carbon-coated copper grid, allowed to dry at room temperature, and then analyzed using a microscope operating at 200 kV. The TEM was used to analyze the shape and morphology of the nanoparticles, while EDX spectroscopy and elemental mapping were used to investigate the elemental distribution of the nanoparticles.

2.5. Data Analysis

The BAF and BSAF represented in Equations (1) and (2), respectively, were adopted to correlate the concentration of silver in the water or sediment to that of the fishes found at a sampling station, thus evaluating the degree of the ongoing silver pollution [42,43]. BAF and BSAF were calculated using Formulas (1) and (2):

$$\text{BAF} = C_{\text{fish}}/C_{\text{water}}, \quad (1)$$

$$\text{BSAF} = C_{\text{fish}}/C_{\text{sediment}} \quad (2)$$

where C_{fish} (mg/kg) is the total concentration of Ag in the fish at a specific sampling station, and C_{water} refers to the Ag concentration in the river water at the same station normalized against the 'normal' Ag concentration of 0.0002 mg/L [44]. For comparison purposes, the average concentration of Ag during the sampling period was also used in the calculation. For BSAF calculations, C_{sediment} refers to the total concentration of Ag in the sediment at a sampling station.

3. Results

3.1. Concentration of Ag in the Aquatic Environment

Analysis of water samples using ICP-MS revealed the fluctuating Ag concentrations at each station throughout the one-year data collection period (Figure 2a). Overall, the lowest concentration of Ag detected was 0.001 mg/L, whereas the highest was 0.505 mg/L. Figure 2b indicates the average Ag concentration by sampling station where water pollution by Ag was greatest at the Lee Rubber station (0.082 ± 0.04 mg/L), followed by Impian Emas (0.040 ± 0.02 mg/L), Bandar Putra (0.039 ± 0.01 mg/L) and Pengkalan Rinting (0.011 ± 0.003 mg/L).

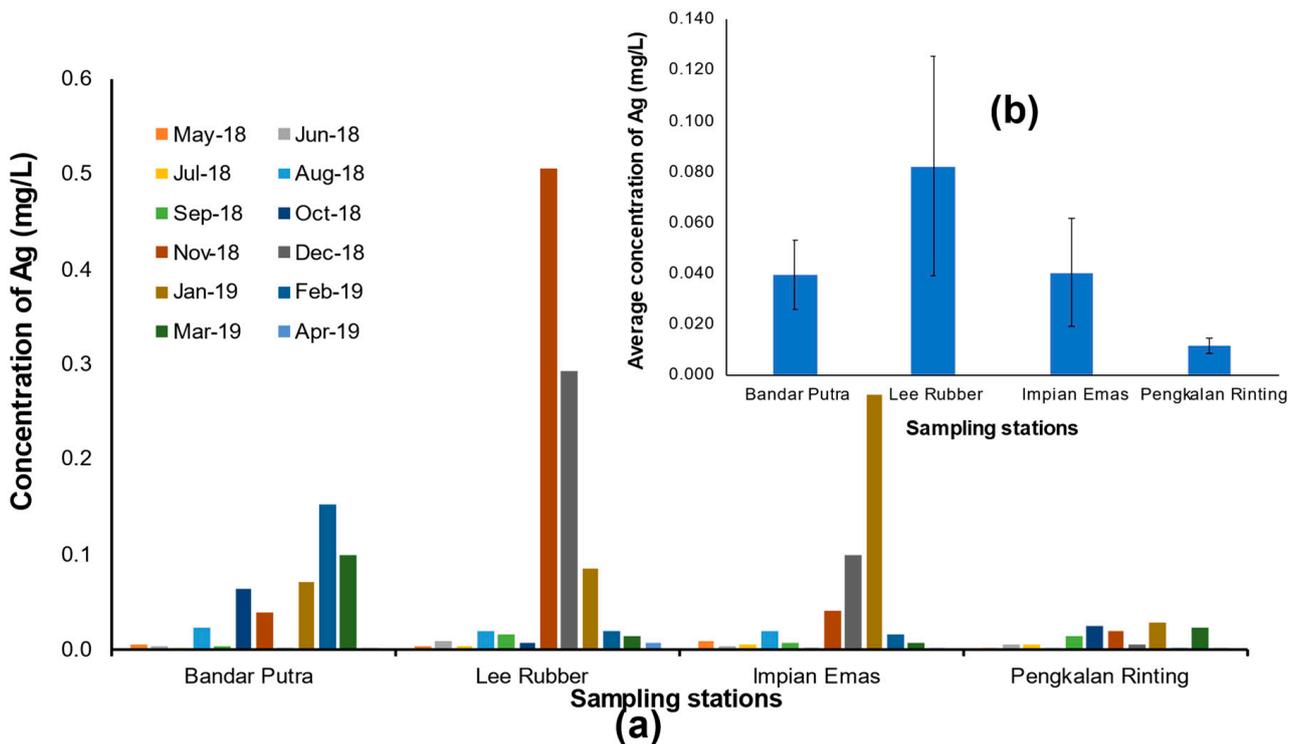


Figure 2. (a) Monthly concentration of Ag over a one-year period and (b) average concentration of Ag in Skudai River water samples by sampling stations.

3.2. Analysis of Silver Nanoparticles in the Aquatic Environment

TEM-EDX analysis was employed to investigate the formation of AgNPs via agglomeration of Ag ions in water samples. This combination of TEM and EDX has successfully confirmed the presence and distribution of Ag in all samples. Micrograph images in Figure 3 depict the tiny spherical or semi-spherical shape of the Ag nanoparticle, with the detected size of AgNPs ranging from 20 nm to 35 nm, demonstrating that agglomeration of Ag ions with other organic and inorganic materials found in the water had occurred. Additionally, by isolating the elemental signatures of Ag from other elements, EDX was able to show the homogenous distribution of AgNPs in the water, regardless of sampling locations (Figure 4). These observations further confirmed that nano-sized Ag particles were present in the Skudai River surface water.

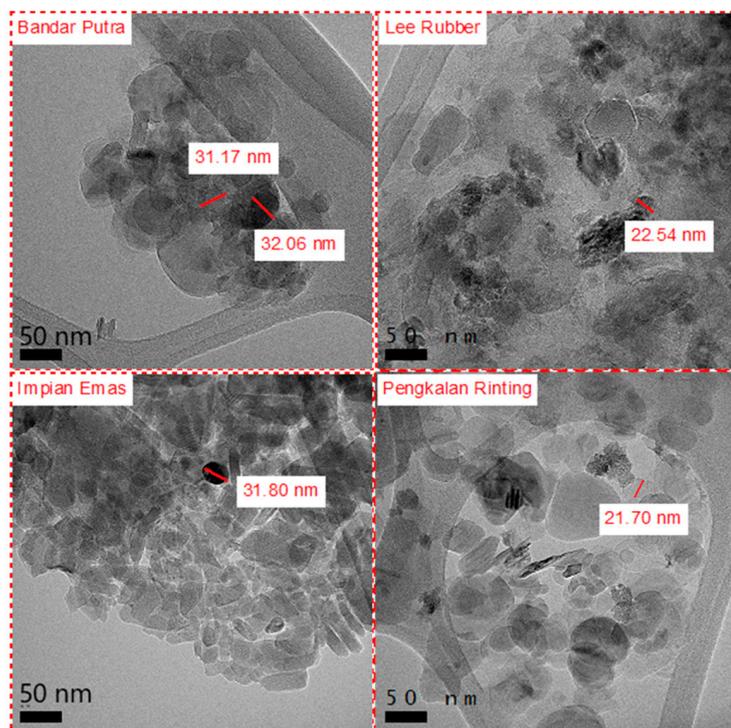


Figure 3. TEM image displaying the nano-size of Ag in water samples.

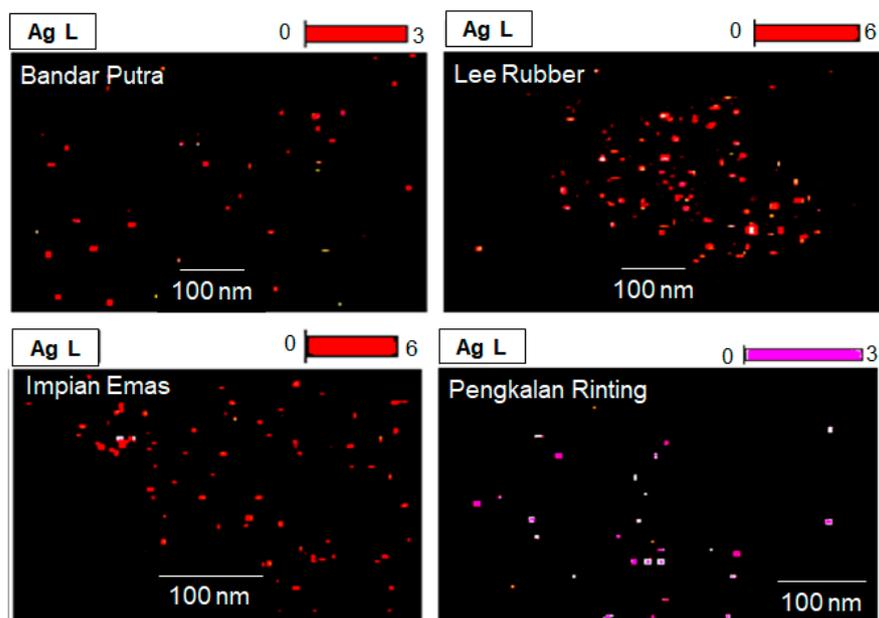


Figure 4. Elemental mapping of Ag by EDX.

3.3. Accumulation of Ag in Sediment Samples

Monthly sediment samples were also analyzed using ICP-MS. The data generated indicated that the amount of detectable Ag had varied dynamically throughout the year, with overall concentrations ranging from 0.036 to 28.115 mg/kg (Figure 5a). Average Ag concentrations according to the sampling station are shown in Figure 5b. Bandar Putra sediment samples contained the highest levels of Ag (4.079 ± 2.19 mg/kg), followed by Lee Rubber (2.529 ± 0.70 mg/kg), Impian Emas (2.324 ± 0.47 mg/kg), and Pengkalan Rinting (0.873 ± 0.17 mg/kg).

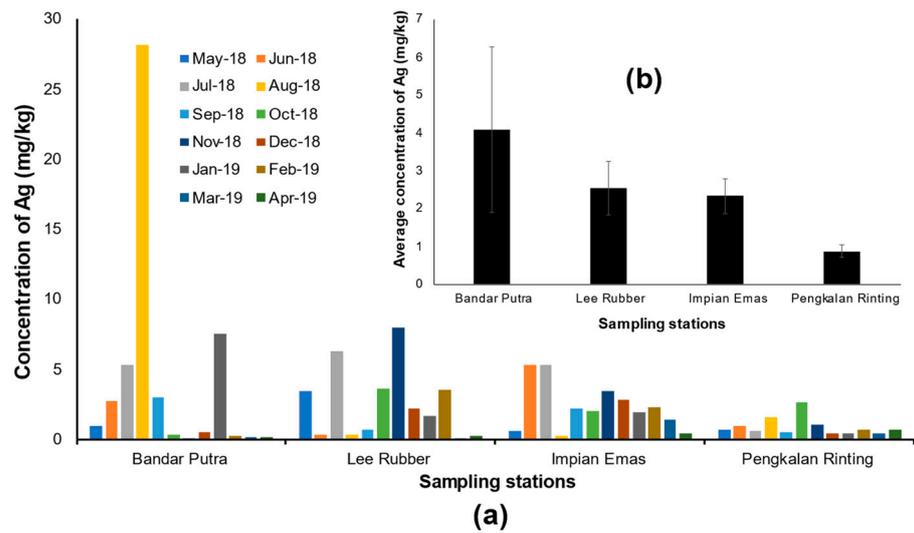


Figure 5. (a) Monthly Ag concentrations in sediment samples over the one-year sampling period and (b) average Ag concentrations by sampling station.

3.4. Accumulation of Ag in Plant Samples

Plants samples were also analyzed using ICP-MS. The data generated indicated that Ag can accumulate in plants with overall concentrations ranging from 0.235 to 4.859 mg/kg (Figure 6a). Average Ag concentrations by sampling station are shown in Figure 6b. Bandar Putra plants samples contained the highest levels of Ag (3.171 ± 1.09 mg/kg), followed by Pengkalan Rinting (2.429 ± 1.72 mg/kg), and Impian Emas (2.260 ± 1.43 mg/kg), while Lee Rubber station has no data due to inaccessible and limited equipment to collect the plant sample.

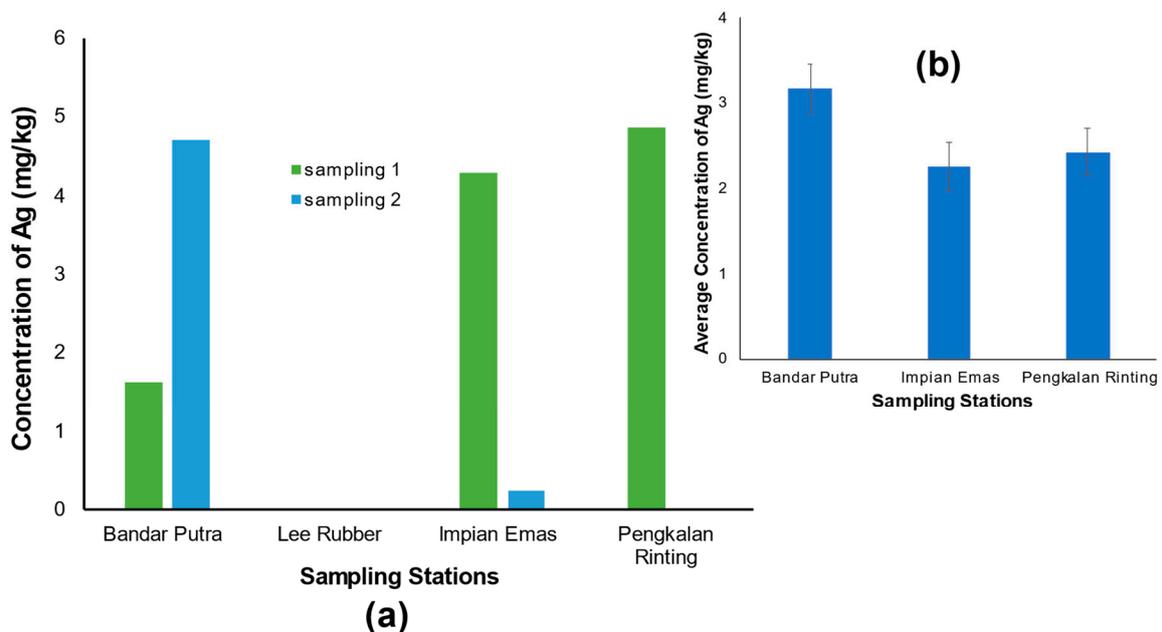


Figure 6. (a) Ag concentrations in plant samples over sampling period and (b) average Ag concentrations by sampling station.

3.5. Accumulation of Ag in Fish Organ

The data generated from ICP-MS indicated that the amount of detectable Ag had varied dynamically throughout the organ and species, with overall concentrations by

species and sampling stations ranging from 3.04 to 161.94 mg/kg (Figure 7a). Average Ag concentrations by species and sampling station are shown in Figures 7b and 7c respectively. Overall, seven species were collected. Accumulation patterns of Ag varied among the species. *Oreochromis niloticus* fishes had the highest accumulative total of Ag (53.784 mg/kg) across all its tissues compared to *Anabas testudineus* (37.174 mg/kg), *Clarias macrocephalus* (33.222 mg/kg), *Pangasianodon hypophthalmus* (30.792 mg/kg), *Barbus schwanenfeldii* (22.176 mg/kg), *Channa striata* (16.526 mg/kg), and *Oreochromis mossambicus* (9.144 mg/kg).

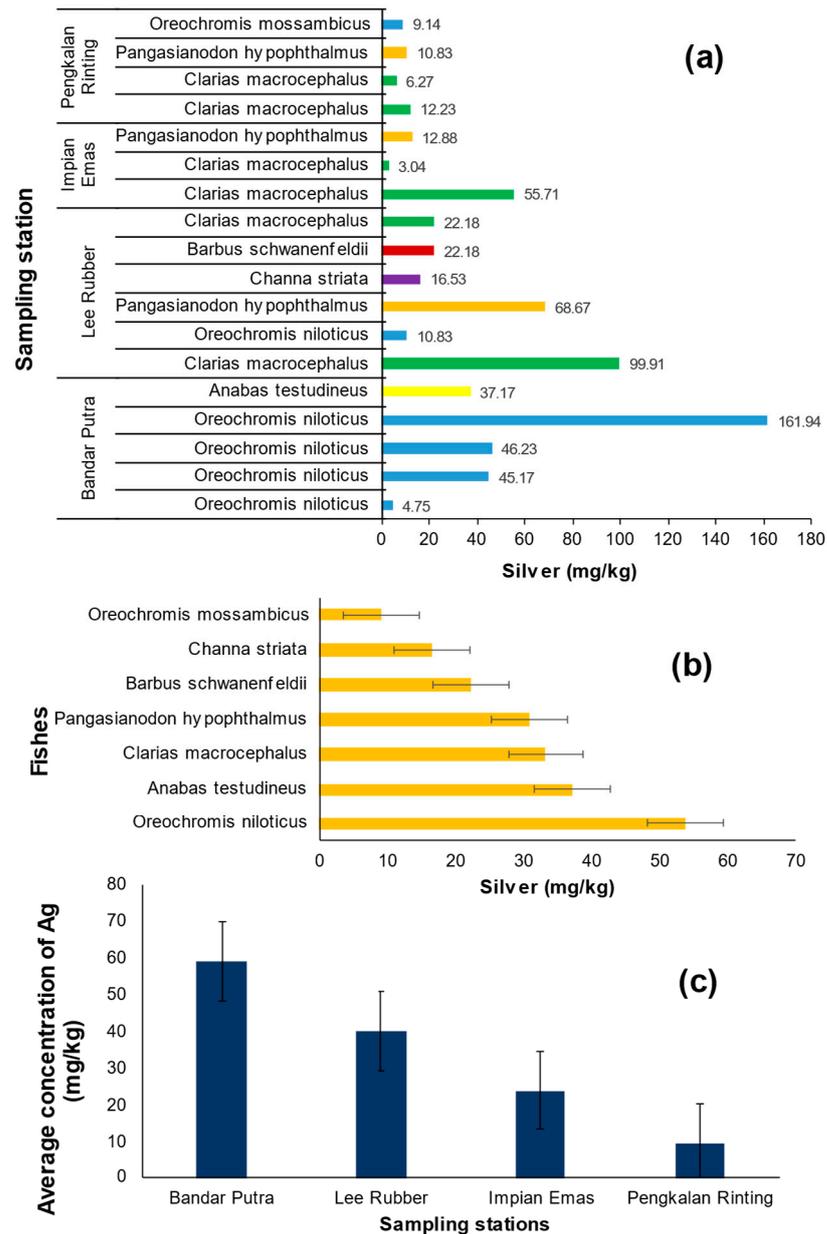


Figure 7. (a) Ag concentrations throughout the fish species and sampling stations, (b) overall concentrations by fish species, and (c) average Ag concentrations by sampling station.

3.6. Values for BAF and BSAF

The BAF and BSAF values were calculated to estimate Ag the accumulation behavior in the water and sediment samples. Both parameters are vital towards estimating the transfer efficiency of Ag from such samples into the aquatic biota.

BAF and BSAF were calculated on the basis of weight against concentration. All data showed non-significant changes according to ANOVA analysis ($p > 0.05$), as suggested by a previous study [43]. As listed in Table 4, Bandar Putra recorded the highest average and relative BAF values, followed by Lee Rubber, Pengkalan Rinting, and Impian Emas. Interestingly, the standardized relative BAF value at Impian Emas was higher than that of Pengkalan Rinting despite its much lower average BAF value. On the other hand, BSAF estimates showed that sediments sampled from the Lee Rubber station imposed the highest bioaccumulation risks, followed by samples gathered from Bandar Putra, Pengkalan Rinting, and Impian Emas. Previous studies have stated that a BSAF value exceeding 2 would indicate that the bio-pollutant could be transferred and accumulated in the aquatic organisms living within the environment [40,41]. Regardless, the overriding conclusion implied by BAF and BSAF calculations suggested that Skudai River was indeed polluted by Ag and AgNPs.

Table 4. List of BAF and BSAF values for each sampling station.

Sampling Station	BAF		BSAF
	Average Ag Concentration in Sampled Surface Water ¹	Relative Limit of Ag Concentration ²	
Bandar Putra	7570.95	1,476,334.75	6.03
Lee Rubber	3733.11	1,530,575.59	10.09
Impian Emas	703.49	140,698.66	1.01
Pengkalan Rinting	2385.52	131,203.74	2.50

Note(s): ¹ Derived from the average concentration of Ag in water samples as shown in Figure 2b. ² Limit of Ag concentration based on National Standard Water Quality, printed in Environmental Quality Report, endorsed by Department of Environment, 2006 (0.0002 mg/L).

4. Discussion

4.1. The Presence of Ag in the Aquatic Environment

The Ag concentrations presented in this study were higher compared to previously published estimates. Figure 2 indicated that different concentrations of Ag were observed in multiple locations along Skudai River. The average levels recorded at urban residential areas (Bandar Putra and Impian Emas) were significantly lower than those of the industrial area (Lee Rubber). The most likely source of Ag in residential areas is discharge effluents from nearby wastewater treatment plants, where inadequate wastewater treatment practices would then lead to its release into the local stream. These observations were in good agreement with previous reports, where more than 5% of the initial amounts of Ag entering wastewater treatment plants would have remained in the effluents released. Additionally, household products that contain AgNPs as an active ingredient may also contribute to the leaching of Ag into the water drainage system, which can ultimately lead to its release into the local stream [45,46].

Furthermore, Figure 2 showed that the Ag concentrations were highly detected at the Lee Rubber and Impian Emas sampling stations from November 2018 to January 2019. This period coincided with the annual North-East Monsoon season, where heavy rain was expected along the West Coast of Peninsular Malaysia including Johor. The increased Ag levels could have therefore been caused by greater water discharge to the selected areas. A study by Syafiuddin et al. 2018 also attributed the high Ag concentrations they reported in rural or industrial areas to the same factor [47]. An alternative explanation is that the increased stream flow instigated by heavier precipitation eventually led to the deposition of minerals, including Ag, from elsewhere to the sampling station areas. Additionally, research conducted by Deycard et al. 2017 indicated that due to the shortcomings of the current process employed by wastewater treatment plants, the efficiency of Ag removal decreases with the increment of average rainfall [46]. This too could have factored into the sudden increments seen in Ag concentrations.

Moreover, Ag and AgNPs could enter the aquatic environment through human activities such as manufacturing, leaching, and mining along the main river. This is particularly concerning as heavy rainfall can lead to a flushing effect that may cause an increase in Ag levels in the water [48–51]. Discharge effluents from industrial processes are long-identified sources of heavy metals in river systems [52,53]. This exposure may occur over several phases of the Ag lifespan, from its synthesis and manufacturing, distribution, end-product use, and end-of-life disposal of everyday Ag-containing consumer products [41–44]. Ag released into the environment via industrial wastewater streams and effluents are emitted into the environment and remain there for extended periods by leaching into the groundwater or subsoil from landfills [45,54,55].

Figure 5 indicated a notable difference in Ag concentrations in the sediments sampled from all stations. Bandar Putra displayed a higher concentration of sedimental Ag compared to the others. At this sampling station, the sediment samples were found to contain more natural organic matter, a factor that greatly influences the stability and bioavailability of nanoparticles [56]. The high likelihood that the AgNPs in the river water could have incorporated with the organic matter and thus settled on the riverbed sediments [57]. This interaction is encouraged by the availability of Ag⁺ cations, which react with the oxygen (O₂) groups of sediment material to induce the chemical transformation of AgNPs, a process known as oxidation dissolution [58]. Previous studies have also demonstrated the existence of electrostatic forces between the positively charged dissolved Ag and negatively charged organic matter, which serves as yet another reason behind the high Ag-adsorbing capability sediments [59,60].

In the environment, AgNPs may stay in suspension, aggregate or agglomerate, and dissolve or react with the different species present in the aquatic system [61–63]. Riverbed sediments are considered a significant sink for released nanoparticles [57,58]. This could be the reason that sediment (Figure 5) has a higher concentration of Ag compared to surface water (Figure 2). Natural organic materials (NOMs) on the surface of sediments such as fulvic and humic acids react with AgNPs, creating a protective coating on the surface of AgNPs before settling as sediments [64,65]. AgNPs mainly sink to the surface sediment (0–1 cm), a fraction that accounts for 70% by weight of the total amount of Ag. Residual AgNPs either stay in the water phase or accumulate in biofilms or aquatic organisms. Once Ag enters a freshwater aquatic environment, it is immediately absorbed by the sediments or suspended particles at the discharge site and becomes immobilized [66–68]. A small amount of Ag will be kept in solution by colloidal and complexed materials, before being transported downstream towards lakes, estuaries, or the sea. Here, Ag is delivered to organisms in the soil, water, and sediments. Over an extended period, these AgNPs may act as sources of ionic silver [63].

Figure 6 showed the accumulation of Ag in plants where these aquatic weeds were collected randomly at Skudai River's bank. Though the plan was to obtain three samples of the same aquatic weed species from each sampling station, the study could not proceed as planned due to accessibility issues. Nevertheless, it was found that these aquatic weeds can accumulate silver (Ag). These Ag nanoparticles (AgNPs) can enter and accumulate in aquatic plants through their roots or leaves [56,69,70]. The cell wall of the root cells was the primary site for AgNPs to enter plant cells, while smaller-sized AgNPs can pass through the pores of the cell wall [71,72]. AgNPs can also penetrate plant leaves through stomata [73,74]. Aquatic macrophytes have been shown to accumulate large amounts of metals when exposed to metallic ions or nanoparticles, which can pose a threat to the aquatic ecosystem's food webs as they can serve as a point of entry for different kinds of anthropogenic toxicants.

The study's findings reveal that the Lee Rubber station had the highest average concentration of silver (Ag) in Skudai River water samples, while Bandar Putra station had the highest average concentration of Ag in sediment, plant, and fish samples. To explain this, the study examined the details of the results. The concentration of silver (Ag) was highest at Lee Rubber with an average of 0.08 mg/L. Lee Rubber is located in an industrial

area which numerous factories in the vicinity utilizing Ag as their raw material, surrounded by a few squatter settlements, a sewerage plant, a housing estate, and the towns of Kulai and Senai. The study suggests that the presence of Ag in the river water is likely due to industrial and residential activities and wastewater treatment, which are common sources of AgNPs in aquatic ecosystems [16,45,75]. Previous studies have shown that the current wastewater treatment process cannot effectively remove AgNPs from the wastewater before its release into the river [17]. Therefore, it is expected to find a high concentration of Ag in the sample water at Lee Rubber.

On the other hand, the sediment in Bandar Putra had the highest average concentration of Ag, with a significant increase detected in August, which is believed to be caused by anthropogenic activities. However, the specific activities remain unidentified. Plant data were not available for Lee Rubber due to inaccessibility, but it is predicted that they may have high accumulations of Ag due to the high concentration of surface water and sediment in the area. Previous research works indicated that AgNPs released can enter the plant rhizosphere, where they are inevitably taken up by plants and enter the food chain [76,77]. Bandar Putra also had the highest accumulation of Ag in fish samples; however, since the fish were purchased from local fishermen and were of random and different species for each sampling station, it is difficult to make a fair comparison of average Ag concentrations by station.

This present study showed that the levels of Ag varied significantly among fish species (Figure 7). Accumulation of such metals varied over the sampling period, with Ag displaying different affinities to different fish tissues. Fish living in polluted waters tend to contain high concentrations of heavy metals in their tissues. Generally, this accumulation was shown to be attributable to environmental conditions, geographical distribution, species-specific factors, biotic characteristics (size, age, sex, and physiological conditions of organisms), and abiotic parameters (metal concentration, time of exposure, way of metal uptake, site-specific water quality, i.e., water temperature, pH, hardness, or salinity) [78–80]. Moreover, Ag⁺ ions have a great propensity to bioconcentrate in organisms since their chemical properties allow for the efficient uptake of these ions via cell membrane ion transporters [26,62].

A previous study at the Asakawa River in Tokyo, Japan, found that Ag was accumulated in the entrails of *C. auratus langsdorfi*, reaching a concentration of 12 µg/g [81]. Accumulation of Ag in the fish tissue begins with the absorption of AgNPs via the respiratory system. Water received through the gills circulates the fish body via the blood system before agglomerating in the liver, kidney, or muscle tissue [82].

4.2. Nano-Size of Ag in the Aquatic Environment

As shown in Figures 3 and 4, TEM-EDX confirmed the presence of nano-sized Ag in the samples. The spherical colloids were the dominant structure during the growth stage. However, the shape and size can be altered during environmental transformations. With prolonged irradiation, triangular nano-prisms might appear and later disappear, gradually displaced by large irregular aggregations [83,84].

AgNPs released from commercial textiles during washing and from outdoor facades after rainfall events [85,86] would likely transform into agglomerates once dissolved in the aqueous solution [87–91]. Other than that, the combination of oxidation and reduction for Ag under light encourages the increased agglomeration of AgNPs as well. Dissolving organic materials (DOMs), irradiation, and pH are essential in driving the reductive reformation of AgNPs. Other factors, including redox potential, dissolved oxygen, and temperature, could also affect the process [83,92,93]. Numerous studies have reported that Ag⁺ can be chemically reduced to AgNPs under high-energy irradiation. In the environment, free Ag⁺ can be reduced by DOMs to form AgNPs under sunlight irradiation and through a charging–discharging mechanism [92,94].

4.3. Bioaccumulation of Ag in the Aquatic Ecosystem of Skudai River

Bioaccumulation factor (BAF) implies the ability of aquatic organisms to accumulate silver from the surrounding water environment. A BAF value of above 100 indicated that fish populations found in the aquatic ecosystem would exhibit a high potential of accumulating Ag [36,38]. Most researchers specifically aim to obtain a wide range of aquatic vertebrates and invertebrates during the capturing exercise to represent this data. However, in this study, the fish samples were wildly and randomly collected from the sampling stations. Thus, the BAF value was instead calculated only on a station-by-station basis to signify the level of accumulation.

In addition, the corresponding BSAF value expresses the ability of the aquatic organisms to absorb or accumulate metal from river sediments [39]. Table 2 indicated that fishes from Bandar Putra, Lee Rubber, and Pengkalan Rinting are classified as macro-concentrators, as their BSAF values were higher than 2. In contrast, fishes collected at Impian Emas could only be classified as micro-concentrators. This classification is due to the innately higher storage levels of AgNPs detected at macro-concentrator sites, as reported in Figure 7a. The BSAF values also show that sediments found along the riverbed could efficiently become a primary reservoir for nanoparticulate Ag, exposing invertebrates and vertebrates akin to the danger of Ag [32].

By contrast, the average Ag concentration within sediment samples gathered from Pengkalan Rinting was significantly lower than that of the other sampling stations. The station is situated near the end of Skudai River and the mouth of the sea. Thus, there is a greater possibility that AgNPs stored in the sediments there would have been washed out to the ocean rather than remaining around the locale. Nevertheless, both the BAF and BSAF values calculated at Pengkalan Rinting were still significant. This implied that the release of Ag from organic sediment layers into the water would in any way reach the fishes, resulting in eventual metal accumulation. Despite outwardly low Ag concentrations, should the natural environment be particularly rich in organic matters—as would the brackish waters of the Pengkalan Rinting delta—the high redox potential of surrounding sediments would promote the rather than curb the release of Ag ions into the water [95,96].

4.4. Trophic Transfer of Ag through the Aquatic Food Chain

These results highlight the ecosystem health risk posed by the Ag compound, which can be transferred through entire food webs (Figure 8). The accumulation of Ag in natural ecosystems is most likely due to cross-correlation factors and uptake routes. Ag taken up from the aquatic environment either via the water phase or food could result in toxicity [80]. Heavy metals absorbed by small organisms such as bacterioplankton, phytoplankton and zooplankton followed by their unintentional uptake by larger fish due to their waterborne nature could have also contributed to Ag accumulation [97]. There are several sources of evidence that Ag and AgNPs can be transferred in the food chain. Examples include the transfer of AgNPs in a simple freshwater food web from sediment-dwelling worms (*T. tubifex*) to pelagic fish (*Danio rerio*) [98], from protozoa to rotifer [97], and algae (*Pseudokirchneriella subcapitata*) to zooplankton (*Ceriodaphnia dubia*) [99].

The findings from this study mirrored those in the previous study, which suggested that the factors affecting the trophic transfer of Ag were environmental transformations of its compounds such as AgNPs, Ag sedimentation, uptake, and the accumulation of Ag in plants, all of which affect the internal fate and localization of Ag in the fish [98]. The association of nanoparticles with sediments might be a critical process in transferring intact particles within aquatic food webs. Meanwhile, the accumulation of Ag and AgNPs in primary producers such as phytoplankton or plants could be available to the next level of predators in the food chain, leading to broader ecological effects in the higher stiles of the chain [97]. Indeed, plants play a crucial role as producers in the ecosystem, sustaining the entire food chain. AgNPs accumulated in plant tissues can be transferred to consumers through the food chain, causing lethal effects on non-tolerant species. Their roles as the primary producers and a source of food for waterfowl, fish, and small invertebrates, and

dwellings for several tiny organisms, meant that they too could have contributed towards the concentration of Ag within the aquatic ecosystem [100,101].

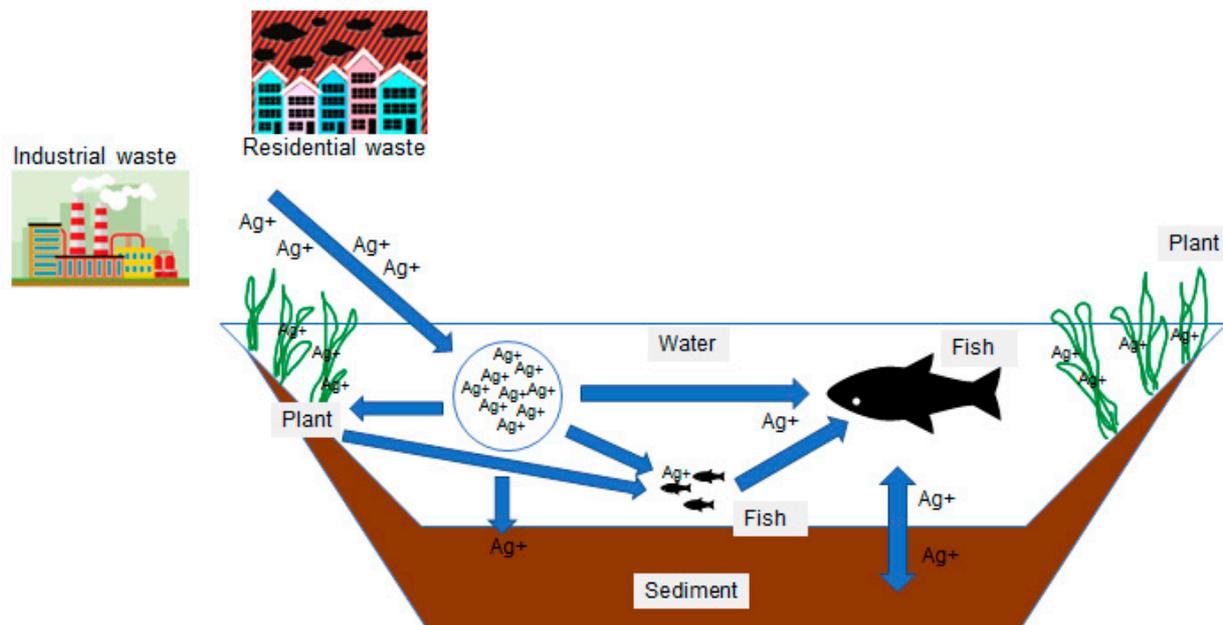


Figure 8. Trophic transfer of Ag through the aquatic food web.

There was a study showed that various species had taken up large quantities of Ag from the amounts released into aquatic and terrestrial ecosystems [48]. Therefore, there is a possibility that Ag will enter and pass through aquatic food webs, transfer between individuals of different species, and have minor or significant effects on natural communities, organisms, and higher trophic levels [102–104]. An example of an adverse effect of the accumulation of metals is that accumulated Ag might cause structural lesions and functional disturbances in various fish organs [80]. Notably, natural organic matter (NOM) possibly enhances nanotoxicity by promoting the accumulation of either Ag particles or Ag ions in organisms [102,103]. For example, AgNPs could damage the gills and guts of adult *D. rerio* as their minute size allows the particles to pass through the organs' mucosal barrier [105]. Furthermore, synthetic AgNPs in *D. rerio* were neurotoxic, embryotoxic, and cardiotoxic and led to oxidative stress, causing global gene expression profile alterations. These results suggested that the risks posed by Ag (AgNPs and ionic Ag) to ecosystems increased with long-term exposure from months to years [106]. Resultantly, bioaccumulation of Ag and trophic transfer through the food chain can threaten the environment and human health [107].

5. Conclusions

Silver compounds are widely used in industries and are released into the environment during manufacturing and other activities. Silver and silver nanoparticles (AgNPs) can end up in aquatic ecosystems, where they can accumulate in animals at higher levels of the food chain, including humans. Studies have shown that there is a high potential risk of Ag contamination in Skudai River, which suggests an Ag pollution situation that has surpassed the danger level. However, the toxic mechanisms of Ag or AgNPs to aquatic organisms are still not fully understood. Moreover, the detection of Ag in the water samples analyzed indicates a necessity for better wastewater treatment. Therefore, to address these emerging pollutants, further studies that consider environmental factors, food web complexity, and the differences between nanomaterials are required to facilitate ecologically relevant toxicity assessment and to better understand the impact of nanomaterials on natural communities and human health. Additionally, effective treatment techniques can be

employed to eliminate or reduce their presence before discharge. Adopting environmentally friendly methods, such as using plant extracts for AgNP synthesis, and restricting the utilization of Ag and AgNPs in consumer goods can assist in reducing their discharge into the environment. Regulating the concentration of Ag in wastewater and implementing penalties for non-adherence can further mitigate their effects. Finally, promoting public awareness and responsible disposal habits can also aid in minimizing their release.

Author Contributions: Conceptualization, Z.M.L., S.S. and N.Z.A.; methodology, Z.M.L., M.M., M.R.M.H. and M.R.S.; software, Z.M.L. and M.M.; validation, Z.M.L., S.S. and M.M.; formal analysis, Z.M.L., S.S. and N.Z.A.; investigation, Z.M.L., M.R.M.H. and M.R.S.; resources, Z.M.L., N.Z.A. and S.S.; data curation, Z.M.L., N.Z.A. and S.S.; writing—original draft preparation, Z.M.L.; writing—review and editing, Z.M.L., S.S., M.M., N.Z.A., E.L.Y. and S.A.; visualization, M.R.M.H.; supervision, M.M. and S.S.; project administration, S.S., E.L.Y. and S.A.; funding acquisition, S.S. and M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Water Security and Sustainable Development Hub funded by the UK Research and Innovation's Global Challenges Research Fund (GCRF) (grant number: ES/S008179/1), as well to the Ministry of Higher Education (Malaysia) and Universiti Teknologi Malaysia for the Fundamental Research Grant Scheme (FRGS/1/2018/WAB05/UTM/02/4), and UTM Zamalah for providing a scholarship in favor of the undertaken project.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the Water Security and Sustainable Development Hub funded by the UK Research and Innovation's Global Challenges Research Fund (GCRF) (grant number: ES/S008179/1), as well to the Ministry of Higher Education (Malaysia) and Universiti Teknologi Malaysia for the Fundamental Research Grant Scheme (FRGS/1/2018/WAB05/UTM/02/4), and UTM Zamalah for providing a scholarship in favor of the undertaken project.

Conflicts of Interest: The authors declare no conflict of interest.

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