water

MDPI

Article

Heavy Metals and Nutrients Loads in Water, Soil, and Crops Irrigated with Effluent from WWTPs in Blantyre City, Malawi

Raymond S. Malikula, Chikumbusko C. Kaonga *, Harold W. T. Mapoma, Fabiano G. D. Thulu and Petra Chiipa

Physics and Biochemical Sciences Department, Malawi University of Business and Applied Sciences (MUBAS), P/Bag 303, Chichiri 312225, Blantyre 3, Malawi; reoraymond@gmail.com (R.S.M.); hmapoma@poly.ac.mw (H.W.T.M.); fthulu@poly.ac.mw (F.G.D.T.); pchiipa@poly.ac.mw (P.C.)

* Correspondence: ckaonga@poly.ac.mw; Tel.: +265-888-855-399

Abstract: Heavy metals may cause acute and chronic toxic effects to humans and other organisms, hence the need to treat wastewater properly, as it contains these toxicants. This work aimed at assessing zinc, copper, cadmium, and chromium in water, soil, and plants that are irrigated with effluent from Manase and Soche Wastewater Treatment Plants (WWTPs) in Blantyre, Malawi. Atomic Absorption Spectrophotometry (AAS) was used to assess the heavy metals. Heavy Metal Health Risk Assessment (HMHRA) on plants (vegetables) around both WWTPs was also conducted. Average daily dose (ADD) and target hazard quotients (THQ) were used to assess HMHRA. Physicochemical parameters were determined using standard methods from American Public Health Association (APHA). The heavy metal ranges were below detection limit (BDL) to 6.94 mg/L in water, 0.0003 to 4.48 mg/kg in soil, and 3 to 32 mg/L in plants. The results revealed that plants irrigated with effluent from WWTP had high values of aforementioned metals exceeding the Malawi Standards and WHO permissible limits. Furthermore, the health risk assessment values showed that vegetables consumed for a long period of time from Manase WWTP were likely to cause adverse health effects as compared to those from Soche WWTP.

Keywords: heavy metals; health risk assessment; wastewater; biological parameters; wastewater treatment plants

check for updates

Citation: Malikula, R.S.; Kaonga, C.C.; Mapoma, H.W.T.; Thulu, F.G.D.; Chiipa, P. Heavy Metals and Nutrients Loads in Water, Soil, and Crops Irrigated with Effluent from WWTPs in Blantyre City, Malawi. *Water* **2022**, *14*, 121. https://doi.org/10.3390/w14010121

Academic Editor: Stavroula Tsitsifli

Received: 29 September 2021
Accepted: 13 November 2021
Published: 5 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

1. Introduction

Wastes generated from industries, homes, marketplaces, and any other areas need to be treated to avoid polluting the environment. According to Kalulu et al. [1], many developing countries lack the infrastructure for waste treatment. In some instances, this is due to lack of land caused by high population growth. Other countries struggle to treat wastes in their existing centralized wastewater treatment systems due to dysfunctional equipment and inadequate treatment capacity. This leads to an appropriate-to-partial treatment, which later affects the water bodies they are discharged in [2]. It is worth noting that sewage effluent may lead to increase in levels of biochemical oxygen demand and nutrient loads in water bodies. The Government of Malawi established dumping sites, such as landfills and wastewater treatment facilities, to combat these problems. The facilities are only established in the cities. In Blantyre, there are three main WWTPs, namely Soche, Limbe, and Manase (Blantyre) [3].

In Malawi, like many developing countries, wastewater generation has increased mostly due to rapid population growth and urbanization, which have resulted into treatment facilities failing to keep up with the demand. Most of the treatment facilities in Malawi are either old, non-functional, or their efficiency is greatly compromised due to numerous challenges. For example, it was observed that Soche WWTP had only one trickling filter (out of three) working at the time this study was being conducted. Limbe WWTP was not functional due to a broken sewer line feeding the plant from the source, and Blantyre/Manase WWTP had all the three trickling filters not working due to blockage and vandalism. At Manase (Blantyre) WWTP, it was only stabilization ponds that were working, but they were in poor condition. The reasons that resulted in non-functional WWTPs were overloading due to the handling of larger volumes of wastewater than the intended capacity and lack of financial muscle to support rehabilitation. Due to the aforementioned challenges, these WWTPs contribute to water-quality degradation of water bodies in Malawi [4].

The reuse of wastewater for irrigation is a common phenomenon across the globe [5,6] for sufficient food production and combating of water scarcity. Regulation standards on minimum water quality for reuse in agriculture were established by the European Union to avoid challenges that emanated from the reuse of wastewater in irrigation [7]. The challenges are based on the composition and origin of the wastewater, as it has multiple sources, including hospitals, residential areas, and industrial areas. The composition of wastewater affects the growth of different plants positively; on the other hand, they may be a source of dangerous pollutants, such as heavy metals (zinc, cadmium, chromium) that bring disruption of complex biochemical cycles, which may threaten the survival of plant and animal life, including humans [2].

The term "heavy metals" refers to metals that often create a number of challenges when released into the environment [8]. Heavy metals are environmental pollutants due to their toxicity, persistence, and bioaccumulative nature. Examples of such heavy metals include zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), cadmium (Cd), chromium (Cr), and others. Although some of them are also essential to plants for their growth, on the other hand, they mostly become harmful at high concentrations. However, some heavy metals, namely cadmium (Cd), lead (Pb), and chromium (Cr), are even harmful at low concentration. Heavy metals are not the only problem in wastewater effluent, as it may also contain phosphates, nitrates, and pathogens. Nitrate and phosphate are also necessary nutrients for the growth of plants; however, high concentration of these in surface and ground water is harmful to the environment and could cause serious problems to aquatic life [9,10] due to their ability to cause eutrophication. Nitrates can also harm human beings. Consequently, the concentration of nitrates in potable water is limited to 50 and 10 mg/L for adults and babies, respectively [11]. Phosphate generally arises from the elemental phosphorous and affects water quality by the disproportionate development of algae, and its excessive concentration results in the eutrophication process, which decreases the amount of dissolved oxygen in aquatic systems [10].

Due to the dangers posed by partially treated wastewater for irrigation, it is always important to monitor its composition. Therefore, what necessitated this study, apart from the fact that partially treated wastewater is released into surface water bodies, is that raw effluent is also used at times to irrigate crops by small-scale farmers. These crops, for example, vegetables, apart from being consumed by the farmers, are also sold in local produce markets, which poses a danger to the locals.

2. Materials and Methods

2.1. Description of Study Area

Figure 1 is map of Blantyre City showing rivers that surround Manase and Soche WWTPs. It also shows sampling fields, rivers, and the position of the aforementioned treatment plants. The fields are irrigated with effluent from the WWTP before discharge into Mlambalala River. These WWTPs are managed by Blantyre City Assembly (BCA). The outcome from one facility shows a good picture of results from other facilities since they are managed by one institution.

2.2. Collection of Crop Samples

Plant samples were collected from the fields that are located within the Soche and Manase WWTPs. The crop plants collected were maize (*Zea mays*), Chinese cabbage (*Brassica chinensis*), and pumpkin leaves (*Telfairia occidentalis*). The crops were sampled randomly from the upper, middle, and lower parts of the farmers' fields. These crops are irrigated with wastewater from Soche and Manase WWTPs, respectively. The crops were washed with de-ionized water to remove any debris. Next, the samples were collected in polyethylene bags. Thereafter they were taken to the laboratory, where they were oven dried. The oven-dried samples were then stored for further analysis.

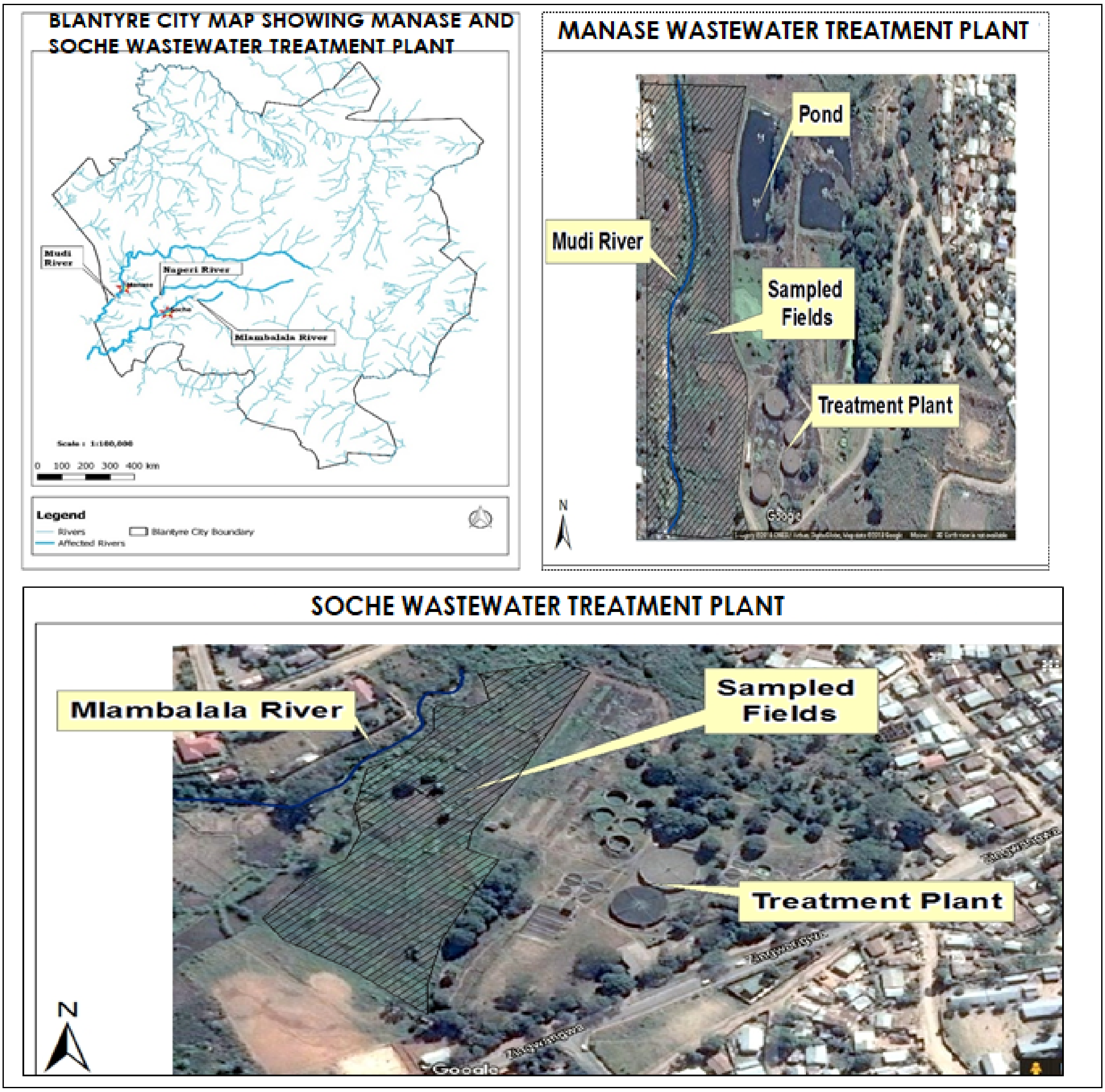

Figure 1. Map of Blantyre showing rivers that surround Manase and Soche Wastewater Treatment Plants and boundary of Blantyre city and aerial view showing sampled fields, the rivers, and positioning of the two WWTPs, respectively.

2.3. Collection of Soil Samples

Soil samples were collected using a handheld auger. The soil samples were collected randomly at a depth of 5 cm to 30 cm in the crop fields at the WWTPs. Then, the samples were collected in polyethylene bags and taken to the laboratory for further analysis.

The fresh soil samples were used to estimate microbes using membrane filtration method. The rest of the soil samples were dried in an oven at 105 °C for 6 h, then ground and sieved through a 2-mm mesh sieve. The sieved samples were kept and sealed in polythene plastic bags.

2.4. Collection of Water Samples

Effluent samples were collected using the grab sampling method. The effluent samples were collected in strategic points, at the outlet of the WWTPs and inlet and outlet of the fields. Temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured on-site [2].

2.5. Chemical Analysis

Instruments and Other Analytical Issues

The study used Atomic Absorption Spectrophotometry (Atomic Absorption Spectrophotometer AA-6200 model) to determine heavy metals [12], and Ultraviolet-Visible Spectrophotometer (UV/VIS) model Spectronic 20, Milton Roy Company (Ivyland, PA, USA), was used to determine phosphates and nitrates. Wagtech pH meter (serial # 1518360) was used to determine pH and temperature, while EC and TDS were determined using MP-4 EC meter (serial # M401468) [2]. BOD was determined by Winkler Method of oxygen measurement in samples before and after incubation for 5 days at 20 °C [13].

Sampling bottles were cleaned with 5 % HNO_3 and rinsed with double-distilled water. The samples were then sealed in sterilized glass bottles and then placed in a cooler box with some ice blocks in order to keep the temperature at 4 °C.

2.6. Analytical Methods

The study used the titrimetric method to determine COD (APHA 1995).

COD is given by:

$$\mathrm{COD}\left(\frac{O_2}{L}\right) = \left(\frac{(A-B)\times M\times 8000}{V\ sample}\right)$$

where A = Volume of ferrous ammonium sulfate (FAS) used for blank (mL); B = Volume of FAS used for sample (mL); M = molarity of FAS; and 8000 = milli equivalent weight of oxygen (8) × 1000 mL/L.

Fecal coliforms were determined using membrane filtration method. A total of 1 mL of each sample was diluted with distilled water in 9-mL test tubes; then, from these samples, 1 mL was taken into a 9-mL test tube while topping up the sample with distilled water. Thereafter, 1 mL was taken from each sample and put under filtration, where 100 mL of distilled water was added and filtered. The filtered papers were put in membrane pads, which were soaked with 1.5 mL of broth, then later were incubated at 37 °C.

Phosphate was determined by using the Vanadomolybdophosphoric acid colorimetric method. Firstly, 10 mL of each sample was placed in a 50-mL volumetric flask. Then, 10 mL of vanadate-molybdate reagent was added to the samples and diluted to the mark with distilled water. Vanadate-molybdate reagent was prepared by mixing solution A and solution B. Solution A was prepared by placing 25 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 300 mL distilled water. Solution B was prepared by heating up and boiling 1.25 g ammonium metavanadate, NH_4VO_3, in 300 mL distilled water. Then, the solution was cooled, and 330 mL concentrated hydrochloric acid (HCl) was added to it. Next, solution B was cooled to room temperature before adding solution A to it and diluted to 1 L with distilled water. The absorbance was measured from the samples at 470 nm wavelength using a Spectrophotometer (Spectronic 20, Milton Roy Company, Ivyland, PA, USA). Using standard solution values, a calibration curve was plotted, which was used to determine the concentrations, which are recorded in the Table 1. Nitrates were determined using Salicylate calorimetric method using a Spectrophotometer (Spectronic 20, Milton Roy Company) [2].

Table 1. Mean and standard deviation of nitrate, phosphate, physical, and biological parameters in effluent and soil at Manase and Soche WWTPs.

In Effluent										
Dry Season	**Nitrate (mg/L)**	**Phosphate (mg/L)**	**Temp (°C)**	**pH**	**EC (µs/cm)**	**TDS**	***E. coli* (CFU/g)**	**Total Coliforms (CFU/g)**	**COD**	**BOD**
Manase WWTP	39 ± 34	2 ± 0.2	17	6.9 ± 0.06	1224 ± 44	859 ± 28	185,800 ± 60,895	433,333 ± 194,415	195 ± 89	78 ± 45
Soche WWTP	37 ± 18	1.2 ± 0.5	22	7.66 ± 0.16	705 ± 2	479 ± 1	200,233 ± 82,323	647,000 ± 239,380	285 ± 86	69 ± 23
Rainy season										
Manase WWTP	75 ± 56	1.4 ± 0.3	25	6.77 ± 0.18	450 ± 40	298 ± 28	111,466 ± 65,121	266,666 ± 30,550	137 ± 5	73 ± 30
Soche WWTP	445 ± 92	1.75 ± 0.12	26	6.98 ± 0.11	483 ± 23	320 ± 16	108,453 ± 40,896	408,666 ± 204,081	133 ± 0.6	73 ± 23
MW (MS579:2013)	50	0.15								
EPA		5 mg/L								
In Soil Samples										
Dry Season	**Nitrate (mg/L)**	**Phosphate (mg/L)**		**pH**	**EC (µs/cm)**	**TDS**	***E. coli* (CFU/g)**	**Total Coliforms (CFU/g)**		
Manase WWTP	187 ± 175	649 ± 97		5.4 ± 0.22	1813 ± 43	1289 ± 33	171,000 ± 101,424	723,000 ± 547,029		
Soche WWTP	84 ± 45	688 ± 174		5.54 ± 0.5	2409 ± 158	1752 ± 124	77,077 ± 21,752	723,000 ± 547,029		
Rainy season										
Manase WWTP	1.89 ± 0.14	567 ± 98		4.85 ± 0.21	1793 ± 14	1272 ± 10	1,887,266 ± 854,892	15,280,000 ± 19,505,856		
Soche WWTP	12 ± 7	582 ± 106		4.78 ± 0.32	1769 ± 58	1255 ± 44	526,543 ± 227,594	253,233 ± 11,551		

2.7. Soil Analysis

After being ground, 20 g of soil was weighed and put in a beaker. Then, 50 mL of calcium chloride was added to extract nitrates and phosphates. Next, the beaker was shaken gently for 2 h and allowed to settle for a day and was filtered with 42-size Whatman filter paper. pH, total dissolved solids, electrical conductivity, and temperature were measured on the supernatant. Thereafter, nitrates and phosphates were analysed as explained earlier.

Heavy metals were analysed using APHA method [13]. A total of 3.0 g of each soil sample was weighed and then digested with a mixture of 10 mL concentrated hydrochloric acid (HCl) and 3.5 mL of concentrated nitric acid (HNO_3). The mixture was left overnight under a fume hood and the next day was heated for 2 h at 105 °C. Thereafter, distilled water was added, and the sample was filtered with Whatman filter paper. The filtrate was topped up to 100 mL in a volumetric flask. Next, the sample was taken for analysis by AAS machine.

For fecal coliforms, 25 g of each sample was weighed and put in 225 mL of distilled water. Then, 1 mL from 225 mL was diluted in 9-mL test tubes with distilled water and another 1 mL from the 9 mL was distilled further into 9 mL. Then, 1 mL of each sample was filtered using a membrane, and 100 mL of distilled water was added and filtered. The filtered membrane of each sample was put in 47-mm petri dishes that were first soaked in broth; thereafter, they were put in an incubator, which was set at 37 °C. The samples were incubated for 18 to 24 h. After incubation, colonies were identified and counted. The blue-colored colonies represented *E. coli,* while as the combination of blue, pink, and purple represented total coliforms on the petri dishes. The colonies were counted three times on each dish, and the mean value was recorded as a reading. The number obtained was then multiplied by 100 mL then divided by the dilution factor.

2.8. Plant Heavy Metal Analysis

At the lab, the plant samples were further washed to remove any possible contaminants. They were then chopped into small pieces and oven dried at 60 °C for 12 h. The dried samples were then ground using a ceramic mortar.

A total of 1 g of each dried and ground sample was put in a crucible and transferred to a furnace for 2 h to ash. Then, 5 mL of nitric acid (HNO_3) was added to each sample and boiled to almost dryness. Next, 10 mL of hydrochloric acid (HCL) was added and diluted to 100 mL volume, which was then taken for analysis by AAS.

Microsoft Excel 2013 was used to come up with descriptive statistics, while as Analysis of Variance (ANOVA) was used to compare results based on seasons and areas.

The potential health risks associated with long-term consumption of vegetables contaminated with heavy metals was assessed using the average daily dose (ADD) of heavy metals [14] and target hazard quotient (THQ). Average Daily Dose (ADD) was calculated using the formula below.

$$\mathrm{ADD} = \frac{Ci \times IR \times ED}{BW \times AT}$$

where Ci is metal concentration in the vegetable; IR is ingestion rate (2.2 g/day); ED is Exposure Duration (64 average life expectancy in Malawi); BW is body weight of consumer (60 kg); and AT is average time ($ED \times 365$ days/year) [15].

Target hazard quotient (THQ) is a ratio of the determined dose of a contaminant to oral reference dose considered detrimental. If the ratio is greater than or equal to 1, an exposed population is at risk [14,15]. This was calculated based on the formula below.

$$\mathrm{THQ} = \frac{\mathrm{ADD}}{\mathrm{Rfd}}$$

where ADD is the average daily dose, and Rfd is the reference dose. The health risk was assessed in relation to its non-carcinogenic as well as carcinogenic effects based on the calculation of ADD estimates and defined toxicity according to the relationships that follow [14,16].

3. Results and Discussion

Firstly, the physicochemical parameters and microbiological issues for samples taken in the WWTPs are presented and discussed. This is then followed by presentation and discussion of heavy metals in water, soil, and plants. The section ends with a discussion on the risk assessment of the heavy metal results. The results of the study are also compared to WHO maximum permissible limits [17] and Malawi Standards (MS579:2013) [18] wherever appropriate. This is in line with the main objective of the study, which is about heavy metal and nutrient loads for samples from a wastewater treatment facility and the associated risks.

3.1. pH, Temperature, Electrical Conductivity, and Total Dissolved Solids in Effluent and Soil Samples

As shown in Table 1, pH range in effluent at both Manase and Soche WWTPs was within the WHO [17] limit and Malawi standards [18] but was high in dry season as compared to rainy season. In effluent, pH registered a maximum mean value of 7.65 and a minimum mean value of 6.77, as shown in Table 2. pH in soil samples was below WHO permissible limit (6 to 9). Maximum mean value was registered as 5.5, and the minimum mean value was 4.74, as shown in Table 1. This is an indication that the soil samples in the study area are acidic. This pH range in soils is not conducive for the survival of macro-organisms, like earthworms, who are irritated by low pH.

Table 2. Mean and standard deviation of heavy metals in water, soil, and plants at Manase and Soche WWTPs.

Heavy Metals in Effluent (Water)								
	Rainy Season				**Dry Season**			
	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)
Manase	0.298 ± 0.23	0.01 ± 0.009	BDL	BDL	6.94 ± 0.41	0.41 ± 0.23	BDL	BDL
Soche	0.236 ± 0.17	0.004 ± 0.004	BDL	BDL	BDL	BDL	BDL	0.55 ± 0.08
MW (MS 579:201)	2	5	0.05	0.05	2	5	0.05	0.05
WHO (1996)	0.017	0.2	0.05	0.05	0.017	0.2	0.05	0.05
Heavy Metals in Soil								
	Rainy Season				**Dry Season**			
	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)
Manase	0.20 ± 0.2	0.159 ± 0.14	0.002	0.38 ± 0.05	0.48 ± 0.10	2.33 ± 0.75	2.32 ± 0.79	4.48 ± 0.26
Soche	0.114 ± 0.62	0.625 ± 0.47	0.0003 ± 0.0001	0.446 ± 11	0.87 ± 0.4	4.415 ± 5	0.062 ± 0.08	0.06 ± 0.07
WHO (1996)	50	36	100	0.8	50	36	100	0.8
Heavy Metals in Plants								
	Rainy Season				**Dry Season**			
	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)
Manase	10 ± 6	25 ± 15	11 ± 11	12 ± 4	12 ± 7	32 ± 19	15 ± 15	14 ± 4
Soche	3 ± 1	39 ± 13	14 ± 5	4.7 ± 4.8	0.8 ± 0.3	14 ± 5	17 ± 11	7 ± 5
WHO (1996)	10	0.6	1.3	0.02	10	0.6	1.3	0.02

Temperature was within the range of 17 °C to 25.9 °C, as shown in Table 1. High values were recorded in rainy season as compared to dry season both at Manase and Soche WWTPs. Minimum mean value in effluent was registered at 17 °C, and the maximum mean value was 25.9 °C. High values of temperature affects the values of BOD and COD since it enhances the growth of bacteria [19].

In effluent, TDS and EC registered high mean values in dry season as compared to rainy season, as shown in Table 1. Broad array of chemical contaminants are shown in water through presence of TDS.

In soil, for TDS the minimum mean value was 1289 ppm, and the maximum mean value was 1752 ppm, as shown in Table 1. There was not much difference in terms of TDS for rainy and dry season in soil, as shown in Table 1. EC in effluent registered a maximum mean value of 1224 µs/cm and a minimum of 450.4 µs/cm, as shown in Table 2. EC plays an important part in plant growth; higher values of EC mean less availability of water to plants even if the soil is wet. The plants compete for water with ions in solution; hence, irrigating with water containing high EC values reduces yield [20].

3.2. Fecal Coliform

On fecal coliforms, both Manase and Soche WWTPs registered high values for *E. coli* and total coliforms, which were above WHO permissible limits. The high values were noted in mostly dry season as shown in Table 1. The presence of fecal coliforms is an indicator of potential health risk for people who are exposed to the water [21]. Data from prospective epidemiology studies in Israel and USA on spray or sprinkler irrigation, which used wastewater, suggest that $\leq 10^5$ fecal coliform bacteria per 100 mL was safe from causing infections transmitted through direct contact or aerosols from wastewater to the farm workers or nearby community, but values $\geq 10^6$ cause excess bacterial infection [22]. The study established that most of the values were $\geq 10^6$, which poses threat of bacterial infections. These high values are also an indication that the wastewater treatment plants are deteriorating; hence, they need attention because their efficiency is reducing. High values are due to poor performance of the system, as it is failing to remove or reduce these biological parameters.

Results also show that total coliforms in effluent were higher in dry season at Soche and Manase WWTPs than in rainy season, as shown in Table 1. This is attributed to warm water, which encourages multiplication of bacteria. In the soil, total coliforms concentration was high in rainy season at Manase WWTPs as compared to dry season. According to Hong et al. [23], external environmental factors, such as precipitation and location, affect the concentration levels of coliforms, which could be the case at Manase and Soche WWTPs. In rainy season, surface water run-off washes away all the dirt along its pathway and deposits it into the system, which also contributes to high levels in the soil. The results further showed high *E. coli* levels in soils as compared to water in both rainy and dry season. Similar studies have found that apart from the human tract, *E.coli* can also survive and reproduce in soil and sand in subtropical temperatures [24]. High concentration of these bacteria is a threat to human beings, as they can cause diseases, such as dysentery, diarrhea, urinary tract infections, and kidney failure in children.

3.3. BOD

The value of BOD upstream (Mlambalala and Mudi Rivers) was within the WHO permissible limit of 20 mg/L at both Manase and Zingwangwa WWTPs, as shown in Table 1. On the other hand, the BOD values in the rivers after effluent release points were above WHO and Malawi permissible limits, as shown in Table 1. The high BOD values in the rivers after the effluent release points are an indication that the WWTPs are not efficient. Most of the organic matter that enters the WWTPs is leaving the systems without being removed. This in turn increases the oxygen demand by bacteria in the receiving waters to break down the organic matter aerobically. At the end of it all, the BOD values of such kinds of waters is very high and in most cases exceeds the maximum permissible limits. High levels of BOD were also recorded at Kauma WWTP in Lilongwe Malawi [25], which potentially could negatively impact the receiving waters [2]. High values of BOD are an indication that the water is polluted with organic matter; as such, it could indicate incomplete treatment of sewage at the WWTPs. When the BOD is high, some organisms that cannot survive at low oxygen levels suffer in water [25].

3.4. COD

On COD, the study found that the results exceeded both the Malawi standard permissible limit and the WHO maximum permissible limit, as shown in Table 1. High concentration of COD shows that the presence of oxygen for aquatic life is at stake in these rivers where effluent is fed, as it indicates the presence of organic compounds in water [26]. High COD indicates high oxidizable organic materials, which reduces oxygen levels, hence jeopardizing aquatic life growth in streams. It is also an indication that the rivers are polluted. Both the BOD and COD levels imply that the WWTPs efficiency has decreased, and there is a need for maintenance to improve the system, as it poses a threat to the environment in particular aquatic life.

3.5. Nitrate in Water Sample

The study registered high values of nitrates as shown in Table 1. This correlates with results of BOD discussed earlier, which points to the fact that the WWTPs are not efficient. The WWTPs are not able to remove organic matter or organic nitrogen compounds. In an efficient system, the nitrogen compounds (in the form of ammonium compounds, nitrites, and nitrates) are supposed to end up being released as nitrogen gas mostly to the atmosphere. However, the non-efficient WWTPs release nitrogen compounds with no or very little removal rate. This then translates to high nitrates and other nitrogen forms in effluent. In effluent, high mean concentration of nitrates were observed in rainy season. There was no significant difference in nitrate levels between the two WWTPs ($p > 0.05$). High concentration of nitrates is dangerous to human health, as it causes diseases, such as methemoglobinemia [21]. According to Grant et al. [27], ingestion of high levels of nitrates by pregnant women could cause abortion.

Nitrate in Soil Samples

In soil samples, the results for nitrates were different from that observed in effluent. High mean values were observed in dry season both at Manase and Soche WWTPs. During this season (dry), farmers who cultivate close to these WWTPs (Manase and Soche) use effluent from the treatment plants, and there is no excessive dilution, as is the case in rainy season. The effects of nitrate at Manase WWTP are clearly seen, as some of the ponds are covered with plants to the point that the situation calls for the deployment of workers to remove them. This is a sign of eutrophication, which can harm aquatic ecosystems.

Nitrate in soil samples in rainy and dry season at Soche WWTP showed that there was no significance difference ($p > 0.05$), while, when compared between WWTPs (Manase and Soche), the results also showed that there was no significant difference ($p > 0.05$).

Nitrate in effluent samples in rainy season showed that there was a significant difference ($p > 0.05$) between Manase and Soche WWTPs unlike in dry season, which showed no significance difference ($p < 0.05$).

3.6. Phosphates

Phosphate values in effluent were above Malawi standards and WHO maximum permissible limit, as shown in Table 1. High levels of phosphate in effluent increase algae and aquatic plants growth, which can choke water ways [21]. The study showed that Mudi and Naperi River are at a high risk of eutrophication; hence, aquatic organisms could be affected due to a potential depletion of oxygen levels arising from eutrophication since phosphates are a limiting nutrient in that their concentration in water determines whether there will be eutrophication or not.

The study observed that there was not much difference in phosphate values in rainy season as well as in dry season for both Manase and Soche WWTPs, as shown in Table 1. The mean concentration values observed exceed Malawi standard maximum permissible limit. Phosphate in soil samples showed no significant difference between the two sites both in rainy and dry season ($p > 0.05$). Similarly, in effluent the trend for phosphates was the same.

3.7. Heavy Metals

In soil, it was observed that the mean concentration of cadmium at Manase WWTP exceeded WHO and Malawi standard permissible limits, as shown in Table 2. The other heavy metals were below permissible limits in both WWTPs. This was attributed to the source of the wastewater, which feeds this WWTP. Manase WWTP receives wastewater from an industrial area (Makata) of the city of Blantyre.

In plants (vegetables), the study observed that the mean concentration of heavy metals was very high in the two WWTPs in both seasons. The values were above Malawi standard and WHO permissible limits, as shown in Table 2. The results showed that high values were obtained in dry season as compared to rainy season, as shown in Table 2. Masona et al. [28] and Namezi (2012), who did a similar study in Semnan, Iran, found similar observations. According to Masona et al. [28], wastewater increases the levels of heavy metals in plants and soil. These heavy metals are transferred to the plants when they absorb water from the soil.

As shown in the box plots in Figure 2, median values in plants were high as compared to those in soil and effluent in both WWTPs. Chromium Inter Quantile Range (IQR) was also higher in plants than in soil and water. This clearly shows that plants have more pollutants in their system than both soil and water. Zinc concentration levels in water at Manase had a wider range, with a median of 4 mg/l, unlike at Soche WWTP, which is almost negligible. On the other hand, zinc range in plants at Soche is wider than Manase, with a median of 10 and 13, respectively. In soil, the range is also higher at Soche than Manase WWTP. The median of heavy metals in water and plants was higher at Manase than Soche WWTP. Overall, Manase WWTP had higher concentration of heavy metals than Soche WWTP. This is because the Manase WWTP receives 70% of its wastewater from industries [4]. The fact that heavy metals were detected in both the WWTPs in all samples, including vegetables, poses a danger to consumers. High levels of heavy metals in plants found in this study are attributed mainly to the use of effluent in irrigation.

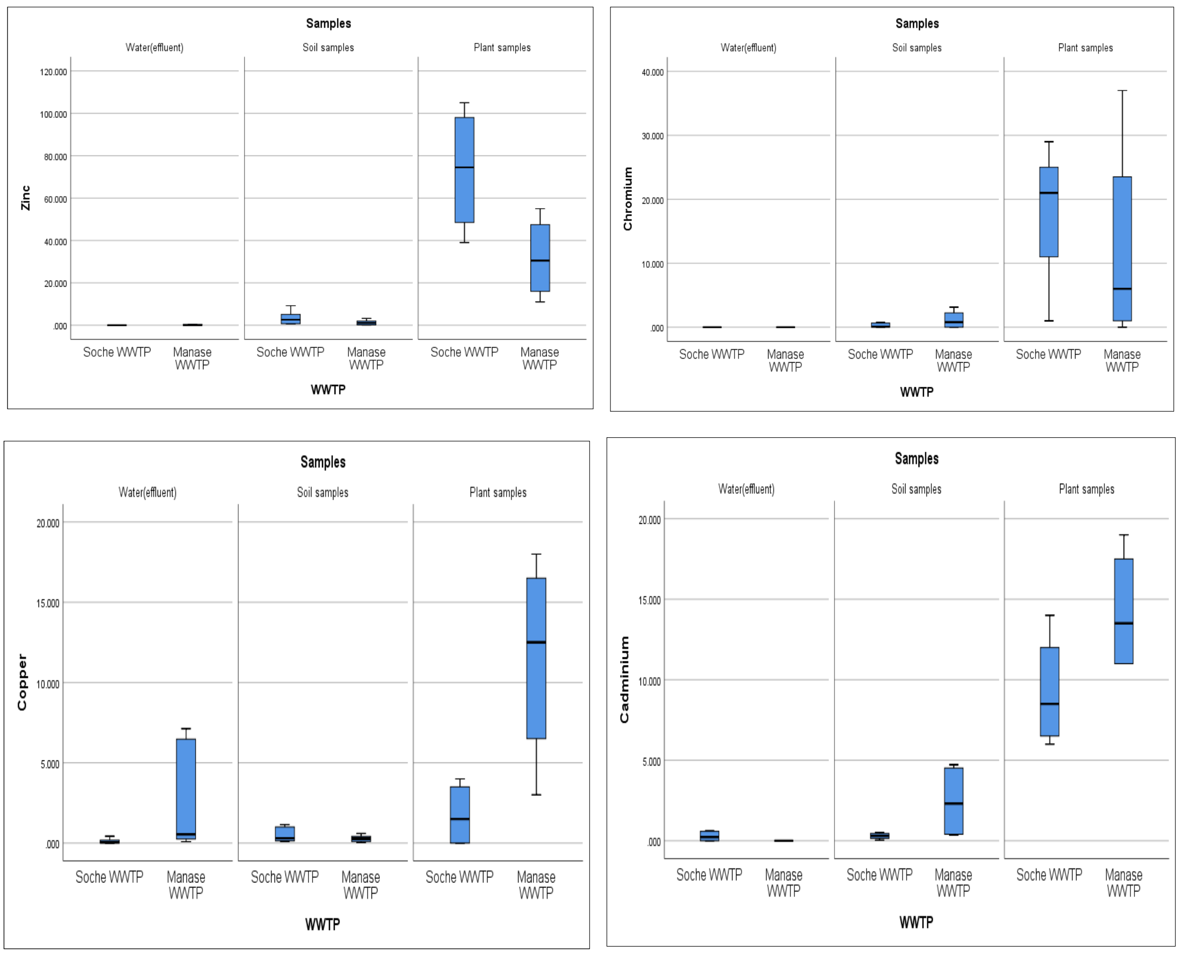

Figure 2. Box plots of heavy metal concentration (mg/L) at Manase and Soche Wastewater Treatment Plants.

3.8. Health Risk Assessment

Average Daily Dose (ADD) and Target Hazard Quotients (THQ) were also determined in this study. The results are shown in Tables 3 and 4 below. There were no significant differences ($p > 0.05$) in ADD values for Manase and Soche WWTP, an indication that the level of exposure (the dose) to heavy metals by consuming vegetables from each of the individual sites was the same. There were also no significant differences ($p > 0.05$) in THQ values between Manase and Soche WWTPs. However, the results show that at Manase WWTP all the THQ values were greater than 1 except for chromium, while for Soche WWTP, only the cadmium value was greater than 1. The values of THQ that are greater than 1 are an indication that there is a high health risk to those who consume these vegetables that are irrigated with effluent, as heavy metals are well known carcinogens. The accumulation of heavy metals, which translates to THQ values to being greater than 1, has also been reported by Zhou et al. [29] in China. On the other hand, vegetable accumulation of heavy metals is also dependent on the concentrations found in soil, as reported in a study by Sulaiman et al. [30] in Malaysia, which found low heavy metal levels, translating to THQ values of less than 1 for vegetables grown in an agricultural area.

Table 3. Average Daily Dose (ADD) and Target Hazard Quotient (THQ) at MANASE WWTP.

Heavy Metal	ADD	THQ
Cu	0.16	4
Zn	0.43	1.4
Cr	0.2	0.13
Cd	0.187	187

Table 4. Average Daily Dose (ADD) and Target Hazard Quotient (THQ) at SOCHE WWTP.

Heavy Metal	ADD	THQ
Cu	0.01	0.27
Zn	0.19	0.62
Cr	0.23	0.15
Cd	0.09	94

4. Conclusions

This study assessed heavy metal and microbiological and physicochemical parameters in samples from Manase and Soche WWTPs in Blantyre, Malawi. pH range in effluent for both WWTPs was within the WHO and Malawi standard acceptable limits, and it was higher in dry season as compared to rainy season in both WWTPs. In effluent TDS and EC registered high mean values in dry season as compared to rainy season. In soil, for TDS the minimum mean value was 1289 ppm, and the maximum mean value was 1752 ppm. Fecal coliforms registered high values for *E. coli* and total coliforms, which were above WHO permissible limit in both WWTPs. Furthermore, total coliforms in effluent were high in dry season than in rainy season. The value of BOD upstream was within the WHO permissible limit of 20 mg/L in both WWTPs. In effluent, high values of nitrates were observed in rainy season. In soil, the results of nitrate were different from that observed in effluent, with high mean values observed in dry season in both WWTPs. In plants (vegetables), it was observed that the mean concentration of heavy metals was very high in the two WWTPs in both seasons, with values above Malawi standard and WHO permissible limit. Lastly, on healthy risk assessment, at Manase WWTP, all the THQ values were greater than 1 except for chromium, while for Soche WWTP, only the cadmium value was greater than 1. These values designate a potential health risk to individuals who consume heavy metal contaminated vegetables. The concentration of these parameters was also an indication of performance of these WWTPs, i.e., they are not efficient in the treatment of heavy metals. It is recommended that the WWTPs should be rehabilitated so as to increase their efficiency.

Author Contributions: Writing—review and editing, R.S.M.; supervising—review and editing, C.C.K. and H.W.T.M.; manuscript consolidation, editing, and layout, F.G.D.T. and P.C. All authors have read and agreed to the published version of the manuscript.

Funding: There was no external funding for this research.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank F. Kamwani and staff at Blantyre City Assembly for the support that they rendered during the sampling process.

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

References

1. Kalulu, K.; Thole, B.; Mkandawire, T.; Kululanga, G. Application of process intensification in the treatment of pit latrine sludge from informal settlements in Blantyre City, Malawi. *Int. J. Environ. Res. Public Health* **2020**, *17*, 3296. [CrossRef]
2. Kayira, F.; Wanda, E.M.M. Evaluation of the performance of Mzuzu Central Hospital wastewater oxidation ponds and its effect on water quality in Lunyangwa River, Northern Malawi. *Phys. Chem. Earth* **2021**, *123*, 103015. [CrossRef]
3. Vunain, E.; Mike, P.; Mpeketula, G.; Monjerezi, M.; Etale, A. Evaluation of coagulating e ffi ciency and water borne pathogens reduction capacity of Moringa oleifera seed powder for treatment of domestic wastewater from Zomba, Malawi. *J. Environ. Chem. Eng.* **2019**, *7*, 103118. [CrossRef]
4. Ngoma, W.; Hoko, Z.; Misi, S.; Chidya, R.C.G. Assessment of efficiency of a decentralized wastewater treatment plant at Mzuzu University, Mzuzu, Malawi. *Phys. Chem. Earth* **2020**, *118–119*, 102903. [CrossRef]
5. Abosede, A.; Solomon, O.; Peter, A.; Eromosele, H.; Emmanuel, A. Wastewater conservation and reuse in quality vegetable cultivation: Overview, challenges and future prospects. *Food Control* **2018**, *98*, 489–500. [CrossRef]
6. Rizzo, L. Science of the Total Environment Best available technologies and treatment trains to address current challenges in urban wastewater reuse for irrigation of crops in EU countries. *Sci. Total Environ.* **2020**, *710*, 136312. [CrossRef]
7. Truchado, P.; Garre, A.; Gil, M.I.; Simón-andreu, P.J.; Sánchez, G.; Allende, A. Science of the Total Environment Monitoring of human enteric virus and coliphages throughout water reuse system of wastewater treatment plants to irrigation endpoint of leafy greens. *Sci. Total Environ.* **2021**, *782*, 146837. [CrossRef] [PubMed]
8. Pourret, O. It's Time to Replace the Term 'Heavy Metals' with 'Potentially Toxic Elements' when Reporting Environmental Research. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4446. [CrossRef]
9. Letshwenyo, M.W.; Sima, T.V. Phosphorus removal from secondary wastewater effluent using copper smelter slag. *Heliyon* **2020**, *6*, e04134. [CrossRef]
10. Alagha, O.; Manzar, M.S.; Zubair, M.; Anil, I. Comparative Adsorptive Removal of Phosphate and Nitrate from Wastewater Using Biochar-MgAl LDH Nanocomposites: Coexisting Anions Effect and Mechanistic Studies. *Nanomaterials* **2020**, *10*, 336. [CrossRef] [PubMed]
11. Al-housni, M.; Hussein, A.H.; Yeboah, D.; Al Khaddar, R. Electrochemical removal of nitrate from wastewater electrochemical removal of nitrate from wastewater. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *888*, 012037. [CrossRef]
12. Taghipour, H.; Mosaferi, M. Heavy Metals in the vegetables collected from production sites. *Health Promot. Perspect.* **2013**, *3*, 185–193. [CrossRef]
13. Duruibe, J.; Ogwuegbu, M.O.C.; Egwurugwu, J.N. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* **2007**, *2*, 112–118.
14. APHA. *Standard Methods for the Examination of Water and Wastewater*, 16th ed.; American Public Health Association: New York, NY, USA, 1985.
15. Ametepey, S.T.; Samuel, J.C.; Felix, J.A.; Abudu, B.D.; Zita, N.A. Health risk assessment and heavy metal contamination levels in vegetables from Tamale Metropolis, Ghana. *Int. J. Food Contam.* **2018**, *5*, 1–8. [CrossRef]
16. Usepa, I.R.I.S. *Integrated Risk Information System*; Environmental Protection Agency Region I: Washington, DC, USA, 2011.
17. WHO. *Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, Switzerland, 2011; Volume 216, pp. 303–304.
18. Malawi Bureau of Standards (MBS). *Malawi Standard, Drinking Water—Specification*; MS 214:2005, ICS 13.030.40 (First Revision); Malawi Standards Board: Blantyre, Malawi, 2005.
19. Balkhair, K.S. Microbial contamination of vegetable crop and soil profile in arid regions under controlled application of domestic wastewater. *Saudi J. Biol. Sci.* **2016**, *23*, S83–S92. [CrossRef] [PubMed]
20. Bauder, T.A.; Waskom, R.M.; Davis, J.G. *Irrigation Water Quality Criteria*; Fact Sheet No 0.506; Colorado State University, Cooperative Extension: Fort Collins, CO, USA, 2004.
21. Kumar, M.; Avinash, P. A review of permissible limits of drinking water. *Indian J. Occup. Environ. Med.* **2012**, *16*, 40–44. [CrossRef] [PubMed]

22. Blumenthal, U.J.; Duncan, D.M.; Anne, P.; Guillermo, R.P.; Rebecca, S. Guidelines for the microbiological quality of treated wastewater used in agriculture: Recommendations for revising WHO guidelines. *Bull. World Health Organ.* **2000**, *78*, 1104–1116.
23. Hong, H.; Qiu, J.; Yan, L. Environmental factors influencing the distribution of total and fecal coliform bacteria in six water storage reservoirs in the Pearl River Delta Region, China. *J. Environ. Sci.* **2010**, *22*, 663–668. [CrossRef]
24. Ishii, S.; Michael, J.S. Escherichia coli in the environment: Implications for water quality and human health. *Microbes Environ.* **2008**, *23*, 101–108. [CrossRef]
25. Mtethiwa, A.H.; Munyenyembe, A.; Jere, W.; Nyali, E. Efficiency of oxidation ponds in wastewater treatment. *Int. J. Environ. Res.* **2008**, *2*, 149–152.
26. Ekhator, O.C.; Udowelle, N.A.; Igbiri, S.; Asomugha, R.N.; Igweze, Z.N.; Orisakwe, O.E. Safety evaluation of potential toxic metals exposure from street foods consumed in mid-west Nigeria. *J. Environ. Public Health* **2017**, *2017*, 8458057. [CrossRef]
27. Grant, W.; Steele, G.; Isiorho, S.A. Spontaneous abortion possibly related to ingestion of nitrate-contaminated well water—LaGrange County, Indiana, 1991–1994. *MMWR Morb. Mortal. Wkly. Rep.* **1996**, *45*, 569-572.
28. Masona, C.; Loveness, M.; Stenly, M.; Revai, M. Assessment of heavy metal accumulation in wastewater irrigated soil and uptake by maize plants (*Zea mays* L.) at Firle Farm in Harare. *J. Sustain. Dev.* **2011**, *4*, 132. [CrossRef]
29. Zhou, H.; Yang, W.; Zhou, X.; Liu, L.; Gu, J.; Wang, W.; Zou, J.; Tian, T.; Peng, P.; Liao, B. Accumulation of heavy metals in vegetable species planted in contaminated soils and the health risk assessment. *Int. J. Environ. Res. Public Health* **2016**, *13*, 289. [CrossRef] [PubMed]
30. Sulaiman, F.R.; Ibrahim, N.H.; Ismail, S.N.S. Heavy metal (As, Cd, and Pb) concentration in selected leafy vegetables from Jengka, Malaysia, and potential health risks. *SN Appl. Sci.* **2020**, *2*, 1430. [CrossRef]