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Ecological Risk Assessment and Sustainable Management of Pollutants in Hydroponic Wastewater from Plant Factories

Hong-Duck Ryu, Jae-Hoon Kim *, Hyeyeol Han, Ju-Hyun Park and Yong Seok Kim

Water Environment Research Department, National Institute of Environmental Research, Hwangyoung-ro 42, Seo-gu, Incheon 22689, Republic of Korea; nanumenv@korea.kr (H.-D.R.); hanhyeyeol@korea.kr (H.H.); soyang@korea.kr (J.-H.P.); nierkys@korea.kr (Y.S.K.)

* Correspondence: jaehoonk800@gmail.com

Abstract: Although the plant factory (PF) industry is expanding worldwide, there are currently no regulatory measures for wastewater discharged from PFs in South Korea. This study aims to present the characteristics of major pollutants discharged from PFs that have not been reported in the literature and suggest effective management measures for them. The occurrence of 17 pollutants in hydroponic wastewater (HW) from 33 PFs was analyzed, and their potential ecological risk (PER) to aquatic life was assessed. Water samples were collected up to three times from each PF. The detection frequencies of 11 pollutants, including total organic carbon, total nitrogen, total phosphorus, Mn, Ni, B, Mo, Cr, Cu, Zn, and Ba, in HW exceeded 50%. Ni, Cr, and Ba are notably not recommended components of nutrient solutions in South Korea. Among the micropollutants, the concentration of Cu, which is a recommended component, was the highest, at 10.317 mg/L. The PER assessment identified Cu and Zn as "high-hazard" pollutants, with Cu, Zn, Ni, Mn, and B prioritized for management. To ensure the sustainability of hydroponic cultivation, these five pollutants must be managed. Nature-based techniques, such as the implementation of constructed wetlands and phyto-filtration, are recommended for effective treatment.

Keywords: plant factory; hydroponic wastewater; potential ecological risk; nutrient solution; treatment technique; nature-based technique

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1. Introduction

Smart farming agriculture (SFA) integrates information technology, including the Internet of Things, big data, and artificial intelligence, into traditional agriculture to enhance sustainability and efficiency [1–3]. The global smart farming market is projected to grow at a rate of 9.8%, from USD 13,800 million in 2020 to USD 22,000 million in 2025 [4]. In South Korea, the plant factory (PF) market within SFA reached approximately USD 268 million in 2020, marking the early stages of market formation. Its share in the overall smart farm market increased from 5.0% in 2015 to 6.6% in 2020 [5].

PFs primarily employ hydroponic cultivation (HC), where a nutrient solution (NS) is supplied to support crop growth [6–8]. Typically, the NS comprises major elements, such as nitrogen (N), phosphorus (P), and potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), boron (B), copper (Cu), zinc (Zn), and molybdenum (Mo) [9]. HC operates in two main ways, depending on the NS supply method. The first method, recycling cultivation, maximizes the reuse of nutrients and water in crop production. After use by plants, the NS is treated and recycled back into the plant growth system, eventually generating wastewater [10–12]. The second method, non-recycling cultivation, discharges the NS as wastewater when its nutrients are depleted [13,14].

PFs, which are regarded as point sources of pollution, are not subject to effluent limitation criteria in South Korea and therefore lie in a management blind spot. Therefore, in order to manage PFs effectively as point sources, it is vital to understand the occurrence

characteristics, such as the concentration and detection frequency, of pollutants discharged by PFs.

Meanwhile, most previous studies have focused mainly on the organic matter and nutrient (mainly N and P) compositions of NS and hydroponic wastewater (HW) [6–8,15–17], rather than the occurrence characteristics of various pollutants in HW. That is, research on the wastewater of HC plant growth systems has addressed the concentration ranges of key pollutants, such as organic matter, N, and P, and their treatment characteristics [16,18–20]. Little information is available on the occurrence characteristics of other major pollutants in HW, such as heavy metals, likely to be discharged from PFs. Obtaining information on the detection frequency of major pollutants discharged by PFs that have not been discussed to date is essential for managing HW. Moreover, to our best knowledge, no studies have been conducted on the toxic effects of wastewater discharged by PFs on aquatic life in surface water. Therefore, further research is needed to investigate the impact of pollutants in wastewater on the aquatic environment and aquaculture, along with the detection levels (concentration and frequency) of various nutrients in wastewater. Regarding HW treatment technology, most studies have focused on treating organic matter, N, and P [18–20]. Thus, effective treatment technologies for major pollutants likely to be discharged from PFs should be proposed.

This study aims to provide information on the occurrence characteristics of the main pollutants discharged by PFs. Additionally, we aimed to assess the potential ecological risk (PER) posed by these pollutants to the water environment. Further, this study explores treatment techniques for the main pollutants discharged by PFs through a literature review and proposes rational treatment techniques for sustainable HC agriculture.

2. Materials and Methods

2.1. Plant Factories

To investigate the pollutant characteristics of wastewater from HC agriculture, 33 PFs in South Korea were selected (Table 1). The crops cultivated in these hydroponic farms included strawberries, tomatoes, cucumbers, lettuce, and paprika. Only the H32 facility used the NS supply method to reuse the NS in the plant growth system. The other 32 facilities discharged nutrient-depleted wastewater into nearby rivers or sewers without treatment. Of these, 23 facilities discharged wastewater into nearby rivers, and 9 facilities through sewers. Although the overall quantity of discharged wastewater from each PF was not substantial, facilities H14, H21, H22, H24, H29, and H33 discharged relatively high volumes, exceeding 6 m^3/day, compared with the others.

Table 1. Details of plant factories.

Plant Factory	Cultivated Plants	Substrate Types	Nutrient Solution Reuse	Wastewater Discharge Location	Quantity of Wastewater (m^3/d)
H1	SB [1]	C [6]	No reuse	River	0.6
H2	SB	N [7]	No reuse	River	0.1
H3	SB	PL [8], C	No reuse	River	1.5
H4	SB	PL, C	No reuse	Sewer	0.25
H5	SB	PL, C	No reuse	Sewer	1
H6	SB	PL, C	No reuse	River	1.5
H7	SB	PL	No reuse	River	0.1
H8	SB	PL, C	No reuse	Sewer	0.3
H9	SB	PL, C	No reuse	River	1.5
H10	SB	C	No reuse	River	2.5
H11	SB	C	No reuse	River	0.525
H12	SB	PL, C	No reuse	River	3
H13	SB	PM [9]	No reuse	River	4

Table 1. *Cont.*

Plant Factory	Cultivated Plants	Substrate Types	Nutrient Solution Reuse	Wastewater Discharge Location	Quantity of Wastewater (m^3/d)
H14	SB	N	No reuse	Sewer	9
H15	SB	PM	No reuse	River	3
H16	SB, T [2]	N	No reuse	River	0.5
H17	T	C	No reuse	River	0.02
H18	T	C	No reuse	River	0.15
H19	T	GRW [10]	No reuse	Sewer	0.2
H20	T	C	No reuse	River	0.2
H21	T	C	No reuse	River	10
H22	T	GRW	No reuse	Sewer	6
H23	T	GRW	No reuse	River	3
H24	T	C	No reuse	Sewer	7.5
H25	T	PL, C	No reuse	River	1.2
H26	CC [3]	C	No reuse	Sewer	0.15
H27	CC	C	No reuse	River	0.525
H28	CC	N	No reuse	River	0.2
H29	CC	C	No reuse	River	6
H30	L [4]	PL	No reuse	River	1.5
H31	L	N	No reuse	River	0.3
H32	L	DFT [11]	Reuse	No discharge	NA [12]
H33	P [5]	C	No reuse	Sewer	6

[1] Strawberry; [2] tomato; [3] cucumber; [4] lettuce; [5] paprika; [6] cocopeat; [7] nursery media; [8] perlite; [9] peatmoss; [10] granular rock wool; [11] deep flow technique; [12] not available.

2.2. Selection of Pollutants

The pollutants in wastewater discharged from PFs in South Korea are of concern due to their potentially significant impact on aquatic ecosystems during HC. These pollutants were selected based on their status as major inorganic pollutants regulated according to effluent standards in South Korean wastewater treatment plants (WWTPs). Additionally, the recommended nutrients for HC in South Korea, including C, H, O, N, P, K, Ca, Mg, S, Fe, Mn, B, Zn, Cu, Mo, and Cl [21], were considered when selecting pollutants. Among the 17 selected pollutants, 9 (Mn, Ni, Cu, Zn, As, Sb, Ba, Pb, and Se) are managed by water quality criteria in the USA (Table S1) [22]. The selected 17 pollutants are presented in Table 2.

Table 2. Seventeen selected pollutants.

Category	Pollutants
Organics	TOC [1]
Inorganics	TN [2]
	TP [3]
	Mn
	Ni
	B
	Mo
	Cr
	Cu
	Zn
	As
	Cd
	Sn
	Sb
	Ba
	Pb
	Se

[1] Total organic carbon; [2] total nitrogen; [3] total phosphorus.

2.3. Ecological Risk Assessment

An ecological risk assessment was conducted on micropollutants (MPs) discharged from 33 PFs to determine their impact on the aquatic environment. This assessment was performed by calculating the hazard quotient (HQ) using Equation (1), a method commonly used to assess the toxicological risk of hazardous materials, as established by the European Union [23–28].

$$HQ = \frac{PEC_{surface\ water,m}}{PNEC_{lowest}} \quad (1)$$

where $PEC_{surface\ water,m}$ is the predicted environmental concentrations for pollutants in receiving water; the median concentration from the collection of values for a single chemical measured at an individual location was used; and $PNEC_{lowest}$ is the lowest predicted no-effect concentration, derived from the quantitative structure–activity relationship and experimentally based values.

The $PEC_{surface\ water,\ m}$ values for pollutants detected in HW were determined using the median value after complete mixing in the receiving water with a dilution factor of 10, as initially proposed for EU sewage treatment plants [29]. This dilution factor is commonly utilized in studies predicting diluted concentrations of target pollutants when wastewater enters rivers [30,31]. The lowest $PNEC_{lowest}$ value for pollutants was obtained from the Norman Ecotoxicology Database [32] (Table 3).

Table 3. $PNEC_{lowest}$ values suggested in the Norman Ecotoxicology Database [32].

Pollutants	$PNEC_{lowest}$ (µg/L)
TOC	NA [1]
TN	NA
TP	NA
Mn	123
Ni	4
B	0
Mo	136
Cr	3.4
Cu	1
Zn	7.8
As	0.5
Cd	0.08
Sn	NA
Sb	7.2
Ba	NA
Pb	1.2
Se	0

[1] not available.

2.4. Sample Collection and Analysis

Samples were collected from the wastewater storage tanks at each of the 33 PFs. The target number of sample collections per facility was set at three, but in cases where facilities were uncooperative, one or two sample collections were conducted. TOC, TN, TP, Mn, Ni, Cr, Cu, Zn, As, Cd, Sn, Sb, Ba, Pb, and Se were analyzed following Korean Standard Methods [33], while B and Mo were analyzed according to US Environmental Protection Agency Methods [34]. Table 4 shows the quality control results of 17 pollutants, which were determined via the following data quality control measures suggested by Korean Standard Methods [33] and US Environmental Protection Agency Methods [34]. TOC was measured using a TOC analyzer (Model: TOC-L CPH, Shimadzu, Kyoto, Japan). TN and TP were measured using an auto TN and TP analyzer (Model: AA3 AutoAnalyzer, SEAL Analytical, Mequon, WI, USA). Heavy metals (Mn, Ni, Cr, Cu, Zn, As, Cd, Sn, Sb, Ba, Pb, and Se) were measured using inductively coupled plasma–mass spectrometry (ICP-MS) (Model: US/820-MS, Analytik Jena, Jena, Germany). B and Mo were measured using inductively

coupled coupled plasma–optical emission spectrometry (ICP-OES) (Model: 5100 ICP-OES, Agilent, Santa Clara, CA, USA).

Table 4. Quality control results for 17 pollutants.

Pollutant	MDL (mg/L)	LOQ (mg/L)	Precision (%)	Accuracy (%)	Recovery (%)	Regression Coefficient (R^2)
TOC	0.1	0.3	10.3	107.0	99.7	0.9997
TN	0.01	0.03	3.7	104.5	99.0	0.9996
TP	0.001	0.003	1.7	102.9	94.7	0.9996
Mn	0.0002	0.0005	3.2	97.1	97.3	1.0000
Ni	0.0006	0.002	3.2	98.6	96.0	0.9999
B	0.001	0.004	1.3	101.3	98.2	0.9999
Mo	0.003	0.010	5.5	92.3	101.0	0.9999
Cr	0.00006	0.0002	2.5	98.2	98.6	0.9996
Cu	0.0006	0.002	3.0	100.9	98.6	0.9999
Zn	0.002	0.006	2.7	101.5	101.1	1.0000
As	0.002	0.006	2.4	103.4	102.3	1.0000
Cd	0.0006	0.002	1.2	97.3	99.4	0.9999
Sn	0.00003	0.0001	1.1	101.8	102.6	0.9998
Sb	0.0001	0.0004	2.0	101.7	101.0	0.9995
Ba	0.001	0.003	3.3	97.1	102.3	0.9995
Pb	0.0006	0.002	1.6	97.0	92.8	0.9992
Se	0.01	0.03	4.1	95.3	104.9	0.9996

Abbreviations: MDL: method detection limit; LOQ: limit of quantification.

3. Results and Discussion

3.1. Occurrence of Pollutants in Nutrient Solution and Hydroponic Wastewater

The analysis of the occurrence characteristics of 17 pollutants from 33 PFs revealed that 16 pollutants, excluding Cd, were detected in both the NS and HW (Table 5). Some significant findings were observed regarding the occurrence of pollutants in HW. First, the concentration deviation of the 17 pollutants discharged by the PFs was very large. The levels of most pollutants detected in HW exhibited high standard deviations, indicating that improved technology is required for the effective removal of these pesticides in PW.

Second, the concentration of MPs in HW tended to be high (Table 5). Table 6 presents the influent concentration ranges of 14 MPs (Mn, Ni, B, Mo, Cr, Cu, Zn, As, Cd, Sn, Sb, Ba, Pb, and Se) in sewage wastewater treatment plants reported in previous studies [35–49]. Notably, the maximum concentrations of nine MPs (Mn, B, Mo, Cu, Zn, As, Ba, Pb, and Se) in HW were much higher than those in sewage treatment plant influents (Table 6). Specifically, the maximum concentrations of Mn, Mo, Se, Zn, and As observed in this study were approximately 11, 9, 7, 6, and 5 times higher than those reported in the literature, respectively. It should be noted that, among nine MPs (Mn, B, Mo, Cu, Zn, As, Ba, Pb, and Se), Mn, B, Cu, Zn, and Ba exhibited detection frequencies in HW of 100%, as shown in Table 5. Therefore, these five MPs (Mn, B, Cu, Zn, and Ba) will be highly important in managing HW discharged from PFs. In this study, the detection frequency refers to the proportion of samples detected above the limit of quantification (LOQ) among the analysis values of all samples. A high detection frequency for a specific pollutant indicates that the need for the management of that pollutant is relatively high. Although some studies have reported the concentrations of major ions in HW, such as NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, B^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, and Mo^{6+} [13,50–55], to our best knowledge, this is the first attempt to simultaneously analyze the concentration range and detection frequency of various metals likely to be discharged from PFs in order to identify those that require management. Additionally, the detection of Cr, As, Sn, Sb, Ba, and Se in HW in this study is novel—to our best knowledge, the detection of these metals in HW has not been reported in previous studies.

Table 5. Concentration and detection frequency of 17 pollutants in nutrient solution and wastewater.

Pollutant	LOQ [4] (mg/L)	Plant Factories					
		Nutrient Solution			Wastewater		
		N [5]	Concentration (mg/L) Av. [6] ± SD [7] (Min. [8]–Max. [9])	DF [11] (%)	N	Concentration (mg/L) Av. ± SD (Min.–Max.)	DF (%)
TOC [1]	0.3	62	24.8 ± 54.0 (0.4–265.4)	100	56	56.9 ± 87.7 (6.1–454.8)	100
TN [2]	0.03	62	877.6 ± 2302.9 (1.9–10,940.6)	100	56	220.9 ± 280.8 (3.1–1920)	100
TP [3]	0.003	62	101.2 ± 311.9 (0.2–1543.5)	100	56	28.3 ± 23.5 (0.1–82.1)	100
Mn	0.0005	52	1.6219 ± 5.2173 (0.0018–23.4340)	100	43	0.3743 ± 0.8462 (0.0012–5.4498)	100
Ni	0.002	52	0.012 ± 0.027 (n.d. [10]–0.155)	75	43	0.021 ± 0.061 (n.d.–0.397)	97.7
B	0.004	62	1.012 ± 3.036 (0.011–20.202)	100	56	0.619 ± 0.668 (0.041–4.271)	100
Mo	0.01	62	0.09 ± 0.31 (n.d.–1.82)	66.1	55	0.02 ± 0.04 (n.d.–0.20)	58.2
Cr	0.0002	52	0.0075 ± 0.0174 (0.0004–0.0859)	100	43	0.0031 ± 0.0031 (0.0010–0.0175)	100
Cu	0.002	52	0.177 ± 0.708 (n.d.–4.969)	94.2	43	0.313 ± 1.564 (0.008–10.317)	100
Zn	0.006	52	0.889 ± 2.158 (0.011–11.248)	100	43	0.832 ± 1.677 (0.014–8.988)	100
As	0.006	52	0.011 ± 0.048 (n.d.–0.282)	9.6	43	0.001 ± 0.004 (n.d.–0.021)	9.3
Cd	0.002	52	0 ± 0 (n.d.–n.d.)	0	43	0 ± 0 (n.d.–n.d.)	0
Sn	0.0001	52	0.0005 ± 0.0017 (n.d.–0.0107)	36.5	43	0.0002 ± 0.0008 (n.d.–0.0054)	2.3
Sb	0.0004	52	0.0002 ± 0.0007 (n.d.–0.0037)	7.7	43	0.0001 ± 0.0003 (n.d.–0.0010)	11.6
Ba	0.003	52	0.030 ± 0.023 (0.003–0.110)	100	43	0.060 ± 0.062 (0.003–0.265)	100
Pb	0.002	52	0.001 ± 0.002 (n.d.–0.010)	26.9	43	0.009 ± 0.049 (n.d.–0.322)	37.2
Se	0.03	52	1.91 ± 13.15 (n.d.–94.89)	55.8	43	0.01 ± 0.03 (n.d.–0.12)	20.9

[1] Total organic carbon; [2] total nitrogen; [3] total phosphorus; [4] limit of quantification; [5] data number; [6] average; [7] standard deviation; [8] minimum; [9] maximum; [10] not detected; [11] detection frequency.

Third, Ni, Cr, As, Sn, Sb, Ba, Pb, and Se, which are not recommended nutrients in NSs, were observed in the discharge from PFs (Table 5). In particular, the detection frequencies of Ni, Cr, and Ba in wastewater were extremely high, at 97.7, 100, and 100%, respectively.

Fourth, the average concentrations or detection frequencies of six pollutants (TOC, Ni, Cu, Sb, Ba, and Pb) were higher in wastewater than in the NS, indicating low utilization efficiency by the cultivated plants and leading to their accumulation in wastewater. Although previous studies have reported higher concentrations of organic matter and nutrients in drainage water compared with NS [13,50], the accumulation of Ni, Cu, Sb, Ba, and Pb in drainage water has not been previously reported.

In summary, the results revealed that the Mn, B, Cu, Zn, and Ba in HW should be of great concern in terms of concentration and detection frequency. It should be noted that Ba is not a recommended component of NS in South Korea. Further studies are required to determine how Ba was detected in HW at such a high concentration and frequency in the future.

Table 6. Concentration ranges of micropollutants reported in sewage wastewater treatment plant influents.

Pollutants	Concentration Ranges in Influent (µg/L)	Wastewater Type	References
Mn	77.8–151.8	SeW + IW	[35]
	150	SeW	[36]
	67	SeW + IW	[37]
	42–217	SeW	[38]
	75.68–508.5	SeW + IW	[39]
	30	SeW + IW	[40]
Ni	3.51–6.25	SeW + IW	[35]
	10	SeW	[36]
	770	SeW + IW	[37]
	n.d.–202	SeW	[38]
	12	SeW	[41]
	4.88–116.6	SeW + IW	[39]
	1.9–3.6	SeW + IW	[42]
	4	SeW + IW	[40]
	5	SeW	[40]
B	100	SeW	[43]
	1400	SeW	[44]
	190	SeW + IW	[40]
	100	SeW	[40]
Mo	1.06–21.52	SeW + IW	[39]
	6	SeW + IW	[45]
	1	SeW + IW	[40]
	2	SeW	[40]
Cr	n.d.–4.88	SeW + IW	[35]
	40	SeW + IW	[37]
	174–2120	SeW	[38]
	9	SeW	[41]
	2.87–72.54	SeW + IW	[39]
	1.7–19	SeW + IW	[42]
	2	SeW + IW	[40]
Cu	45.8	SeW + IW	[46]
	66.1–125	SeW + IW	[35]
	300	SeW	[36]
	79	SeW + IW	[37]
	9–400	SeW	[38]
	65	SeW	[41]
	13.99–5657	SeW + IW	[39]
	6.2–78	SeW + IW	[42]
	110	SeW + IW	[40]
Zn	91.3	SeW + IW	[46]
	82.9–163	SeW + IW	[35]
	390	SeW	[36]
	470	SeW + IW	[37]
	58.05–1569	SeW + IW	[39]
	85–610	SeW + IW	[42]
	250	SeW + IW	[40]
	135	SeW	[40]
As	n.d.–2.28	SeW + IW	[35]
	0.76–3.9	SeW + IW	[42]

Table 6. *Cont.*

Pollutants	Concentration Ranges in Influent (μg/L)	Wastewater Type	References
Cd	0.08–0.4	SeW + IW	[35]
	10	SeW	[36]
	3.3	SeW + IW	[37]
	n.d.–137	SeW	[38]
	0.6	SeW	[41]
	n.d.–17.16	SeW + IW	[39]
	0.055–0.12	SeW + IW	[42]
Sn	0.98	SeW	[47]
	367–468	SeW + IW	[48]
Sb	7	SeW + IW	[45]
	0.3	SeW	[40]
	209–380	SeW + IW	[48]
	1.73	SeW	[49]
Ba	21.9–51.9	SeW + IW	[35]
	100	SeW	[36]
	90	SeW + IW	[45]
	35	SeW + IW	[40]
	41	SeW	[40]
Pb	3.64	SeW + IW	[46]
	2.19–3.98	SeW + IW	[35]
	40	SeW	[36]
	39	SeW + IW	[37]
	1–358	SeW	[38]
	18	SeW	[41]
	2.93–79.33	SeW + IW	[39]
	7	SeW + IW	[40]
	12	SeW	[40]
Se	n.d.–17	SeW + IW	[42]
	3	SeW + IW	[45]

Abbreviations: n.d.: not detected; SeW: sewage wastewater; IW: industrial wastewater.

3.2. Potential Ecological Risk Assessment of Pollutants Discharged by Plant Factories

The PER was assessed to determine the impact of pollutants discharged from PFs on freshwater aquatic life. The frequency of exceeding the $PNEC_{lowest}$ values in surface water (with a dilution factor of 10) for 12 pollutants (B, Cu, Zn, Se, Ni, As, Mn, Pb, Mo, Cr, Cd, and Sb) was calculated, excluding the 5 pollutants (TOC, TN, TP, Cd, and Ba) with no applicable $PNEC_{lowest}$ values among the 17 studied (Table 3). The frequencies of B, Cu, and Zn exceeding the lowest $PNEC_{lowest}$ were 100, 95, and 79%, respectively, indicating a high necessity for managing these substances in the HW discharged by PFs. Additionally, Se, Ni, As, Mn, and Pb were observed to exceed the $PNEC_{lowest}$ value (Figure 1). The frequency of Mo, Cr, Cd, and Sb exceeding the $PNEC_{lowest}$ values was zero.

Considering a dilution factor of 10, HQ values were calculated using Equation (1). The PER was assessed according to the criteria provided in previous studies using the calculated HQ value. $HQ \geq 1$ indicates a high level of hazard, $1 > HQ \geq 0.1$ indicates a medium level of hazard, and $HQ < 0.1$ indicates a low level of hazard [56–58]. A total of 10 pollutants (Mn, Ni, Mo, Cr, Cu, Zn, As, Cd, Sb, and Pb) were evaluated for PER, excluding the 5 pollutants (TOC, TN, TP, Sn, and Ba) with no applicable $PNEC_{lowest}$ values and 2 (B and Se) with a $PNEC_{lowest}$ value of 0 (Table 3). The risk assessment results demonstrated that Cu and Zn in HW posed a "high-hazard" ecological risk. Cu exhibited the highest observed maximum concentration (10.317 mg/L) in the wastewater (Table 5). The element has high toxicity that reduces the biological treatment efficiency in WWTPs [59–61] and negatively affects aquatic life when it enters surface water [62,63]. The maximum concentration (8.988 mg/L)

of Zn in HW was the second highest. Ni and Mn posed a "medium-hazard" ecological risk, while Cr, Mo, As, Cd, Sb, and Pb posed a "low-hazard" ecological risk (Figure 2), indicating that the HQ values of As, Cd, Sb, and Pb were zero.

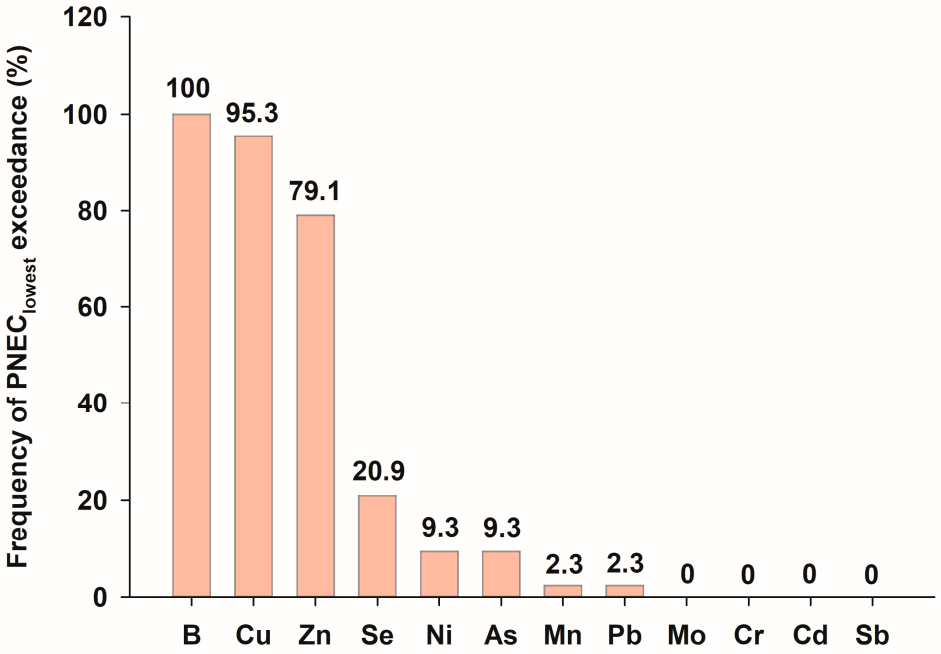

Figure 1. Frequencies of 10 pollutants diluted 10 times in surface water exceeding $PNEC_{lowest}$. The number above each bar indicates the frequency of each pollutant exceeding the $PNEC_{lowest}$ value.

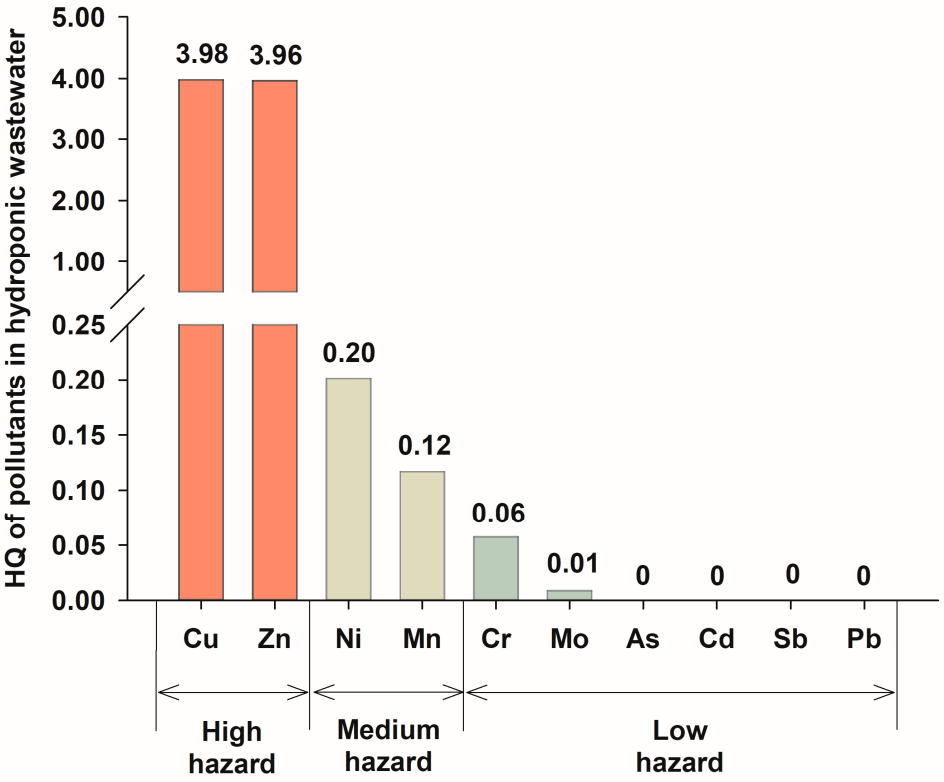

Figure 2. Ecological risk assessment of 10 pollutants in hydroponic wastewater (HW) using the hazard quotient (HQ). The number above each bar indicates the HQ value of each pollutant.

Studies on the ecological risk assessment of metals discharged into aquatic environments from PFs or wastewater treatment plants are very rare, and few have reported the ecological risk of heavy metals in sewage sludge or those in the surface water and sediment in areas receiving wastewater discharge. The results reported in these studies differ from our findings. In the ecological risk assessment of heavy metals in sewage sludge, they were ranked in the following order: Cd > Hg > Cu > As > Ni > Pb > Zn > Cr [64]. Roy et al. [65] reported that Hg > Pb > As > Cr had high ecological risk factors in that order when conducting an ecological risk assessment of heavy metals in the sediment of sewage treatment plant ponds. Kwon and Lee [66] reported that the potential of adverse biological effects of metals in the sediments of a wastewater discharge site decreased in the following order: Zn (69.8%) > Pb (35.8%) > Cu (29.1%) > Cr (21.1%).

When considering the $PNEC_{lowest}$ exceedance frequency (Figure 1) and HQ values (Figure 2), the priority pollutants for management in PFs are Cu, Zn, Ni, Mn, and B. B is included in the priority pollutants list owing to its high aquatic toxicity ($PNEC_{lowest}$ value of 0) and its 100% $PNEC_{lowest}$ exceedance frequency. Cr and Mo were classified as "low hazard," and their 0% $PNEC_{lowest}$ exceedance frequency excluded them from the priority list. Ba was also excluded from the priority pollutants list owing to its relatively low concentration compared with Cu, Zn, Ni, Mn, and B, although the detection frequency in HW was 100%. Despite the small amount of wastewater discharged from PFs into surface water (Table 1), the discharge of HW raises concerns due to the presence of these five priority pollutants (Cu, Zn, Ni, Mn, and B). The results of this study are valuable, as they have not been reported in previous research, to our best knowledge.

3.3. Suggested Treatment Techniques for Five Priority Pollutants

In Section 3.2, five priority pollutants (Cu, Zn, Ni, Mn, and B) discharged from PFs are suggested. However, to date, there have been no studies to suggest treatment technologies to be used in PFs for removing these pollutants. The common treatment technologies for these pollutants (Cu, Zn, Ni, Mn, and B) reported in the literature are summarized in Table 7 [67–101]. Cu, Zn, Ni, Mn, and B can be usually treated using four major technologies: flocculation, electrocoagulation, adsorption, and constructed wetlands (CWs), as shown in Table 7. CW technologies are nature-based techniques (NBTs) that utilize various hydrophilous plants. Based on the four treatment technologies, the removal efficiencies of the five priority pollutants decreased in the following order: electrocoagulation (98.0 $\pm$ 2.7%) > adsorption (88.6 $\pm$ 15.3%) > CW (83.9 $\pm$ 21.2%) > flocculation (76.1 $\pm$ 22.8%) (Figure 3).

The treatment technologies for HW considered in previous studies included filtration, chemical oxidation, NBTs (CW and phyto-filtration), activated carbon treatment, and biological treatment using activated sludge [16,18–20,50,102–106]. However, these studies predominantly focused on the treatment of organic matter (TSS, BOD, and COD), as well as N and P. The removal of MPs from HW has rarely been reported, though the effective removal of heavy metals, such as Cd, Cu, Zn, Pb, Cr, and As, has been achieved using hydroponic plants and bioelectrochemical techniques [15,102,107]. Interestingly, there have been no documented cases of the application of commonly used coagulation and flocculation treatment techniques to HW, probably due to the additional costs associated with treating the secondary sludge generated by this method.

Overall, adsorption and CWs could be considered as effective treatment technologies for treating HW as they have been proven to be effective in removing organic matter, N, and P from PF wastewater and the five priority pollutants from other types of wastewater (Table 7 and Figure 3). However, activated carbon adsorption requires periodic activated carbon regeneration or replacement, which would be the greatest limitation in applying this technology to HW treatment. We suggest that electrocoagulation technology could be used for treating HW, which is not only effective in treating pollutants (Table 7), but has also been proven cost-effective in treating pollutants in previous studies [108,109]. In particular, NBTs offer significant advantages over other techniques in terms of operational simplicity,

cost-effectiveness, and the absence of secondary sludge generation during treatment [55]. Therefore, NBTs are strongly recommended as sustainable treatment technologies for HW discharged by PFs.

Table 7. Removal efficiencies of five priority pollutants based on major treatment techniques.

Pollutant	Treatment Technique	Removal (%)	Wastewater Type	Operating Conditions				References
				Reactor Scale	Reaction Time	pH	Comments	
Cu	FL	99.9	IW	LAB	32 min	11	• Coagulant: $Al_2(SO_4)_3 \cdot 18H_2O$ or $FeCl_3 \cdot 6H_2O$	[67]
		86.79	IW	LAB	33 min	4.5	• Coagulant: $Al_2(SO_4)_3 \cdot 18H_2O$	[68]
		84.07	IW	LAB	33 min	4.5	• Coagulant: $FeCl_3$	[68]
	EC	99.9	IW	LAB	20 min	3.0	• Current density: 10 mA/cm^2	[67]
		96	IW	Full	NA	7	• Power consumption: 112 W h/m^3	[69]
	AD	99	SyW	LAB	120 min	NA	• Adsorbent: Chitosan-based biodegradable composite	[70]
		100	IW	LAB	NA	NA	• Adsorbent: Clinoptilolite	[71]
	CW	97.1	IW	Pilot	NA	5.1	• Plant: *Leersia hexandra* • HRL: 0.1 $m^3/m^2 \cdot d$ • Temp.: 25 ± 2 °C	[72]
		100	SW	Bench	72 h	NA	• Plant: *Typha d.* and *Eleocharis c.*	[73]
Zn	FL	80.47	IW	LAB	33 min	4.5	• Coagulant: $Al_2(SO_4)_3 \cdot 18H_2O$	[68]
		78.81	IW	LAB	33 min	4.5	• Coagulant: $FeCl_3$	[68]
	EC	99	IW	LAB	30 min	5	• Current density: 98 A/m^2 • Temp.: 30 °C	[74]
		100	SyW	LAB	5 min	7	• Current density: 15 mA/cm^2	[75]
	AD	100	IW	LAB	NA	NA	• Adsorbent: Clinoptilolite	[71]
		94	SyW	LAB	240 min	NA	• Adsorbent: AC • Temp.: 22 ± 0.5 °C	[76]
	CW	96	SW	Bench	96 h	NA	• Plant: *Typha d.*	[73]
		83	SeW	Full	100 d	7.5–8.0	• Total Zn removal • Native plants • Temp.: 9.6–12.6 °C	[77]

Table 7. *Cont.*

Pollutant	Treatment Technique	Removal (%)	Wastewater Type	Operating Conditions				References
				Reactor Scale	Reaction Time	pH	Comments	
Ni	FL	74.15	SyW	LAB	36 in	5	• Ni(II) removal • Coagulant: $Fe_2(SO_4)_3$ • Temp.: 35 °C	[78]
		63	IW	LAB	12 min	7	• Coagulant: PAC	[79]
	EC	97.8	IW	LAB	92 min	8.40	• Current density: 6.26 mA/cm^2 • Temp.: 50 °C	[80]
		99.4	IW	LAB	90 min	9.2	• Current density: 10 mA/cm^2 • Temp.: 25 °C	[81]
	AD	99.0	SyW	LAB	NA	7.0	• Ni(II) removal • Adsorbent: GAC • Temp.: 35 °C	[82]
		96.23	SyW	LAB	NA	5.0	• Ni(II) removal • Adsorbent: PAC • Temp.: 25 °C	[83]
	CW	94.3	IW	Pilot	NA	5.1	• Plant: *L. hexandra* • HRL: 0.1 m^3/m^2·d • Temp.: 25 ± 2 °C	[72]
		83.6	SyW	LAB	72 h	NA	• Plant: *Cyperus alternifolius*	[84]
Mn	FL	90.3	BW	LAB	20 min	6.2	• Coagulant: Alum	[85]
		99.8	SyW	LAB	NA	9.5	• Mn(II) removal • Coagulant: $AlCl_3$ • Pre-oxidation with $KMnO_4$	[86]
		15	GW	LAB	26 min	7.37	• Mn(II) removal • Coagulant: $Al_2(SO_4)_3$ • Pre-oxidation with O_2	[87]
		50	GW	LAB	26 min	7.37	• Mn(II) removal • Coagulant: $Al_2(SO_4)_3$ • Pre-oxidation with $KMnO_4$	[87]
	EC	100	IW	LAB	90 min	6	• Power consumption: 112 W h/m^3	[88]
		91.3	IW	LAB	60 min	7	• Current density: 10 mA/cm^2	[89]
	AD	79.1	IW	LAB	60 min	7	• Mn(II) removal • Adsorbent: GAC • Temp.: 25 °C	[90]
		87.7	SyW	LAB	180 min	4–6.5	• Mn(II) removal • Adsorbent: PAC • Temp.: 25 °C	[91]

Table 7. *Cont.*

Pollutant	Treatment Technique	Removal (%)	Wastewater Type	Operating Conditions				References
				Reactor Scale	Reaction Time	pH	Comments	
Mn	CW	99	SyW	LAB	144 h	4	• Plant: *C. bicolor*	[92]
		90	SW	LAB	15 d	NA	• Plant: *P. australis* • Temp.: 9.3–32.3 °C	[93]
B	FL	87	IW	LAB	8 h	12.4	• Coagulant: $Ca(OH)_2$ • Temp.: 60 °C	[94]
		80	IW	LAB	32 min	8	• Coagulant: $Al_2(SO_4)_3$ or $FeCl_3$	[95]
	EC	99.7	SyW	LAB	89 min	6.3	• Current density: 17.4 mA/cm^2	[96]
		97	SyW	LAB	120 min	8.0	• Current density: 3.0 mA/cm^2 • Supporting electrolyte: $CaCl_2$ • Temp.: 25 °C	[97]
	AD	80	IW	LAB	1 h	8.0	• Adsorbent: POMB bottom ash	[98]
		51.3	SyW	LAB	24 h	7	• Adsorbent: GAC • Temp.: 20 ± 1 °C	[99]
	CW	32	IW	LAB	15 d	NA	• Plant: *P. australis and T. latifolia*	[100]
		64	SyW	LAB	14 d	NA	• Plant: *T. latifolia*	[101]

Abbreviations: FL: flocculation; EC: electrocoagulation; AD: adsorption; CW: constructed wetland; IW: industrial wastewater; SyW: synthetic wastewater; SW: swine wastewater; SeW: sewage wastewater; BW: borehole water; GW: groundwater; LAB: laboratory; NA: not available; HRL: hydraulic loading rate; Temp.: temperature; AC: activated carbon; PAC: powdered activated carbon; GAC: granular activated carbon; POMB: palm oil mill boiler.

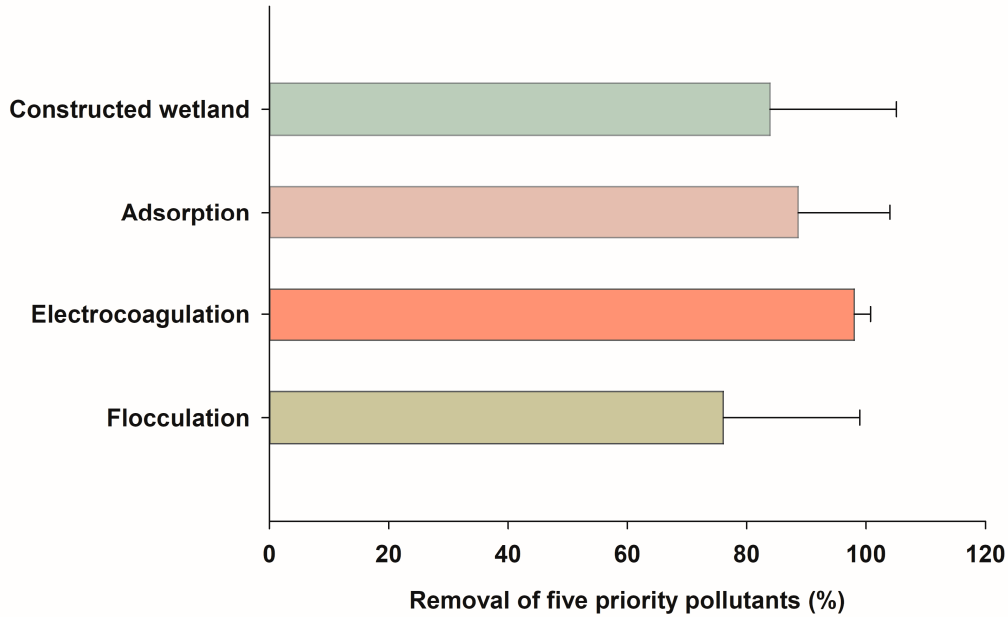

Figure 3. Average removal efficiencies of five priority pollutants (Cu, Zn, Ni, Mn, and B) based on four major treatment technologies. Error bars indicate standard deviation.

4. Conclusions

The main objective of this study was to explore the characteristics of HW discharged by PFs and assess the PER to aquatic life posed by pollutants contained in the HW. Additionally, this study proposed rational treatment techniques for the main pollutants discharged by PFs through a comprehensive literature review. The conclusions are as follows:

1. An analysis of 17 pollutants in HW from 33 PFs detected 8 pollutants (Ni, Cr, As, Sn, Sb, Ba, Pb, and Se) that are not recommended as components of NS in South Korea.
2. In the HW, 11 pollutants (TOC, TN, TP, Mn, Ni, B, Mo, Cr, Cu, Zn, and Ba) exhibited a detection frequency of over 50%. Notably, Cu, a recommended component of NS and highly toxic element to aquatic organisms, exhibited the highest maximum concentration (10.317 mg/L) among MPs, excluding TOC, TN, and TP.
3. The PER assessment of MPs discharged by PFs revealed that Cu and Zn posed a high ecological risk to aquatic life. Additionally, Cu, Zn, Ni, Mn, and B were identified as the five priority pollutants in wastewater that should be managed first.
4. To ensure the sustainability of HC agriculture, appropriate treatment methods for the five priority pollutants discharged into the aquatic environment by HC systems are necessary. For these treatment techniques, NBTs such as CW and phyto-filtration are recommended.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su16177688/s1: Table S1: US EPA surface water quality criteria for 17 pollutants.

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Abbreviations

B, boron; Ca, calcium; Cu, copper; CW, constructed wetland; EU, European Union; Fe, iron; HC, hydroponic cultivation; HQ, hazard quotient; HW, hydroponic wastewater; K, potassium; Mg, magnesium; Mn, manganese; Mo, molybdenum; MPs, micro-pollutants; N, nitrogen; NBTs, nature-based techniques; NS, nutrient solution; P, phosphorus; PER, potential ecological risk; PFs, plant factories; PNEC, predicted no-effect concentration; S, sulfur; SFA, smart farming agriculture; Zn, zinc.

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