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Organic Micropollutants in the Agricultural Chain of Production of Strawberries by Irrigation with Treated Wastewater and Assessment of Human Health Implications

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Abstract: Treated water reuse is vital for sustainable water management and reducing the strain on freshwater resources, particularly in agriculture, which has a great impact on freshwater withdrawal. Despite the benefits, the reuse of treated wastewater carries risks due to residual chemical and microbiological contaminants, such as the organic micropollutants polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), which are not fully removed by current treatment processes and can affect plant growth and human health when used for irrigation. This study focuses on monitoring the PAHs and PCBs in wastewater used for irrigating strawberries, assessing their transfer to crops and potential health risks. The effluents of four wastewater treatment plants were monitored for two years (2017 and 2018) and used to irrigate strawberries grown in plot installations. Effective and robust analytical methodologies (60–99% recoveries, optimal reproducibility) were developed for wastewater and strawberry analysis. The analysis of the treated wastewaters showed the presence of residual PAH and PCB concentrations at hundreds of ng/L. The strawberry crops were further analyzed to measure the PAHs and PCBs. Since two PAHs were present in strawberries, a risk assessment was performed (EPA methodology), finding that the residual contamination of treated waters does not pose a significant health risk, for both adults and children, through the consumption of fruits.

Keywords: PAHs and PCBs; treated wastewaters; reuse; agricultural chain; strawberry crop

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1. Introduction

Water scarcity is a critical global issue, exacerbated by several factors such as climate change, population growth, and increased industrial and agricultural activities. Water reuse is a key strategy in addressing water scarcity. For this purpose, wastewater from various sources, including industrial, agricultural, and domestic ones, must be treated to a safe level for reuse for various purposes like irrigation, industrial processes, and even potable water supply [1]. Water reuse can significantly alleviate the pressure on freshwater resources and contribute to sustainable water management, especially in sectors with a high water demand, such as agriculture, which accounts for a withdrawal of freshwater of about 70% [2]. In the European Union, the European Commission has adopted key legislation for the reuse of urban wastewaters, focusing on sustainable water management and addressing water scarcity challenges. Specifically, Regulation (EU) 2020/741, which entered into force

in June 2023 [3], outlines the minimum requirements for the safe reuse of treated urban wastewaters in agricultural irrigation, with the aim of ensuring protection for both the environment and human health. Even if crop irrigation with wastewater is widespread in water-scarce areas [4], the reuse of treated wastewater may have adverse effects on plant growth and productivity, necessitating the careful consideration of various environmental and health factors due to the residual chemical and microbiological contamination in the irrigating waters. Organic micropollutants are the main compounds accounting for the residual chemical contamination of treated wastewaters. Nevertheless, organic micropollutants are not considered to be parameters of minimum quality prescriptions by Regulation (EU) 2020/741, which sets limits for BOD_5, TSS, turbidity, and *E. coli* contamination which vary according to the technological object of the plant.

Within the class of organic micropollutants, PAHs and PCBs still deserve attention. They are priority pollutants that originate from both natural (e.g., volcanic eruptions, forest fire) and anthropogenic processes (e.g., combustions), are not removed by activated carbon refinement treatment processes [5], and, hence, can lead to both point source and diffuse emissions [6]. Exposure to PAHs and PCBs impacts human health. Long-term exposure can lead to cancer and immune and reproductive systems' disorders, while the assessed short-term effects are gastrointestinal discomfort and skin irritations [7,8].

The amount of PAHs and PCBs in treated wastewater varies depending on the treatment plant and methods used and can achieve concentrations as high as 860 ng/L for PAHs [9] and 6 ng/L for PCBs [10]. Residual PAHs and PCBs may enter the soil and water cycle during their reuse in irrigation practices and be transferred to crops, with implications for human health.

It should be mentioned that few works are devoted to the evaluation of the possible transfer of hazardous species to crops cultivated with treated wastewaters, mainly focused on vegetables [11]. Only a reduced number is devoted to assessing chemical contamination in fruits and, in particular, in strawberries, which are widely enjoyed by children. Hence, the necessity to improve existing knowledge about residual chemical wastewater contamination and study its impact on crop safety under irrigation with treated wastewater is highly demanding.

Taking into account the aspects mentioned above and considering the lack of studies on the possible transfer of organic micropollutants directly to crops, this study aims to achieve the following: (i) monitor the residual contamination of 13 PAHs and 14 PCBs (including dioxin-like congeners) in effluents from urban and industrial wastewater treatment facilities used as irrigating waters; (ii) evaluate the potential transfer of residual PAHs/PCBs to strawberries irrigated with treated wastewaters; and (iii) assess the health risks for adults and children arising from the consumption of these fruits. A two-year monitoring period (2017 and 2018 campaigns) has been considered.

2. Materials and Methods

2.1. Abbreviations of Analytes

PAHs. AcPY (acenaphthylene), Flth (fluoranthene), Phe (phenanthrene), Ant (anthracene), Pyr (pyrene), BaA (benzo[a]anthracene), Chr (chrysene), BbFl[#] (benzo[b]fluoranthene), BkFL[#] (benzo[k]fluoranthene), BaP[#] (benzo[a]pyrene), Ind[#] ((indeno[1,2,3-cd]pyrene), DBA (dibenzo[a,h]anthracene), and BP[#] (benzo[ghi]perylene). PAHs marked with (#) are included within the European directive EU 2020/2184 on drinking water [12].

PCBs. PCB11 (3,3′-dichlorobiphenyl), PCB 15 (4,4′-dichlorobiphenyl), PCB 28 (2,4,4′-trichlorobiphenyl), PCB 52 (2,2′,5,5′-tetrachlorobiphenyl), PCB 81* (3,4,4′,5-tetrachlorobiphenyl), PCB 101 (2,2′,4,5,5′-pentachlorobiphenyl), PCB 118* (2,3′,4,4′,5-pentachlorobiphenyl), PCB 123* (2′,3,4,4′,5-pentachlorobiphenyl), PCB 138 (2,2′,3,4,4′,5-hexachlorobiphenyl), PCB 153 (2,2′,4,4′,5,5′-hexachlorobiphenyl), PCB 167* (2,3′,4,4′,5,5′-hexachlorobiphenyl), PCB 169* (3,3′,4,4′,5,5′-hexachlorobiphenyl), PCB 180 (2,2′,3,4,4′,5,5′-heptachlorobiphenyl), and PCB 189* (2,3,3′,4,4′,5,5′-heptachlorobiphenyl). PCBs marked with (*) are dioxin-like PCBs.

2.2. Reagents

PAH standard stock solution (containing the priority compounds listed by the EPA) was purchased from Sigma Aldrich-Merck (Darmstadt, Germany). PCB standard stock solutions, purchased from LGC Standards (Milan, Italy), contains mono- to epta-chlorine and dioxin-like congeners.

The labelled isotope compounds from PAHs and PCBs were from Wellington Laboratories (Guelph, ON, Canada) and were used as the internal standards (see Table S1 of the Supplementary Materials Section) and as surrogates to obtain calibration curves and extraction recoveries, respectively.

Reagent-grade CH_2Cl_2, 2-propanol, and $MgSO_4$, were from Sigma Aldrich-Merck. An Elix-Milli Q Academic system (Millipore-Merck, Vimodrone, Italy) was used to produce ultrapure water (18.2 MW cm resistivity at 25 °C).

2.3. Instrumentation

The PAHs and PCBs were analyzed by gas chromatography–mass spectrometry (GC-MS), equipped with a (5%-Phenyl)-methylpolysiloxane column (HP 5 ms, 30 m × 0.25 mm × 25 µm, Agilent, Santa Clara, CA, USA). The analysis was performed in a single-ion monitoring (SIM) mode, at a proper m/z ratio (Table S1 of the Supplementary Materials Section). A total of 2 µL volume was injected in the pulsed, splitless mode, with the pressure set to 40 psi for 2.5 min. The GC oven ramp parameters are reported in the Supplementary Materials Section. The total run time for the complete separation of PAHs and PCBs was around 45 min. In Figure S1 of the Supplementary Materials Section, the sequential single-ion monitoring (SIM) gas chromatogram of the PAHs and PCBs included in this work is shown.

2.4. Treated Wastewaters

Treated wastewaters (TWs) were provided from wastewater treatment plants located in Tuscany (center of Italy), selected according to the type of inlet wastewater and the treatment adopted. The TWs used are fully described in Table 1. The selected area is rich in textile industries.

Table 1. Details of the treatments of the wastewater treatment plants considered in this study.

Wastewater Effluent	Source	Treatment	Point of Discharge
TW1	mixed urban/industrial	Primary settling, biological oxidation, secondary settling, clariflocculation, and ozonization	River or to TW2 or TW3 plants
TW2	TW1 effluent	Clariflocculation, sand filtration, activated carbon, and disinfection with hypochlorite	Inlet of the industrial aqueduct
TW3	TW1 effluent	Clariflocculation, sand filtration, dilution with river water, and disinfection with hypochlorite	Inlet of the industrial aqueduct
TW4	mixed urban/industrial and pretreated [(1)] septic tank and landfill leachate sewage	Primary settling, biological oxidation, secondary settling, clariflocculation, and ozonization	

Note: [(1)] pretreatments: aeration for septic tank sewage and filtration with membrane for landfill leachate sewage.

Freshwater (FW) was also tested as the control. The sampling period ranged from June to August 2017 and from June to August 2018. The TWs were provided by the wastewater treatment plants every fifteen days and stored in dark tanks at the irrigation site. The samples were withdrawn on the first and eight day from the filling of the tanks and stored at −10 °C until their analysis. The physicochemical and chemical characteristics of the TWs and the FW were monitored within the irrigation period (2017–2018) and are reported in Table S2 of the Supplementary Materials. For each sample, an aliquot was filtered through a paper filter (Whatman) prior to analysis.

2.5. Strawberry Cultivation

Five rows of seven pots (each one containing ten *Fragaria Ananassa* plants) were regularly irrigated using the four TWs and the FW from June to August 2017/2018. The details of pot installation can be found in the Supplementary Materials Section. The pots were filled with commercially available topsoil for fruits and vegetables. To exclude the leaching of target pollutants from soil to crops, soil characterization was performed using the protocol previously developed [6].

After the harvest, the strawberries were washed, dried, and frozen at −4 °C until the analysis.

2.6. Extraction Procedures

Water samples. A water sample (1 L), spiked with surrogate solutions of PAHs and PCBs at a 2 µg/L concentration, was added to 100 mL of 2-propanol. For PAH and PCB extraction, a STRATA XL cartridge (Phenomenex, Torrance, CA, USA), which had reversed phase characteristics, was used. The cartridge was previously conditioned with 5 mL of the following solvents (5 mL/min): CH_2Cl_2, 2-propanol, and H_2O. The PAHs and PCBs were eluted with two aliquots of CH_2Cl_2, of 1 mL each. A total of 1 mL extract was spiked with the internal standard solution of PAHs and PCBs prior to GC-MS analysis, (5 µg/L concentration). After extraction, the concentrations of PCBs and PAHs were calculated using matrix-matched calibration (by spiking the same ^{13}C surrogates in the supernatant obtained after the extraction of an aliquot of strawberry). In such a way, the matrix effect was considered in the evaluation of the recoveries.

Strawberries. A total of 5 g of strawberries was spiked with 250 µL of PAHs ^{13}C surrogates (160 µg/L) and 250 µL of PCBs ^{13}C surrogates (160 µg/L), corresponding to 8 µg/kg for PCBs and 8 µg/kg for PAHs. Then, the strawberries were placed in a container with 10 mL of CH_2Cl_2, 400 mg of $MgSO_4$, and 1 g of NaCl. This mixture was then vigorously shaken and centrifuged at 1507× *g* for 5 min. The clear liquid on top was moved to a new container for purification, containing 50 mg of primary and secondary amine (PSA, Agilent Technologies, Santa Clara, CA, USA) absorbent and 150 mg of $MgSO_4$. The container was shaken and centrifuged at 7871× *g* for 10 min. Finally, 1 mL extract was spiked with the internal standard solution of PAHs and PCBs (5 µg/L concentration) and transferred for analysis by GC-MS. As for the water samples, after extraction, the concentrations of PCBs and PAHs were calculated using matrix-matched calibration.

2.7. Health Risk Assessment

The BaP equivalent concentrations for each PAH observed in the strawberry crops were determined using Equation (1) [13]:

$$BaP_{eq} = \sum [PAH_i \times BaP\ (TEF_i)] \quad (1)$$

where [BaP_{eq}] = BaP equivalent concentration in strawberry, considering the TEF of BaP = 1 [14], PAH_i = concentration of ith PAH (present in strawberry) in mg g^{-1}, and BaP $(TEF)_i$ = BaP toxicity equivalency factors (TEFs) for ith PAH [13] (and reference herein).

The lifetime average daily dose (LADD, mg/kg per day) was determined for both adults and children, as shown in Equation (2), according to the U.S. EPA [15]:

$$LADD = \frac{CF \cdot IR \cdot EF \cdot ED}{AT} \quad (2)$$

where CF = BaP_{eq} concentration in strawberry (mg g^{-1}), IR = ingestion rate of a food product (g/kg per day), EF = exposure frequency (365 days/y), ED = exposure duration (30 years for adults; 6 years for children, 0–6 years old), and AT = averaging time (25,550 days or 70 years).

The intake of strawberries was estimated according to the EPA indications for fruit consumption [16]. The IR values chosen were 0.36 g/kg per day for children (age 1–2 years) and 0.1 g/kg per day for adults (>50 years), since these populations were the ones with the highest mean strawberry consumption, under the precautionary assumption that all the strawberries consumed were only those grown with irrigation using the TWs in this study.

From LADD, the cancer risk (CR) was calculated according to Equation (3) [17]:

$$CR = LADD \times CSF \quad (3)$$

where SF = slope factor 1 (mg kg^{-1}-day)$^{-1}$ for benzo[a]pyrene, as used by Singh and Agarwal [13], according to the US EPA Integrated Risk Information System.

3. Results and Discussion

Before analyzing the PAH and PCB contamination in the TWs and strawberries, the analytical methods described above were validated directly in the matrices to verify their fulfilment with the limits imposed by regulations (where present). Hence, the extraction yields and the method quantitation limits (MQLs) were determined in the TWs and strawberries.

3.1. Treated Wastewaters

3.1.1. Figures of Merit

Method validation indicated good extraction recovery yields, between 60% (^{13}BP) and 99% (^{13}PCB 52). The MQLs, reported in Table S3, were between 1.3 (Phe) and 11.0 ng/L (PCB 169). For benzo[a]pyrene, which is currently the only PAH regulated by the Italian legislative decree n. 185/2003 at 10 ng/L, the MQL obtained was 3.9 ng/L, thus fully satisfying the legislative requirements. The relative standard deviations were below 15% for all the analytes, showing optimal analytical reproducibility.

3.1.2. Monitoring of PAHs and PCBs

The concentrations detected for all the analytes in the TWs sampled in 2017 and 2018 are shown in Tables S3 and S4 for the PAHs and in Tables S5 and S6 for the PCBs in the Supplementary Materials Section.

For each year, the data are represented as boxplot representations of the dispersion of the PAH (Figure 1A) and PCB (Figure 1B) concentrations, considering all the plants and the freshwater.

Overall, the presence of both PAHs and PCBs was higher in the waters withdrawn in 2017 with respect to those sampled in 2018.

The amount of pollutants in the effluents depends upon a large number of factors, such as the type and the amount of industrial wastewater collected by the sewage, the served population (usually expressed as population equivalent, p.e.), the meteorological events, which altogether affect the contamination of the influent water, and, most of all, the level of technology used in the WWTP.

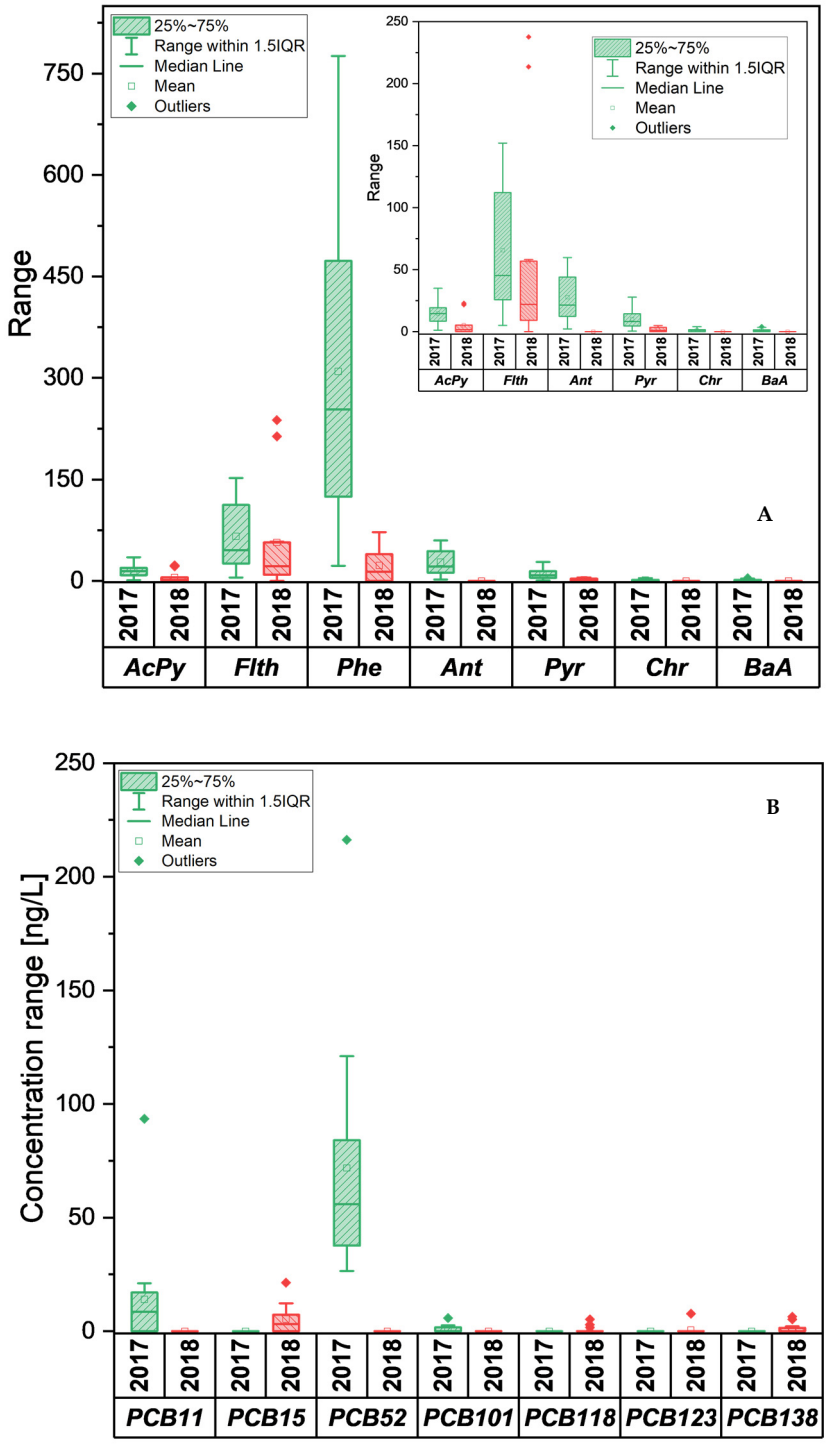

Figure 1. Boxplot representation for the PAH (**A**) and PCB (**B**) concentrations (ng/L) detected in FW and TWs in the 2017 and 2018 campaigns. Each box represents the interquartile range (IQR) of the concentrations, with the line inside the box denoting the median.

PAHs

As for the PAHs, it is interesting to note that the greater contamination was accounted for by the low- and medium-molecular weight (LMW and MMW, respectively) congeners in both years (Figures 2 and 3).

In fact, as shown in Figure 2, phenanthrene (three-ring, LMW) was the compound detected in the highest concentrations, up to 776 ng/L in TW1, with a wide variability, even if significant amounts of fluoranthene (four-ring, MMW), up to 152 ng/L in TW2,

anthracene (three-ring, LMW), up to 60 ng/L in TW4, pyrene (four-ring, MMW), up to 28 in TW2, and acenaphthylene (three-ring, LMW), up to 35 ng/L in TW2, were also detected. Chrysene and benzo[a]anthracene, both four-rings MMW, were the congeners less present in the TWs, around 4.0 ng/L in TW1 and TW2. The presence of LMW and MMW compounds is in agreement with their higher or moderate solubility in water and their persistence.

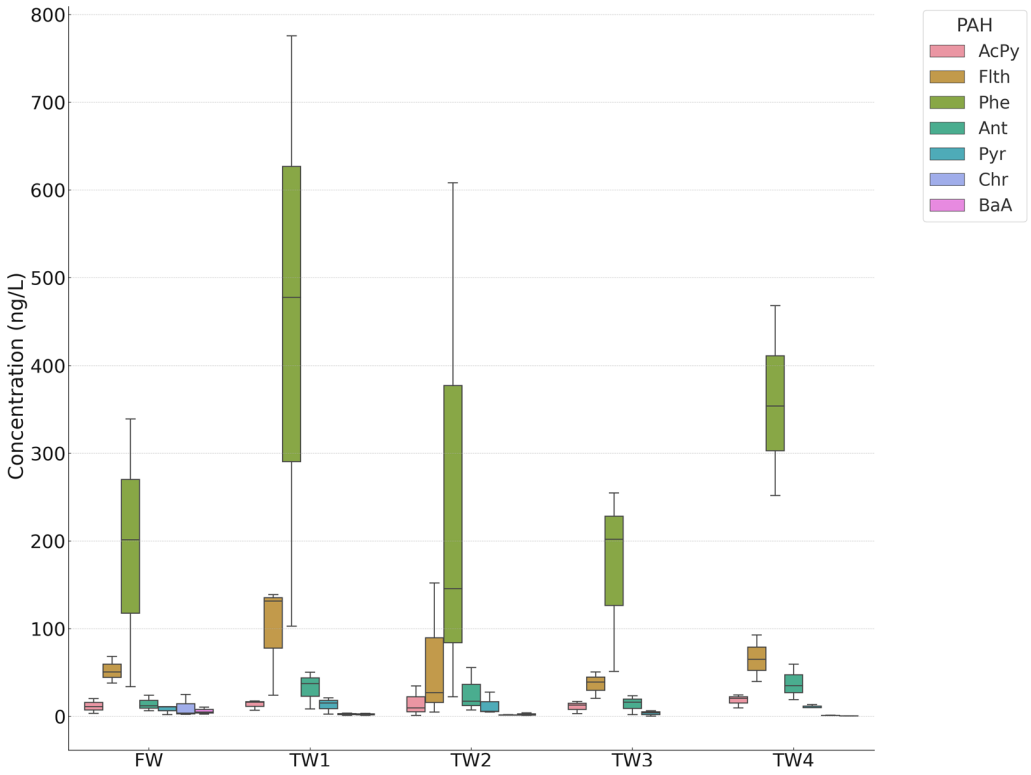

Figure 2. Boxplot distributions for PAHs detected in FW and TWs in 2017.

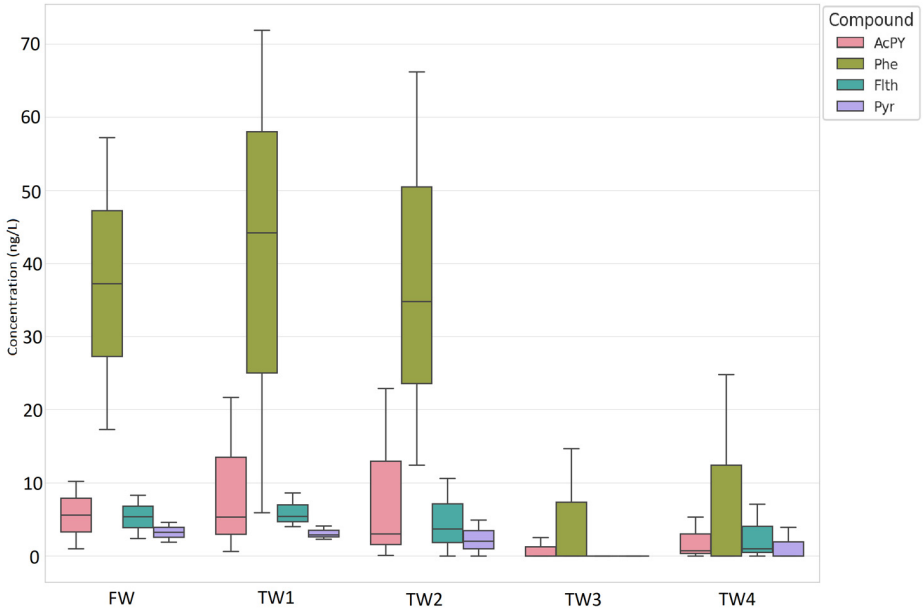

Figure 3. Boxplot distributions for PAHs detected in FW and TWs in 2018.

Within the already published research works on the topic, even if plant parameters such as p.e. and treatment steps are available, a direct comparison within wastewater

quality parameters is generally performed relying only on effluent contamination, which, for PAHs, is expressed as the sum of the total PAHs detected. In this regard, the average contamination observed for the sum of PAHs detected in TW1 (613 ng/L), TW2 (380 ng/L), TW3 (235 ng/L), and TW4 (492 ng/L), which can be seen in Figure 4, was in line or far lower than the contamination levels reported by other studies [15].

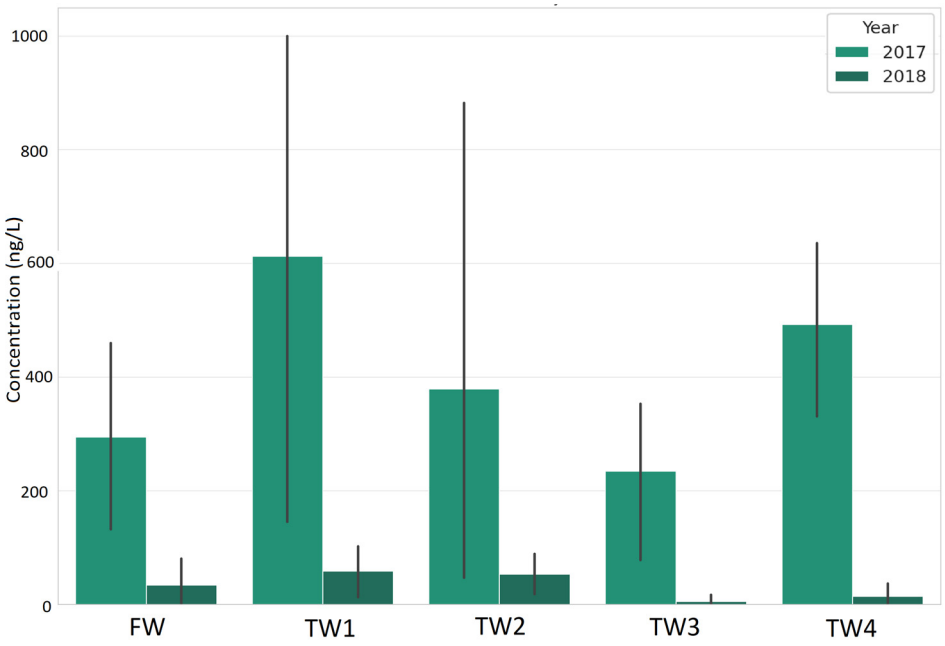

Figure 4. Average of the sum PAHs detected in FW and TWs in the 2017 and 2018 campaigns. The minimum and maximum values are indicated.

The average contamination data for the sum of PAHs in the four effluents studied allow for some considerations. With regard to 2017, the highest contamination observed for TW1 was in line with the fact that TW1 was the less treated water. Despite the fact that the statistical tests (Kruskal–Wallis non-parametric test, $p = 0.05$) showed no statistical dissimilarities between the treatment plants, an effect of different purification technologies could be observed from the data obtained. When the effluent of TW1 underwent activated carbon treatment and disinfection (TW2), its PAH contamination was almost halved, probably due to the significant adsorption of PAHs onto the carbon surface. The amount of PAHs detected in TW3 suggested that activated carbon filtration could be avoided if dilution with river water is performed instead. The quality of TW4, which was similar to the one of TW1, appeared to reflect the characteristics of both the influent type and the treatment processes. In 2018, the same considerations remained true, even if the better quality of TW3 then should be ascribed to a probable better quality of the river water used for water dilution.

As previously mentioned, the contamination of effluent wastewater was higher in 2017 than in 2018, and this held true for each treatment plant. Since, for each treatment plant, the type and the amount of industrial wastewater collected from sewage and the served population were quite constant, the higher contamination observed in 2017 was tentatively explained by the rainfall data in the studied area, which measured 26.4 mm of rainwater in the months of June, July, and August in 2017 and 129.4 mm in the same months in 2018 [18], as correlations between BOD_5 and rainfall intensity had been demonstrated elsewhere [19].

Finally, it is appropriate to point out that the BbFl, BkFl, BaP, Ind, and BP congeners regulated within the EU Directive 2020/2184 on drinking water were not present in any of the TWs analyzed. This result can have positive repercussions for a global water reuse approach.

PCBs

Overall, in the two years monitored, our study revealed the presence of dichlorobiphenyl congeners (PCB11, PCB15), tetrachlorobiphenyl congeners (PCB52, PCB81*), pentachlorobiphenyl congeners (PCB101, PCB118*, 123*), and one hexachlorobiphenyl congener (PCB138), which can be seen in Figures 5 and 6.

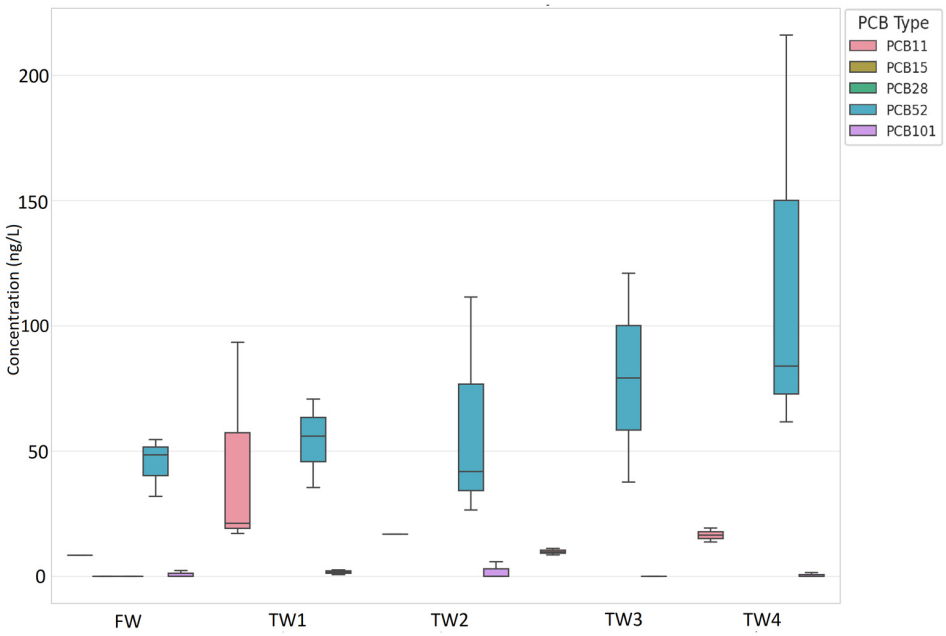

Figure 5. Boxplot distributions for PCBs detected in FW and TWs in 2017.

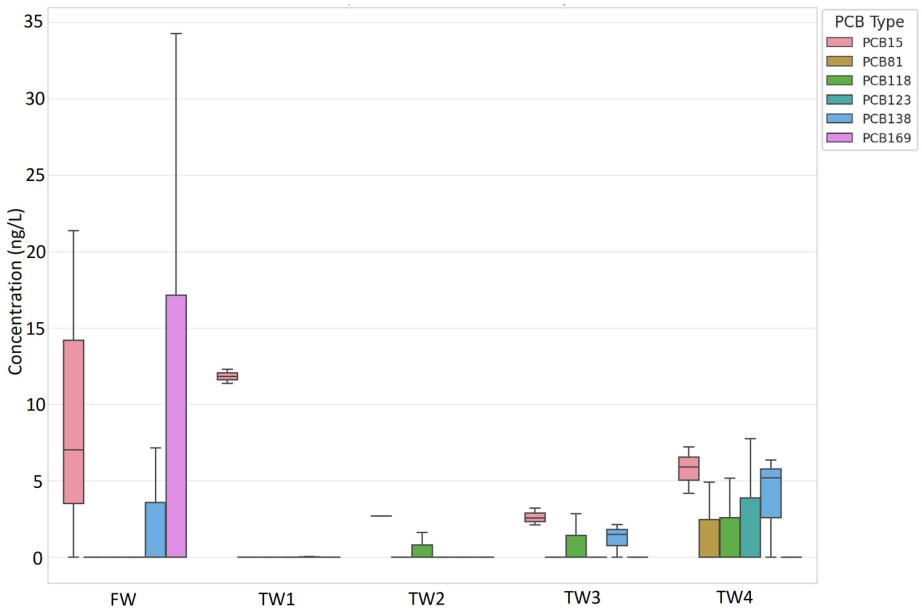

Figure 6. Boxplot distributions for PCBs detected in FW and TWs in 2018.

In 2017, only three congeners were detected (PCB52, PCB11, and PCB101), which accounted for a maximum average total PCB content of 132.6 ng/L in TW4. During the observed period, in 2018, even if a higher number of congeners had been detected (PCB15, PCB81*, PCB118*, PCB123, PCB138, and PCB169*), the average total content was lower and achieved a maximum of 15.6 ng/L in TW4.

PCB11 and PCB52 have been recognized to be side-reaction products during the synthesis of azo pigments starting from chlorinated benzidines [20]. Their presence is,

hence, in agreement with the textile industrial activities in the area studied. The other PCBs compounds detected can be often found, even not as major constituents, in commercial PCB mixtures, such as PCB101 in Aroclor 1248, 1254, and 1260, PCB15 in Aroclor 1221, 1232, 1016, and 1242, PCB81* in low amounts in Aroclor 1248, PCB118* in Aroclor 1248 and 1254, PCB123* in Aroclor 1254, and PCB 138 in Aroclor 1254, 1260, and 1262 [21]. Anyway, the presence and concentration of specific congeners in effluent samples are typically a result of both the original composition of the PCB mixtures used that enter the environment as well as the environmental fate and behavior of the individual congeners during the treatment.

The data obtained in this work can only be tentatively compared with those presented in the literature, mainly due to the difference in the PCB congeners analyzed, the quality of the inlet wastewater, and the plants' efficiency. Nevertheless, our average total PCB concentrations (132.6 ng/L in 2017 and 15.6 ng/L in 2018) were not far from the values reported elsewhere (52 ng/L for 12 PCBs in a WWTP of Paris [22], 250 ng/L for 7 PCBs in a WWTP of Thessaloniki [23], and 123.9 ng/L for 12 PCBs in a WWTP in Jordan [24]).

The content of PCBs in the TWs studied (Figure S2 of the Supplementary Materials Section) shows that the average contamination data for the sum of PCBs were statistically non-dissimilar for the four TWs (Kruskal–Wallis non-parametric test, $p = 0.05$).

No statistical similarities or similar trends between the residual PAH and PCB concentrations were observed (ANOVA test, $p = 0.05$), except for the cumulative lower contamination detected for TWs in 2018, which could be related to the higher rainfall of that year, as previously discussed for PAHs.

3.2. Strawberries

3.2.1. Figures of Merit

For each analyte, the recovery yields of the extraction method and the MQLs achieved are detailed in the Supplementary Materials Section (Figure S3 and Table S8, respectively). Overall, the developed method provided recovery yields from strawberries between 70% (^{13}Ind) and 107% (^{13}BaA), with relative standard deviations lower than 15%. The MQL ranged from 0.96 µg/kg (Phe) to 10.1 µg/kg (PCB169*).

3.2.2. Monitoring of PAHs and PCBs

For the two years considered, the content of the micropollutants in the strawberries is shown in Table 2.

Table 2. Concentrations of PAHs (µg/kg) in the strawberry crops of 2017 and 2018.

Analyte	Year	FW	TW1	TW2	TW3	TW4
BaA	2017	-	1.14 ± 0.05	-	-	-
DBA	2018	1.56 ± 0.09	1.00 ± 0.15	1.18 ± 0.15	1.53 ± 0.16	0.85 ± 0.13

Even though some residual concentrations of PAHs were detected in the TWs, the only PAH analyte present in the crop of 2017 was BaA, which was detected in TW1 at a concentration close to the MQL level (1.17 µg/kg). With regard to 2018, DBA was detected in the crops irrigated with all TWs at concentrations levels close to the MQL level (1.45 µg/kg) and ranging from 0.85 µg/kg (TW4) to 1.56 µg/kg (TW3). The presence of DBA was also found in the control. It should be remarked that the EU normative on food (EU Commission regulations 1881/2006 and 835/2011) regulates the presence of BaP alone and the sum of BaP, BaA, BBFl, and Chr, with limits depending on the kind of food considered.

In this regard, BaP was not detected in any of the strawberry samples (in agreement with its absence also in the TWs), whereas only BaA was detected in one crop at 1.14 µg/kg. If for BaA a possible transfer from TW1 to the crop could not be excluded, the presence of DBA in the strawberries did not derive from water contamination, since it had not been detected in the water used for irrigation.

A limited transfer of PAHs to strawberry crops was also verified by Tozzi et al. [25] using sediments contaminated by PAHs in soilless cultivations and by Wennrich et al. [26], who did not observe a positive relationship between the total PAH burden in strawberries and the cultivating site.

Concerning PCBs, none of the congeners were transferred to the crops, regardless of the number of Cl atoms.

3.2.3. Health Risk Assessment

For the two years under study, human exposure to PAHs expressed as the lifetime average daily dose (LADD) derived from the consumption of strawberry crops obtained under irrigation with TWs and FW and carcinogenic risk were assessed for children and adults according to the EPA indications (Tables 3 and 4). The data obtained for the cancer risk of consuming the crops irrigated with all the TWs in this study were well-below the threshold of 1×10^{-6} set by the EPA [27] for both adults and children and, hence, could be considered acceptable.

Table 3. Risk assessment for the 2017 crops.

Irrigating Water	LADD (mg/kg a Day)		Cancer Risk	
	child	adult	child	adult
TW1	3.5×10^{-9}	1.1×10^{-8}	3.5×10^{-9}	1.1×10^{-8}

Table 4. Risk assessment for the 2018 crops.

Irrigating Water	LADD (mg/kg a Day)		Cancer Risk	
	child	adult	child	adult
FW	9.6×10^{-9}	3.1×10^{-8}	9.6×10^{-9}	3.1×10^{-8}
TW1	3.9×10^{-8}	1.0×10^{-7}	3.9×10^{-8}	1.0×10^{-7}
TW2	3.6×10^{-8}	1.2×10^{-7}	3.6×10^{-8}	1.2×10^{-7}
TW3	4.7×10^{-8}	1.5×10^{-7}	4.7×10^{-8}	1.5×10^{-7}
TW4	2.6×10^{-8}	8.5×10^{-8}	2.6×10^{-8}	8.5×10^{-8}

4. Conclusions

The practice of treated water reuse in agricultural practices is encouraged by the current EU 2020/741 Regulation. For this purpose, the safety of the treated wastewater must be assessed to avoid the transfer of residual contaminants to the crops. PAHs and PCBs are organic micropollutants that can still be detected, even if at low ng/L levels, in treated wastewater. This work took up the challenge of understanding whether the residual contamination of treated wastewater could represent a risk to the health of the consumers of strawberries irrigated with such water. To this aim, analytical methodologies were developed and validated for the determination of PAH and PCB presence in treated wastewater and strawberries. The good recovery rates (60–99% in the wastewaters and 70–107% in the strawberries, with relative standard deviations below 15%) and the good method quantitation limits obtained showed that the methods fulfilled the current regulation requirements. The analysis of four effluents from four different treatment plants located in an industrial (textile sector) area, over two monitoring years, indicated the presence of residual PAH and PCB concentrations at hundreds of ng/L, in line with the overall contamination of treated wastewater reported by the literature. The content of contaminants was correlated with the rainfall data in the area for the periods monitored. The PAHs detected at higher concentrations were low- and medium-molecular-weight compounds (phenanthrene, fluoranthene, anthracene, pyrene, and acenaphthylene), in agreement with their higher solubility in water and their persistence. The PCB congeners detected still reflected their use in the Aroclor mixture and their presence as side-reaction products during the synthesis of pigments used in the textile industry. Despite the presence of residual contaminants, the PCBs were not transferred to the fruits. As for the PAHs,

only benzo[a]anthracene and dibenzo[a,h]anthracene were present in the crops; it is worth mentioning that only benzo[a]anthracene was also present in the treated waters. As verified by applying the EPA methodology, the presence of the compounds detected in the strawberries led to a cancer risk within 3.1×10^{-8} and 1×10^{-7} for adults and within 3.5×10^{-9} and 2.6×10^{-8} for children, which was well-below the acceptable threshold of 1×10^{-6}.

The results here reported confirm that the integration of wastewater reuse in sustainable agriculture requested by the EU 2020/741 Regulation may be implemented without increasing the health risks for the final consumers. This work has a crucial impact on risk communication strategies and on policy recommendations aimed at enhancing the sustainability, safety, and effectiveness of these practices.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w16060830/s1, Figure S1: Total ion gas chromatogram of the PAHs and PCBs included in this work; Figure S2: Average of the sum PCBs detected in FW and TWs in the 2017 and 2018 campaigns. Minimum and maximum values are indicated; Figure S3: Recoveries of PAHs (A) and PCBs (B) from strawberries by the optimized QuEChERS method; Table S1: List of m/z ratios for the compounds studied; Table S2: Average values and standard deviations (in brackets) of the physicochemical and chemical parameters of TWs for the samples collected in 2017 and 2018; Table S3: MQLs expressed on ng/L for PAH and PCB extraction from wastewaters, calculated as 10 × SDxy/b (where SDxy is the standard deviation of the response, and b is the slope of the calibration curve). * Dioxin-like PCBs are marked with an asterisk; Table S4: Content of PAHs expressed in ng/L in the irrigating waters for 2017; Table S5: Content of PAHs expressed in ng/L in the irrigating waters for 2018; Table S6: Content of PCBs expressed in ng/L in the irrigating waters for 2017; Table S7: Content of PCBs expressed in ng/L in the irrigating waters for 2018; and Table S8: MQLs expressed on µg/kg for the QuEChERS method used for PAH and PCB extraction from strawberries, calculated as 10 × SDxy/b (where SDxy is the standard deviation of the response, and b is the slope of the calibration curve). * Dioxin-like PCBs are marked with an asterisk.

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