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## REMOVAL EFFICIENCY OF PAHs IN WASTEWATER: STATISTICAL EVALUATIONS WITH CHEMICAL-PHYSICAL INDICATORS

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### Abstract

Polycyclic aromatic hydrocarbons (PAHs) are very hazardous compounds. This investigation is the third in a series of three experiments carried out in conventional wastewater treatment plants with regard to PAHs. The first experiment regarded the analysis of PAHs in a municipal wastewater sewage system and in the wastewater treatment plant (WWTP) effluent, followed by a comparison between the observed removal efficiency and FATE model (US-EPA) predictions. The second experiment was carried out in the same WWTPs and showed no evident degradation of PAHs after applying a mass balance estimation between the various types of sludge. The aim of the third experiment described in this paper, was to study PAHs in a more extensive area of wastewater, (with a higher population density and with higher PAH values in the wastewater). The evaluations were carried out in different periods of the in order to estimate the removal efficiency of PAHs. The concentrations measured were well below the legal limits, however in a few cases a statistical analysis was carried out in order to identify possible correlations between various chemical-physical indicators, such as  $\log K_{ow}$  and  $\log K_H$ , and PAH removal yield, verified at different stages of the different treatment plants. A strong correlation resulted between the mechanical treatment removal yield and  $\log K_{ow}$  and a very good correlation between yield measures after secondary sedimentation and  $\log K_H$ . This is because the process is strongly influenced by volatilization induced by air insufflation in the oxidation reactor.

*Key words:* environmental indicators, PAHs, removal, wastewater treatment plant

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### 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) represent a very large class of organic compounds (over 600), characterized by the presence of two or more aromatic rings joined by the co-division of a couple of carbon atoms generally forming a single-structure plane (Balducci et al., 2008). They are ubiquitous pollutants originating from anthropogenic (i.e. combustion of organic matter) and natural activities (such as volcanic eruptions and biogenic formation) (Cai et al., 2008; Kriipsalu et al., 2008; Nikolaou et al., 1984).

PAHs are very hazardous compounds (Blanchard et al., 2004; Metcalf & Eddy, 2003; Zhang et al., 2005). Due to their lipophilicity, they can easily cross biological membranes and accumulate inside

organisms, causing damage to the genetic material (Martellini et al., 2012; Scipioni et al., 2012). Their global annual emissions exceed 500 Gg (520 Gg was the estimation for 2004 by Zhang et al., 2005). In wastewater, contaminant concentrations vary from the  $\text{pg kg}^{-1}$  to  $\text{g kg}^{-1}$  range, depending mainly on the quality and type of incoming wastewater (domestic, municipal, or industrial, etc; Fabian et al., 2016; Ratola et al., 2012; Smith, 2000).

The importance of the PAH contamination of urban wastewaters has been reported by many authors (Loganathan et al., 1997; Pham and Proulx, 1997). Urban surfaces receive deposits of PAHs from different sources such as car traffic, industries, waste incinerators, and domestic heating via both atmospheric transport and local activity (Manoli and Samara, 1999). Their most significant role may be in

urban sewer pollution (Bris et al., 1999). Wastewater contamination has been found to be dominated by atmospheric wet deposition for PCBs, whereas PAHs appear to originate mainly from urban runoff which flushes organic deposits from ground surfaces (Blanchard et al., 2001).

Due to their toxic, mutagenic and carcinogenic properties, 16 PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA) and seven are considered as some of the strongest known carcinogenic compounds by the International Agency for Research on Cancer (IARC, 1991). Benzo-a-pyrene (BaP) is the most important PAH and is also the most toxic together with dibenzo(a,h)anthracene (dBahA).

This study represents the third stage of a series of experiments regarding PAHs in wastewater treatment plants in the province of Varese (in northern Italy). This area has a high population density and industrial activity together with significant environmental pressures with great public focus on environmental and related health problems (Di Mauro et al., 2012).

The first study (first step) was developed in one of the four wastewater treatment plants studied in this paper. It is a WWTP with 80,000 as equivalent population, calculated using BOD loading, with mixed wastewater: 75% domestic and 25% industrial. The aim was to compare an experimental removal and theoretical calculation using FATE (Fate And Treatability Estimator, US-EPA model). The evaluations were conditioned by the low values of parameters. However a comparison of some typologies of PAHs was possible and a substantial correlation was found between experimentally measured removal yields and those calculated using the simulation model (Torretta, 2012). This was in accordance with other experiments described in the technical literature (Katsoyannis and Samara, 2004; Katsoyannis et al., 2006).

Due the importance of the environmental concerns regarding PAHs, we decided to extend the first stage of the experiment with a second application regarding a larger WWTP located in Lombardy (the same region as where Varese is located), in the same industrial district (400,000 equivalent population, receiving mixed wastewater: 70% domestic and 30% industrial). Here we studied the occurrence of PAHs in sludges, over a twelve-month period. Benzo[a]anthracene was consistently found to be the most abundant PAH, whereas anthracene (An) had the lowest concentrations. In terms of PAH concentrations in dry matter, the PAHs levels were relatively constant in the four sludge types. This suggests that pre-thickening, anaerobic digestion and dehydration do not remove PAHs through degradation, or any other mechanism. This was also confirmed by applying a mass balance between the various sludges, which resulted in a higher PAH content in the final sludge than in the earlier steps.

Finally, two approaches were used to estimate the raw wastewater concentrations based on the sludge

PAH concentrations. These provided values that were close to those measured in the case of aAn and fluorantene (Fl), but highly overestimated those of pyrene (Py) and chrysene (Chry) (Torretta and Katsoyiannis, 2013).

The third and last step, which is the focus of this study, regarded four WWTPs located in the same district (Raboni et al., 2013; Torretta et al., 2013), two of which had been considered in the two previous studies. A third plant (100,000 equivalent inhabitants, receiving mixed wastewater: 60% domestic and 40% industrial), in the same area, also receives rainwater drained from a very urbanized area, with dense vehicular traffic. It is worth highlighting that traffic sources can generate an array of harmful pollutants such as hydrocarbons and heavy metals into the urban atmosphere (Gunawardena et al., 2012; Mahbub et al., 2011). A portion of the traffic-generated pollutants is deposited directly onto the ground surfaces (and conducted by the rainfall water into the sewage system), whilst the remainder initially accumulates in the atmosphere (Blanchard et al., 2001; Torretta et al., 2012). Finally a fourth WWTP was considered, in the same area (25,000 equivalent inhabitants, receiving mixed wastewater: 65% domestic and 35% industrial).

This study aims at investigating the presence of PAHs in wastewater considering a more extended area, at different periods of the year – spring, summer, fall and some weeks in the winter, in order to estimate the removal efficiency of PAHs in conventional WWTPs. In this application the measured concentrations were below the legal limits, however in a few cases a statistical analysis revealed correlations between various chemical-physical indicators, such as  $\log K_{ow}$  and  $\log K_H$ , and PAH removal yield, verified at various stages of the different treatment plants. These correlations help to assess the level of danger associated with the water effluents of a treatment plant (Park et al., 2006) in relation to the values of some of the statistical indicators considered here. In addition the results of this study help to highlight what could be done to better control the effluents before and after treatment of the PAHs in the WWTPs.

## 2. Material and methods

### 2.1. Theoretical setup

A measure of molecular lipophilicity can be represented by the partition coefficient octanol-water ( $K_{ow}$ ), which represents the accumulation capacity in non-polar phases. This coefficient is widely used. According to US-EPA (1990), compounds with  $\log K_{ow}$  value higher than 3.5 are potentially dangerous for the environment. In relation to the environmental sector, the diffusive pathways of PAHs can change (Antizar-Ladislao et al., 2004). PAHs have a very low solubility in water, which decreases with an increase in molecular weight and with the presence of salts (*salting out*). The solubility can be measured with the constant  $K_s$ , expressed as Eq. (1) (Schlautman et al., 2004).

$$K_s = \{ \log [C_w / C_{w, sal}] \} / [salts] T \quad (1)$$

where:  $C_w$  = the concentration in pure water;  $C_{w, sal}$  = the concentration in water with ionic solutes;  $[salts]$   $T$  = the total concentration of ions.

Despite their low water solubility, PAHs are equally distributed in river basins, and due to rain wash out they end up in river sediments. In fact, if highly soluble compounds have a good dispersion capacity, less soluble PAHs have a great capacity to join water-suspended particles and hence be included in sediments. This phenomenon is described by the distribution coefficient  $K_p$  (Eq. 2):

$$K_p = C_s / C_w \quad (2)$$

where:  $C_s$  = the concentration in the solid phase, and  $C_w$  = the concentration in the water phase.

The determination of  $K_{om}$  (coefficient of distribution between organic matter and water) is important because it represents the trend of the distribution between water and solid phases and constitutes a normalized  $K_p$  with respect to the total amount of organic matter. As such,  $K_{om}$  depends on the total amount of organic carbon (TOC) and, therefore, represents the aqueous phase and the coefficient of distribution of the organic phase, associated with the solid material. Once determined  $K_{om}$  and TOC we can proceed with the determination of  $K_p$ , as follows (Eq. 3):

$$K_p = K_{om} \cdot TOC \quad (3)$$

The experimental method to analyze  $K_{om}$  is quite difficult, thus  $K_{om}$  can be assessed indirectly starting from  $K_{ow}$  given by the ratio between  $C_o$  (solubility in n-octanol of a specific compound) and  $C_w$  (solubility in water). In fact, n-octanol is the organic solvent that behaves most similarly to the organic matter present in environment. The  $K_{om}$  constant can be calculated using a simple empirical law, once the value of constant  $K_{ow}$  is known (Eq. 4):

$$K_{om} = A \log K_{ow} + B \quad (4)$$

where  $A$ ,  $B$  are constants and  $K_{om}$ ,  $K_{ow}$  are partition coefficients.

The PAH partition between water/solid substances depends on the solubility in water and in n-octanol and on the amount of organic matter in the related environment (TOC). Thus, combining the above mentioned equations gives Eq. (5):

$$K_p = (A \log C_o / C_w + B) \cdot TOC \quad (5)$$

where the path described includes the following steps:  $C_w \rightarrow K_{ow} \rightarrow K_{om} \rightarrow K_p$ .

The likelihood of an individual PAH being captured by a particulate increases with the increase in molecular weight.

The depositing of PAHs into sediments and over particles represents a sort of reserve, and the PAHs are slowly released back into the water. Thus soil contamination can cause groundwater contamination (Elsgaard et al., 2001; Jakob et al., 2012; Luciano et al., 2013; Meynet et al., 2012; Richardson et al., 2012).

Even in the case of groundwater, it is rare for contamination to be caused by a single PAH or a single hydro-carbon compound, however a mix of different pollutants is always found, which differs not only in terms of source, but also in terms any degradation caused by microorganisms, light, chemical agents (Xiao et al., 2008).

Some fractions of the part of the PAHs that are not completely mineralized in the treatment of the water line, can be found in the final discharge and end up in the environment, or they can remain trapped in the sludge (Alhafez et al., 2012; Brandli et al., 2007; Dai et al., 2007; Foan et al., 2012; Savić et al., 2016). The current trend is to evaluate the depurative efficiency of a WWTP not only on the basis of the removal of traditional indicators, but also on the removal of other contaminants (Byrns, 2001).

## 2.2. Description of WWTPs

The evaluation of PAHs and their removal efficiency in wastewaters was carried out at different WWTPs, using average values and considering only plants with a prevalent composition of domestic wastewater (60-75%) compared to industrial wastewater (25-40%, however compatible for quality characterization, to be added to domestic wastewaters in conventional treatment)(Table 1).

All four plants are conventional biologic treatment plants with mechanical pre-treatments (gridding, sand/oil removal and primary sedimentation), followed by biological treatment (activated sludge) and final sedimentation and disinfection. The sludge line is complete for all the plants, with anaerobic digestion, thickening, conditioning and final dewatering.

## 2.3. Samplings

The analytical methods used to evaluate the PAHs in the watery matrix included collecting and conserving several samples, extracting PAHs, removing any interfering compounds, and finally, verifying the presence of PAHs.

The following guidelines were also applied:

- respect the instrument specifications and the procedures adopted in order to obtain a sufficient number of samples for analysis;
- calculate the amount of lost PAHs, considering that the selected analytical procedures might involve partial losses of analytes;
- store and conserve the PAHs in sealed bottles, located in a dark and cool place to avoid fermentation and decomposition.

**Table 1.** Characteristics of the four WWTPs – average values

<i>Parameter</i>	<i>Unit</i>	<i>WWTP1</i>	<i>WWTP2</i>	<i>WWTP3</i>	<i>WWTP4</i>
Equivalent inhabitants		80,000	400,000	100,000	25,000
Inflow	[m <sup>3</sup> d <sup>-1</sup> ]	22,000	100,000	27,000	5,500
% urban	%	75	70	60	65
% industrial	%	25	30	40	35
WWTP1 layout	Water line: mechanical pre-treatment (gridding and sand/oil removal), biological treatment (activated sludge) and final sedimentation and disinfection. Sludge line: pre-thickening, anaerobic digestion, conditioning and mechanical dehydration.				
WWTP2 layout	Water line: mechanical pre-treatment (gridding, sand/oil removal and primary sedimentation), biological treatment (activated sludge) and final sedimentation and disinfection. Sludge line: pre- and post-thickening, anaerobic digestion, conditioning followed by the final dewatering.				
WWTP3 layout	Water line: mechanical pre-treatment (gridding, sand/oil removal and primary sedimentation), biological treatment (activated sludge) and final sedimentation and disinfection. Sludge line: pre-thickening, anaerobic digestion, conditioning and dewatering.				
WWTP4 layout	Water line: mechanical pre-treatment (gridding and sand/oil removal), biological treatment (activated sludge) and final sedimentation and disinfection. Sludge line: pre-thickening, anaerobic digestion, conditioning and dewatering.				

Sample collection took place on different days from February-November 2011, with different weather conditions (sunny, cloudy, rainy). Two different samples were collected on each day in three different locations at the plant (sample collection elapsed a specific time, which was defined after calculating the hydraulic retention time existing between the three sampling locations): position “A” just after the gridding device, representing the status at the process entrance; position “B” after the primary sedimentation or mechanical treatment; “C” after the disinfection device, representing the end of the process (water line). The samples were homogenized, lyophilized and purified before GC-MS analyses. Total PAHs (adsorbed and dissolved) were extracted by the liquid-liquid method and analyzed by HPLC and fluorescence revelations (analytical methods: EPA 8270 D2007).

The samples were purified using silica chromatographic columns and analyzed by gas chromatography (Agilent 6890 series system linked to a mass selective detector HP-5972) coupled with mass spectrometry. All solvents and reagents were of chromatographic grade. Calibration standard solutions, internal standards, laboratory and field blanks were routinely used to ensure the quality of results. The recovery of the method ranged between 65 and 85% for the studied PAHs.

At the beginning different types of PAHs were considered, but the low concentration levels focused our attention on a smaller group of compounds. The initial group was also considered in the light of the literature (Katsoyiannis and Samara, 2004; US-EPA, 1990), and consisted of naphthalene (Np), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[ $\alpha$ ]anthracene (B[ $\alpha$ ]An), chrysene (Chry), benzo[ $b$ ]fluoranthene (B[ $b$ ]Fl), benzo[ $k$ ]fluoranthene (B[ $k$ ]Fl), benzo[ $\alpha$ ]pyrene (B[ $\alpha$ ]Py), dibenzo[ $\alpha,h$ ]anthracene (dB[ $\alpha,h$ ]An), benzo[ $ghi$ ]perylene (B[ $ghi$ ]Pe), and indeno[1,2,3- $cd$ ]pyrene (IPy).

The restricted group of target compounds (characterized by significant concentration values of) included anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Chry) and benzo[ $\alpha$ ]anthracene (B[ $\alpha$ ]An). In addition Np, Ph, B[ $b$ ]Fl, B[ $\alpha$ ]Py, B[ $ghi$ ]Pe, B[ $k$ ]Fl and IPy were target compounds, but were always below the detection limits.

For each PAH the average concentration value was calculated, measured in the four WWTPs at the corresponding treatment stages. The lowest values were rejected. The total amount of sampling in 10 months of tests was  $108 \times 4 = 432$  for the watery matrix. Thus for each PAH, three concentrations were identified by evaluating the corresponding removal yields: the average concentration at the entrance of the WWTP, the average after the primary sedimentation (mechanical treatment), and the average after the secondary sedimentation (or disinfection). The removal yield was analyzed with the Eq. (6):

$$R = (C_{in} - C_{out}) \cdot C_{in} \quad (6)$$

where  $R$  is the removal efficiency,  $C_{in}$  and  $C_{out}$  are the concentrations entering and exiting each treatment, respectively.

### 3. Discussion and results

Table 2 shows the concentration averages in the wastewater inflow (stage A), after the primary sedimentation (stage B), after the secondary sedimentation (stage C) and the corresponding removal yields. A first result was that not all the 16 PAHs indicated by the technical literature (Torretta and Katsoyiannis, 2013; US-EPA, 1990) as the main pollutant in the group, are present in significant quantity in the wastewater to be treated. Among these, only a small group of five PAHs is on average present in the influent of all four considered WWTPs, with values between  $0.040 \mu\text{g L}^{-1}$  (B[ $\alpha$ ]An) and  $0.210 \mu\text{g L}^{-1}$  (Py).

**Table 2.** Values measured: rounded averages for the four WWTPs

Compound	$C_{in}$ at stage A	$C_{out}$ at stage B	Partial removal efficiency $R_{BA}$	$C_{out}$ at stage C	Partial removal efficiency $R_{CB}$	Total removal efficiency $R$
	$[\mu\text{g L}^{-1}]$	$[\mu\text{g L}^{-1}]$	$[\%]$	$[\mu\text{g L}^{-1}]$	$[\%]$	$[\%]$
An	0.050	0.022	56.0	0.008	61.3	83.0
Fl	0.170	0.069	59.4	0.028	59.4	83.5
Py	0.210	0.087	58.5	0.035	59.7	83.5
Chry	0.080	0.028	65.0	0.013	53.5	84.0
B[ $\alpha$ ]An	0.040	0.013	67.5	0.005	55.6	86.0

Even if we are considering low values of concentration, it is possible to underline that the percentage of removal related to the mechanical treatments results significant, with yields in the range of 56% (An) and 67.5% (B[ $\alpha$ ]An).

Considering the secondary treatment, in all the cases characterized by the activated sludge process, the removal yields range between 53.5% (Chry) and 61.3% (An) showing an opposite trend compared with the mechanical treatment. For example, the primary treatment results less efficient regarding An removal, whereas the secondary treatment presents the highest efficiency in terms of An abatement. Obviously the obtained results need to be considered with the necessary care, due to the quite low values of the concentrations, but they confirm the great variability and inconsistency among the measured data reported in previous studies (Blanchard et al., 2004; Manoli and Samara, 2008).

As a last step, a specific PAH measurement was taken at the end of the sludge treatment line, in order to evaluate any correlation between PAH concentration and the percentage of industrial wastewater inflow. The monthly average values were considered, regarding the four WWTPs at the end of the treatment (after dewatering). The total number of samplings was  $32 \times 4 = 128$  for sludge line. The average values are reported in the table 3.

Using the average values from all four WWTPs, a good correlation was found between the average concentration values and concentrations analyzed using FATE (the simulation model). The results show how, after primary sedimentation, there were no differences between the experimental (real) values and those calculated by FATE. The maximum difference in percentage between the observed removal and calculated removal was approximately 2-3%. Also in the final effluent, for some PAHs there was good agreement between the theoretical and experimental results, in other cases FATE underestimated the final results.

In order to examine a possible statistical correlation with various indicators of the physical-chemical compound properties, such as  $\log K_{ow}$  and  $\log K_H$ , the second step involved using the removal yields calculated after the primary treatment and after the biological stage. It appeared that in the mechanical treatment (after the primary sedimentation),

compounds with a  $\log K_{ow}$  value higher than 5 present a removal yield of between 60 and 66%, whereas compounds with a  $\log K_{ow}$  value higher than 3.6 and lower than 5 have a removal efficiency lower than 60% (Fig. 2). This result is important because compounds with a  $\log K_{ow}$  value higher than 3.5 are potentially dangerous for the environment and must be removed during mechanical treatments. It confirms the importance to consider the opportunity of not considering the mechanical treatment when, for example, a higher value of organic load is requested in the biological treatment in order to improve the denitrification process. This important aspect has to be considered evaluating the eventual consequences of this choice on PAHs removal.

During the biological treatment, biosorption, biotransformation, biodegradation and volatilization are the most common/effective/feasible removal processes. Within the activated sludge, the injection of diffused air can induce a transfer to the atmosphere (Manoli and Samara, 2008). As volatilization is strongly connected to Henry's law constant, a potential correlation can be revealed between the biological removal yield and the parameter  $\log K_H$ . In this case too, the statistical evaluations highlighted a good correlation (Fig. 3), according to the technical literature (Byrns, 2001; Manoli and Samara, 2008).

A final evaluation considering the PAHs in the dewatered sludge (Hua et al., 2008). The monthly average values of all the four WWTPs were considered, after the end of the treatment (after dewatering).

As in the water line, also in dewatered sludges the presence of Py resulted on average higher respect to the other PAHs. In fact, Py represents the 20% of the total amount of PAHs in the dehydrated sludges, whereas An has the less significant presence (<1%). Considering the occurrence of PAHs in the sludges, the aim of this study was in particular the evaluation of the correspondence with the percentage of industrial component in the wastewater inflow. In fact, as shown in Fig. 4, the proportion of industrial wastewater flowing into the WWTPs was significantly correlated with the total content of PAHs in the sewage sludge, indicating that the proportion of industrial wastewater plays an important role in the total concentration of PAHs in the sludge from different WWTPs.

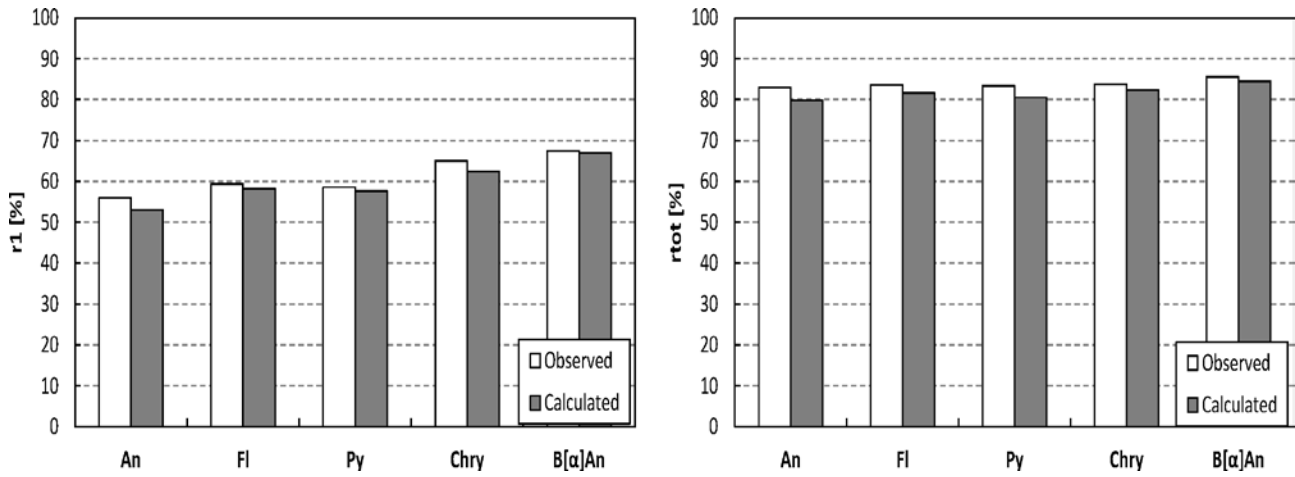


Fig. 1. Comparison between observed and calculated removal percentages

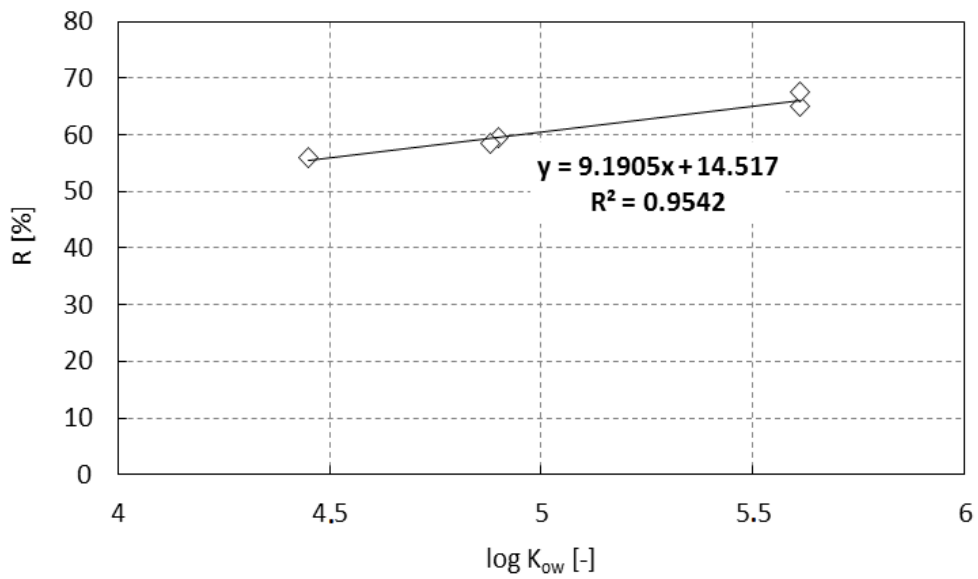


Fig. 2. Correlation between removal efficiency after primary treatment stage and  $\log K_{ow}$

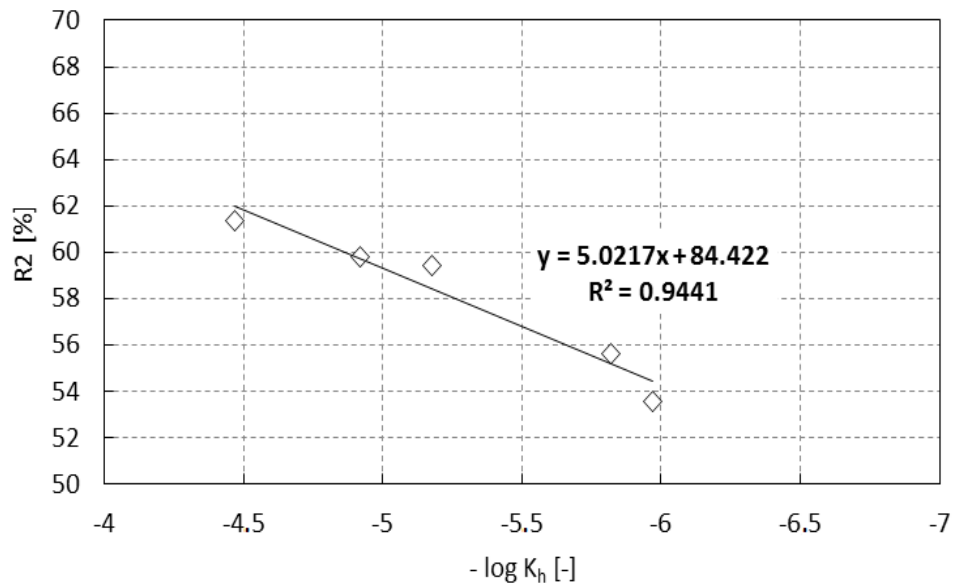


Fig. 3. Correlation between removal efficiency after secondary treatment stage ( $R_2$ ) and  $\log K_h$

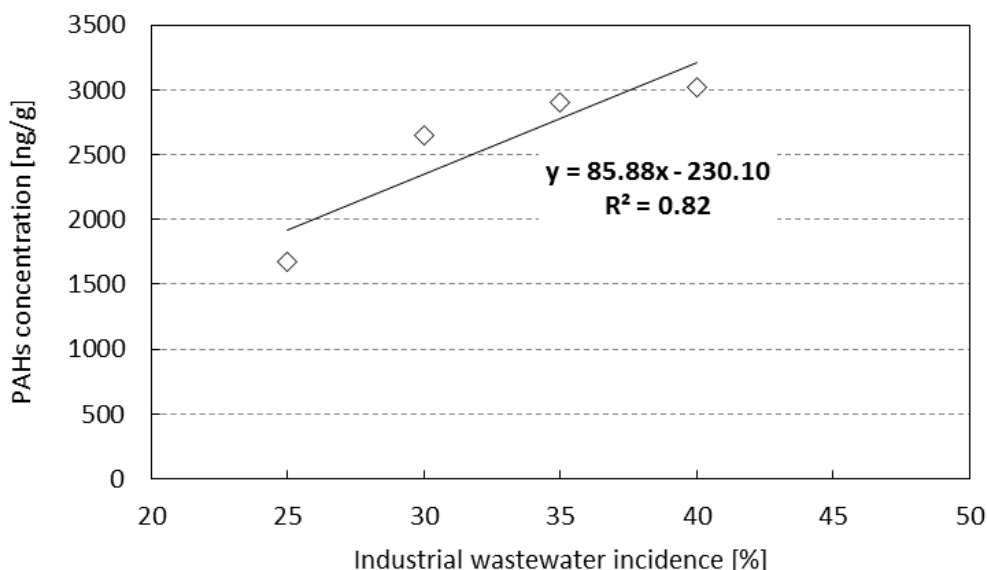


Fig. 4. Concentrations of PAHs in the sludge samples (monthly average)

Table 3. Concentrations of PAHs in the sludge samples (monthly average), final stage (after dewatering). Summary of values measured (rounded averages refer for the four WWTPs)

Compound	WWTP1	WWTP2	WWTP3	WWTP4
	[ng g <sup>-1</sup> ]	[ng g <sup>-1</sup> ]	[ng g <sup>-1</sup> ]	[ng g <sup>-1</sup> ]
Np	235	254	245	215
Ph	300	326	295	275
An	20	25	20	23
Fl	135	177	190	146
Py	350	543	650	510
BaA	170	302	250	400
Chr	160	385	380	490
BbF	60	115	160	140
BaP	35	62	60	70
BghiP	210	456	770	635
ΣPAHs	1675	2645	3020	2904

#### 4. Conclusions

PAHs represent a possible risk for human health, and due the public concern over possible exposure to PAHs, the general attention to this form of pollution increased a lot in the last years. The occurrence and fate of PAHs during wastewater treatment process was subject of several studies and experiences, but there is much inconsistency and variability among the data reported in the technical literature.

The removal of PAHs from municipal WWTPs was examined in four conventional WWTPs where the wastewater influent presents a significant percentage of industrial discharge. Two different approaches were employed for the quantification of removal yields of PAHs. The first approach was the experimental removal calculations, based on effective measurement campaign with sampling analysis, while the second one was the FATE (Fate and Trearability Estimator) predictive model application. Good agreement between the measured data and those calculated by FATE application was observed for the

whole process, but with a small underestimation of the final results by FATE.

In all our tests conducted at the considered WWTPs, the measured concentrations resulted below the limits fixed by regulations. However in a few cases a statistical analysis identified possible correlations between various compound chemical-physical indicators, such as  $\log K_{ow}$  and  $\log K_H$ , and PAH removal yield, considering different stages of the WWTPs.

Higher PAH concentrations enable evaluate the level of correlation to be evaluated between the PAH removal efficiency and the indicators. A strong correlation resulted between the mechanical treatment removal yield and  $\log K_{ow}$  and a very good correlation between yield measures after secondary sedimentation and  $\log K_H$ . This is because the process is strongly influenced by volatilization induced by air insufflation in the oxidation reactor.

Clearly, the presence of PAHs in wastewater inflows is related to the contribution of industrial wastewater. This is of great importance from an environmental point of view, considering the effects on surface water quality and soil quality due to water

effluent discharges from WWTPs and dewatered sludge disposal, respectively. Regarding the latter and considering the sludges, a good correlation was observed between the percentage of industrial wastewater in inflows and PAH presence in the sludges. The correlations that we found in the four WWTPs would suggest that the chemical and physical indicators outlined in this paper give an accurate picture of the presence of PAHs in WWTPs and in the related effluents. We thus believe that our results can be exploited in developing accurate controls of PAHs in the sewage treated at WWTPs, thereby ensuring higher removal rates. The result would be that the environment would be protected and the risk to human health reduced considerably.

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