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PAHs in wastewater: removal efficiency in a conventional wastewater treatment plant and comparison with model predictions

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Polycyclic aromatic hydrocarbons (PAHs) are very hazardous compounds and, owing to their lipophilicity, they can easily cross biological membranes and accumulate inside organisms, causing damage to the genetic material. The scientific interest in PAHs is related to their demonstrated or supposed genotoxicity (cancer-causing characteristics of B[α]Py and dB[α , h] first suspected in the 1930s). This study tried to detect the presence of PAHs in wastewater and to estimate their removal efficiency in a conventional wastewater treatment plant (Varese Olona). The PAHs' presence in municipal wastewater sewage system and in the WWTP effluent was determined by a specific analytical campaign, and afterwards a comparison between observed removal efficiency and FATE model (US-EPA) predictions was carried out.

Keywords: PAHs; wastewater; wastewater treatment plant; removal; modelling

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a very large class of organic compounds (more than 600), characterized by the presence of two or more aromatic rings joined by the co-division of a couple of carbon atoms making a single-structure generally oriented on a plane surface [1]. They do not contain heteroatoms (an atom that is not H or C). Polycyclic aromatic hydrocarbons have some physical–chemical characteristics in common (high boiling point and fusion, not very water soluble, high lipophilicity), such as:

- PAHs with two or three rings (simple structure) can be found in gas format at environmental temperature;
- PAHs with three or five ring (intermediate structure) can be found both as gas and as liquid, associated with suspended particulates;
- heavy compounds (five and more aromatic rings) exist only in aerosols (however, in high temperature emissions, PAHs can be gaseous); they can be inhaled, reaching the lungs (highest level of toxicity is related to the form with four to seven rings);
- linear structures are less stable than the ramified ones;
- PAHs with N-group have a greater carcinogenicity (for example PAHs contained in diesel engine emission).

With the exception of naphthalene, PAHs have a high fusion and boiling temperature, and usually a low vapour tension, that is inversely proportional to the number of rings and/or to molecular mass. The molecular structure

determines the stability: as already mentioned, a lower level of stability is related to the linear structure.

Polycyclic aromatic hydrocarbons are very hazardous compounds [2–3] and, because of their lipophilicity, they can easily cross biological membranes and accumulate inside organisms, causing damages to the genetic material.

A measure of the molecular lipophilicity is the octanol–water partition coefficient (K_{ow}), which represents the accumulation capacity in non-polar phases, as, for example, lipid tissues of organisms:

$$K_{ow} = \frac{[S]_{octanol}}{[S]_{water}}, \quad (1)$$

where [S] = the concentration of substance S expressed in ppm. This coefficient is widely used; according to the US EPA, compounds with a $\log K_{ow}$ value higher than 3.5 are potentially dangerous for the environment [13].

Diffusion pathways of PAHs are different in different environmental sectors: atmosphere, water and soil [4]; in particular, PAHs have a very low solubility in water, even if solubility increases when some organic liquids are presents. Solubility decreases with the increasing of molecular weight. Solubility decreases further if salts are present (*salting out*) and it can be measured by the constant K_s , expressed with the following formula:

$$K_s = \frac{\left\{ \log \left[\frac{C_w}{C_{w,sal}} \right] \right\}}{[salts]T}, \quad (2)$$

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where C_w = the concentration in pure water, $C_{w,sal}$ = the concentration in water with ionic solutes, and $[salts]_T$ = the total concentration of ions. This effect is very important in systems where saltiness can change (e.g. a fluvial estuary). An organic substance results more hydrophobic in contact with water when the constant value is higher.

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

$$K_p = \frac{C_s}{C_w}, \quad (3)$$

where C_s = the concentration in the solid phase, C_w = the concentration in the water phase. The coefficient depends on many factors, i.e. temperature, concentration and typology of ionic solutes, solid phase characteristics and presence of organic matter.

Moreover, K_{om} (distribution coefficient between organic matter and water) represents a normalized K_p compared with the total amount of organic matter present. The coefficient K_{om} assumes a relevant importance because the distribution trend between the water and solid phases depends on the total amount of organic carbon (TOC). Therefore, K_{om} is the water phase and organic phase distribution coefficient, associated with solid material; K_p can be calculated after the determination of K_{om} and TOC:

$$K_p = K_{om} \cdot TOC. \quad (4)$$

The experimental way to determine K_{om} is quite difficult, so it can be indirectly assessed from K_{ow} , given by the ratio between C_o (solubility in n-octanol of a specific compound) and C_w (solubility in water). As a matter of fact, n-octanol is the organic solvent having the most similar behaviour to organic matter present in the environment. It is possible to evaluate K_{om} using a simple empirical law, once the value of K_{ow} is known:

$$K_{om} = A \cdot \log K_{ow} + B, \quad (5)$$

where A and B are constants.

The partitioning of PAHs between water and solid substances will depend on the solubility in water and in n-octanol and on the quantity of organic matter (TOC) present in the environment under study. In conclusion, combining the above-mentioned equations, it is possible to obtain:

$$K_p = \left(\frac{A \log C_o}{C_w + B} \right) \cdot TOC, \quad (6)$$

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

The tendency of a single PAH to be captured by particulates grows with the increase in molecular weight. The deposition of PAHs in sediments and on particles represents a sort of reserve, and the slow release of PAHs causes a new presence in water. Thus soil contamination may cause groundwater contamination. Even in the case of groundwater, it is rare to face a contamination caused by a single PAH or a single hydrocarbon compound: a mix of different pollutants is usually found, whose composition can vary depending not only on the source but also on the eventual degradation caused by microorganism, light and chemical agents.

Important sources of PAH contamination in wastewater to be treated by a WWTP include tube and tank coatings, run-off water, the air and wastewater derived from human activities.

2. Material and methods

2.1. WWTP description

The evaluations of PAH presence in wastewater and PAH removal efficiency were made at Varese Olona WWTP (mixed wastewater: 70% domestic and 30% industrial with 80,000 as the population equivalent, calculated using BOD loading). It is a conventional biologic treatment plant with mechanical pretreatment (screening, sand/oil removal and primary sedimentation), followed by biological treatment (activated sludges process) and final sedimentation and disinfection. Treated water is discharged to the Olona river. The sludge line includes sludge anaerobic digestion and mechanical dehydration.

2.2. Sampling and analysis

The analytical methods used to determine the PAHs in the watery matrix involved the collection and conservation of several samples, PAH extraction, removal of interfering compounds, and final analytical determination of PAHs present. All these stages were done according to precise instruction, in order to avoid analytical errors. These steps had to be followed:

- respect the instruments' specifications and obtain a sufficient number of samples for the analysis phase;
- use some sagacity when evaluating the amount of lost PAHs, taking into account that the selected analytical procedures may cause a partial loss of analytes;
- store and conserve the PAHs in sealed bottles, in a dark and cool place to avoid fermentation and decomposition.

The sample collection took place on three, non-consecutive, days in February and March 2010, with different weather conditions (sunny, cloudy, rainy). Two different sets of samples were collected on each day (named 'P' and

'S': from *primo* and *second* – first and second in Italian) from three different locations at the plant: position 'A' just after the gridding device, representing the status at the process entrance; position 'B' after the primary sedimentation; 'C' after the disinfection device, representing the end of the process. A specific time elapsed between the 'P' and 'S' collections, defined after calculating the hydraulic retention time existing between the three sampling locations. So, on the first day, samples were collected at the three locations (A, B, C) at three times during the first phase (P), starting at 9.00 a.m. The period of time between the sampling was calculated on the basis of the incoming flow-rate measured at the sampling time and the volumes of the sedimentation and biological treatment steps. This procedure was followed for the next sampling as well. The third sample was collected at 9:57 p.m. The second phase (S) started at 1.30 p.m. at location 'A' and ended at 11.33 p.m. at location 'C'. Eighteen samples were collected in total.

The samples, managed according to well-known handling methods, were homogenized, lyophilized and purified before GC-MS determinations. Specifically, total PAHs (adsorbed and dissolved) were extracted by the liquid-liquid method and determined by HPLC and fluorescence detection (analytical method: EPA 8270 D2007). The identification of the different PAHs was based on the comparison with a solution which contains a known amount of the following PAHs [5–6]: naphthalene, acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[α]anthracene (B[α]An), chrysene (Chry), benzo[*b*]fluoranthene (B[*b*]Fl), benzo[*k*]fluoranthene (B[*k*]Fl), benzo[α]pyrene (B[α]Py), dibenzo[α,h]anthracene (dB[α,h]An), benzo[*ghi*]perylene (B[*ghi*]Pe) and indeno [1,2,3-*cd*]pyrene (IPy).

For each PAH, the partial reduction rate (after primary treatment) and the final rate (final effluent) were calculated.

2.3. Theoretical removal rate by FATE model

If the PAHs are not totally mineralized inside a treatment system, some fractions may be released to the surrounding environment in the final effluent or in the sludge or in the air [7–8]. The current trend foresees the evaluation of depurative efficiency of a WWTP based not only on the removal of traditional indicators but also on the removal of other contaminants [9].

Because of their hydrophobic behaviour, the PAHs are adsorbed on organic matter particles and, considering their affinity with particulates, are expected to be significantly removed during primary and secondary sedimentation.

To evaluate the PAH removal (including the 16 chosen for this experiment) in a traditional WWTP, the FATE (Fate and Treatability Estimator) model is frequently applied. This model was developed by the Technology Industrial Division of the US Environmental Protection Agency in

1990. The model consists of two sub-models: one to evaluate the removal of the organic fraction, the other to evaluate the inorganic one.

The 'organic' sub-model applied in this study takes into consideration the primary sedimentation, the aeration and the secondary sedimentation, considering the following removal processes: primary phase absorption and adsorption, and volatilization and biodegradation in the secondary phase. The outgoing concentration from primary sedimentation is assumed to be equal to the incoming one at the aeration tank and secondary sedimentation [11–12]. The outgoing pollutant concentrations from primary and secondary sedimentation are, respectively:

$$S_0 = \frac{QS_{in}}{[Q + Q_p X_p (4.1 \cdot 10^{-5}) K_{ow}^{0.35}]} \quad (7)$$

$$S = \frac{(QS_0)}{[(Q + \frac{GH}{RT} + Q_w X_v) (3.06 \cdot 10^6 K_{ow}^{0.67}) + K_1 X_a V]} \quad (8)$$

where

S_0 = organic pollutant concentration outgoing from primary sedimentation

$Q = Q_0$ = incoming flow rate = outgoing flow rate from secondary sedimentation (Q_c water + Q_w)

S_{in} = incoming organic pollutant concentration at WWTP

Q_p = sludge flow rate extracted from primary sedimentation

Q_w = sludge flow rate extracted from secondary sedimentation

X_p = dry substances concentration in primary sedimentation (%)

S = organic pollutant concentration outgoing from secondary sedimentation

X_v = pollutant concentration in secondary sludge

X_a = active cells concentration in the biological reactor (assumed as 0.64 of the SS in the mixed liquor)

G = air flow rate in aeration compartment

H = Henry's constant

$R = 8.206 \times 10^5$ ($m^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)

T = aeration compartment temperature

K_1 = first-order biodegradation coefficient

As already done with measured data, once the outgoing concentrations had been determined, the percentage removal values were calculated according to the model.

3. Results and discussion

A comparison between the real values, obtained from the analysis, and the values obtained from the FATE model was made. A specific spreadsheet was devised and used to allow this comparison. The spreadsheet guaranteed the traceability of the whole process and the correct application

Table 1. Comparison between observed and calculated removals.

	Observed removal (%)	Calculated removal (%)	Difference (%)
Anthracene	85.71	84	0.02
Fluoranthene	95.24	94	0.01
Pyrene	94.44	92	0.03
Chrysene	83.33	81	0.03
Benzo[α]anthracene	80	78	0.03

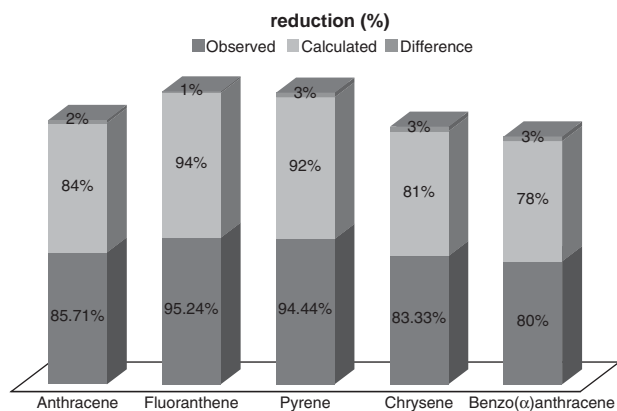


Figure 1. Removal percentages.

of the data (sampling date, position, lab acceptance date, etc.).

In the sampled matrix were found concentrations of: acenaphthene (Ace), dibenzo[α ,i]pyrene, dibenzo[α ,l]pyrene, naphthalene (Np), dibenzo(a,h)pyrene phenanthrene (Ph), anthracene (An), acenaphthylene (Acy), fluoranthene (B[k]Fl) and fluorene (F).

The obtained results show how, after primary sedimentation, there are no differences between experimental (real) values and calculated values (from FATE model). Anyway the concentration values measured with the analysis are very little and show small differences between the plant entrance and exit. The removal efficiency is, consequently, very low; for this reason, the test appears to be not representative.

In the final effluent, for all the analyses made, there is a substantial agreement between theoretical and experimental results for some PAHs; however, for other PAHs, the FATE model underestimates the final results. However, even in this case, the very low levels of concentration cannot allow further considerations about the results obtained (see Table 1 and Figure 1).

4. Conclusions

Polycyclic aromatic hydrocarbons are of concern for human health, but, in general, their presence in fresh water is not representative. In the experiment conducted at Varese WWTP, the measured concentrations were very low – well below the legal limits. The measurements were made

on different days and at different times of the day, with different weather conditions, but they always showed very low values.

The comparison with theoretical modelled values did not give representative results because of low pollutant concentrations; however, there was a small underestimation by the FATE model.

It was impossible to evaluate the connections between the PAHs' $\log K_{ow}$ and the removal efficiency, as foreseen at the beginning of the study.

It is the author's opinion that it may be more useful to repeat this experiment in another area, with a higher population density and with higher PAH values in the wastewater, and to define an analytical protocol which takes into account autumn–winter and spring–summer periods. Higher PAH concentrations may allow the evaluation of the level of correlation between the PAHs' $\log K_{ow}$ and the removal efficiency (particularly after primary sedimentation).

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