Polycyclic Aromatic Compounds

Distribution and Removal of Polycyclic Aromatic Hydrocarbons in Two Italian Municipal Wastewater Treatment Plants in 2011–2013

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Distribution and Removal of Polycyclic Aromatic Hydrocarbons in Two Italian Municipal Wastewater Treatment Plants in 2011–2013

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PAH (Polycyclic Aromatic Hydrocarbons) analyses were carried out on samples from two Wastewater Treatment Plants (WWTPs) in Lombardy, similar for treatment sequences but fed on different influents: industrial component accounts for 70% at Alto Seveso plant while it is absent in Nosedo plant. Sampling concerned the influent and the effluent from activated sludge reactor and the final effluent after disinfection (ozonation for Alto Seveso and peracetic acid treatment for Nosedo). The concentrations of total PAHs were 5.3 ± 4.0 μg L^{-1} and 2.4 ± 1.3 μg L^{-1} in Alto Seveso and Nosedo influent, respectively. The lowest molecular weight PAHs had the highest concentrations in both plants; acenaphthene and naphthalene were the most important components in the influent to Alto Seveso and Nosedo WWTPs, respectively. The higher molecular weight compounds had the lowest concentrations and benzo(g,h,i)perylene and dibenzo(a,h)anthracene were never detected. Most of the PAH load entered biological treatment in dissolved form. For both plants PAHs were mostly removed in the biological section (96.5% and 89.5% for Alto Seveso and Nosedo, respectively), while disinfection had a minor role. Peracetic acid (Nosedo) seemed more efficient than ozone (Alto Seveso) in the removal of PAHs (4.18% and 0.89%, respectively). It is now necessary to confirm this result by using the same effluent for the two disinfection treatments.

Key Words: Dissolved phase, economic crisis, particulate phase, Polycyclic Aromatic Hydrocarbons (PAH), wastewater treatment

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INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are environmental contaminants including a large number of molecules essentially made of two or more aromatic rings arranged in various configurations, differing among them in molecular weight and structure, octanol-water partition coefficient, etc. They are generally considered as a group of hazardous and toxic compounds and classified as priority pollutants according in the Water Framework Directive 2000/60/EC. Many of them have been identified to be potent carcinogens (1) and to bioaccumulate in food chains (2). 16 PAHs are included on the U.S. EPA and WHO list of priority pollutants to be monitored in water and wastes.

Their formation is related to incomplete combustion (related to natural fires or to anthropic activities) so that they are generally classified as atmospheric pollutants (3). Due to their origin and to the low water solubility of most of them, regulations for water discharge generally do not include limits for PAHs. They are frequently found in surface water where they are classified as hazardous pollutants and their concentration is one of the parameters contributing to water quality classification. EU Directive 105/2008, for instance, sets environmental quality standards in surface waters for fluoranthene (0.1 and 1 μg L^{-1} as Annual Average (AA) and Maximum Admissible Concentration (MAC), respectively), naphthalene (AA = 2.4 μg L^{-1}), anthracene (AA = 0.1 μg L^{-1}, MAC = 0.4 μg L^{-1}), benzo(a)pyrene (AA = 0.05 μg L^{-1}, MAC = 0.1 μg L^{-1}), and for the sums of benzo(b)fluoranthene and benzo(k)fluoranthene (AA = 0.03 μg L^{-1}) and of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene (AA = 0.002 μg L^{-1}).

The most widely accepted way PAHs reach surface water is related to atmospheric deposition, as non point source pollution. Wastewater may also contain significant PAH loads due to some industrial contribution, but, especially, to the input of runoff water in combined sewers. Studying the influence of rain on PAH concentration in wastewater in Paris area (France), Blanchard et al. (4) demonstrated that the contribution of the atmospheric compartment to PAH pollution of wastewater was minor with respect to the input from urban runoff, as also shown by Bomboi and Hernandez (5).

This last mechanism is responsible for the shift of non point loads to point source ones for different kinds of pollutants and micropollutants. The presence of pollutants in wastewater fed to wastewater treatment plants should allow their removal and, thus, the decrease of the load reaching surface waterbodies.

Significant removal of PAHs is reported for municipal wastewater treatment plants (WWTPs) (4, 6, 7). The experiments carried out by Wlodarczyk-Makula[6] showed that the removal was due to a significant extent to adsorption on sewage sludge. The following anaerobic digestion of the sludge involved a partial biodegradation of acenapthylene, chrysene, benzo(k)fluoranthene, naphthalene, and benzo(b)fluoranthene, while in the same conditions

acenaphtene, anthracene, fluorene, indeno(1,2,3-cd)pyrene, benzo(a) anthracene, and benzo(a)pyrene seemed to have been released in the gaseous phase. Lab scale experiments carried out by Manoli and Samara (8) showed the influence of volatilization on the removal of PAHs also during secondary treatment (more than 50% for anthracene). Tian et al. (2) found that biosorption, biotransformation/biodegradation, and volatilization were the most likely removal processes in the primary and secondary stages of WWTPs but that the extent of removal, in the different treatment steps, was strongly dependent on the physicochemical properties of each compound and was also affected by the influent concentration. Haritash and Kaushik (9) report that PAHs may undergo adsorption, volatilization, photolysis, and chemical degradation, but microbial degradation is the major degradation process in soil and water. Sun et al. (10), working with a PAH rich wastewater (15.2 μg L^{-1}) where the most abundant PAHs were naphthalene, benzo(g,h,i)perylene, and pyrene (accounting for 86.4%), found a significant relationship between the removal efficiency and log K_{ow} of the PAH compounds in the preliminary treatment stage for log K_{ow} higher than approximately 5.

As hydraulic retention time in WWTPs is normally much shorter than needed for biodegradation, it is likely that the dominant role in removal is played by other mechanisms, first of all adsorption, due to the high octanol/water partitioning coefficient of many PAHs. In many cases, then, the removal achievable in WWTPs is not enough to comply with the quality standard in the receiving waterbody: even where WWTPs includes chemical oxidation or Advanced Oxidation Processes, their efficiency on specific molecules may be reduced by the presence of a number of oxidant demanding substances in the influent.

Combined sewers are provided with overflows discharging untreated water during strong rain events, when the flow exceeds the acceptable level and this causes the point input of greater loads of various pollutants, PAHs included.

The critical aspect of PAH discharge is not related to the compliance to standard limits for discharge (which, as previously told, in most cases do not exist), but rather to the final concentration in the receptor. When the effluent input concerns low flow waterbodies, the so-called effluent dominated streams, where no dilution of the input load occurs, the target concentration in the effluent should be the same as the acceptable level in the receptor.

The present article includes the results of a series of analyses on the influent and the effluent of two WWTPs in the same geographic area but in different urban contexts. The aim of the research was to evaluate the input load of hazardous PAHs in the dissolved and in the solid fraction of wastewater, the contribution of the various sources to the input loads and the removal efficiency in the WWTPs.

The analyses were carried out in two consecutive years, in order to compare the results and to discuss them in the light of socio-economic factors.

EXPERIMENTAL

Description of the Wastewater Treatment Plants

The survey concerned two WWTPs in Lombardy, similar for treatment sequences (sieving, sand removal, degreasing, pre-denitrification, biological oxidation/nitrification – carried out in activated sludge systems-, secondary settling and disinfection) but fed on quite different influents. Alto Seveso WWTP (about 140,000 population equivalent (PE)) is located in the province of Como. About 70% of the COD (Chemical Oxygen Demand) load and about 40% of the flow entering the plant is of industrial origin and derives chiefly from textile dyeing settlements. Nosedo WWTP, located in the city of Milan, is much larger (2,550,000 PE). It receives only domestic sewage from Milan urban area through combined sewers carrying high flows of runoff water. Final disinfection is performed by peracetic acid (PAA) at Nosedo WWTP, while Alto Seveso WWTP has ozonation as final polishing step; moreover ozone is used to remove the residual colour present in the wastewater. As in many similar plants in this area, Alto Seveso WWTP, discharging into an effluent dominated streams, needs a strong color removal, and the most suitable solution is the ozonation (11).

Collection and Preparation of Samples

Wastewater samplings were carried out monthly from June 2011 to May 2012 in three points along the treatment processes, in dry weather conditions: the influent to biological treatment (In-BIO), downflow preliminary treatments; the effluent from biological treatment, after the secondary settling (Out-BIO) and the final effluent after ozonation (Out-O$_3$) and PAA disinfection (Out-PAA) processes, for Alto Seveso and Nosedo plants, respectively. A second sampling campaign was carried out in 2013 on the effluents from biological treatment (Out-BIO).

The samples were collected in pre-cleaned 2.5 L amber glass bottles and, immediately after collection, were transported to the laboratory in a cool bag. In the laboratory, samples were divided in four 200 mL aliquots. Each aliquot was vacuum filtered through GF/C filters (90 mm, 1.2 μm, Whatman International Ltd., Maidstone, UK) pre-treated at 450°C for 4 h in a muffle and pre-weighed. For each sample, one filtered wastewater aliquot (aqueous phase) and one filter with collected suspended solids (solid phase) were stored, respectively, at 4°C for maximum 12 hours and at −18°C for maximum 24 h before extraction processes. The remaining three filters were weighed, after drying at 105°C overnight, to obtain the concentration of suspended solids (mg L^{-1}).

Reagents and Materials

16 PAHs (naphtalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene,

benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah) anthracene, benzo(ghi)perylene, and indeno(1,2,3-c,d) pyrene) were purchased from Restek (Bellefonte, PA, USA) as a mixed solution at 2000 μg mL^{-1} in dichloromethane. Even if acenaphtylene was present in the mixture, it was non detected because weakly fluorescent.

The surrogate standard solutions, 1-methylanthracene (10 μg mL^{-1}) in cyclohexane and 6-methylchrysene (10 μg mL^{-1}) in acetonitrile, were obtained from Dr. Ehrenstorfer (Augsburg, Germany).

The solvents used for sample extraction (dichloromethane, isopropyl alcohol, dimethyl sulfoxide, and hexane) and for LC analyses (HPLC grade water and acetonitrile) were purchased from Panreac (Barcelona, Spain). Anhydrous sodium sulfate (Na_2SO_4) (Sigma-Aldrich, St. Louis, MO, USA) was heated at 450°C for 4 h and stored in a drier. Milli-Q water was obtained by a Millipore system.

Cartridges used for SPE were Oasis HLB (60 mg, 3 mL) from Waters (Milford, MA, USA). Oasis SPE polymer cartridges contained a balanced mixture of hydrophilic and lipophilic (HLB) monomers. A VAC ELUT SPS 24 (Varian, Palo Alto, CA, USA) was used to simultaneously process up to 24 SPE cartridges.

Samples were pre-concentrated by a Syncore automatic evaporator (Büchi, Flawil, Switzerland) and evaporated with nitrogen gas (Sapio, BG, Italy).

Dissolved Phase Extraction

The dissolved phase was extracted by SPE[12]. Before extraction, 30 mL of isopropyl alcohol were added to 200 mL of the filtered sample and the solution was mixed thoroughly to avoid adsorption of PAHs upon glassware. Then the surrogate standards (20 ng) were added. SPE cartridges were conditioned first with 5 mL of dichloromethane, then with 5 mL of isopropyl alcohol, and finally with 5 mL of a Milli-Q water and isopropyl alcohol solution (85:15, v/v). Thereafter, 200 mL aqueous phase samples were passed through the cartridges at a flow rate of 2.5 mL min^{-1}. Then the cartridges were rinsed with 5 mL of Milli-Q water and isopropyl alcohol solution (85:15, v/v) and then vacuum dried for 30 min. Finally, PAH elution was performed with 5 mL of dichloromethane and hexane (50:50, v/v). 50 μL of dimethyl sulfoxide were added to the extract to avoid the loss of light PAHs during evaporation process. Then the extract was evaporated at room temperature under a gentle nitrogen flux until only dimethyl sulfoxide was present. In the end, 950 μL of acetonitrile were added to reach 1 mL final volume (13).

Particulate Phase Samples Extraction

Particulate phase samples were put in a glass centrifuge tube, spiked with surrogate standards (20 ng) and, after 10 min, were extracted for 20 min with 30 mL of dichloromethane using an ultrasonic bath (14). Then solid-phase filter

was put out, 1 g of Na_2SO_4 was added and the solution was centrifuged for 20 min at 4000 rpm. The extract, after removing Na_2SO_4, was filtered through a 0.45 μm PTFE syringe filter and 50 μL of dimethyl sulfoxide were added. Thereafter the extract was transferred in a glass tube and pre-concentrated to 1 mL with Syncore evaporator (Büchi) at 36°C and 200 mbar. 1 mL was put in a vial and evaporated at room temperature under a gentle nitrogen flux until dimethyl sulfoxide only was present. Ultimately, 950 μL of acetonitrile were added to reach 1 mL final volume.

Instrumental Analysis

LC separations were performed in an HPLC-1100 system (Agilent, Santa Clara, CA, USA), using Vydac C18-RF column, 5 μm, 250 mm × 4.6 mm I.D. (Grace, Columbia, MD, USA) and coupled with a fluorescence detector (Agilent-1100). The column was kept at 30°C. Mobile phase was composed of a solvent A (water) and a solvent B (acetonitrile) at a constant flow rate of 1.5 mL min^{-1}. The gradient was programmed to increase the amount of solvent B from an initial 30% to 100% in 35 min, returning to the initial conditions (70% A) in 5 min. This condition was maintained until 5 min. The sample volume injected into the HPLC system was 20 μL. A mixed iso-concentrated solution (1000 μg L^{-1}) of PAHs, 1-methylantrhacene and 6-methylchrysene was prepared in acetonitrile. The solutions, for constructing the calibration curves, were prepared by dilution of the iso-concentrated solution with acetonitrile. The calibration curves ranged from 0–100 μg L^{-1} and the correlation coefficients (R^2) were > 0.998. The 0 μg L^{-1} values were determined analyzing the acetonitrile for three times. The LOD values were in the range $1.06 \cdot 10^{-3}$ – $14.27 \cdot 10^{-3}$ μg L^{-1} (calculated as LOD = 3*st.dev. blank, according to Miller and Miller (15).The mean surrogate recoveries for dissolved and particulate samples were: 1-methylantrhacene, 89±22 and 92 ± 19%; 6-methylchrysene, 68 ± 13 and 82 ± 5%, respectively. The PAH concentrations were corrected according to the recoveries of the surrogate standards. The PAH concentrations were also corrected subtracting the average values of concentrations in blank samples (n = 6). Finally, PAH concentrations determined in the extract were reported to the volume of the sample aliquots (200 mL).

RESULTS AND DISCUSSION

2011–2012

Inflow Concentrations

The concentration of total PAHs entering the WWTP secondary treatment stage is highly variable. In the period 2011–2012, average values are more

than double in Alto Seveso than in Nosedo WWTP (5.34 and 2.41 μg L^{-1}, respectively), as reported in Table 1. Both are in the same order of magnitude as literature data (2,16–20) while considerable differences are reported about the concentrations of the single compounds which have shown to be highly variable also within our analytical campaign. No specific information is available for PAH concentrations in wastewaters from textile dyeing industries.

In both cases, the most important fraction is made of 2 ring compounds, which are the most water soluble ones, representing 86 and 85% of the total in the two WWTPs, respectively.

Two rings compounds are the prevailing fraction both in dissolved and in particulate fraction in the two cases, as is shown in Figure 1, whereas the distribution of the other components differs for the greater importance of $\sum$PAH$_3$ in the particulate of Nosedo plant. The determinations on dissolved and particulate samples show that the concentrations of all the tested compounds were higher in the dissolved than in the particulate fraction in both plants. This is probably due to the fact that samplings were performed downflow from the primary treatments, where most of PAHs bound to the particulate matter had been removed (21). Opposite to Alto Seveso, in Nosedo samples the fraction of higher molecular weight (PAH$_4$ and PAH$_{5-6}$) is greater in the particulate than in the dissolved phase. This is likely to depend on the higher concentration of non ionic surfactants in the influent to Alto Seveso WWTP (about 7 mg L^{-1}) than in the influent to Nosedo WWTP (about 1.5 mg L^{-1}). The presence of non ionic surfactants, in fact, is reported to enhance the solubility of PAHs in wastewater (22) as well as their desorption from soil particles (23).

The most abundant compound is acenaphthene (PAH$_2$) for Alto Seveso, with 3.08 μg L^{-1} average total concentration (89% in dissolved form), and naphthalene (PAH$_2$) for Nosedo (2.38 μg L^{-1} average total concentration, 92% in dissolved form). The influent of Alto Seveso plant includes 70% industrial contribution from textile dyeing settlings and it is reported that
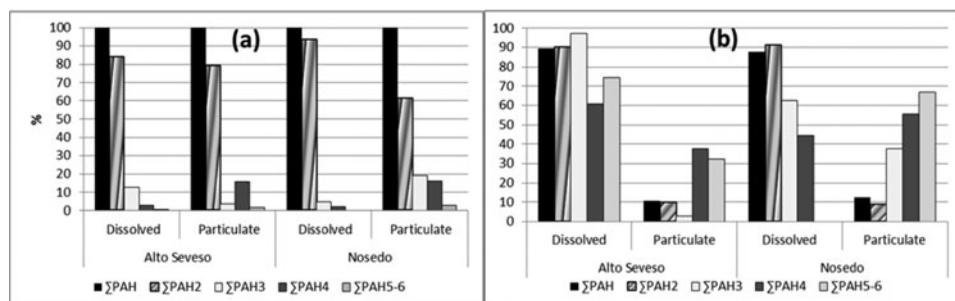
Figure 1: PAH groups analyzed at the inlet to secondary treatment. Percent distribution between dissolved and solid samples (a) and percent partition between dissolved and solid phase (b).

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Table 1: Average concentrations (μg L^{-1}) of total PAHs ($\sum$PAH) and of PAHs grouped by the number of aromatic rings ($\sum$PAH$_n$) at the secondary treatment inlet to Alto Seveso and Nosedo WWTPs in dissolved and particulate phases

	Alto Seveso			Nosedo		
	Dissolved phase	Particulate phase	Total	Dissolved phase	Particulate phase	Total
$\sum$PAH	4.77 ± 3.74	0.57 ± 0.23	5.34 ± 3.75	2.11 ± 1.12	0.3 ± 0.21	2.41 ± 1.14
$\sum$PAH$_2$	4.25 ± 2.77	0.46 ± 0.19	4.71 ± 2.78	1.97 ± 1.16	0.19 ± 0.16	2.16 ± 1.17
$\sum$PAH$_3$	0.64 ± 1.55	0.02 ± 0.02	0.66 ± 1.55	0.1 ± 0.04	0.06 ± 0.03	0.16 ± 0.05
$\sum$PAH$_4$	0.15 ± 0.03	0.09 ± 0.06	0.240 ± 0.07	0.04 ± 0.02	0.05 ± 0.03	0.09 ± 0.04
$\sum$PAH$_{5-6}$	0.02 ± 0.03	0.011 ± 0.006	0.031 ± 0.03	0.004 ± 0.002	0.008 ± 0.004	0.012 ± 0.004
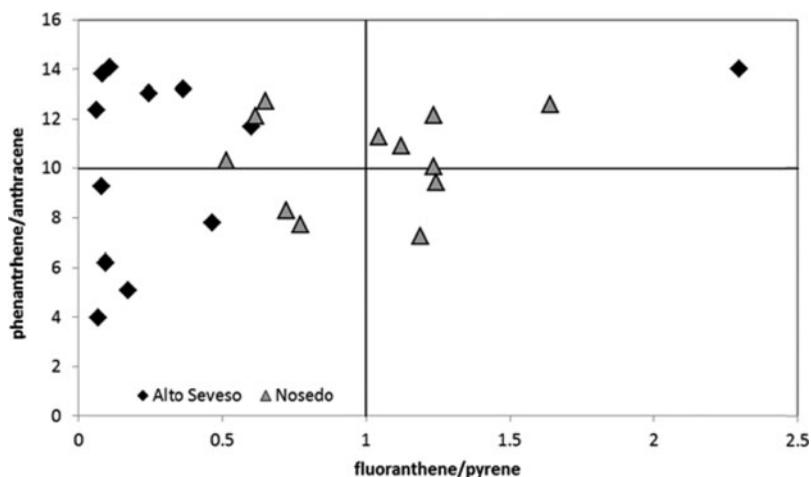
Figure 2: Ratio phenanthrene/anthracene vs, fluoranthene/pyrene in the influents to Alto Seveso and Nosedo WWTPs.

the lower molecular weight PAHs (naphthalene, acenaphtene, fluorene, and phenanthrene) are used in dye production (8). This could justify the high level of acenaphtene (73%) and naphthalene (27%).

On the contrary, Nosedo influent is only domestic, so the load of PAHs could be due to some household products containing them (e.g., naphthalene is used in powders, bathroom products, deodorants, and insecticides) (21).

In the other groups, the most represented compounds are phenanthrene, pyrene and benzo(a)pyrene for PAH_3, PAH_4 and PAH_{5-6}, respectively, but their concentrations are orders of magnitude lower.

The origin of PAH inputs was estimated basing on the ratios fluoranthene/pyrene and phenanthrene/anthracene, according to Sun et al. (24) and to Wang et al. (25). Values <1 for fluoranthene/pyrene ratio and >10 for phenanthrene/anthracene ratio would indicate a petrogenic origin of PAHs, meaning a direct input of PAHs in the sewers. Opposite to this situation, values >1 for fluoranthene/pyrene ratio and <10 for phenanthrene/anthracene ratio would be related to combustion (of various kinds of natural and synthetic compounds) and, thus, to the deposition from atmosphere and the following runoff.

The origin of the PAH loads does not seem to be clearly related to one source or another, while they probably depend on both as it is shown by the values of the above mentioned ratios, calculated on the basis of total concentrations, for all the analyzed samples for Alto Seveso and Nosedo WWTPs (Figure 2). On the other hand, the fact that samples have been collected only in dry weather conditions prevents to assess definitely the specific role of runoff.

Removal Efficiency

For 2011–2012 removal efficiency for the biological section (activated sludge + secondary settling) and for the disinfection was calculated as:

$$\% \text{ Removal } BIO = 100 \cdot (C_{in-BIO} - C_{out-BIO})/C_{in-BIO}$$

and

$$\% \text{ Removal } DIS = 100 \cdot (C_{out-BIO} - C_{out-DIS})/C_{out-BIO},$$

where $C_{out\text{-}DIS}$ is the PAH concentration in the effluent from the disinfection. The overall removal was equal to the sum of % Removal BIO and % Removal DIS.

It has to be considered that in both cases disinfection is an oxidative treatment, performed by means of different reagents, i.e., ozone for Alto Seveso and PAA for Nosedo WWTP, respectively, and could potentially affect the final concentrations of organic compounds.

In Figure 3, percent removal values are reported, and in Table 2 the concentrations at the outlet of the biological section (out-BIO) and of the disinfection treatment (out-O_3 or out-PAA) are reported. These concentrations were compared by *t*-test at 95% confidence level with the inlet concentrations (Table 1) and resulted significantly different, with the exception of the higher weight molecules (PAH_4 and $PAH_{5\text{-}6}$) in Nosedo plant.

The overall removal was comparable and very high for both plants (98% for Alto Seveso and 97% for Nosedo) and, as expected, depended essentially on the performance of the biological treatment. These results are in the same order of magnitude as literature data: Vogelsang et al. (26) reported a total
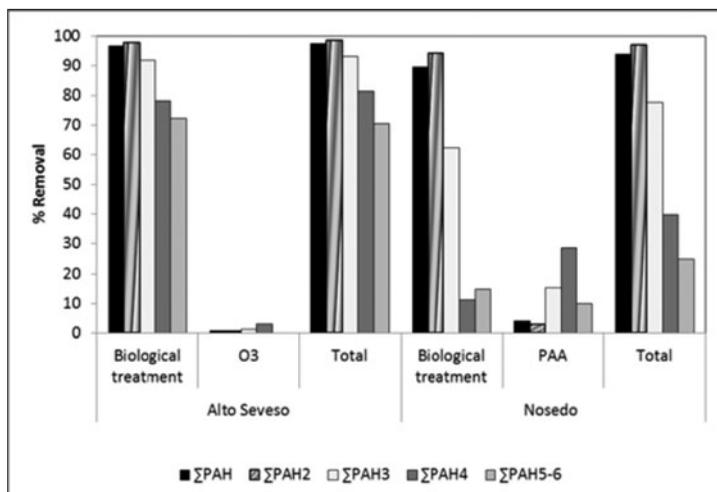
Figure 3: Percent removal of total PAHs and of the different groups in Alto Seveso and in Nosedo WWTPs.

Table 2: Average concentrations (sum of dissolved and particulate phase, μg L^{-1}) of total PAHs ($\sum$PAH) and of PAHs grouped by the number of aromatic rings ($\sum$PAH$_n$) outflowing biological treatment and disinfection in the two WWTPs

	Alto Seveso		Nosedo	
	out-BIO	out-O$_3$	out-BIO	out-PAA
$\sum$PAH	0.19 ± 0.16	0.15 ± 0.13	0.26 ± 0.16	0.15 ± 0.07
$\sum$PAH$_2$	0.11 ± 0.10	0.09 ± 0.08	0.21 ± 0.17	0.07 ± 0.07
$\sum$PAH$_3$	0.05 ± 0.03	0.04 ± 0.03	0.06 ± 0.04	0.04 ± 0.02
$\sum$PAH$_4$	0.06 ± 0.04	0.05 ± 0.04	0.08 ± 0.04	0.06 ± 0.02
$\sum$PAH$_{5-6}$	0.008 ± 0.004	0.009 ± 0.004	0.014 ± 0.008	0.013 ± 0.005

PAH removal (calculated for the whole of 16 EPA PAHs) of 94–100% in activated sludge plants with simultaneous chemical precipitation, while according to Fatone et al. (21) PAH removals in secondary treatment ranged from 10–90%. On the other hand, the removal in the biological section depends not only on biodegradation but also on adsorption. In our study, no mass balance could be done as we did not analyze sewage sludge, but the role of adsorption can be roughly estimated on the basis of the modified partitioning of PAHs between dissolved and particulate phase in the samples collected after secondary settling: the percent of total PAH in the dissolved phase decreased by 10% in Nosedo WWTP and by 15% in Alto Seveso WWTP and a corresponding increase was observed in the particulate phase. Such variations were chiefly due to variations in the partitioning of the smallest molecules (PAH$_2$).

Considering disinfection, PAA seems to be more effective than ozone. Only PAH removal with PAA (Nosedo plant) results are statistically significant (t-test at 95% confidence level). Alderman and Nyman (27), however, working with PAA concentrations in the order of percent, had obtained considerable PAH removal (removal of benzo(a)pyrene in 24 h was 60% with 1.7% PAA, > 80% with 9.2% PAA).

Due to the prevailing importance of PAH$_2$, in Alto Seveso plant the removal of PAH and PAH$_2$ are comparable, while for the larger molecules it was lower. These results can be explained by the higher biodegradability of smaller compound, as also reported by Vogelsang et al. (26) and by their high initial concentration. On the other hand, larger compounds are characterized by a higher number of double bonds which can be attacked by oxidation and are thus more likely to be removed by chemical treatment. However, their percent removal may be misleading because, as their starting concentrations are lower, small variations result in high percent values.

For Nosedo, the trend was similar for PAH and PAH$_2$, while the removal of PAH$_3$ was lower, but the starting concentration of this group compounds was a smaller fraction of the total with respect to Alto Seveso WWTP.
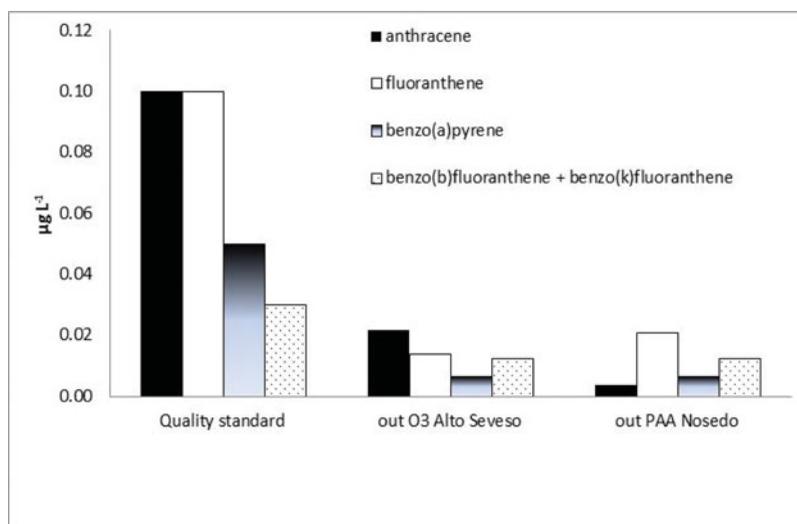
Figure 4: Comparison between the quality standards set by EU Directive 105/2008 for some PAHs and the average total concentrations (dissolved + particulate phase) measured in the two WWTPs.

Comparison with Water Quality Standards

As previously mentioned, no discharge standard exists for the concentrations of PAHs in treated effluents. However, where the receiving water body provides no dilution, as it is often the case in Italy (and, in particular, in the two considered case studies), the environmental impact of PAH (as well as of other hazardous pollutants) input to watercourses must be carefully evaluated. So, the obtained data have been compared to the quality standards for surface water set by the EU Directive 105/2008 which includes reference values for naphthalene (2.4 μg L^{-1}), anthracene (0.1 μg L^{-1}), fluoranthene (0.1 μg L^{-1}), benzo(a)pyrene (0.05 μg L^{-1}), and for the sums of benzo(b)fluoranthene and benzo(k)fluoranthene (0.03 μg L^{-1}), and of benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene (0.002 μg L^{-1}). Figure 4 shows that the concentrations of such compounds (considering the sum of total and dissolved forms in accordance to EU Directive 105/2008) at the outlet of WWTPs were below the water quality standards for anthracene, fluoranthene, benzo(a)pyrene and for the sum of benzo(b)fluoranthene and benzo(k)fluoranthene. For the sum of benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene in many cases the analytical result was below the LOD: for Alto Seveso and Nosedo WWTP benzo(g,h,i) perylene was always below the LOD; indeno (1,2,3-c,d) pyrene was below the LOD in 8 samples out of 12 for Alto Seveso WWTP and in 7 samples out of 12 for Nosedo WWTP. So, the overall average values have been calculated assuming that the values below the LOD were equal to half the LOD (i.e., 0.0005 μg L^{-1}). On the basis of such calculation, the value for Alto Seveso also complies with the water quality standard
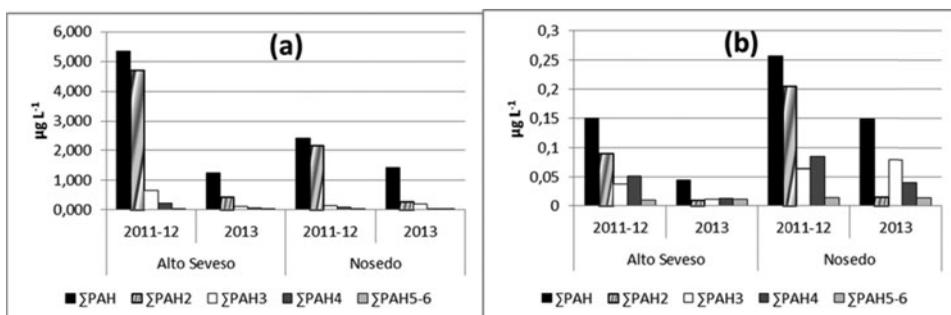
Figure 5: Comparison between the average of total PAHs (μg L^{-1}) and of the different groups at the inlet and at the outlet of biological treatment in Alto Seveso and in Nosedo WWTPs in 2011–2012 and in 2013 (2013 inlet data are calculated).

and the Nosedo one is just at the limit, being 0.0016 and 0.0024 μg L-1, respectively.

2013

In 2013 the analyses were performed only on samples collected after biological treatment. An estimate of the inflowing concentrations was thus made using the percent removal efficiency observed in 2011–2012 for the two WWTPs. The results are compared to the 2011–2012 data in Figure 5, along with a comparison between the analytical data at the outlet of biological treatment. A dramatic drop can be observed and is likely to depend on the effects of the economic crisis on both vehicular traffic and industrial production, which are also related between them. Data from INRIX Scorecard (28) show that, in Italy, traffic decreased by 34% in 2012 (32% in Milan area) and by a further 23% in the first 4 months of 2013, due to the fewer people driving to go to work (or elsewhere). In Italy, the correlation between the decrease of traffic and the increase of unemployment is very strong: according to the official Italian statistics (29), the unemployment has grown by 1.6% from April 2012 to April 2013 and the average industrial production in the first semester of 2013 has decreased by 4% with respect to the average value of the first semester of 2012. PAH emissions are strongly dependent on the type of vehicles and, especially, on the kind of fuel used (30), so, sound evaluations could be done only basing on specific investigations. However, due to the chief sources of PAH pollution, economic and social indicators can provide relevant information about the trend of the polluting load reaching wastewater and, thus, surface waters.

CONCLUSIONS

The results show that in 2011–2012 the influent concentration of total PAH was nearly double in the influent to Alto Seveso WWTP than in the influ-

ent to Nosedo WWTP. In both cases the ratio between selected compounds (phenanthrene/anthracene and fluoranthene/pyrene) shows that the primary source of PAHs could not be clearly identified as petrogenic or pyrolytic. Nosedo WWTP is located in the city of Milan, while Alto Seveso is in the province of Como, in a less urbanized area, but they belong to the same geographical area and are likely to receive comparable loads of atmospheric pollutants. For Alto Seveso the industrial contribution could play an important role, due to the significant industrial component in the influent, while Nosedo WWTP is only fed on municipal sewage and this could partly account for the observed difference.

Despite the different influent composition, the distribution of PAHs, based on the aromatic ring numbers ($PAH_2 > PAH_3 > PAH_4 > PAH_{5-6}$), was very similar in the two plants. PAH_2 were nearly 90% of the total PAHs (88% and 89% for Alto Seveso and Nosedo, respectively) and the most represented compounds, in the PAH_2 group, are acenaphtene for Alto Seveso and naphthalene for Nosedo.

PAHs were mostly removed in both plants in the biological section (activated sludge + secondary settling) while disinfection had a minor role. This could be expected, as the oxidant doses used for disinfection are enough to remove bacteria but too low to provide an effective chemical oxidation of organic pollutants. PAA (Nosedo) was more efficient than ozone (Alto Seveso) in the removal of PAHs after biological treatment, but no definite conclusion can be drawn on this point because only two plants were compared and treated wastewaters may have had differences explaining the different results obtained.

For both plants the concentrations in the effluent complied to the water quality standards set by EU Directive 105/2008 for naphthalene, anthracene, fluoranthene, benzo(a)pyrene, and for the sums of benzo(b)fluoranthene and benzo(k)fluoranthene and of benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene ($0.02~\mu g~L^{-1}$). This is particularly important because both plants discharge into small streams where the flow is made mostly or completely by the input effluents.

It is interesting to observe that the same analyses, repeated one year after, have shown the dramatic drop of concentration of PAHs in both treatment plants as a probable consequence of the economic crisis which was a cause of decrease of both vehicular traffic and industrial production, which are the main sources of PAH pollution.

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