Effectiveness of measures adopted for the reduction of nonylphenol emission in European river basins: a case study of the River Lambro, Northern Italy

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Abstract

According to the Water Framework Directive 2000/60/EC, nonylphenol (NP) has been included in the list of priority hazardous substances and subject to cessation or phasing out of discharges, emissions and losses within an appropriate timetable not exceeding 20 years. The present work analyzed monitoring data on NP and its precursors (mono- and di-ethoxylates, nonylphenol-mono-ethoxylate and nonylphenol-di-ethoxylate) collected in a highly impacted river basin in Northern Italy in order to assess the effectiveness of the adopted measures for NP reduction, during two monitoring campaigns in 2003/04 and 2009/10, respectively, before and after the entry into operation of three new wastewater treatment plants (WWTPs) in Milan. The River Lambro is the main source of pollutants also for the River Po and the Adriatic Sea. Data collected in the present work showed that in the last 7 years the reduction of the different analytes was from 70% to 90%. Most of the reduction can be attributed to the substitution of nonylphenolethoxylates in industrial uses as demonstrated by a survey in the textile industrial district. The entry into operation of the new municipal WWTPs in Milan contributes about 10% of the reduction of the total NP load discharged by the River Lambro.

Keywords: Monitoring; Nonylphenol; Nonylphenolethoxylates; Partitioning; Reduction measures; River quality

1. Introduction

In recent years an increasing number of studies found a global increase in harmful effects on the endocrine and reproductive systems both in animals and humans, such as alterations in sexual characteristics, decreased fertility and reduction in the rate of growth of the population (Park et al., 2010;

Meier *et al*., 2011; Giusti *et al*., 2013; Marques-Pinto & Carvalho, 2013; Souza *et al*., 2013). Several hypotheses have been put forward to explain the causes of such evidences; the incidence of endocrine disruption is generally attributed to the increasing spread in the environment of numerous chemical compounds which, due to their characteristic to interfere with the hormonal system, have been defined as endocrine disruptors. Some of these molecules are common in consumer products, such as phthalates and bisphenol A, additives of plastics, or the alkylphenols (AP), degradation products of alkylphenolethoxylates (APE), non-ionic surfactants employed for more than 40 years. Since the widespread use of APE in several industrial processes and domestic products, large quantities of these compounds and their transformation products have been dispersed in the aquatic environment, in particular by the effluents of municipal and industrial wastewater treatment plants (WWTPs). Municipal effluents in fact contain up to a few hundred micrograms per liter of APE (Ying *et al*., 2002), while effluents from paper or textile industries may contain much greater quantities, up to milligrams per liter (European Commission, 2002). In domestic detergents APE have been substituted by surfactants of lower environmental impact, such as alcohol ethoxylates, but APE cannot be replaced in many other industrial applications because of their efficacy combined with their low production costs.

Among the APE the most commonly used compounds are the nonylphenolethoxylates (NPE), which are used as emulsifying agents, wetting agents and dispersants, in products for household cleaning, for industrial detergents, for applications in the textile and metallurgic industry, as components in metal-working fluids, paper mills and in processing of coal, in agriculture, in the production of plastics, and also in the pharmaceutical industry of contraceptives as spermicides (Soares *et al*., 2008). NPE are degraded in nonylphenol (NP) and its short-chain ethoxylates (nonylphenol-mono-ethoxylate (NPE1) and nonylphenol-di-ethoxylate (NPE2)) (Ahel *et al.*, 1994a) (Figure 1).

In the 1990s the European production of NP was estimated to be about 80,000 t/year (European Commission, 2002). In the official documents of the EU or international organizations, data on production and commercialization of NP and NPE generally date back before the EU restrictions were introduced. Recently REACH (Registration, Evaluation, Authorisation and restriction of Chemicals) registration data reported that for branched 4-NP (CAS 85852-135-3) the total production and import is in the range of 10,000–100,000 t/year, while NPE (under CAS 8412-54-14) are registered in the range of 2,000–20,000 t/year (SUBSPORT, 2013).

As there was evidence that NPs elicit estrogenic activity on aquatic communities (Routledge & Sumpter, 1996), they have been subject to EU restrictive regulation on marketing and use since 2003 (Directive 2003/53/EC). The Directive, which should have been implemented in all Member States by the beginning of 2005, stated that NP and NPEs 'may not be placed on the market or used as a substance or constituent of preparations in concentrations equal to or higher than 0.1% by mass'. These restrictions for NP and NPEs were also confirmed and included in Annex XXVII of the REACH regulation (2006/1907/EC). From June 2013 (ED/69/2013) NPEs are included together with NP in the Candidate List for Annex XIV (Substances of Very High Concern, SVHC) because there is unequivocal scientific evidence that these compounds are precursors of NP in their environmental degradation (Mao *et al*., 2012).

According to the Water Framework Directive 2000/60/EC, NP has been included in the list of priority hazardous substances for aquatic ecosystems and therefore subject to cessation or phasing out of discharges, emissions and losses within an appropriate timetable not exceeding 20 years. During the transitional phase before elimination, two kinds of standards were set: environmental quality standard
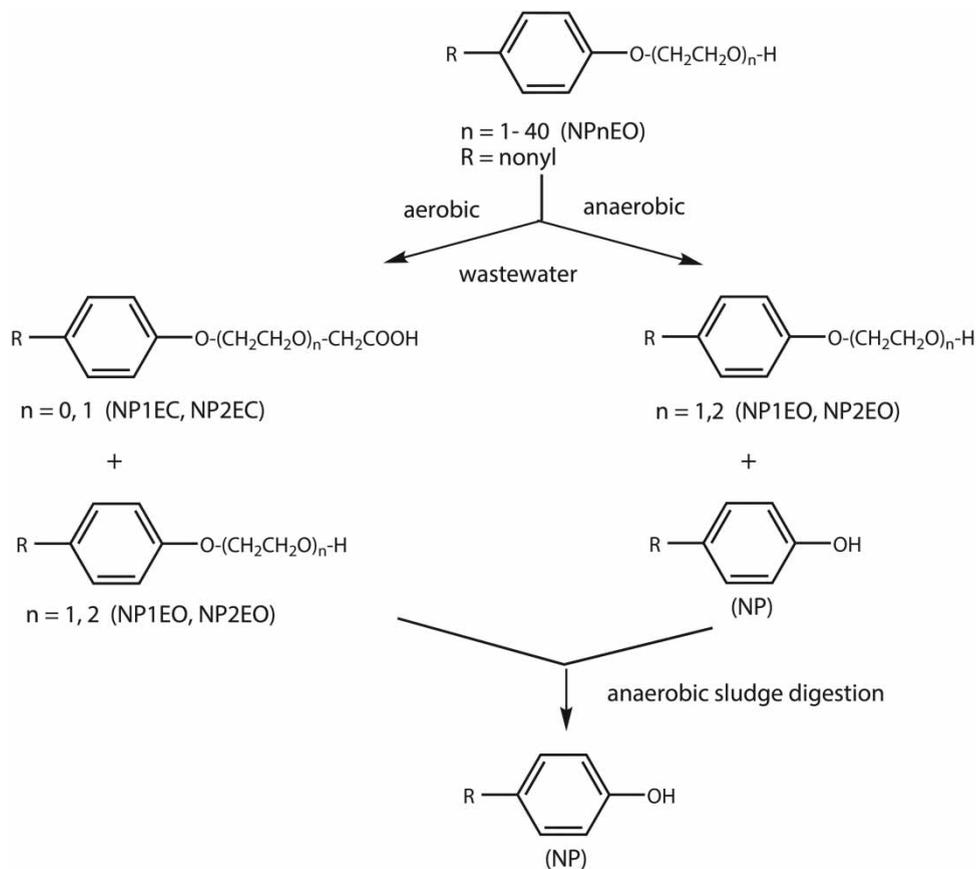
Fig. 1. Aerobic and anaerobic degradation of NPE; modified from Ahel *et al.* (1994a).

(EQS), which should be checked against the annual average of the concentrations, and maximum allowable concentration (MAC), which is the concentration that can never be exceeded since it refers to the acute toxicity of the compound. EQS and MAC for NP are 0.3 μg/L and 2.0 μg/L, respectively (Directive 2008/105/EC) and both of them refer to total concentrations measured in the 'whole water', i.e. water and suspended matter (Ademollo *et al.*, 2012).

Member States should provide programs of measures to achieve the goal of discharge reduction and to comply with the EQS. The adopted measures have been mainly restrictions in use and improvement of WWTPs.

The present work aims to study the concentrations and load trends of NP and its ethoxylates in a time lapse of about 7 years in order to verify the efficacy of normative and reduction measures in an impacted basin characterized by mixed urban and industrial sources. The selected study area was the basin of the River Lambro, a tributary of the River Po, which has already been demonstrated to be the principal source of NPs in the River Po (Mingazzini *et al.*, 2002; Viganò *et al.*, 2006), which in turn discharges into the Adriatic Sea, significantly impacting marine organisms (Ferrara *et al.*, 2001, 2005).

2. Materials and methods

2.1. Study area

The length of the River Lambro is 144 km and the catchment, with closure at Orio Litta, has an area of 1,950 km^2. The mean flow rate before flowing through Milan is about 12 m^3/s while at the basin closure it is about 60 m^3/s. Downstream of Monza, the River Lambro receives the discharge of the WWTP 'Consorzio Alto Lambro, ALSI', then downstream of Milan it is impacted by the waters of channel Vettabia, which receives discharges of the WWTP 'Milano Nosedo', Redefossi and Naviglio della Martesana, which collects waters from the River Seveso.

At Sant'Angelo Lodigiano the River Olona, called also the Southern Lambro, flows into the River Lambro, after having collected waters from an industrialized area (county of Varese) and from the WWTP 'Milano San Rocco'. A few kilometers after Sant'Angelo Lodigiano, the River Lambro flows into the River Po near Orio Litta (Figure 2).

The characteristics of the WWTPs sited within the study area are as follows:

- WWTP 'Consorzio Alto Lambro, ALSI' (TP1 in Figure 2), sited in Brugherio, treats the wastewater of approximately 480,000 inhabitants and 4,500 industrial facilities, with a size of about 700,000 population equivalent (p.e.). The plant has not been significantly renewed over the years.
- WWTP 'Milano Nosedo' (TP2) is located in south-east Milan. The first module with a capacity of 300,000 p.e. has been working since 22 April 2003, while the second module, with further treatment capacity for 600–700,000 p.e., has been working since 31 January 2004. The complete system has been working since 30 October 2004 and has a treatment capacity of 1,250,000 p.e.
- WWTP 'Milano San Rocco' (TP3) is located in the southern part of Milan. The Milano San Rocco plant, for the treatment of urban wastewater of 1,050,000 p.e., has been operating at its full potential since December 2004.
- WWTP 'Peschiera Borromeo' (TP4) is located east of Milan: on 20 June 2005 the second line treatment of the plant was inaugurated. The treatment capacity of the plant is 566,000 p.e.

With regard to the industrial sector, the main manufacturing classes affecting the study area are the following: textiles, chemicals and synthetic fibers, metal products, mechanical equipment manufacturing, and publishing.

2.2. Sampling period and stations

Data on NP and NPE are available for 2 yearly periods with a monthly sampling frequency: the first one from September 2003 to November 2004 (with a single further sampling in February 2005) represents the environmental situation before the restriction ratified by 2003/53/EC and preceding the commissioning of three WWTPs (Milano Nosedo, Milano San Rocco and Peschiera Borromeo, TP2-4); the second one from July 2009 to July 2010 takes a snapshot of the situation several years after the coming into force and operation of the legislative restriction and the new WWTPs.

Whole water sampling was performed monthly in Brugherio and Orio Litta sampling sites. The first station (Brugherio, north of Milan, S2 in Figure 2) is located downstream of the ALSI WWTP, which
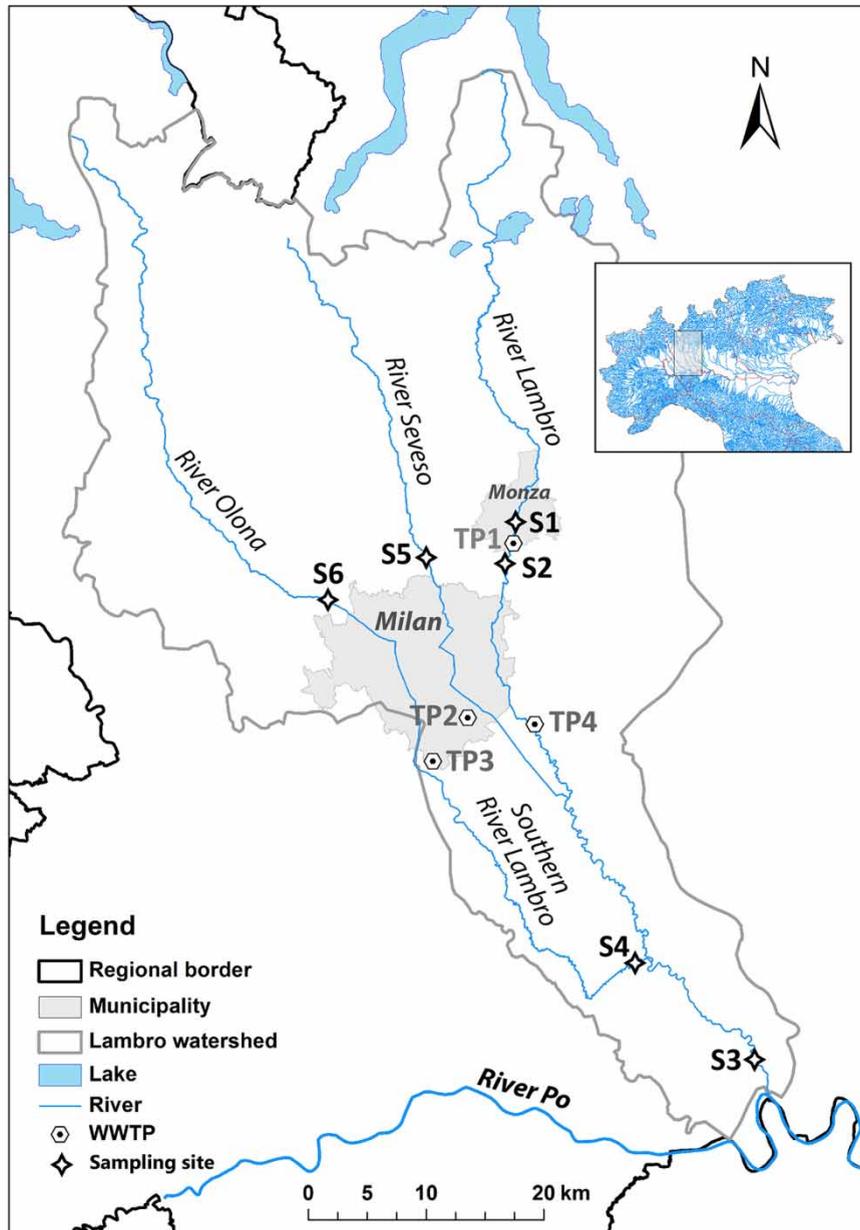
Fig. 2. Study area. S = Sampling site; S1: Upstream ALSI; S2: Brugherio; S3: Orio Litta; S4: S. Angelo Lodigiano; S5: Bresso; S6: Rho. TP = Wastewater treatment plant; TP1: WWTP Consorzio Alto Lambro (ALSI); TP2: WWTP Milano Nosedo; TP3: WWTP Milano San Rocco; TP4: WWTP Peschiera Borromeo.

has not been subject to any renovation or substantial change in sewage inputs since 2002; in this case any variation in NP concentrations can be attributed to modification in domestic or industrial uses of this compound. The second station (Orio Litta, S3) is sited at the basin closure and integrates any variation

in uses and treatments of NPs in the basin, including the opening of the new WWTP plants for Milan (TP2-4).

During both monitoring campaigns, in July, water samples were collected in further stations (S4–S6 Figure 2), which are representative of the most polluted and industrialized areas of the River Lambro basin; they are located on some of the tributaries of the Lambro River, which are mostly affected by human pressures: Sant'Angelo Lodigiano (S4) on the Southern Lambro, Bresso (S5) on the River Seveso, and Rho (S6) on the River Olona (Figure 2). The sampling station 'Upstream ALSI' (S1) represents the River Lambro in Monza, upstream of the ALSI WWTP (TP1) input.

2.3. Sampling and analytical methods

Grab samples of river waters were collected from river bridges using a stainless steel bucket and transported in dark glass bottles to the laboratory under refrigeration. For each site three replicates were collected. Samples were processed within 3 h of the sampling.

Analyte concentrations were analyzed in aqueous and in particulate phases, after separation by filtration. Whole water concentrations for compliance checking with EQS were obtained by summing.

A total of 10 L of water was collected from every sampling station into glass bottles, and solid particulate matter (SPM) was recovered by filtering through pre-combusted (4 h at 480 °C) and pre-weighed glass fiber filters (Whatman GF/F, 0.7 µm nominal pore size, 145 mm diameter). The filters were stored at −20 °C and, before extraction, dried at 50 °C overnight and reweighed to determine the particle loading. Dried filters, inserted in a glass fiber thimble, were extracted by an automated extractor (SER 148, Velp Scientifica, Usmate, Italy) based on the Randall technique: immersion for 2 h in 120 mL hot methanol (instrument plate temperature 260 °C) and then washing with solvent under reflux for 3 h. Methanol extracts were concentrated to 1–2 mL by rotary evaporation and transferred on to a column (1.5 cm i.d. × 4.5 cm length) containing neutral alumina deactivated with 15% water; the column was then eluted with 15 mL 10% acetic acid in methanol. The purified extracts were concentrated to 0.5 mL under a gentle stream of nitrogen using a TurboVap®II system (Zymark, USA) and filtered through a 0.45 µm PTFE filter before injection.

A total of 500 mL of filtered river water sample was extracted by solid phase extraction (SPE) on Strata C-18 cartridges (Phenomenex, 500 mg) previously conditioned by sequentially passing methanol (5 mL), acetone (10 mL) and high purity water (10 mL). After the sample loading, cartridges were eluted with 10 mL acetone and the extract was reduced to 0.5 mL under a nitrogen stream by using a TurboVap®II system (Zymark, USA).

Analytical separation was performed with a high-performance liquid chromatography system composed of a gradient PU-1580 pump (Jasco Corporation, Tokyo, Japan), with a 10 µL sample loop, and a FP-920 fluorescence detector (Jasco Corporation), set at λ_{exc} 230 nm and λ_{em} 302 nm. The separation was achieved on a Synergi Polar-RP (150 × 4.6 mm, 4 µm, Phenomenex) by using a mixture of water and methanol for the gradient elution. Quantification was carried out by external calibration with commercial standards purchased by Sigma Aldrich. The detection limits were in the range 0.02–0.03 µg/L and 0.03–0.06 µg/g d.w. for all the analytes, respectively, in aqueous and solid samples. Mean recoveries were in the range 82–96% for all the analytes. The method has also been validated through participation in intercalibration exercises (Loos *et al.*, 2008; Hanke *et al.*, 2012).

3. Results and discussion

3.1. Effectiveness of measures for NP reduction in River Lambro basin

The River Lambro flows through one of the most industrialized and populated areas in Italy around Milan (1,300,000 inhabitants). This river is the last receptor of other small but highly polluted tributaries, i.e. the River Olona and River Seveso, which collect discharges of a large area of about 1,500,000 p.e., including an important textile district in the area south of Como. Until 2003–2005 the critical status of the River Lambro basin was made worse by the absence of treatment plants for Milan: in those years the most important measure adopted by the local authorities was the building of three new WWTPs, pushed by an infringement procedure launched by the EU Commission in 1999.

Concentrations of NP, NPE1 and NPE2 in whole water, measured at the two stations (S2 and S3) before (2003/04) and after (2009/10) the adoption of reduction measures, are shown in Figure 3.
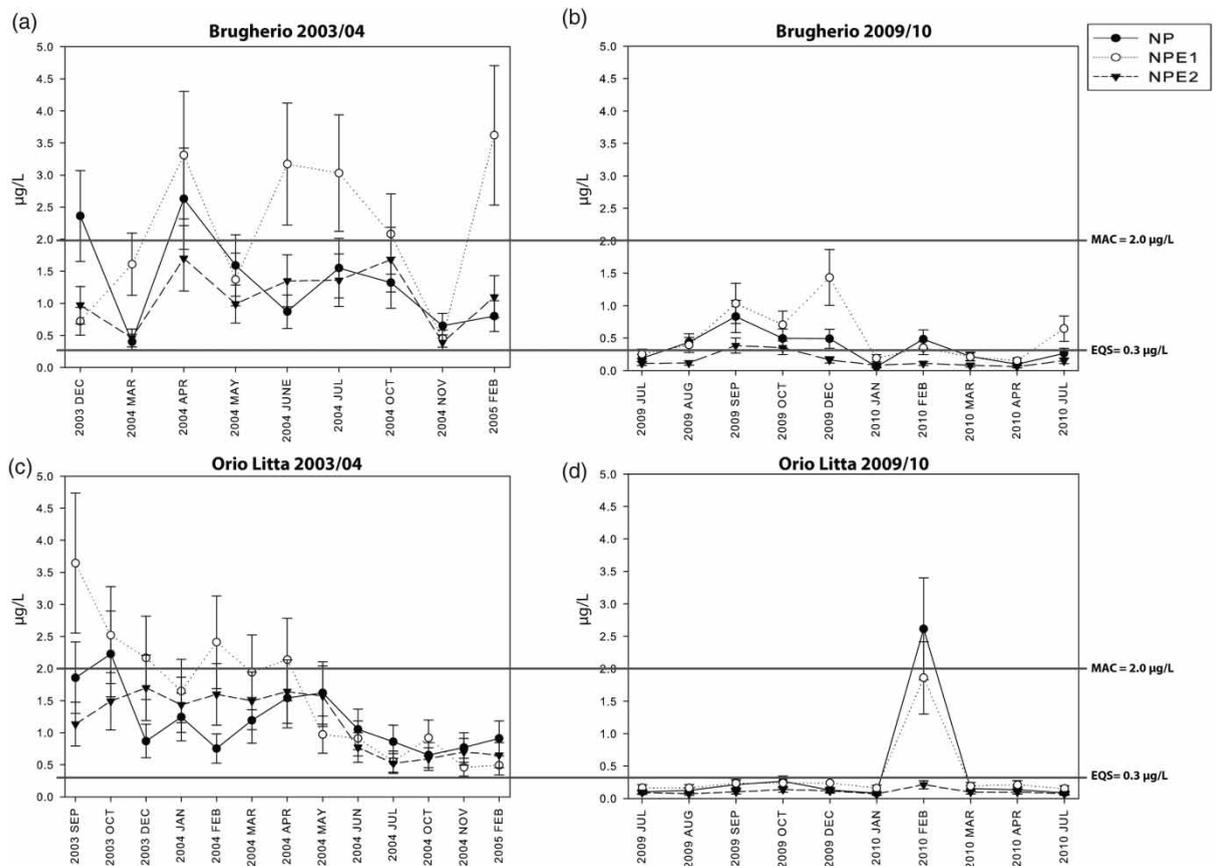

Fig. 3. NP, NPE1 and NPE2 concentrations measured in two sampling campaigns, in two sample sites: (a) Brugherio (S2) 2003/04, (b) Brugherio (S2) 2009/10, (c) Orio Litta (S3) 2003/04, (d) Orio Litta (S3) 2009/10. Bars are one standard deviation ($n = 3$).

At first glance it is evident that concentrations measured in the sampling periods are very different. During the 2003/04 campaign (Figure 3(a) and 3(c)) concentrations were constantly above the risk threshold identified by the value of EQSs (0.3 µg/L), while during the 2009/10 campaign (Figure 3(b) and 3(d)) there were only sporadic exceedances of the EQS of NP in Brugherio (S2), while in Orio Litta (S3) NP exceeded the EQS only once, also exceeding the MAC (2 µg/L) in this instance, in February 2010. This anomalous sample was collected just 2 days after an intentional and relevant (2,600 t) fuel oil spill into the River Lambro originating from an oil storage tank in Villasanta (MB). Thereby, NP concentrations in the water rose to 2.6 µg/L in Orio Litta, which is really different from the annual average concentrations (Figure 4(a)). It is interesting to note that as early as the following month the usual concentrations recovered.

The graph of Figure 3(c) shows a decrease, in the Orio Litta site, of the nonylphenolic compounds concentrations, especially for NPE1, in the last months of 2004, very likely because some modules of the new WWTPs in Milan had come into operation.

The boxplots in Figure 4 show the concentrations of NP, NPE1 and NPE2 in whole water sampled in the two sites during the two monitoring periods. In 2009/10, the outlier values of February 2010 were excluded. In 2003/04 data, variability was larger than in the later monitoring period (Figure 4(a)), and all data exceeded the EQS. On the contrary in 2009/10 the NP means (dotted line) were constantly below (at Orio Litta) or close (at Brugherio) to the EQS required by law (Figure 4(a)). A substantial decrease also for NPE1 and NPE2 during the years can be seen in Figure 4(b) and 4(c): these two compounds can be sources of NP during degradation in WWTPs. This decrease can be attributed to a reduced use of the compounds as well as a better efficiency of degradation in treatment plants.

Considering the percentage differences between the medians of the two monitoring campaigns calculated for Brugherio and Orio Litta (excluding the February 2010 sample for both stations), the decrease in NP concentrations in water was about 77% and 88% at Brugherio and Orio Litta, respectively. At the first station the decrease can be attributed to the reduction in the use of these substances due to normative restrictions, while at Orio Litta the entry into operation of the new WWTPs in Milan contributed to a further decrease of NP.

A recent review (Soares *et al.*, 2008) highlighted that concentrations of NPs in the environment are decreasing in developed countries. From our data we are able to calculate the reduction of the daily load
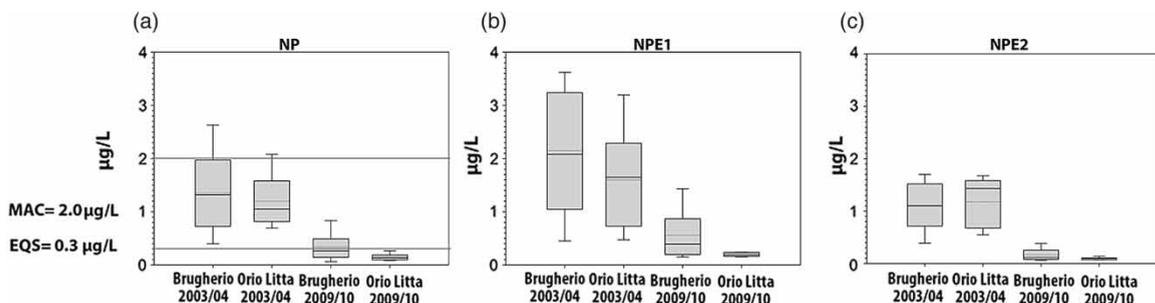

Fig. 4. NP (a), NPE1 (b) and NPE2 (c) concentrations in two sampling campaigns, in two sample sites (Brugherio (S2) 2003/04, Orio Litta (S3) 2003/04, Brugherio (S2) 2009/10, Orio Litta (S3) 2009/10). Vertical boxes represent 25th and 75th percentiles, whiskers are at 10th and 90th percentiles, median (continuous line) and mean (dotted line) values. (a) Mean values for NP are, respectively, from left to right 1.35 µg/L, 1.20 µg/L, 0.34 µg/L, 0.15 µg/L.

per inhabitant for nonylphenolic compounds in the two sampling points, starting from the average concentrations of the analytes, the average flow rates of the River Lambro, and the population equivalent that burdens those two sites (Table 1).

The data presented in Table 1 confirm the reduction from 70% to 90% of all the nonylphenolic compounds in this basin, and the highest reduction percentage has been obtained for NPE2.

To carry out a survey of the NP sources in the Lambro basin, in July 2004 and July 2010 sampling campaigns of the main tributaries, representative of the most polluted areas in the basin, were carried out: the sampling stations were Sant'Angelo Lodigiano (S4) on the Southern Lambro, Bresso (S5) on the River Seveso, and Rho (S6) on the River Olona (Figure 2). The sampling station 'Upstream ALSI' (S1) represents the River Lambro in Monza, upstream of the ALSI WWTP (TP1) discharge. In Figure 5 the concentrations of NP, NPE1 and NPE2 measured in the two different years are compared in order to appreciate the significant (*t*-test; $p < 0.05$) decrease in the concentrations of nonylphenolic compounds along the entire basin.

The concentrations of NP in the station Upstream ALSI were low and similar in both years, suggesting that the River Lambro has not been significantly affected by sewages up to Monza. On the contrary the substantial decrease of nonylphenolic compounds in all the tributaries of the River

Table 1. Daily load per population equivalent (p.e.) of nonylphenol (NP), nonylphenolmonoethoxylate (NPE1) and nonylphenoldiethoxylate (NPE2).

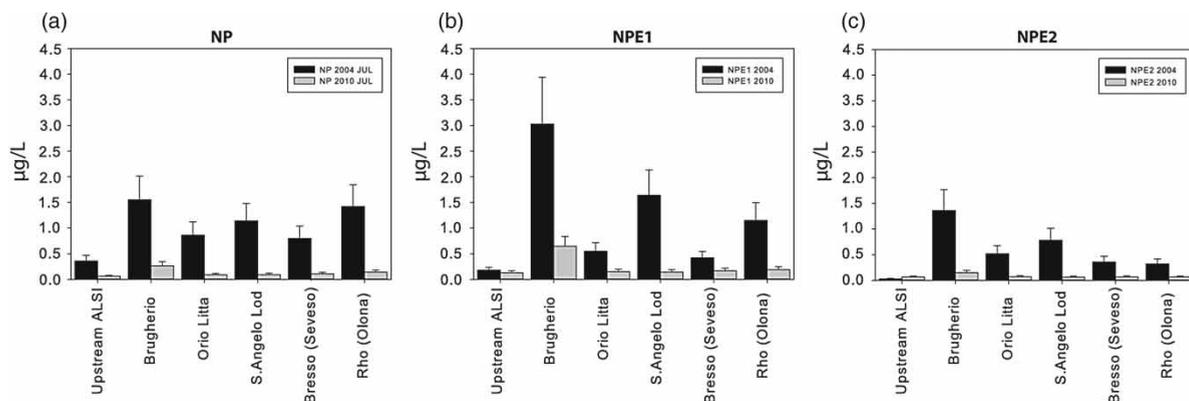|	NP	NPE1	NPE2
	mg/d p.e.		
Brugherio (S2) 2003/04	2.0	3.2	1.6
Brugherio (S2) 2009/10	0.5	0.8	0.2
Orio Litta (S3) 2003/04	2.2	2.9	2.1
Orio Litta (S3) 2009/10	0.7	0.7	0.2

Fig. 5. Concentrations of NP (a), NPE1 (b) and NPE2 (c) measured in the two different years (2004 July and 2010 July) in six sampling stations: Upstream ALSI (S1), Brugherio (S2), Orio Litta (S3), S. Angelo Lodigiano (S4), Bresso (S5), Rho (S6). Bars are one standard deviation ($n = 3$).

Lambro is evident, confirming the effectiveness of mitigation measures and NPE replacement in everyday products as required by the European Commission.

The reduced discharge of NP compounds from the River Lambro into the River Po can also be highlighted by the decreasing trend in NP concentrations measured in the River Po at the basin closure station in Pontelagoscuro (FE), Emilia Romagna region. The first data available on NP date back to 1994–96 when maximum concentrations up to 158 µg/L were measured (Davì & Gnudi, 1999); in January 2002 we measured 720 ng/L during an important event of drought (unpublished data); then an average of 66 ng/L was measured during a European intercalibration exercise in 2006 (Hanke *et al*., 2012) and, finally, monitoring carried out in 2009/10 by the local water company shows that NP in the River Po is always under detection limits (<0.50 ng/L) by then (Hera, 2011).

3.2. NP partitioning and whole water monitoring

As indicated by the legislation, the analyte concentrations must be measured in the whole water, since the measurement of the dissolved fraction underestimates the total concentrations in water for lipophilic compounds (Ademollo *et al*., 2012). Owing to the medium lipophilicity of these compounds ($\log K_{ow}$: NP 4.48; NPE1 4.17; NPE2 4.20; Ahel & Giger, 1993), they can adsorb on the particulate phase in function of river regime, suspended matter concentration and organic carbon (Ahel *et al*., 1994b; Ferguson *et al*., 2001). The process is regulated at the equilibrium by the partition coefficient that is expressed as the ratio between concentration in SPM and concentration in water (Karickoff *et al*., 1979). Although dissolved and particulate organic carbon are generally considered significant parameters in NP partitioning (Arditsoglou & Voutsa, 2010), plots of NP concentrations in water or SPM versus dissolved organic carbon (DOC) or particulate organic carbon (POC) content for the two sampling seasons (figures not shown) indicate that there is not a significant correlation ($p > 0.05$) between the analyte concentrations and the organic carbon amount.

Figure 6 shows the percentage distribution of NPs between aqueous and solid phase for each sampling data. Percentages in solid phase ranged from 14% to 76% and from 4% to 53%, respectively, in Brugherio 2003/04 and 2009/10, while in Orio Litta they ranged from 13% to 66% and from 2% to 13%, respectively, in 2003/04 and 2009/10. Throughout, the 2003/04 partition data had a large variability, which has been clearly reduced in 2009/10 in Orio Litta. One important source of variability is the hydrological regimes as exemplified by comparing the data collected in May and July 2004 in both sampling sites, Brugherio and Orio Litta: samples collected during a high flow event (266 m³/s in May 2004) had the highest percentage in SPM, greater than 50%, while samples collected during low discharge (63 m³/s in July 2004) showed the minimum percentages (about 15%). A high flow rate in the river greatly affects the partitioning in favor of the fraction adsorbed and carried on SPM. In the former hydrological condition, the high solid phase partitioning could be explained by the run-off or re-suspension of NP-enriched sediment (Meyer *et al*., 2007). Our data are in agreement with Li *et al*. (2004) who found in the Han River (Korea) 60% of NPs in suspended particles during the rainy season and only 28% during the dry season.

As shown in the histograms in Figure 6, during the 2003/04 monitoring campaign the contribution of the particle-bound NP to the total concentration was more important than in the most recent campaigns in Brugherio (S2) and Orio Litta (S3). The decrease in Orio Litta was greater than in Brugherio and this fact confirms that the implementation of the new WWTPs has been effective in the reduction of SPM by sedimentation.
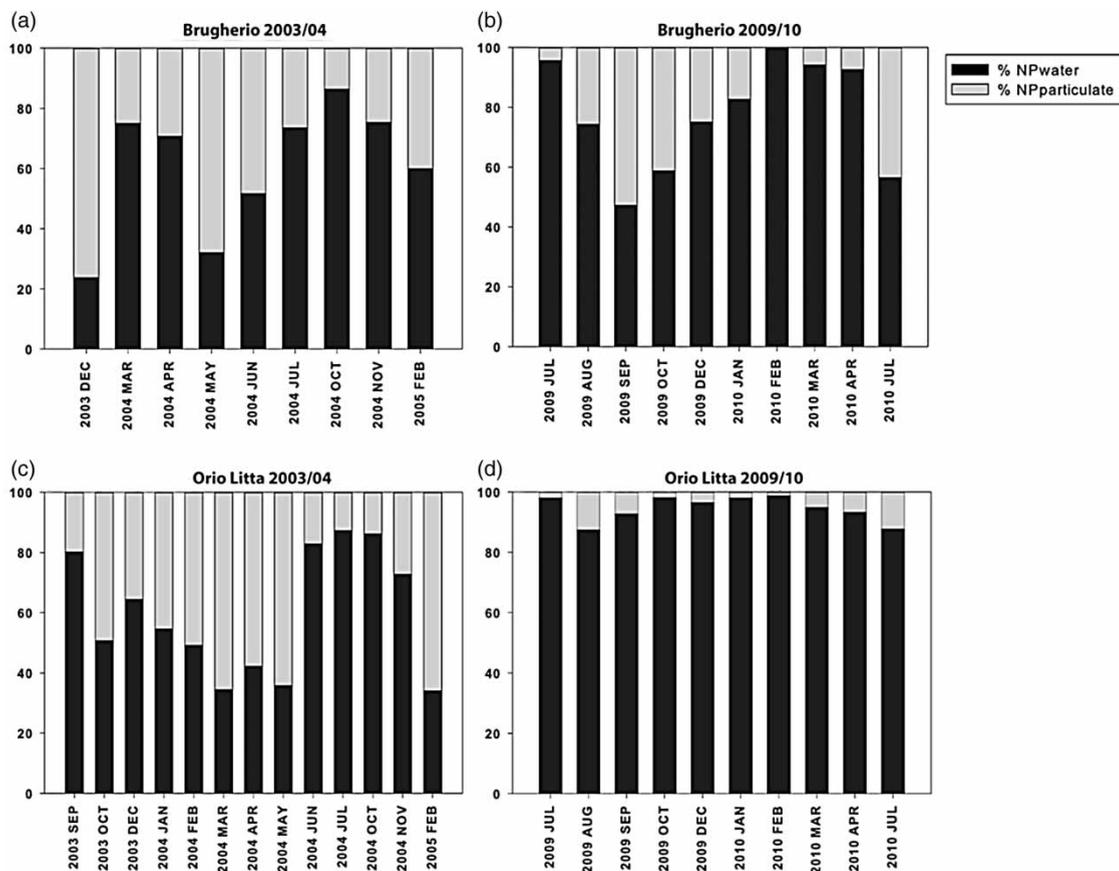
Fig. 6. Percentage of NP dissolved in water vs percentage adsorbed to SPM in two sampling campaigns, in two sample sites: (a) Brugherio (S2) 2003/04, (b) Brugherio (S2) 2009/10, (c) Orio Litta (S3) 2003/04, (d) Orio Litta (S3) 2009/10.

Experimental K_{oc}s were calculated according to the equation reported by Isobe *et al*. (2001), which approximately represents the equilibrium state:

$$K_{oc} = (C_s/C_w)/f_{oc}$$

C_w (µg/L) and C_s (µg/kg) are, respectively, the analyte concentrations in water and SPM, and f_{oc} is the organic carbon mass fraction of the SPM. Table 2 summarizes minimum, maximum and mean values of calculated log K_{oc} in both sites in both sampling periods.

As shown in Table 2, the experimental log K_{oc}s decreased over the years, more markedly at Orio Litta than at Brugherio (22% and 11%, respectively, calculated on mean values for NP) so that the minimum values were very close to the theoretical log K_{oc} that represents the partitioning equilibrium. Theoretical log K_{oc}s, predicted from K_{ow}s according to the equation reported in Sabljic *et al*. (1995), are 3.63, 3.46 and 3.47.

The field-measured K_{oc}s are generally much higher than those predicted by K_{ow} (Ferguson *et al*., 2001; Heemken *et al*., 2001; Patrolecco *et al*., 2006; Wang *et al*., 2006; Arditsoglou & Voutsa,

Table 2. Calculated log K_{oc} for NP, NPE1 and NPE2; minimum, maximum and mean values.

	NP			NPE1			NPE2		
	min	max	mean	min	max	mean	min	max	mean
Brugherio (S2) 2003/04	4.54	5.43	5.04	4.21	5.38	4.95	4.61	5.13	4.95
Orio Litta (S3) 2003/04	4.94	5.52	5.26	4.75	5.35	5.04	4.60	5.37	5.01
Brugherio (S2) 2009/10	4.04	5.31	4.74	4.28	5.33	4.73	4.15	5.47	4.65
Orio Litta (S3) 2009/10	3.67	4.80	4.21	3.81	4.84	4.42	3.64	5.44	4.34
Theoretical[a]			3.63			3.46			3.47

[a]Sabljic *et al.* (1995).

2010), and the common interpretation is that nonspecific hydrophobic interactions are not the predominant sorption mechanism for this group of compounds, and other chemical interactions such as hydrophilic interaction with mineral components (John *et al.*, 2000) may occur.

In our case, particularly in 2003/04, the enrichment in SPM could be derived from the sewage emission of particulates, enriched in particle-bound NP or nonylphenolethoxylate surfactants, which can degrade in NP in river conditions (Ahel *et al.*, 1994b). In 2009/10 at a sampling site very close to a WWTP discharge (Brugherio), the SPM percentage is still relevant, while at Orio Litta, after the introduction of modern WWTPs in Milan and the consequent effective abatement of particulates, the field-measured log K_{oc} tends to theoretical values, showing that this riverine system, at the basin closure, is close to a pseudo-equilibrium state.

As a practical consequence in monitoring, we can conclude that at the river basin closure the NP determination can be carried out on the dissolved phase without a relevant loss in accuracy, but whole water analysis, which is much more expensive and time-consuming, is still necessary in sampling sites downstream of the main sources such as WWTPs.

4. Conclusions

The inclusion of NP into the priority substance list of the Water Framework Directive led to the adoption of control measures that, at European level, were based on restrictions in NP and NPE use imposed by a specific regulation (Directive 2003/53/EC), but which, at local and national level, should mainly act on the improvement of treatment facilities in order to reduce emission sources. In this context, a key policy question is how the effectiveness of the adopted measures can be estimated: thereby, several models have been proposed and applied to target molecules (see e.g. Marinov *et al.*, 2014) but they need to be validated by field measurements.

The present work analyzed monitoring data on NP and its short-chain precursors collected in a highly impacted river basin in Northern Italy in order to assess the effectiveness of the adopted measures for emission reduction. The availability of data collected in stations subject to different pressures and where different measures have been undertaken allowed us to differentiate the effectiveness of the various reduction approaches.

Data collected in the present work showed that in the last 7 years the reduction of the different analytes was from 70% to 90% of all the nonylphenolic compounds in the studied basin. From the data analysis we attributed most of the reduction to the substitution of NPE in industrial uses. The entry

into operation of new WWTPs for the treatment of urban sewage in Milan contributed a further 10% to the reduction of the total nonylphenolic load discharged by the River Lambro into the River Po. The plant efficiency in sedimentation reduces the supply of SPM to the river from the city, and, as a consequence, the fraction of NP bound to particles. Thereby, nonylphenolic compounds discharged by the River Lambro are for more than 90% in the dissolved phase, reducing also the risk of NP deposition in the River Po sediment during the mixing of the two river waters.

The significant decrease in concentrations in the last 7 years is a positive signal for a future definitive elimination of these molecules from the aquatic environment and demonstrates the effectiveness of the control measures that the European Union put in place against priority hazardous substances. The confirmation of a continuous concentration reduction of NP and NPE compounds over time could also lead to a reduction of monitoring costs and resources allocated for the control of the substance NP.

Acknowledgements

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