Alkylphenols in atmospheric depositions and urban runoff
A. Bressy, M. -C. Gromaire, C. Lorgeoux and G. Chebbo

ABSTRACT
A sampling campaign was conducted in order to determine alkylphenol (AP) concentrations in stormwater as well as potential AP sources in suburban environments. An analytical procedure was developed to quantify APs in bulk atmospheric deposition, building runoff, road runoff and stormwater. Both nonylphenols and octylphenols could be quantified in each sample. Median stormwater concentrations amounted to: 470 ng/l for nonylphenols, and 36 ng/l for octylphenols. These concentrations are 3 times higher than those found in atmospheric deposition, thus proving that local human activity constitutes a significant source of contamination. The contributions of the various sources to stormwater have been assessed from mass balances at the catchment scale. 70% of AP mass in stormwater originates from building and road emissions. Annual AP fluxes have been extrapolated from the total AP mass measured over our sampling periods for atmospheric depositions (44 to 84 μgNP/m²/yr) and stormwater (100 to 190 μgNP/m²/yr).

Moreover, since APs were mainly found in the dissolved fraction, runoff treatment devices based on settling are unlikely to be very efficient.

Key words | alkylphenol fluxes, atmospheric deposition, sources, stormwater, urban runoff

INTRODUCTION
Runoff from urban areas constitutes a major source of water quality degradation in surface water (Burton & Pitt 2002; Brombach et al. 2005). In order to achieve the objective of elevating the aquatic environment to a "good ecological status" by 2015, as required by the Water Framework Directive (2000/60/EC), it would be necessary to quantify pollutant fluxes within stormwater and identify their sources and evolution through the environment (Eriksson et al. 2007). Moreover, this Directive established a list of 33 priority substances for mandatory monitoring, with alkylphenols (APs) included as one of them; according to the Directive, the discharge of these substances to surface water must be minimised.

APs are in fact metabolites of alkylphenol ethoxylates, which are compounds widely used as surfactants in domestic, industrial and agricultural products. Among the family of APs, 4-nonylphenol (NP) and 4-tert-octylphenol (OP) are the main ones present in commercial formulations. They have proven to be toxic for aquatic ecosystems due to their persistence and ability to mimic natural hormones, thereby inducing endocrine disruption for aquatic species (Laws et al. 2000). Many studies have reported their widespread occurrence in the environment; in addition, their concentrations in receiving waters often lie above the Predicted No Effect Concentration (PNEC) level defined in the Framework Directive (2008/105/EC) (Ying et al. 2002; Cailleaud et al. 2007; Soares et al. 2008). Only limited data are available however on APs in urban runoff and on their sources, even though such data are necessary for developing successful water management strategies: for example, NPs have been measured at between 100 and 1,200 ng/l in urban stormwater in Sweden (Bjorklund et al. 2009), while the figure in France has been measured over the range 300 to 9,200 ng/l (Zgheib 2009).

The main objectives of this study consist of providing an order of magnitude for both NP and OP contamination in urban runoff, determining the AP distribution between the dissolved phase and suspended solids, in addition to comparing contributions from the atmosphere versus local human activities.
MATERIALS AND METHODS

Site characterisation and sampling strategy

A residential catchment (Figure 1) has been studied within a suburban area built over the past 20 years near Paris (France). This catchment encompasses a land area of 8,210 m² and contains: 28% roads and parking lots, 42% buildings (with tile, zinc and flat roofs), and 30% green space (on top of slabs). Moreover, it is drained by a separate sewer system and characterised by low-density traffic, without any industrial activity in the vicinity. The decision was made to conduct works on a small scale in order to avoid the effects of in-sewer processes (i.e. sedimentation, erosion, adsorption).

Four points were sampled, extending from the atmosphere to the catchment outlet (see Figure 1). Bulk atmospheric deposition (both dry and wet) was sampled using an amber glass bottle connected to a 1-m² stainless steel collector set up on the highest roof nearly 400 m from the site. The sampling period included the studied rain event as well as the preceding dry weather period. Water from building runoff (including the roof, flat roof and green space), road runoff and residential catchment was extracted by automatic samplers controlled through a Sigma 950 flow-meter (height measured from the bubble pipe and velocity by means of the Doppler Effect) to obtain average concentrations throughout the rain event.

A total of 15 events were sampled for bulk atmospheric deposition, 11 events for residential catchment, 9 for the building catchment and 2 for the road catchment. These events spanned all four seasons, although most samples were produced during autumn and winter. The dates of events examined herein are shown in Figure 2; various characteristics are also given in Table 1.

Analytical procedure

An analytical method has been developed to quantify the APs in rainwater and stormwater, along with two other families of pollutants, i.e. polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), both of which have already been studied in our laboratory (Jung et al. 2008). A simultaneous extraction protocol allows saving time and reducing the sample volume. This method is based on separating dissolved from particulate fractions (limit: 0.45 μm) as a means of preventing contaminant loads from being underestimated (Zgheib et al. 2009) and offering valuable information regarding contaminant speciation (Coquery et al. 2005). All steps of this analytical protocol are shown in Figure 3.

The solvents introduced were of chromatographic grade: heptane (Picograde, LGC Promocem), ethyl acetate, methylene chloride and methanol (Suprasolv, Merck, VWR). All analytical procedures were performed using glassware first cleaned with detergent, then with MilliQ water, and finally calcined at 500°C for 8 hours.

Between two and four litres of sample were filtered through a glass fibre filter (GFF Whatman). Samples were filtered immediately after completion of the sampling procedure and at most one day after the rain event in order to preserve speciation.

![Figure 1](https://iwaponline.com/wst/article-pdf/63/4/671/445402/671.pdf) Map of the studied catchments.
Dissolved fractions, spiked with internal standard (IS = deuterated APs from CDN isotopes: 4-n-octylphenol-D11 and 4-n-nonylphenol-D4), were extracted by means of Solid-Phase Extraction (SPE) on a 2-g C18 cartridge (Macherey-Nagel), with a 2.5-litre sample maximum on each cartridge. The cartridges were rinsed with 8 ml methanol and then 8 ml of MilliQ water under atmospheric pressure. Subsequently, the samples were percolated under pressure; the cartridges were cleaned using 0.8 ml of methanol and dried before elution with 12 ml of methylene chloride/ethyl acetate (80:20, v/v). Once solvent had been removed from the extracts under a nitrogen stream, each resulting residue was dissolved once again in 300 ml of heptane prior to purification.

Particulate fractions were extracted by Microwave-Assisted Extraction (Soxwave 3, Prolabo). Between 50 and 500 mg of solid were extracted using methylene chloride/methanol (87.5:12.5, v/v) spiked with IS. Extracts were filtered, then the solvent was removed and the residue dissolved in 300 ml of heptane before purification.

The three pollutant families were separated during the purification step. A 2.1-g silica column was conditioned with

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**Table 1** | Characteristics of the sampled events (median and 1st–9th deciles)

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of sampled events</th>
<th>Rainfall (mm)</th>
<th>Max. 6-min rainfall intensity (mm/hr)</th>
<th>Exposure time (days)</th>
<th>Cumulative rainfall (mm)</th>
<th>Cumulative exposure time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>15</td>
<td>7.6</td>
<td>7.6</td>
<td>6.1</td>
<td>107</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2–11.8</td>
<td>4.0–18.8</td>
<td>1.8–14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Building catchment</td>
<td>9</td>
<td>8.0</td>
<td>8.0</td>
<td>9.6</td>
<td>80</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6–13.2</td>
<td>5.2–23.1</td>
<td>2.5–14.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Road catchment*</td>
<td>2</td>
<td>2.2, 4</td>
<td>8.0, 8.3</td>
<td>13.1, 13.3</td>
<td>6.2</td>
<td>26.4</td>
</tr>
<tr>
<td>Residential catchment</td>
<td>11</td>
<td>8.0</td>
<td>8.0</td>
<td>9.0</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2–12.4</td>
<td>4.2–22.7</td>
<td>2.3–13.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Since only two measurements are provided for the road catchment, no median value can be derived.
4 ml of heptane. The PCB fraction was eluted with 15 ml of heptane, followed by a PAH fraction elution with 10 ml of heptane/methylene chloride (80:20, v/v) and an AP fraction elution with heptane/ethyl acetate (80:20, v/v). The solvents were removed under a nitrogen stream and each resulting residue was then dissolved in heptane before analysis.

A GC/MS (Focus DSQ, Thermo Fisher Scientific) was used to perform the trace analysis of APs. A 1-μl aliquot of each extract was injected using the splitless mode. The analytes were separated with a RXI-5Sil MS fused silica capillary column (60 m long, 0.25 mm internal diameter, and 0.25 μm film thickness, Restek), and the gas carrier introduced was helium. The molecules were detected by a quadrupole mass analyser operating in Selected Ion Monitoring mode (SIM), following ionisation by means of electron impact. The specific ions and internal standards for each analyte are listed in Table 2. Each AP concentration has been corrected in accordance with the recovery of internal standards, and overall calibration was verified by a calibration check standard applied every 12 samples. Blanks were taken during each sequence in order to control for laboratory contamination. The standards used for calibration and reference materials were para-tert-octylphenol and branched 4-nonylphenol (Pestanal, Riedel de Haeën).

**Analytical validation**

To test for the effective separation of PCBs, PAHs and APs during the purification step, the three eluted fractions were analysed for PAHs, while the PAH fraction (i.e. the 2nd eluted fraction) was also analysed for PCBs and APs. Less than 5% of each contaminant family (by area of chromatographic peak) was detected in one of the other elution fractions.

The limits of quantification (LOQ) and limits of detection (LOD) have been determined for each molecule according to the XPT-90-210 Standard and are provided in Table 2.

The analytical methods employed for the dissolved fraction have been evaluated on the basis of an extraction in triplicate of a runoff water sample spiked with standards. Both the accuracy and repeatability (Table 2) of the analytical method prove to be satisfactory. Recoveries between extracted water and control ranged between 73% and 111%. The relative standard deviation over the three replicates varied from 11% to 13%.

Standard reference material (SRM) 1944 was extracted nine times in order to evaluate the analytical method for particulate fractions. No certified value for APs is available to obtain recoveries, as only the repeatability could be given. The relative standard deviations equal 16% for NPs and 34% for OPs.

**RESULTS AND DISCUSSION**

**Occurrence of alkylphenols in atmospheric depositions and runoff**

Branched NPs and OPs have been quantified in each sample and in both the particulate and dissolved fractions. The median concentrations, loads and percentages of particles...
are listed in Table 3 for the various sampling sites. OP concentrations are 10 to 20 times less than NP concentrations, as observed in previous studies (Ying et al. 2002).

**AP concentrations found in different types of runoff**

The median NP concentration equals 560 ng/l in building runoff, 1,700 ng/l in road runoff and 470 ng/l in residential catchment stormwater (respectively 26 ng/l, 160 ng/l and 36 ng/l for median OPs). The variability between samples however remains rather high. Concentrations can indeed vary by a factor of ten from one rain event to the next.

The highest concentrations were measured for the road catchment and amount to 3 to 4 times greater than other samples, as observed in Bjorklund et al. (2009). Yet the number of rain events for the road runoff statistic is insufficient to draw any conclusions. Building runoff concentrations are close to those measured at the residential catchment outlet.

Only a limited amount of data on stormwater is available. A comparison using our data would therefore be difficult to perform. The existing data however all present the same order of magnitude as our data. Bjorklund et al. (2009) reported NP concentrations ranging from 100 ng/l (suburban residential catchment) to 1,200 ng/l (a high-density traffic catchment). Rule et al. (2006) obtained concentrations between 1,700 and 4,900 ng/l at various times for the same rain event on an industrial catchment. The median concentrations measured in urban runoff during this study all lie above the PNEC for NPs (PNEC = 300 ng/l) and below this threshold for OPs (PNEC = 100 ng/l) (Framework Directive 2008/105/EC).

**AP concentrations in bulk atmospheric deposition and comparison with runoff**

The median NP and OP concentrations in bulk atmospheric deposition (dry and wet) equal 170 ng/l and 9 ng/l, respectively; these results are significantly less than runoff concentrations: three times less than NP concentrations in building runoff and residential catchment stormwater, and ten times less than the NP concentration in road runoff (for OP, these differences are three and twenty times less, respectively).

The local contribution to building and road runoff from NPs and OPs can therefore be predicted. APs are in fact degradation products of the alkylphenoletethoxylates found in detergent, paints, plastics, civil engineering materials and pesticide formulations (European Chemicals Bureau 2002; Ying et al. 2002; Soares et al. 2008).

These concentrations measured in atmospheric deposition are comparable to those cited in the literature for rainwater samples. Fries & Puttmann (2004) evaluated NPs at between 30 and 950 ng/l in rainwater.

**APs in particulate fractions**

The association of APs with particles is a key process in controlling the evolution of APs in the environment and their behaviour in stormwater management systems. Table 3 summarises the main characteristics of APs within particles. APs display moderate octanol-water partition coefficients (logKow = 4.5 for NPs and 4.1 for OPs (Ying et al. 2002)). A portion of the APs thus make their way into the suspended matter.

| Table 3 | Concentrations in total samples (median and 1st - 9th deciles in ng/l), proportions of particles (%) and loads in the particulate fraction (μg/g) for branched NPs and OPs |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | NPs             | OPs             |                |                |                |
|                | Concentration   | % in particles | Load in particles | Concentration | % in particles | Load in particles |
|                | (ng/l)          |                 | (μg/g)          | (ng/l)        |                 | (μg/g)          |
| Bulk atmospheric deposition (n = 15) | 170 | 21 | 1.5 | 8.4 | 26 | 0.12 |
| | 49–340 | 4–45 | 0.51–4.3 | 3.0–30 | 5–66 | 0.03–0.41 |
| Building runoff (n = 9) | 560 | 35 | 0.80 | 26 | 15 | 0.05 |
| | 150–750 | 7–53 | 0.26–2.2 | 18–36 | 10–67 | 0.03–0.13 |
| Road runoff (n = 2)* | 1500, 1900 | 14, 70 | 3.8, 5.8 | 110, 210 | 23, 67 | 0.53, 0.53 |
| Urban runoff (n = 11) | 470 | 27 | 3.7 | 36 | 20 | 0.27 |
| | 160–920 | 17–43 | 1.9–7.6 | 13–69 | 7–44 | 0.12–0.46 |

*Since only two measurements are provided for the road catchment, no median value can be derived.
The particulate fraction of APs accounts for between 15% and 35% in runoff. It is worth noting that this distribution is similar for NPs and OPs and does not change between atmospheric deposition and runoff.

Stormwater pollution is usually considered as being strongly correlated with particulates (Gromaire-Mertz et al. 1999), hence most stormwater treatment devices are based on settling. Yet APs are more highly dissolved than the other typical parameters measured in runoff, meaning that this kind of treatment will not be sufficiently efficient for APs.

The observed data provided in Table 3 suggest that loads in the form of particulate fractions depend on the type of site. The lowest concentrations were measured in building runoff (0.80 μg/g for NP and 0.05 μg/g for OP) and atmospheric deposition (1.5 μg/g for NP and 0.12 μg/g for OP), while the highest were recorded in residential catchment stormwater (3.7 μg/g for NP and 0.27 μg/g for OP) and road runoff (4.8 μg/g for NP and 0.53 μg/g for OP). The lower loads found in building runoff may be correlated with the greater supply of relatively uncontaminated suspended solids from ground erosion on the green space.

The differences in particulate loads between the various types of runoff might be due to the speciation of APs from different sources: dissolved from paints, pesticides or material emissions, and particulates from road erosion or vehicle wear.

Fluxes and mass balances at various scales

Annual fluxes of APs in bulk atmospheric deposition and stormwater

AP fluxes have been extrapolated from the total mass of APs measured over our sampling periods to an annual scale, for both atmospheric fallout and residential catchment stormwater. Since it is not known whether the main process for AP emission is the build-up during dry weather periods or lixiviation by rainfall, two distinct hypotheses have been formulated. According to Hypothesis 1, the emission of APs is considered to be proportional to the duration of exposure, while Hypothesis 2 considers the emission of APs to be proportional to the depth of rainfall. The data input for each hypothesis as well as the results are given in Table 4.

The atmospheric flux of NPs lies between 44 and 84 μg/m²/yr and the flux of OPs between 2.5 and 4.9 μg/m²/yr. Bjorklund (2010) estimated a flux of 110 μg/m²/yr for NPs and their ethoxylates (NPEOs) in Sweden. If we consider, in accordance with the literature (Ying et al. 2002; Patrolecco et al. 2006; Bjorklund et al. 2009), NPEOs to be of the same order of magnitude as NPs, then the value produced by Bjorklund (2010) is in the same range as the findings of this study.

For stormwater fluxes, NPs range between 100 and 190 μg/m²/yr and OPs between 6.5 and 12 μg/m²/yr. Stormwater fluxes are at least 2.5 times higher than atmospheric fluxes.

The contributions of the various sources can be obtained from mass balances, and the following subsection is intended to make this determination.

Mass balances at the watershed scale

In order to evaluate the relative contributions of atmospheric deposition and both building and road emissions to runoff contamination, entry-exit mass balances have been calculated for the three experimental catchments and the nine rain events, which were simultaneously sampled on at least three sampling sites.

For the contribution from bulk atmospheric deposition, the atmospheric alkylphenol fallout on urban surfaces was considered both to equal what had been measured on the atmospheric collector and to stream like rainwater without any change in concentration. The mass of APs originating from the atmosphere within the runoff of the considered

Table 4 | Evaluation of annual NP and OP fluxes

<table>
<thead>
<tr>
<th></th>
<th>Atmospheric fallout</th>
<th>Stormwater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hypothesis 1</td>
<td>Hypothesis 2</td>
</tr>
<tr>
<td>Sampling period</td>
<td>115 days</td>
<td>107 mm</td>
</tr>
<tr>
<td>Annual period</td>
<td>365 days</td>
<td>650 mm</td>
</tr>
<tr>
<td>Annual fluxes (μg/m²/yr)</td>
<td>NPs</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>OPs</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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catchment \((M_{atm})\) can thus be calculated from Equation (1), where: \(C_{atm}\) is the AP concentration measured in the atmospheric collector; \(H\) the depth of rainfall; \(S_r, S_b\) and \(S_g\) the surface areas of roads, buildings and green space on the considered catchment; and \(R_{Cr}, R_{Cb}\) and \(R_{Cg}\) the runoff coefficients of roads, buildings and green space:

\[
M_{atm} = C_{atm} \cdot H \cdot (R_{Cr} \cdot S_r + R_{Cb} \cdot S_b + R_{Cg} \cdot S_g) \tag{1}
\]

The contribution of building emissions was calculated from Equation (2), in which \(M_{build}\) denotes the mass of APs originating from building emissions (buildings and green space), and \(C_{build}\) the AP concentration in runoff from the building catchment, i.e.:

\[
M_{build} = (C_{build} - C_{atm}) \cdot H \cdot (R_{Cb} \cdot S_b + R_{Cg} \cdot S_g) \tag{2}
\]

The contribution of road emissions was calculated in two ways. First, at the scale of the road catchment and for the two sampled rain events, this contribution was calculated from Equation (3), where \(M_{road}\) is the mass of APs originating from road runoff, and \(C_{road}\) the AP concentration in road runoff:

\[
M_{road1} = (C_{road} - C_{atm}) \cdot H \cdot R_{Cr} \cdot S_r \tag{3}
\]

Second, at the scale of the overall residential catchment, road runoff data were not available for most of the studied rain events; therefore, the road contribution was estimated as the difference between the mass load measured at the sewer outlet \((M_{outlet})\) and mass loads estimated for atmospheric fallout and building emissions (Equation (4)):

\[
M_{road2} = M_{outlet} - (M_{atm} + M_{build}) \tag{4}
\]

Runoff coefficients were estimated from the literature values; they have been adjusted for each rain event such that the calculated runoff volume \((V_r\) in Equation (5)) corresponds to the volume measured at the sewer outlet. These values thus vary depending on both rainfall intensity and initial catchment wetness: \(R_{Cb} = 0.7\)–1; \(R_{Cr} = 0.6\)–0.9; and \(R_{Cg} = 0\) (for 4 rain events)–0.7.

\[
V_r = H \cdot (R_{Cr} \cdot S_r + R_{Cb} \cdot S_b + R_{Cg} \cdot S_g) \tag{5}
\]

The results are described below. The percentages (expressed in mass for the sum of the nine events) of the various contributions are shown in Figure 4.

For the building catchment, atmospheric depositions represent less than 30% of the mass of APs in runoff. One possible explanation would be that nonylphenol ethoxylates are used in the civil engineering industry as admixtures in cements and certain plastic materials (European Chemicals Bureau 2002) as well as in pesticide formulations (Ying et al. 2002).

For the road catchment, the contribution of atmospheric deposition is significantly less than that of the building catchment (13%), which proves that traffic constitutes a considerable source of alkylphenols in runoff. Nonylphenol ethoxylates are actually an additive to bitumen emulsions in

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**Figure 4** | Contributions of the various sources to AP contamination in runoff.
lubricants, fuel and car care products (European Chemicals Bureau 2002; Bjorklund 2010).

At the watershed scale (i.e. the residential catchment in Figure 4), buildings appear to be the main source of alkylphenols, followed by the road. It should also be noted that this evaluation probably overestimates atmospheric contributions: the deposition and washout processes on urban surfaces may indeed differ from those measured on the atmospheric collector (e.g. due to the wind causing more spreading of atmospheric APs, the possible adsorption of APs in green space, fewer washouts on rougher surfaces like tiles and roads). Consequently, road and building contributions will be even greater than those predicted in the calculations.

CONCLUSION

An analytical procedure has been developed for alkylphenols (APs) and applied to bulk atmospheric deposition, building and road runoff, and residential catchment stormwater within a small suburban area near Paris (France).

Nonylphenols and octylphenols have been quantified in each sample using median concentrations of 470 ng/l and 36 ng/l, respectively, in residential catchment stormwater. These concentrations often lie above European environmental quality standards for surface waters. As part of the implementation of the Water Framework Directive, stormwater must be considered as a substantial contributor to the AP contamination of surface waters.

AP fluxes have been extrapolated from the total mass of APs measured over our sampling periods to an annual scale; the results are significantly lower in atmospheric deposition than in runoff, thus proving that local human activity constitutes a major source. Mass balances at the watershed scale reveal that building emissions and road runoff represent more than 70% of APs in residential catchment stormwater, with building runoff being the most predominant source.

Moreover in closing, we would like to underscore the fact that APs are more highly dissolved than the other standard parameters measured in runoff. Treatment devices based solely on settling will thus not be as effective for APs as what is generally considered for stormwater pollution.

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