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# Impact of dry weather discharges on annual pollution from a separate storm sewer in Toulouse, France

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## HIGHLIGHTS

- Dry weather discharges from storm sewers have an impact on annual pollution load.
- The more urbanized the outlet is, the more important the pollution is.
- Correlations between some overall pollution parameters have been revealed by PCA.
- No seasonal variation in stormwater pollution was found.

*Keywords:*
Trace organic compounds
Storm sewer discharge
Separate sewer system
Dry weather
Wet weather
Principal component analysis

## ABSTRACT

The city of Toulouse with its separate sewer system is ideal for studying stormwater. However, during dry weather, the storm sewer also discharges water into the environment, and it is the impact of these discharges on annual pollution from storm sewer that is the object of this study.

Samples have been taken from the outlets of two storm drains located in heavily and moderately urbanized areas. Sampling has been undertaken during wet weather and during dry weather between January 2010 and February 2011. Three dry weather and two wet weather samples have been taken every three months and from each outlet. The overall pollution parameters have been analyzed (chemical oxygen demand, biological oxygen demand, total nitrogen, ammonium, nitrate, total phosphorus, suspended solid matter, volatile suspended matter, pH, conductivity, turbidity). Characterization has been completed by analysis of trace organic compounds: polycyclic aromatic hydrocarbons, total hydrocarbons, methyl *tert*-butyl ether, diethylhexylphthalate, nonylphenols, hormones (estradiol, ethinylestradiol). For certain parameters, the results obtained did not conform to legislative requirements concerning discharge into the natural environment. Correlations between these parameters have been studied, and identified between several of them using principal component analysis. The most important correlation observed was between conductivity and concentration in total phosphorus for one of the outlet. Results showed that dry weather had an impact on annual pollution load from separate storm sewer and that level of urbanization was also a factor. The effect of season has been studied but no significant impact was found.

## 1. Introduction

Municipalities have for long considered stormwater as a purely hydraulic phenomenon. However, it is now recognized as a pollution source for the receiving environment (Clark et al., 1971). At present, stormwater may be collected in the same system as wastewater, i.e. combined sewer system, or else in an independent network, i.e. separate sewer system. And it is important to study stormwater in the latter because it is discharged directly into the natural environment. Pollution of stormwater can be from different sources: rainwater quality, urban runoff from roofs/roads, illicit connections, illegal

*Abbreviations:* $BOD_5$, 5-days Biological Oxygen Demand; Bvds, Boulevards outlet; COD, Chemical Oxygen Demand; DEHP, DiEthylHexylPhthalate; EQS, Environmental Quality Standard; MTBE, Methyl *Tert*-Butyl Ether; NP, NonylPhenol; NP1EO, NonylPhenol MonoEthOxylate; NP2EO, NonylPhenol DiEthOxylate; PAHs, Polycyclic Aromatic Hydrocarbons; PCA, Principal Component Analysis; SSM, Suspended Solid Matter; TH, Total Hydrocarbons; TN, Total Nitrogen; TP, Total Phosphorus; TOC, Trace Organic Compounds; VSM, Volatile Suspended Matter.

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dumping, discharges from authorized companies and leaks from the wastewater sewer (Walker et al., 1999).

Worldwide, numerous studies have already been made on stormwater characterization especially concerning overall pollution parameters (Lee and Bang, 2000; Teemusk and Mander, 2007; Terzakis et al., 2008; Zgheib et al., 2011; Zhang et al., 2010), but only a few (Kim et al., 2007; Zhang et al., 2010) have covered correlations between these parameters in stormwater. Other studies have covered certain priority organic pollutants, notably polycyclic aromatic hydrocarbons (Chedeville et al., 2010; Terzakis et al., 2008; Zgheib et al., 2011), diethylhexylphtalate (Bjorklund et al., 2009; Zgheib et al., 2011), methyl *tert*-butylether (Achten et al., 2001), total hydrocarbons (Barraud and Fouillet, 2006; Chedeville et al., 2010; Legret and Pagotto, 1999), and 4-nonylphenol (Bjorklund et al., 2009; Bressy et al., 2011; Zgheib et al., 2011). No work on testing for hormones in stormwater has been published so far. Only Pailler et al. (2009) and Peng et al. (2008) have presented results covering presence of these hormones in river water.

Concerning a seasonal influence, Lee et al. (2004) identified a seasonal first flush phenomenon on Mediterranean climate for total organic carbon, minerals and metals. Furthermore, a seasonal effect for PAH has been reported in publications on rainwater quality (De Rossi et al., 2003; He and Balasubramanian, 2010; Polkowska et al., 2000). So there could be a possible seasonal influence on stormwater quality for other pollution parameters or other pollutants.

Certain companies such as car wash stations, are authorized to discharge their wastewater into the storm sewer after a pretreatment, resulting in a constant, observable flow here even in dry weather without rain. Moreover, a study by Sablayrolles et al. (2010) has shown that the impact of car wash stations on the overall quality of stormwaters was not negligible. It accounted indeed for up to 100% of the pollution source for certain priority organic pollutants. Similarly, in a separate internal study, Sablayrolles et al. (2008) have shown the influence of dry weather on the annual pollutant load (two dry weather sampling points).

For almost sixty years now, the city of Toulouse in South West France has opted for a separate system. The city's stormwater is discharged directly into the River Garonne with no prior treatment and so must conform to certain requirements concerning overall pollution parameters under the French 2nd February 1998 Water Act (Arrêté du 2 février, 1998). Regarding trace organic compounds, the Water Framework Directive and its daughter directives have established a list of priority organic pollutants to be monitored in surface waters in addition to the overall water quality pollution parameters, and environmental quality standard (EQS) limit values have been set.

The present study was thus carried out in order to characterize the overall pollution of the water discharge from the two main storm drain outlets in Toulouse, and to evaluate the impact of dry weather discharges. To this end, the water discharge from storm sewer was monitored over a year and 40 samples were taken. Respect of the 1998 Act limit values was checked and trace organic component pollution levels were compared to requirements under the Water Framework Directive (Directive 2000/60/EC).

Principal component analysis enabled correlations between the classical parameters to be established and seasonal influence to be studied.

## 2. Materials and Methods

### 2.1. Studied Sites

Two major outlets in the Toulouse storm sewer have been selected. The first, the Boulevards outlet, drains runoff water from the heart of downtown. Its watershed extends over an area of 439 ha and represents a heavily urbanized zone.

The second, the Mirail outlet, drains runoff water from a residential zone composed of houses and blocks of flats with gardens. Its watershed extends over an area of 1428 ha.

### 2.2. Sampling Methods

Sampling was carried out from January 2010 to February 2011 Two wet weather samples were collected and three dry weather samples were collected per season and per outlet. Dry weather samples were collected following a minimum of two successive dry weather days. Wet weather samples were taken on selected days forecasted for heavy rain of 24 h, in order to obtain ideally at least 3 mm rainfall corresponding to the minimum necessary for satisfactory rooftop runoff. These samples were collected after the rain has started so the first flush flow was not sampled. For each wet weather sample, the daily precipitation was determined thanks to rain gauges placed near the two outlets.

Each time, the water was collected over 24 h using a time based autosampler (ISCO 3700) to obtain a representative average sample. The samples were collected in an 18 L glass bottle and then transferred into amber glass bottles and stored at −25 °C for subsequent analysis. Flow was measured throughout the sampling.

### 2.3. Analyses

Initially, classical parameters were measured for the raw samples: pH, turbidity, and conductivity. Commercially available tests (Spectroquant®, Merck) were used to determine the chemical oxygen demand, total nitrogen and total phosphorus in the raw samples, as well as for ammonium ion ($NH_4^+$) and nitrate ($NO_3^-$) ion analyses in filtered samples. Suspended solid matter and volatile suspended matter were assessed by filtration according to NF-T90-105-1 and NF-T90-029 standards respectively. The 5-day biological oxygen demand was analyzed according to the NF-EN-1899-1 standard.

Characterization was completed by analysis of trace organic compounds. Sixteen polycyclic aromatic hydrocarbons were selected using data from the Environmental Protection Agency: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. These molecules were analyzed using liquid–liquid extraction and liquid chromatography with fluorescence detection according to NF EN ISO 17993. Limit of quantification (LOQ) for these molecules was 0.02 μg/L. The diethylhexylphthalate was analyzed by liquid–liquid extraction and gas chromatography with mass spectrometry using EPA 606, with a limit of quantification of 0.5 μg/L. The 4-nonylphenol, 4-nonylphenol-monoethoxylate and 4-nonylphenol-diethoxylate were also analyzed by liquid–liquid extraction and gas chromatography with mass spectrometry. The limit of quantification obtained for these three molecules was 0.1 μg/L. The methyl *tert*-butyl-ether was analyzed according to NF EN ISO 10301 with gas chromatography with mass spectrometry after headspace extraction, with a limit of quantification of 1.0 μg/L. Total hydrocarbons from C10 to C40 were analyzed using liquid–liquid extraction and a gas chromatograph fitted with a flame ionization detector according to NF EN ISO 9377-2. The limit of quantification was 50 μg/L. The selected hormones (estradiol and ethinylestradiol) were analyzed by liquid–liquid extraction and liquid chromatography—mass spectrometry with a limit of quantification of 0.01 μg/L.

These analytical methods were validated in accordance with a validation protocol. No contamination was observed.

### 2.4. Multivariate Analyses

Principal component analysis (PCA) was carried out in order to visualize the correlations between the variables studied (= overall pollution parameters) and to identify homogenous groups of observations or conversely, atypical ones.

## 3. Results and Discussion

### 3.1. Annual Concentrations

#### 3.1.1. Overall Pollution Parameters

The average and median values plus standard deviations were calculated for each sampling weather condition and for each outlet studied (a total of 40 samples: 12 dry weather samples and 8 wet weather samples for each outlet). An LOQ/2 value was applied for calculations when values were below the LOQ (Directive, 2009/90/CE). Results are shown in Table 1. Some data from literature are included in this table, articles cited in this table refer to recent stormwater study in Europe.

Box plots for each outlet and each type of weather were drawn to illustrate dispersion of data, and are shown in Fig. 1 representing also average–median, minimum–maximum and extreme values.

In general, as illustrated in Fig. 1, the concentrations of the overall pollution parameters are very different from one outlet to the other, with wide variations between the various samples taken from the same outlet under identical meteorological conditions, as shown by the relatively high standard deviations obtained.

According to the French 1998 Water Act (Arrêté du 2 février, 1998), water pH values must be between 5.5 and 8.5 inclusive. Seven wet weather samples and seven dry weather samples from the Boulevards outlet did not come within this range. Similarly, from the Mirail outlet there were three wet weather samples and four dry weather samples that did not conform to this pH standard. Thus some of the samples taken were more alkaline than stipulated in the legislation.

Overall, the chemical oxygen demand is low compared to previous internal studies made using these same outlets in 2004 (average COD Bvds = 103.8 mg $O_2$/L; average COD Mirail = 49.3 mg $O_2$/L, Xaumier et al., 2004) and 2007 (average COD Bvds = 80 mg $O_2$/L; average COD Mirail = 61 mg $O_2$/L, Sablayrolles et al., 2008). The data is also low compared to literature values (Bressy et al., 2011; Terzakis et al., 2008; Zgheib et al., 2011). No sample exceeds the 125 mg $O_2$/L threshold value. The biological oxygen demand is also very low and concentration values above the limit of quantification have only been found in two samples from the Boulevards outlet and for only one sample from the Mirail outlet. The median $BOD_5$/COD ratios for the Boulevards outlet are 0.11 and 0.22 for wet weather and dry weather respectively. Thus the biodegradability of the storm sewer waters studied can be classified as poor (ratio less than 0.3), and this data agrees with some literature values (Teemusk and Mander, 2007; Zhang et al., 2010). Nevertheless, the biodegradability of stormwater would appear to vary because higher $BOD_5$/COD ratio values were also found (Lee and Bang, 2000; Luo et al., 2009).

All of the samples from the Mirail and Boulevards outlets conform to the legislation limit values for total phosphorus and total nitrogen. However, this is not the case for quantity of suspended solid matter in the water, because all but one wet and one dry weather sample from the Boulevards outlet had SSM concentrations over the 35 mg/L limit value. Whereas for the Mirail outlet because the observed concentrations were lower, only two wet and eight dry weather samples did not conform to the current standard. Finally, samples taken from the Boulevards outlet have higher concentrations overall than those taken from the Mirail outlet. In addition, the values obtained from dry weather samples are much higher overall than those obtained for wet weather ones from both outlets studied, except for chemical oxygen demand and pH where the opposite was observed.

#### 3.1.2. Trace Organic Compounds

The average and median values, plus the standard deviation were calculated for each type of sampling weather and for each outlet studied. For values below the LOQ, LOQ/2 was used in calculations (Directive, 2009/90/EC). Results are shown in Table 1. Since there are no specific amendments to the law covering trace organic compounds in stormwaters, these results were compared with the environmental quality standards (EQS) for surface waters as defined in Directive (2008/105/EC), daughter directive of the EU Water Framework Directive set out in the 25 January 2010 Order.

Overall, the concentrations in trace organic compounds found in the storm sewer water were very low from both outlets. The compounds were only quantifiable in very few of the samples taken, as shown by the low occurrence percentages. Only PAHs, nonylphenol ethoxylates and estradiol were quantified in at least 25% of the same nature samples.

Of the sixteen PAHs studied, only five of them were quantifiable at least once: naphthalene, fluorene, acenaphthene, phenanthrene and pyrene. Moreover, the concentrations found were very low compared to an internal study on these same outlets in 2004: ([PAH]average Bvds = 0.11 μg/L; [PAH]average Mirail = 0.05 μg/L, Xaumier et al., 2004) and also in the literature (Bressy et al., 2011; Terzakis et al., 2008; Zgheib et al., 2011). However, another internal study in 2007 also gave average and median PAH concentrations lower than the limit of quantification (= 0.01 μg/L) for these same outlets (Sablayrolles et al., 2008). Of the five quantifiable PAHs, only naphthalene is given an average annual Environmental Quality Standard (EQS); 2.4 μg/L (Directive, 2008/105/EC). The average concentrations of naphthalene found in the twenty samples from each outlet were all less than this EQS.

Similarly, the maximum concentration in total hydrocarbons must not exceed 10 mg/L (Arrêté du 2 février, 1998). None of the samples taken attained this value. In fact, only three of the forty samples had a concentration above the limit of quantification of 50 μg/L. These figures are low relative to literature values for stormwater runoff (Barraud and Fouillet, 2006; Legret and Pagotto, 1999). Nonetheless, they agree with the equally low PAH concentrations.

There is also an Environmental Quality Standard of 0.3 μg/L for 4-nonylphenol. Average concentrations of 4-NP were lower than this EQS annual average. 4-nonylphenol was indeed only found in one of the forty samples analyzed.

Overall, the Boulevards outlet showed slightly higher concentrations of trace organic compounds than Mirail outlet.

### 3.2. Dry Weather Loads and Impact

#### 3.2.1. Overall Pollution Parameters

The pollution generated by each outlet is due to the pollutant concentrations during samplings but also to the flow, because the higher the latter the greater the quantity of pollutants that will be carried along. Thus, to make a significant comparison between the outlets and the sampling weather for this pollution, it is better to look at pollutant loads.

The annual wet weather pollutant load was thus calculated using Eqs. (1) and (2) and was expressed as pollutant mass per year. The annual dry weather pollutant load was also calculated using Eqs. (3) and (4). For values below the LOQ, LOQ/2 was used in calculations.

Eq. (1). Wet weather pollutant load for a sample (i). $x_{i,p,j}$ is the pollutant load of sample (i) in wet weather for the pollutant (p) for the particular outlet (j) expressed in mg/mm. $c_{i,p,j}$ is the concentration of the pollutant (p) when sampled (i) for the outlet (j) expressed in μg/L. $Q_{i,j}$ is the flow measured on sampling (i) at the particular outlet (j) expressed in $m^3$/h. $t_i$ is the duration of sampling (i) expressed in h and is equal to 24 h. $P_i$ is the quantity of rain falling when sample taken (i) expressed in mm.

$$x_{i,p,j} = \frac{c_{i,p,j} \times Q_{i,j} \times t_i}{P_i}. \quad (1)$$

Eq. (2). Annual wet weather pollutant load. $X_{p,j}$ is the annual wet weather pollutant load for the pollutant (p) and the particular outlet (j) expressed in mg/yr. $x_{i,p,j}$ is the pollutant load of the sample (i) for

**Table 1**
Results of analyses of overall pollution parameters and trace organic compounds for the two stormwater outlets studied.

| | Units | Wet weather | | Dry weather | | Standard | Literature data |
|---|---|---|---|---|---|---|---|
| | | Data | Occurrence % (n = 8) | Data | Occurrence % (n = 12) | | |
| *Boulevards outlet* | | | | | | | |
| Rainfall | mm | 13.1 ± 12.4 (12.5) | | | | | |
| Flow | $m^3/h$ | 728 ± 475 (645) | | 296 ± 156 (397) | | | |
| pH | – | 8.9 ± 0.3 (8.8) | | 8.7 ± 0.4 (8.6) | | 5.5–8.5[a] | 6.75[c]–7.35[d] |
| Conductivity | μS/cm | 362 ± 203 (349) | | 500 ± 61 (499) | | | 14[c]–1316[d] |
| Turbidity | NTU | 9.8 ± 5.3 (9.8) | | 16.2 ± 5.0 (14.6) | | | |
| COD | mg $O_2$/L | 20.1 ± 9.1 (19.0) | 100 | 17.8 ± 11.1 (16.0) | 100 | 125[a] | 23[f]–256[c] |
| $BOD_5$ | mg $O_2$/L | 2.9 ± 2.9 (2.0) | 12.5 | 3.9 ± 2.7 (3.5) | 8.3 | 25[a] | 2.9[e]–7[e] |
| TP | mg P/L | 0.45 ± 0.16 (0.47) | 100 | 0.65 ± 0.17 (0.63) | 100 | 2[a] | 0.5[c]–8.5[c] |
| TN | mg N/L | 5.5 ± 2.5 (5.5) | 100 | 7.2 ± 3.0 (6.5) | 100 | 30[a] | 0.4[c]–7.3[c] |
| $NH_4^+$ | mg N/L | 0.89 ± 0.55 (0.87) | 87.5 | 2.0 ± 1.0 (1.8) | 100 | | |
| $NO_3^-$ | mg N/L | 3.1 ± 1.1 (2.9) | 100 | 4.2 ± 0.95 (4.2) | 100 | | 0.2[c]–0.9[c] |
| SSM | mg/L | 54.2 ± 18.3 (55.1) | 100 | 70.1 ± 29.1 (68.0) | 100 | 35[a] | 15[f]–430[d] |
| VSM | % MES | 35.6 ± 12.5 (36.3) | 100 | 22.1 ± 5.9 (23.3) | 100 | | |
| ∑ PAH (16) | μg/L | 0.068 ± 0.115 (0.013) | 37.5 | 0.058 ± 0.112 (0.010) | 33.3 | | 0.07[c]–40.75[g] |
| DEHP | μg/L | <2 | 0.0 | <2 | 0.0 | 1.3[b] | <1.0[h]–60.9[d] |
| MTBE | μg/L | <0.5 | 0.0 | <0.5 | 0.0 | | 0.03[i]–1.174[i] |
| TH | mg/L | 0.031 ± 0.016 (0.025) | 12.5 | 0.131 ± 0.368 (0.025) | 8.3 | 10[a] | <0.0002[g]–25.9[j] |
| 4-NP | μg/L | <0.1 | 0.0 | <0.1 | 0.0 | 0.3[b] | <LOQ[d]–1.2[h] |
| NP1EO | μg/L | 0.054 ± 0.024 (0.05) | 12.5 | 0.163 ± 0.218 (0.050) | 41.7 | | <LOQ[h]–1.1[h] |
| NP2EO | μg/L | 0.143 ± 0.195 (0.05) | 37.5 | 0.282 ± 0.732 (0.050) | 25.0 | | <LOQ[h]–2[h] |
| Estradiol | μg/L | 0.012 ± 0.014 (0.005) | 25.0 | 0.006 ± 0.002 (0.005) | 8.3 | | |
| Ethinyl-estradiol | μg/L | <0.01 | 0.0 | 0.005 ± 0.001 (0.005) | 8.3 | | |
| *Mirail Outlet* | | | | | | | |
| Rainfall | mm | 12.0 ± 12.9 (7.5) | | | | | |
| Flow | $m^3/h$ | 694 ± 483 (626) | | 399 ± 227 (524) | | | |
| pH | – | 8.6 ± 0.4 (8.5) | | 8.4 ± 0.4 (8.3) | | 5.5–8.5[a] | 6.75[c]–7.35[d] |
| Conductivity | μS/cm | 278 ± 120 (264) | | 367 ± 206 (321) | | | 14[c]–1316[d] |
| Turbidity | NTU | 12.4 ± 6.0 (14.2) | | 13.2 ± 5.4 (12.4) | | | |
| COD | mg $O_2$/L | 6.1 ± 5.2 (5) | 75.0 | 7.7 ± 11.8 (2.5) | 58.3 | 125[a] | 23[f]–256[c] |
| $BOD_5$ | mg $O_2$/L | 4.5 ± 6.0 (2.5) | 12.5 | <3 | 0.0 | 25[a] | 2.9[e]–7[e] |
| TP | mg P/L | 0.08 ± 0.01 (0.09) | 100 | 0.07 ± 0.02 (0.08) | 100 | 2[a] | 0.5[c]–8.5[c] |
| TN | mg N/L | 4.5 ± 1.9 (4.5) | 100 | 5.1 ± 2.0 (5.5) | 91.7 | 30[a] | 0.4[c]–7.3[c] |
| $NH_4^+$ | mg N/L | <0.1 | 0.0 | <0.1 | 0.0 | | |
| $NO_3^-$ | mg N/L | 2.6 ± 1.4 (2.2) | 100 | 3.4 ± 1.6 (2.5) | 100 | | 0.2[c]–0.9[c] |
| SSM | mg/L | 29.8 ± 7.0 (29.1) | 100 | 42.0 ± 12.4 (41.1) | 100 | 35[a] | 15[f]–430[d] |
| VSM | %MES | 28.4 ± 6.9 (30.4) | 100 | 21.2 ± 4.6 (20.1) | 100 | | |
| ∑ PAH (16) | μg/L | <0.02 | 0.0 | 0.016 ± 0.014 (0.010) | 8.3 | | 0.07[c]–40.75[g] |
| DEHP | μg/L | <2 | 0.0 | <2 | 0.0 | 1.3[b] | <1.0[h]–60.9[d] |
| MTBE | μg/L | <0.5 | 0.0 | <0.5 | 0.0 | | 0.03[i]–1.174[i] |

*(continued on next page)*

**Table 1** (*continued*)

| | Units | Wet weather | | Dry weather | | Standard | Literature data |
|---|---|---|---|---|---|---|---|
| | | Data | Occurrence % (n = 8) | Data | Occurrence % (n = 12) | | |
| *Mirail Outlet* | | | | | | | |
| TH | mg/L | 0.029 ± 0.012 (0.025) | 12.5 | <0.05 | 0.0 | 10[a] | <0.0002[g]–25.9[j] |
| 4-NP | μg/L | 0.078 ± 0.078 (0.050) | 12.5 | <0.1 | 0.0 | 0.3[b] | <LOQ[d]–1.2[h] |
| NP1EO | μg/L | <0.1 | 0.0 | <0.1 | 0.0 | | <LOQ[h]–1.1[h] |
| NP2EO | μg/L | 0.063 ± 0.035 (0.050) | 12.5 | <0.1 | 0.0 | | <LOQ[h]–2[h] |
| Estradiol | μg/L | <0.01 | 0.0 | <0.01 | 0.0 | | |
| Ethinyl-estradiol | μg/L | 0.009 ± 0.011 (0.050) | 12.5 | 0.006 ± 0.002 (0.005) | 8.3 | | |

Average ± Standard deviation (Median).

[a] Order of 2 February 1998 concerning waste water discharged into the natural environment.
[b] Directive, 2008/105/CE. 16 December 2008 setting out environmental quality standards for water.
[c] Terzakis et al. (2008).
[d] Zgheib et al. (2011).
[e] Teemusk and Mander (2007).
[f] Bressy et al. (2011).
[g] Chedeville et al. (2010).
[h] Bjorklund et al. (2009).
[i] Achten et al. (2001).
[j] Barraud and Fouillet (2006).

the pollutant (p) for the particular outlet (j) expressed in mg/mm. $P_{2010}$ is the 2010 annual rainfall expressed in mm/yr.

$$X_{p,j} = Median\, x_{i,p,j} \times P_{2010}. \quad (2)$$

During the year 2010, 599 mm of rain fell on the Toulouse region. This rainfall is 90% of the normal annual rainfall measured over the period 1971–2000.

Eq. (3). Dry weather pollutant load for a sample (i). $y_{i,p,j}$ is the pollutant load of the sample (i) in dry weather of the pollutant (p) for the particular outlet (j) expressed in mg/h. $c_{i,p,j}$ is the concentration of the pollutant (p) when sampled (i) for the particular outlet (j) expressed in μg/L. $Q_{i,j}$ is the flow measured when sampled (i) at the outlet (j) expressed in $m^3$/h.

$$y_{i,p,j} = c_{i,p,j} \times Q_{i,j}. \quad (3)$$

Eq. (4). Annual dry weather pollutant load. $Y_{p,j}$ is the annual dry weather pollutant load for the pollutant (p) and the particular outlet (j) expressed in mg/yr. $y_{i,p,j}$ is the pollutant load of the sample (i) in dry weather for the pollutant (p) for the particular outlet (j) expressed in mg/h. $t_{DW,2010}$ represents the duration of the dry weather (DW) over the year 2010 expressed in h.

$$Y_{p,j} = Median\ \ y_{i,p,j} \times t_{DW2010}. \quad (4)$$

During the year 2010 there were 260 days dry weather, thus 6240 h.

Thus the total annual load is the sum of the annual wet weather load and the annual dry weather load, which allows the proportion of the total annual load due to dry weather to be calculated. The results for each outlet are illustrated in Fig. 2 where each bar represents the total annual load and is separated in two parts: one corresponding to dry weather load and the other to wet weather load. The figure also shows the percentage impact of dry weather on the annual pollutant load.

The load calculations showed that overall, the most polluted storm sewer water came from the Boulevards outlet. The most important difference between the two outlets was for COD, a value of 53 t/year was found for the Boulevards outlet and the value of COD loads for Mirail outlet was 16 t/year. This can be explained by the nature of the watershed of Boulevards outlet which is a more heavily urbanized zone than that feeding the Mirail outlet. Indeed, a heavily urbanized zone generates an important quantity of organic matter represented in this study by the COD. Only the annual total nitrogen pollutant load was higher in the Mirail outlet discharges: 23 t/year for the Mirail outlet and 15 t/year for the Boulevards outlet. However, the Mirail outlet has a lower nitrate ion pollutant load (12 t/year vs 13 t/year for Boulevards outlet) and negligible ammonium ions (no concentration upper the limit of quantification). The total nitrogen pollutant load was therefore also due to the presence of organic nitrogen which could come from plants (leaves, branches …) or animals (fecal matter …) or from organic fertilizers. An explanation could be the «greener» urban zone nature of the outlet's watershed.

The wet and dry weather load calculations highlight the impact of dry weather discharges on the annual pollutant load and thus on the overall storm sewer water quality. Thus apart from the $BOD_5$, the impact of the dry weather discharges vary between 65% (VSM) and 89% ($NH_4^+$) for the Boulevards outlet and between 53% (COD) and 78% (SSM) for the Mirail outlet. The impacts of dry weather discharges for each parameter are illustrated in Fig. 2 above each bar of histograms.

Student or Mann–Whitney statistical tests were made to verify the significance of the difference between the two outlets and between sampling weathers. The p-value calculated by supposing that the null hypothesis is accepted as shown in Table 2.

These tests confirm a significant difference (at the $\alpha = 0.10$ level) between the pollution resulting from the Boulevards outlet and that from Mirail, for the majority of overall pollution parameters studied, apart from the total nitrogen and the nitrate ion pollution loads. The Boulevards outlet discharges representative of a heavily urbanized zone were 3.4 times more important than Mirail outlet discharges for COD and 6 times higher for total phosphorus.

These same tests comparing the sampling weather showed that the difference in pollutant load between wet and dry conditions was significant for COD, nitrate ions, suspended solid matter and volatile suspended matter at the Boulevards outlet. Therefore, the impact of dry weather discharges on storm sewer water quality was significant for these parameters. For COD, the dry weather discharge had an impact of 69% on annual pollution load, for nitrate ions this impact was equal 74%, for suspended solid matter and volatile suspended matter the impacts of dry weather discharges were 76% and 65% respectively. For the Mirail outlet, only total phosphorus presented a significant impact for the pollution load of dry weather, this impact was equal to 62%.

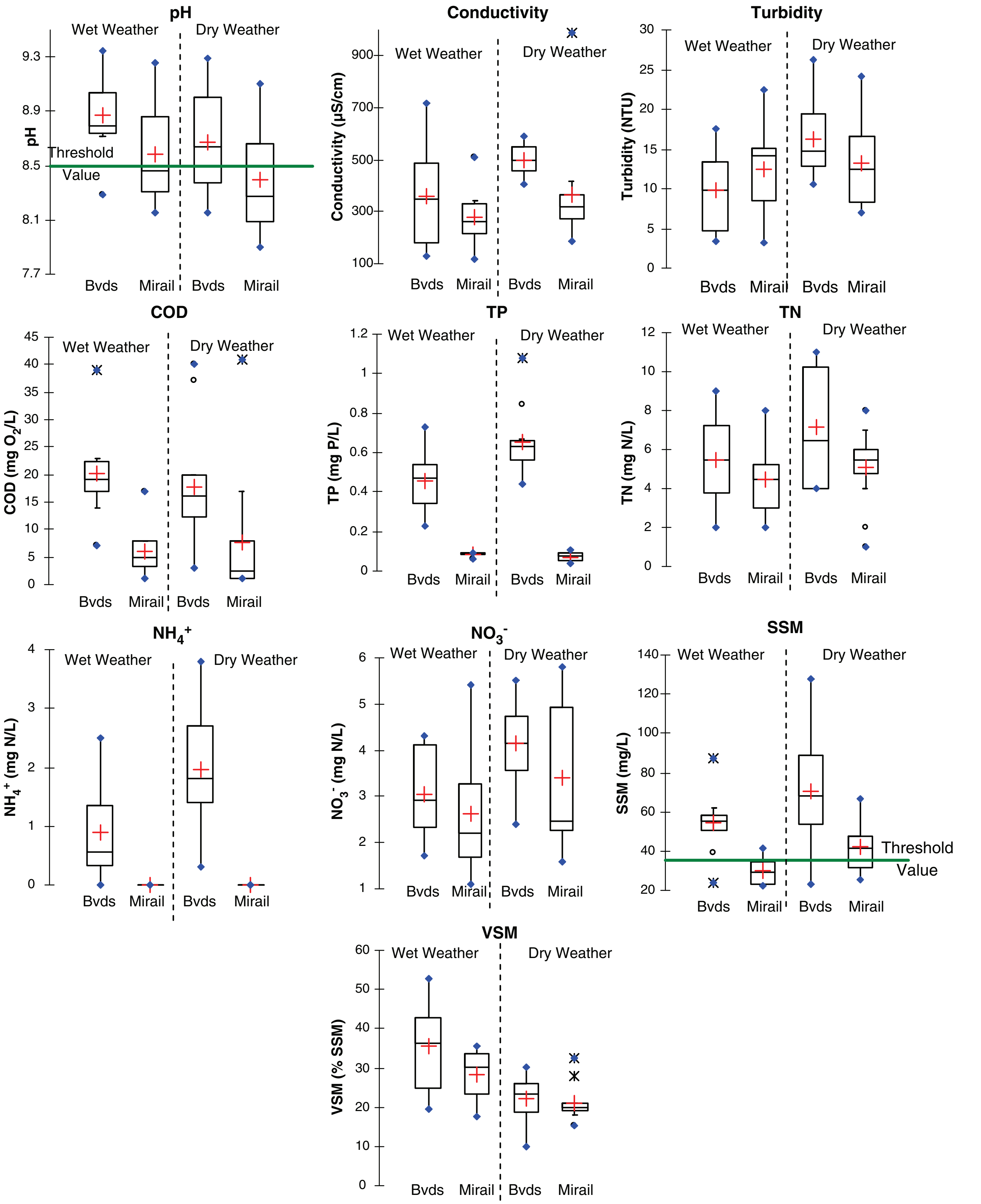


**Fig. 1.** Box and whisker plots representing data distribution for the overall pollution parameters in wet and dry weather discharges—SSM and pH threshold values of French 1998 Water Act are shown by a line. WW: wet weather—DW: dry weather. +: average. *: extreme values. ●: minimum–maximum.

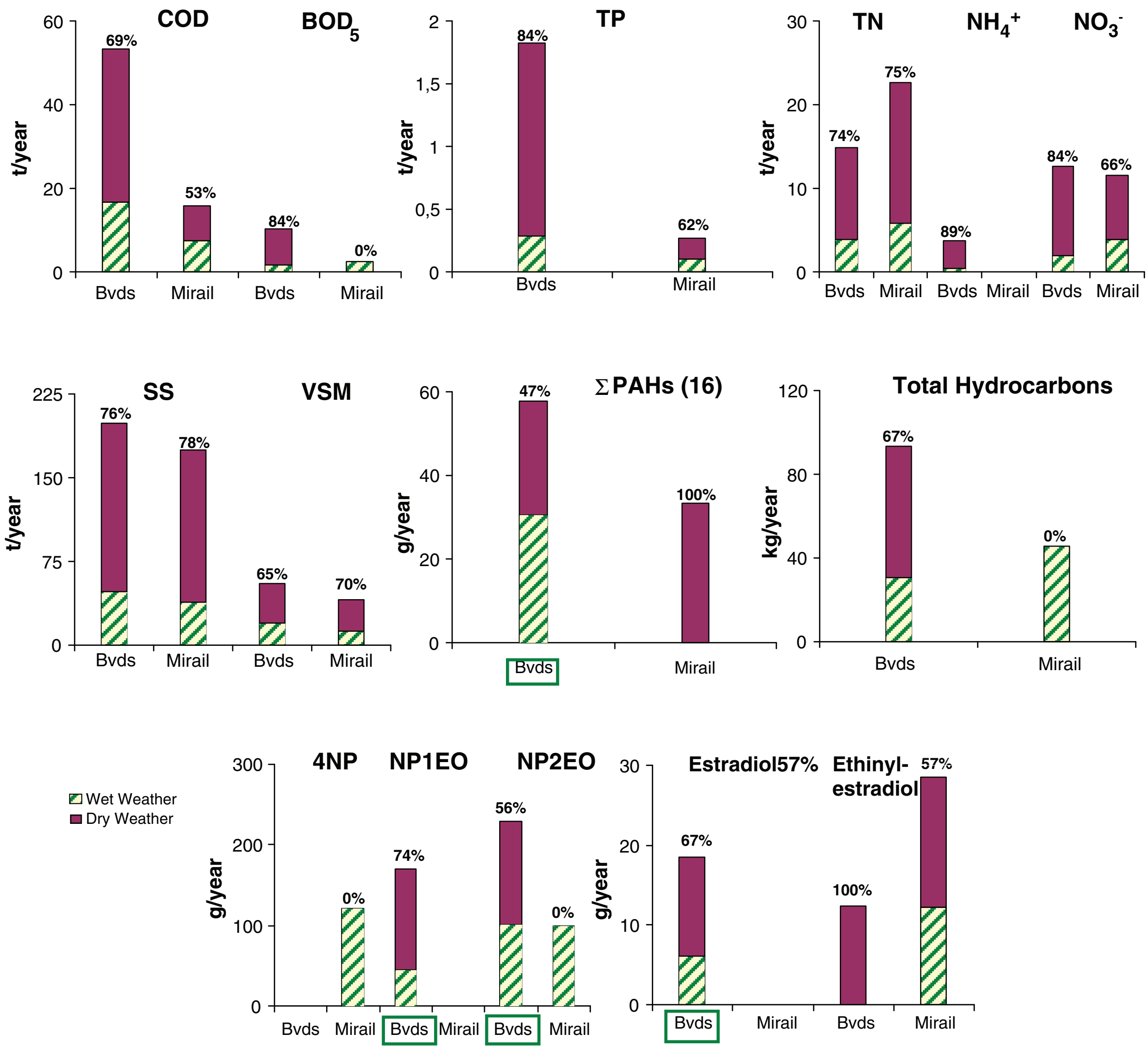


**Fig. 2.** Annual dry and wet weather loads for the overall pollution parameters and the trace organic compounds at the Mirail and Boulevards outlets—the impact of dry weather discharges on the annual pollutant load are expressed as percentages—the trace organic compounds with an occurrence of at least 25% are in boxes.

#### *3.2.2. Trace Organic Compounds*

The annual trace organic compound loads were calculated in the same way as for the pollution parameters (Fig. 2).

In view of the data, from now on it has been decided to only consider the compounds with an occurrence equal to or exceeding 25%.

The load calculations showed that overall, the highest pollutant load was contained in the water discharge from the Boulevards outlet for compounds with an occurrence equal to or exceeding 25%. This can be explained, as for the overall pollution parameters, by the nature of the watershed that is more heavily urbanized than that of Mirail outlet.

Calculations of the wet and dry weather loads highlighted an impact of dry weather discharges on the annual pollutant load in nonylphenol ethoxylates (74% for NP1EO and 56% for NP2EO) and in estradiol (67%).

The PAH pollutant load is almost the same for both dry and wet weathers from the Boulevards outlet. Quantities of PAH seem to be released into the storm sewer from car wash stations, and from road runoff in wet weather. The two effects would thus have a similar impact.

**Table 2**
Null hypothesis p-value obtained with Mann–Whitney or Student's tests.

| p-Value | Comparison between the two outlets Boulevards–Mirail | Comparison between wet and dry weather–Boulevards outlet | Comparison between wet and dry weather–Mirail outlet |
|---|---|---|---|
| COD | **0.5** | *5.9* | 37 |
| TP | <**0.01** | 18 | *8* |
| TN | 57 | 18 | 97 |
| $NH_4^+$ | <**0.01** | 41 | |
| $NO_3^-$ | 38 | 18 | 79 |
| SSM | *7.6* | **3.3** | 91 |
| VSM | **3.2** | **1.5** | 21 |

Bold: p-value < 5%—italics: p-value <10%.

### *3.3. Principal Components Analysis*

At the outset, principal component analysis (PCA) was conducted for all the data from both outlets, concerning the overall pollution parameters and the trace organic compounds (occurrence ≥25%). However, it was found that the trace organic compounds were not well represented on the new F1, F2 and F3 axes generated by the PCA and no trend could be seen. Therefore a new PCA using only the values in overall pollution parameters for the two outlets was made, (Fig. 3). Each point represents one collected sample. Points in black

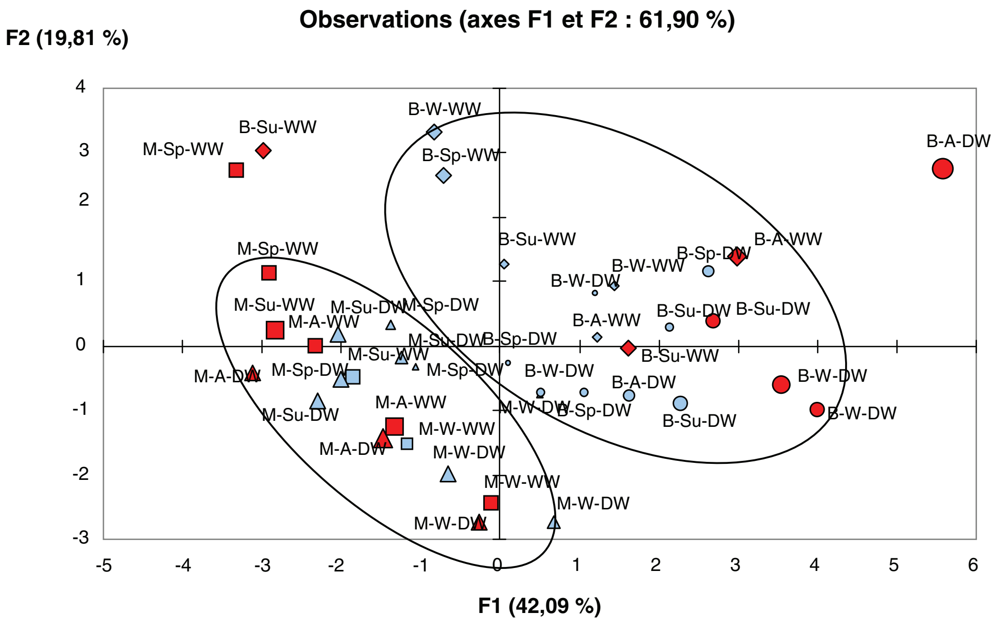


**Fig. 3.** PCA for all samples from the Boulevards and the Mirail outlets—visualization of observations. M = Mirail; B = Boulevards. Wi = winter; Sp = spring; Su = summer; A = autumn; WW = wet weather; DW = dry weather.

have a $\cos^2$ value above 0.7, therefore they are well represented in this PCA. The bigger the size of each point is, the higher the $\cos^2$ value is, the better the sample is represented in the PCA.

This PCA reveals a significant difference between the two outlets. Indeed, the observations from each of the outlets are grouped in two distinct clusters, allowing the previously drawn conclusions to be confirmed. However, grouping together data from both outlets, the data from the Boulevards outlet seem to strongly influence PCA results. It was also decided to conduct another PCA to study them separately. The PCA made for the Boulevards outlet and representing the overall pollution parameters studied is illustrated in Fig. 4. This figure presents two correlation circles with the first three principal components and each line in circles corresponds to the vector of each parameter. This representation permits to underscore correlations between parameters because co-linear variables are significantly correlated.

The first three principal components aggregate 72% of the variance. The F1 component seems to represent the nutrients (TP, TN, $NO_3^-$, $NH_4^+$). F2 can be taken as the organic component (VSM and DCO) and the F3 component mainly corresponds to the pH.

Using these circle interpretations and the Pearson (P) and linear correlation coefficients ($R^2 = P \times P$), significant correlations between certain parameters were made (at an $\alpha = 0.05$ level): TP—$NH_4^+$ ($R^2 = 0.554$); TP—$NO_3^-$ ($R^2 = 0.536$); TP—turbidity ($R^2 = 0.600$); $NO_3^-$—conductivity ($R^2 = 0.667$); $NO_3^-$—turbidity ($R^2 = 0.556$) and conductivity—turbidity ($R^2 = 0.661$). A strong correlation was observed between the conductivity and the concentration in total phosphorus ($R^2 = 0.834$).

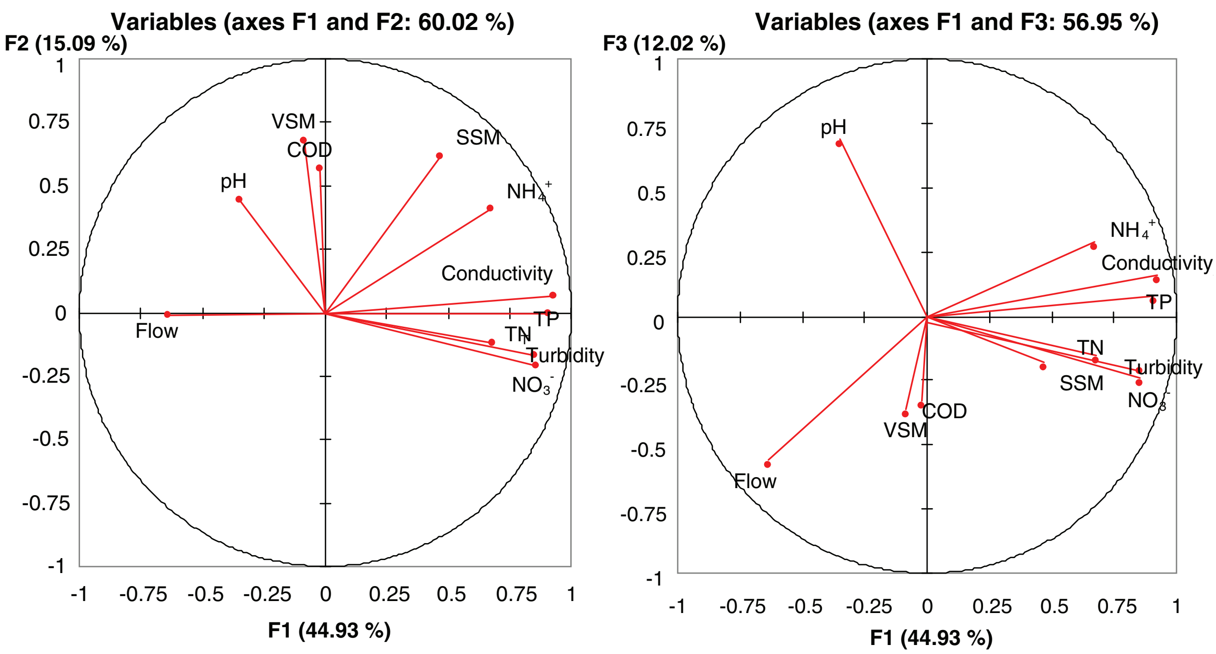


**Fig. 4.** Correlation circles for the F1–F2 and F1–F3 axes constructed from principal component analysis of all the samples from the Boulevards outlet.

The correlation between the total phosphorus and the ammonium ions could be explained by the possible presence of ammonium phosphate, used as a fertilizer or rejected by companies, and the strong correlation between the phosphorus and the conductivity agrees with these hypotheses since it confirms the presence of ionic phosphorus (phosphate ions).

The conductivity and turbidity are also correlated. It is possible that this is due to an ionic colloidal phase, a hypothesis supported by the presence of correlation between these two parameters and the nitrate ions and the total phosphorus (mainly present in the phosphate form as already shown).

PCA was also conducted on the data from the Mirail outlet samples. Only two correlations were found, one between the conductivity and the concentration of nitrate ions ($R^2 = 0.679$) and one between conductivity and flow ($R^2 = 0.531$). Therefore these correlations are specific to the outlet studied and the urbanization rate.

The quantity of total nitrogen for the two outlets studied is not correlated with the quantity of ammonium and nitrate ions present. Therefore organic nitrogen is also present (animal excrement, organic fertilizers, plant matter), a hypothesis already put forward under interpretation of loads, and thus confirmed by these results.

For the trace organic compounds, the Pearson and linear correlation coefficients allowing correlations with or between the overall pollution parameters were determined. They revealed the following, significant correlations (at the $\alpha = 0.05$ level): NP1EO—COD ($R^2 = 0.800$); NP2EO—COD ($R^2 = 0.788$); NP2EO—turbidity ($R^2 = 0.792$); estradiol—conductivity ($R^2 = 0.997$, inverse correlation). Nevertheless, the amount of available data needs to be greater to derive reliable correlations.

The PCA performed on the overall pollution parameters of the Boulevards outlet was also done (Fig. 5). Each point represents one sample collected for the Boulevards outlet.

This perception reveals that the sampling results are very variable in view of the wide dispersion of the data. However, two different groups can be seen: one corresponding to wet weather samples and the other to dry weather samples. No seasonal influence is visible since there is no appropriate aggregation, and this is confirmed by the ANOVA tests made.

## 4. Conclusion

The study of the water quality at two major outlets of the Toulouse storm sewer was completed with the aim of determining the impact of dry weather discharges on the overall quality. Twelve dry weather and eight wet weather events were sampled over a year at each outlet. Analyses were made on average samples taken over 24 h. In addition to the overall pollution parameters (SSM, VSM, pH, conductivity, turbidity, COD, $BOD_5$, TP, TN, $NH_4^+$ and $NO_3^-$), six groups of trace organic compounds were monitored (PAHs, DEHP, MTBE, total hydrocarbons, nonylphenols and hormones).

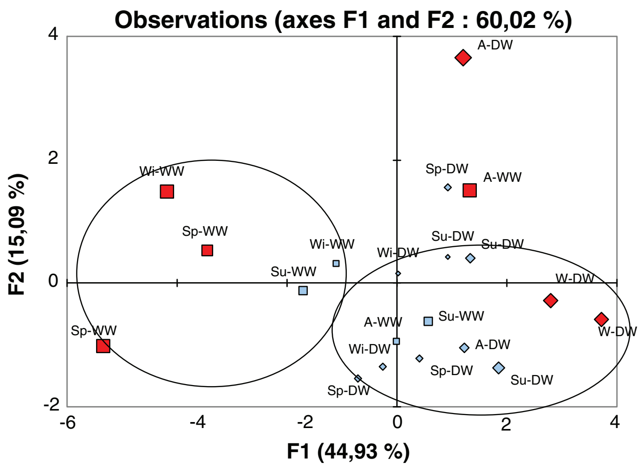


**Fig. 5.** PCA for all samples from the Boulevards outlet—visualization of observations. Wi = winter; Sp = spring; Su = summer; A = autumn; WW = wet weather; DW = dry weather.

Overall, for the two outlets studied, the concentrations and loads determined in dry weather discharge were higher than those obtained in wet weather discharge. The impacts of the dry weather discharges on the annual pollutant load and thus on the quality of the storm sewer water were significant for COD, SSM, VSM and TP.

Certain samples taken had levels of suspended solid matter and pH that did not respect legislation limit values, but for the other overall pollution parameters the requirements were respected. Concerning trace organic compounds, concentrations found in the samples were very low. MTBE and DEHP were not present in any sample and for the other pollutants: PAHs, NPEO, NP, hydrocarbons and hormones were only quantified in very few samples.

Comparing the pollutant loads at the two outlets, that from the Boulevards is, overall, much higher than from the Mirail outlet. The different levels of urbanization of the watersheds can explain it: Boulevards outlet is more heavily urbanized than Mirail outlet.

Principal component analyses were made and revealed correlations between different overall pollution parameters and thus a possible presence of ammonium phosphate, an ionic colloidal phase, and the presence of organic nitrogen. However, these correlations are specific of studied outlet. These multivariate statistical analyses also allowed to reject the hypothesis of a possible seasonal influence on storm sewer water quality in Toulouse.

These results, together with strengthened environmental quality standards raise serious questions as to the necessity for treating storm sewer discharge, prior to discharge into the natural environment.

## Conflict of interest

None.


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## References


Achten C, Kolb A, Püttmann W. Methyl tert-butyl ether (MTBE) in urban and rural precipitation in Germany. Atmos Environ 2001;35:6337–45.

Arrêté du 2 février. relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation—Section II: Eaux pluviales—Article 32 les eaux résiduaires rejetées au milieu naturel respectent par ailleurs les valeurs limites de concentration suivantes, selon le flux journalier maximal autorisé; 1998.

Barraud S, Fouillet B. Caractérisation des eaux pluviales et risques sanitaires. Conférence ASTEE, Eau et santé, Eaux pluviales et assainissement: nouvelles préoccupations sanitaires, Lyon-Villeurbanne; 2006.

Bjorklund K, Cousins AP, Stromvall AM, Malmqvist PA. Phthalates and nonylphenols in urban runoff: occurrence, distribution and area emission factors. Sci Total Environ 2009;407:4665–72.

Bressy A, Gromaire MC, Lorgeoux C, Saad M, Leroy F, Chebbo G. Contamination des eaux pluviales d'un bassin versant résidentiel dense amont. Tech Sci Méthodes 2011;4:28–36.

Chedeville M, Lesage J, Viau JY. Innovation dans la gestion et le traitement des eaux pluviales à la source. J Inform Eaux 2010. [Poitiers, 04-1–04-8].

Clark JW, Viessman W, Hammer MJ. Water supply and pollution control. 2nd ed. International Textbook Company; 197144–5.

Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status Text with EEA relevance.

De Rossi C, Bierl R, Riefstahl J. Organic pollutants in precipitation: monitoring of pesticides and polycyclic aromatic hydrocarbons in the region of Trier (Germany). Phys Chem Earth 2003;28:307–14.

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC,

86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.
He J, Balasubramanian R. Semi-volatile organic compounds (SVOCs) in ambient air and rainwater in a tropical environment: concentrations and temporal and seasonal trends. Chemosphere 2010;78:742–51.
Kim G, Yur J, Kim J. Diffuse pollution loading from urban stormwater runoff in Daejeon city, Korea. J Environ Manage 2007;85:9-16.
Lee JH, Bang KW. Characterization of urban stormwater runoff. Water Res 2000;34:1773–80.
Lee H, Lau S-L, Kayhanian M, Stenstrom MK. Seasonal first flush phenomenon of urban stormwater discharges. Water Res 2004;38:4153–63.
Legret M, Pagotto C. Evaluation of pollutant loadings in the runoff waters from a major rural highway. Sci Total Environ 1999;235:143–50.
Luo HB, Luo L, Huang G, Liu P, Li JX, Hu S, et al. Total pollution effect of urban surface runoff. J Environ Sci-China 2009;21:1186–93.
Pailler JY, Krein A, Pfister L, Hoffmann L, Guignard C. Solid phase extraction coupled to liquid chromatography-tandem mass spectrometry analysis of sulfonamides, tetracyclines, analgesics and hormones in surface water and wastewater in Luxembourg. Sci Total Environ 2009;407:4736–43.
Peng XZ, Yu YJ, Tang CM, Tan JH, Huang QX, Wang ZD. Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China. Sci Total Environ 2008;397:158–66.
Polkowska Z, Kot A, Wiergowski M, Wolska L, Wolowska K, Namiesnik J. Organic pollutants in precipitation: determination of pesticides and polycyclic aromatic hydrocarbons in Gdansk, Poland. Atmos Environ 2000;34:1233–45.
Sablayrolles C., Vialle C., Montréjaud-Vignoles M., 2008. Etude des rejets pluviaux de la ville de Toulouse, VEOLIA Eau – INP-ENSIACET-LCA-CATAR, Unpublished results. pp. 162.
Sablayrolles C, Vialle C, Vignoles C, Montrejaud-Vignoles M. Impact of carwash discharge on stormwater quality (Toulouse, France). Water Sci Technol 2010;62:2737–46.
Teemusk A, Mander U. Rainwater runoff quantity and quality performance from a greenroof: the effects of short-term events. Ecol Eng 2007;30:271–7.
Terzakis S, Fountoulakis MS, Georgaki I, Albantakis D, Sabathianakis I, Karathanasis AD, et al. Constructed wetlands treating highway runoff in the central Mediterranean region. Chemosphere 2008;72:141–9.
Walker WJ, McNutt RP, Maslanka CK. The potential contribution of urban runoff to surface sediments of the Passaic River: sources and chemical characteristics. Chemosphere 1999;38:363–77.
Xaumier F., Montréjaud-Vignoles M., Renner C., 2004. Etude des rejets pluviaux de la ville de Toulouse, VEOLIA Eau – Anjou-Recherche – INP-ENSIACET-LCA-CATAR Unpublished results. pp. 100.
Zgheib S, Moilleron R, Saad M, Chebbo G. Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stormwater catchments? Water Res 2011;45:913–25.
Zhang ML, Chen H, Wang JZ, Pan G. Rainwater utilization and storm pollution control based on urban runoff characterization. J Environ Sci (China) 2010;22:40–6.