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Priority pollutants in stormwater: the 'ESPRIT' project

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ABSTRACT

The ESPRIT collaborative research project (2007-2010) aims to contribute to the identification, evaluation and characterisation of 41 priority substances transported by stormwater, in two experimental sites in Lyon, France (one combined system and one separate system). At the outlet of both catchments, monitoring campaigns are carried out for a large number of storm events and for some dry weather periods. Most of the campaigns will deal with event mean concentrations, and a limited number of pollutographs will also be measured. In both sites, specific prototypes collect both dry atmospheric fallout and rain water, allowing estimating the dry and wet contributions of the atmosphere to the stormwater pollutant loads. In a first phase, screenings of the 41 substances will be performed. In a second phase, more accurate specific analyses for some substances will be carried out if necessary. A special effort will be devoted to evaluate the event variability of concentrations and loads. Models will be developed to extrapolate results to annual and multi-annual time scales and, if possible, to un-monitored catchments with similar characteristics.

KEYWORDS

Combined sewer, monitoring, priority pollutants, priority substances, separate sewer, stormwater.

INTRODUCTION

The European Water Framework Directive (WFD) n° 2000/60/EC (EC, 2000) requires, in its article 16, a progressive reduction of discharges of priority substances into water bodies and the cessation of discharges of priority hazardous substances. In a global and integrated urban water management approach, all sources should be analysed (diffuse agricultural pollution, urban and industrial pollution, emissions from wastewater treatment plants, from separate and combined sewer systems, etc.) and quantified, in order to define priorities for action.

Considering that only limited information is available regarding most priority substances in stormwater, the ESPRIT collaborative research project aims to contribute to the identification, evaluation and characterisation of priority substances transported by stormwater, in both combined and separate sewer systems. It is part of the research cluster Rhodanos and has links with other French research projects (e.g. AMPERES, DEMA...) dealing with priority substances in i) wastewater treatment plant influent, effluent and sludge and ii) in agricultural

discharges. All together, these projects aim to quantify the main sources and pathways of priority substances, to suggest reduction strategies and to contribute to reach the WFD goals. ESPRIT is carried out by a consortium of six partners (INSA-Lyon, Cemagref Lyon, SCA-CNRS, Suez-Environnement, Lyonnaise des Eaux and Grand Lyon). It is funded by various institutions through the Chemistry and Environment Pole of Competitiveness “Axelera” in Lyon, France. ESPRIT started in March 2007 for a period of 3 years.

OBJECTIVES

The main objective of ESPRIT consists to evaluate the concentrations and loads of 41 priority substances transported in stormwater in two experimental sites in Lyon, France. Monitoring campaigns will be carried out at the outlet of both catchments for a large number of storm events, and also for some dry weather periods. Most campaigns will focus on event mean concentrations (EMC), and a limited number of pollutographs will also be measured. In addition, at both sites, specific prototypes have been built to collect both dry atmospheric fallout and rain water. They allow estimating the dry and wet contributions of the atmosphere to stormwater pollutant loads. In a first phase, screenings of the 41 substances will be performed. In a second phase, more accurate specific analyses for some substances will be carried out if necessary and/or appropriate. A special effort will be devoted to evaluate the event variability of concentrations and loads. Models will be developed to extrapolate results to annual and multi-annual time scales and, if possible, to un-monitored catchments with similar characteristics.

SELECTION OF SUBSTANCES MEASURED IN STORMWATER

According to the provisions of article 16 of the WFD, a list of 33 priority substances, which represent a significant risk to or via the aquatic environment at the EU level, has been established by the European Decision n° 2001/2455/EC (EC, 2001). The list of priority substances regulated at European level also includes 8 additional dangerous substances, which are part of the List I in the European Directive on Dangerous Substances (EEC, 1976). The resulting main list of 41 substances to be monitored in the ESPRIT project is given in Table 1. An international literature review was carried out to identify other possible substances of interest to be monitored in stormwater; it includes for instance several metals listed in the dangerous substances directive (Becouze and Dembélé, 2007a).

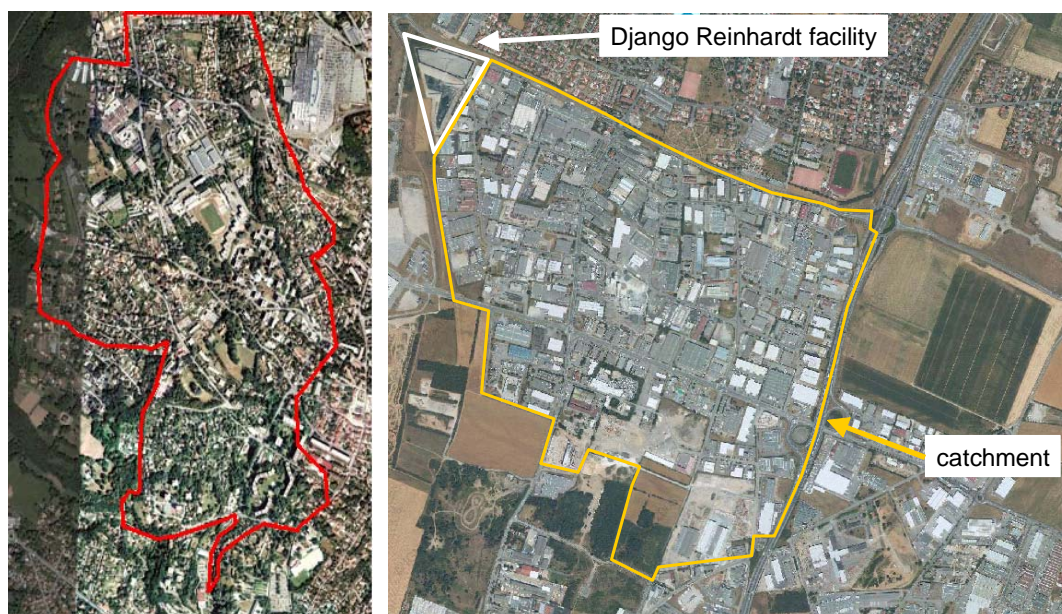
EXPERIMENTAL SITES

Monitoring campaigns are carried out at the outlet of two experimental catchments in Lyon, France: Ecully and Chassieu, which are part of the OTHU (Field Observatory on Urban Hydrology). Ecully (Figure 1, left) is a 245 ha residential area in the Western hilly suburbs of Lyon, equipped with a combined sewer system. The mean slope of the catchment is 2 %, with a coefficient of imperviousness of 42 %. Chassieu (Figure 1, right) is a 185 ha industrial area in the Eastern flat suburbs of Lyon, equipped with a stormwater separate sewer system. The mean slope of the catchment is 0.4 %, with a coefficient of imperviousness of 75 %.

Table 1. List of the 41 priority substances measured in stormwater.

| n° | Name | n° | Name |
|----|--|----|--|
| 1 | Alachlor * ** | 23 | Nickel |
| 2 | Anthracene ** | 24 | Nonylphenols (4-(para)-nonyphenol) ** |
| 3 | Atrazine * ** | 25 | Octylphenols (para-tert-octylphenol) ** |
| 4 | Benzene | 26 | Pentachlorobenzene |
| 5 | Brominated diphenylethers | 27 | Pentachlorophenol |
| 6 | Cadmium | 28 | Polyaromatic hydrocarbons ** (Benzo(b)fluoranthene **, Benzo(g,h,i)perylene **, Benzo(k)fluoranthene **, Indenol(1,2,3-cd)pyrene) ** |
| 7 | C ₁₀ -C ₁₃ -chloroalkanes | | |
| 8 | Chlorfenvinphos * ** | | |
| 9 | Chlorpyrifos * | 29 | Simazine ** |
| 10 | 1,2-Dichloroethane | 30 | Tributyltin compounds (tributyltin cation) |
| 11 | Dichloromethane | 31 | Trichlorobenzenes (1,2,4-Trichlorobenzene) * |
| 12 | Di(2-ethylhexyl)phthalate (DEHP) ** | 32 | Trichloromethane (Chloroform) |
| 13 | Diuron ** | 33 | Trifluralin * |
| 14 | Endosulfan (alpha-endosulfan) * | | |
| 15 | Fluoranthene ** | | |
| 16 | Hexachlorobenzene * | 1 | DDT total (para-para-DDT) * |
| 17 | Hexachlorobutadiene * | 2 | Aldrin * |
| 18 | Hexachlorocyclohexane * (gamma-isomer, Lindane *) | 3 | Dieldrin * |
| | | 4 | Endrin * |
| 19 | Isoproturon ** | 5 | Isodrin * |
| 20 | Lead | 6 | Carbontetrachloride |
| 21 | Mercury | 7 | Tetrachloroethylene |
| 22 | Naphtalene * | 8 | Trichloroethylene |

* GS-MS analysis, ** LC-FLD-MS/MS analysis: see Figure 4 and related text for details.

**Figure 1.** Aerial views and borders of the Ecully (left) and Chassieu (right) catchments.

Both catchments are equipped with similar specific sampling devices. Stormwater samples are collected at the outlet of the catchment by means of a Bühler 4010 volumetric vacuum pumping and refrigerated automatic sampler equipped with either a set of twenty-four 1 L glass bottles or a unique 25 L glass vessel. The 25 L vessel is used for EMC measurements

and the 1 L bottles are used for pollutographs. All sampler components in contact with stormwater are made of or covered with Teflon to avoid any interactions between sampling devices and pollutants to be measured. The sampler is controlled by means of a Sofrel S50 data logger and control system, in order to collect flow proportional samples. The discharge is calculated from 2 minutes time step simultaneous measurements of water level and flow velocity in the outlet sewer pipe (Nivus ultrasonic Nivumaster P06 probe for water level and Nivus Doppler OCM Pro probe for flow velocity). Two seasons (winter and summer) are distinguished for the flow proportional sampling to account for the significantly different storm event characteristics (duration, intensities, antecedent dry periods) observed in past rainfall data sets.

In addition to the automatic sampler, other physico-chemical parameters and pollutant concentrations and loads are measured or estimated by means of 2 minutes time step continuous monitoring of pH, electrical conductivity, turbidity, temperature and UV-visible spectrometry. All sensors (except flow meters) are located in a shelter where a transit flume is continuously supplied with effluent from the outlet sewer by means of a 1 L.s⁻¹ and 1 m.s⁻¹ peristaltic pump (Figure 2). They are initially and then periodically calibrated to ensure data quality and reliability.

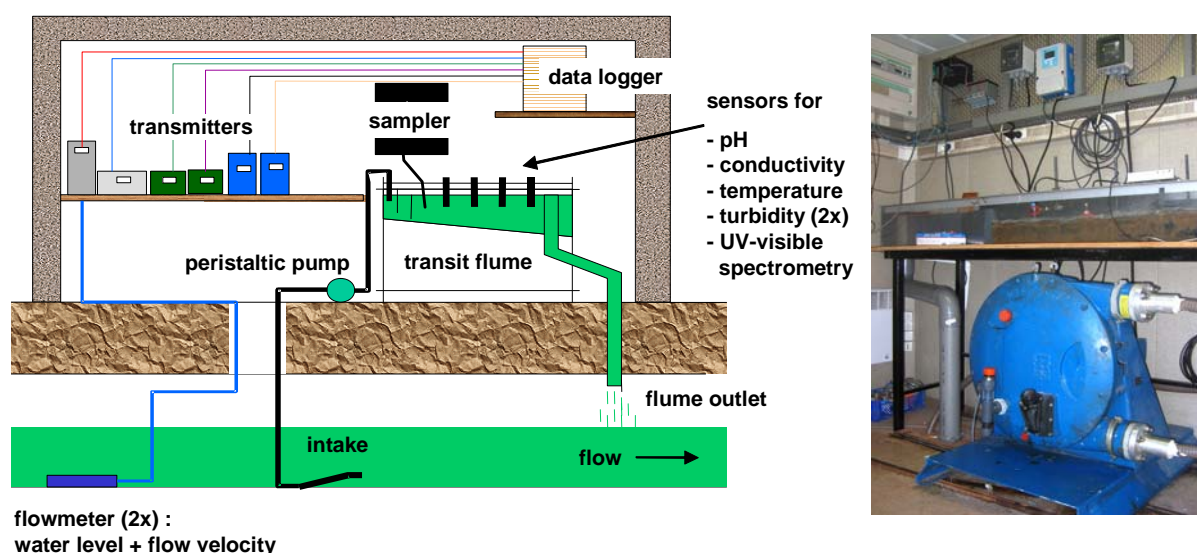


Figure 2. Left: scheme of the monitoring shelter installed on each inlet; Right: photo of the peristaltic pump and of the transit flume inside the shelter (photo JLBK).

In order to estimate both the dry and wet atmospheric contributions to loads of priority substances, specific prototypes for atmospheric sampling have been developed and installed in each catchment. Each prototype is composed of two parallel compartments built with plastic boxes (800×600×220 mm) entirely covered with Teflon (Figure 3). Each compartment is equipped with its own electric shutter. The dry compartment is open during dry weather to collect dry fallout whereas the other one is closed by the shutter. During storm events, the dry compartment is closed and the storm compartment is opened to collect rain water. Shutters opening and closing are controlled according to rainfall intensities measured in situ and on-line by means of OTT Pluvio weighing rain gauges. A specific algorithm has been developed and validated based on past storm data in order to ensure an appropriate control of the shutters (Dembélé, 2007). Dry fallout is collected monthly and rain water is collected after each storm

event: the pollutants to be measured depend on the available mass (for dust) or volume (for rainwater) of collected material. Analyses of organics and metals in both dry fallout and rain water are made with the same protocols as those used for stormwater samples as described in the following section.



Figure 3. Two compartments sampler for atmospheric dry fallout and rain water in Chassieu, with the rain gauge at the forefront (photo AD).

SAMPLING PROTOCOLS AND ANALYTICAL METHODS

Detailed protocols for sampling and samples handling, preservation and conditioning have been established and validated (Becouze and Dembélé, 2007b). Immediately after sampling, samples are conditioned and split in four subsamples:

- one for the analyses of organic compounds;
- one for the analyses of metals;
- one for the analyses of total suspended solids (TSS) and chemical oxygen demand (COD), which give an additional characterisation of the samples;
- one for the analyses of other compounds usually measured in stormwater: total organic carbon (TOC), total Kjeldahl nitrogen (TKN), ammonia, total phosphorous, orthophosphates.

Analyses of organic compounds

A multi-residue method by gas and liquid chromatography coupled to mass spectrometry has been developed and validated for the analysis of 36 priority organic substances listed in the WFD in various water matrices (Barrek *et al.*, 2008). More precisely, the method was developed in three steps, as illustrated in Figure 4. First, automated off-line solid-phase extraction was optimized to trap simultaneously the 36 studied compounds in the filtered water samples. Second, the 20 more volatile compounds were analysed by gas chromatography coupled to mass spectrometry with electron impact ionisation in selected ion monitoring mode (SIM). Third, the last 20 compounds were detected and quantified, in one run, by liquid chromatography coupled to fluorescence detector and mass spectrometry. The compounds measured by GS-MS and LC-FLD-M/MS are marked with * and ** respectively in Table 1.

Recoveries obtained were generally higher than 56 % for all tested waters. Extraction recoveries of substances analysed by GC-MS varied between 59.1 and 100 % with relative

standard deviations (RSD) below 4.5 %. Recoveries of substances analysed by LC-MS varied from 56 % for octylphenol to 100 % for pentachlorophenol. RSD varied from 2.1 % for chlorfenvinphos to 16.8 % for fluoranthene. Limits of detection (LOD) varied between 4 ng/L (pentachlorophenol) to 125 ng/L (octylphenol) for LC-FLD-MS/MS analysis. The limits of quantification (LOQ) for GC-MS analyses were between 6 and 41 ng/L for hexachlorobutadiene and endosulfan, respectively. During the ESPRIT project, the protocols will be adapted and validated for the analysis of organic substances in the suspended particulate fraction of stormwater samples.

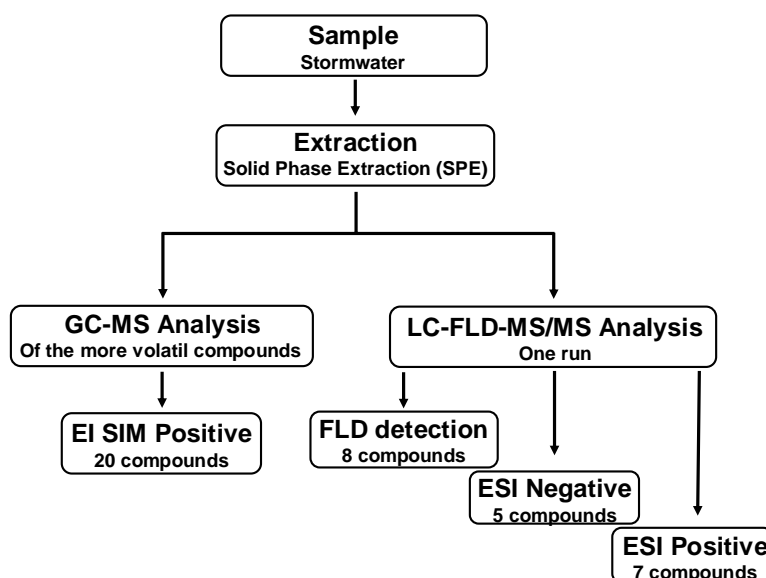


Figure 4. Flow chart of the analytical strategy developed for the sample extraction process and analysis.

Analyses of metals

Thanks to the techniques used, more metals than the four ones listed in Table 1 (Cd, Pd, Ni and Hg) are systematically analysed. All laboratory ware including filters, filtration units and polyethylene bottles are previously washed with 10 % (v/v) HNO₃ and rinsed with ultrapure water (Milli-Q, Millipore). An additional HCl 10 % (v/v) cleaning step is included for all equipment used for Hg analyses.

Water samples are filtered in the laboratory under a clean bench on acid-cleaned and preweighed filters (0.45 µm pore size; PVDF for metals or Teflon for Hg). The filtrate is immediately acidified with ultrapure acids (Suprapur, Merck): 0.2 % v/v HNO₃ for metals and 0.5 % v/v HCl for Hg analyses. Then they are stored at 4°C in darkness until analyses. Filters are put in plastic petri dish, dried for 24 h at 50°C, transferred in a dessiccator and reweighed. They are stored in plastic bags before analyses. Similar manipulations are performed with ultrapure water (Milli-Q, Millipore) to control the cleanness of the sampling and filtration procedures.

Metals are measured in both dissolved and particulate fractions. Filters are first mineralized using aqua regia (HNO₃:HCl, 3:1) in a microwave oven. Samples are analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X7 series II) according to ISO-CEN standard methods (ISO, 2003). The LOQs for the dissolved phase vary between 0.01 µg/L

(for Cd) and 5 µg/L (for Al and Ba) (see Figure 7). Typical precisions (evaluated as expanded uncertainties) vary between 8 and 20 % depending on the element.

Total dissolved mercury analyses in water samples are performed according to the US Environmental Protection Agency standard method (EPA, 2002). Samples are first oxidized with bromine monochloride (BrCl), then hydroxylamine hydrochloride (NH₂OH, HCl) is added to neutralise the remaining BrCl and Hg^{II+} is reduced to Hg⁰ using a stannous chloride (SnCl₂) solution. Mercury is detected after preconcentration on a gold trap using an automated atomic fluorescence spectrophotometer (AFS, Mercur Analytikjena). The LOQ of the method is 0.5 ng/L. Precision, evaluated by replicate analyses, was between 5 and 10 %. The analytical method for Hg in particulate samples is under validation. Particles collected on filters are first mineralized using a mixture of (HNO₃:HCl, 9:1) for 3 h at 90°C, then Hg is measured using the same analytical procedure as described above.

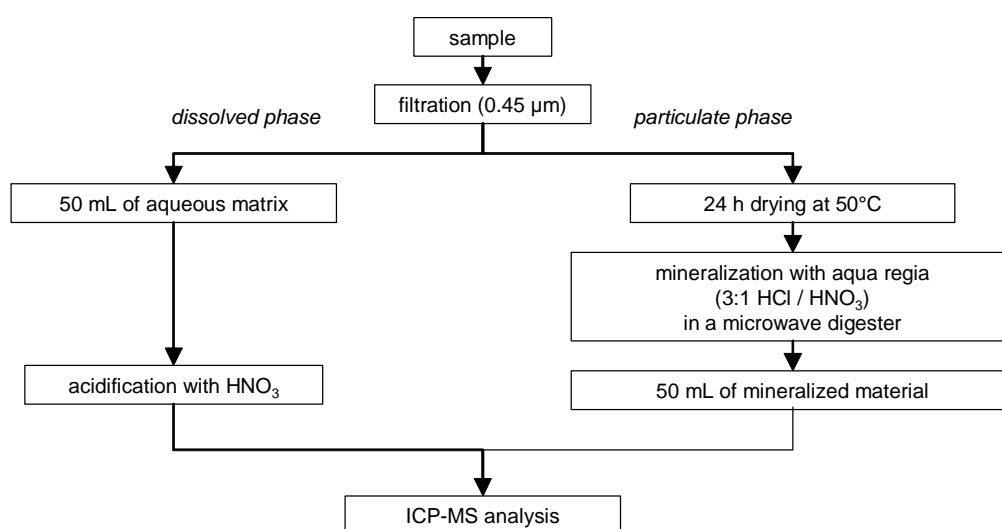


Figure 5. Flow chart of the analytical protocol for metals analysis in dissolved and particulate fractions (except mercury).

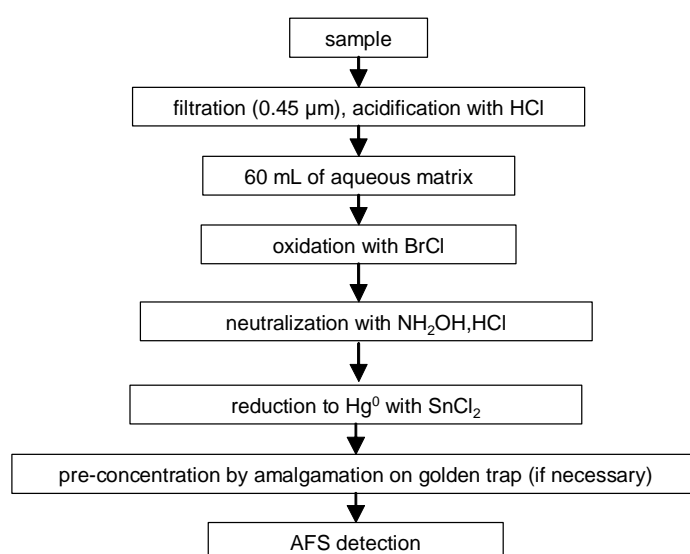


Figure 6. Flow chart of the analytical protocol for mercury analysis in the dissolved fraction.

Analyses of TSS and COD

TSS concentration is measured according to the standard method EN 12880 (2000). COD concentration is measured with the small tube test (STT) standard method (ISO 15705, 2002) with Hach - Dr Lange tubes LCI 500 [0-150 mg/L] and LCI 400 [0-1000 mg/L], after homogenisation with an Ultra-Turrax[®] mixer.

Analyses of other compounds

All other compounds are measured in an external subcontracting certified laboratory according to French and international standard methods.

MONITORING CAMPAIGNS

The planned monitoring campaigns include initial pollutant screenings for both sites, field blank samples for sampling devices, storm event mean concentrations (EMC), dry weather daily mean concentrations (DMC) and a few pollutographs. Samples for EMC measurements are obtained by direct mixing of individual flow proportional sub-samples pumped in the 25 L vessel. Samples for DMC measurements are obtained by off-line flow proportional mixing of hourly sub-samples taken in 1 L bottles.

After cleanup of all sampling devices according to a suitable validated protocol (Becouze and Dembélé, 2007b), field blank samples are obtained by passing off benchmark water samples (BWS) into all sampling devices. BWS must be typical i) of urban wet weather effluent or of dry weather effluent for the automatic sampler and ii) of rainwater for the atmospheric sampler. In the later case, Evian water, which has a pH similar to that of rainwater, is used as BWS. The campaign aims to evaluate possible adsorption of or contamination by priority substances during sampling. Results obtained upstream and downstream sampling devices are compared to detect possible differences. In case significant differences are detected, they will have to be identified for correction in the following campaigns.

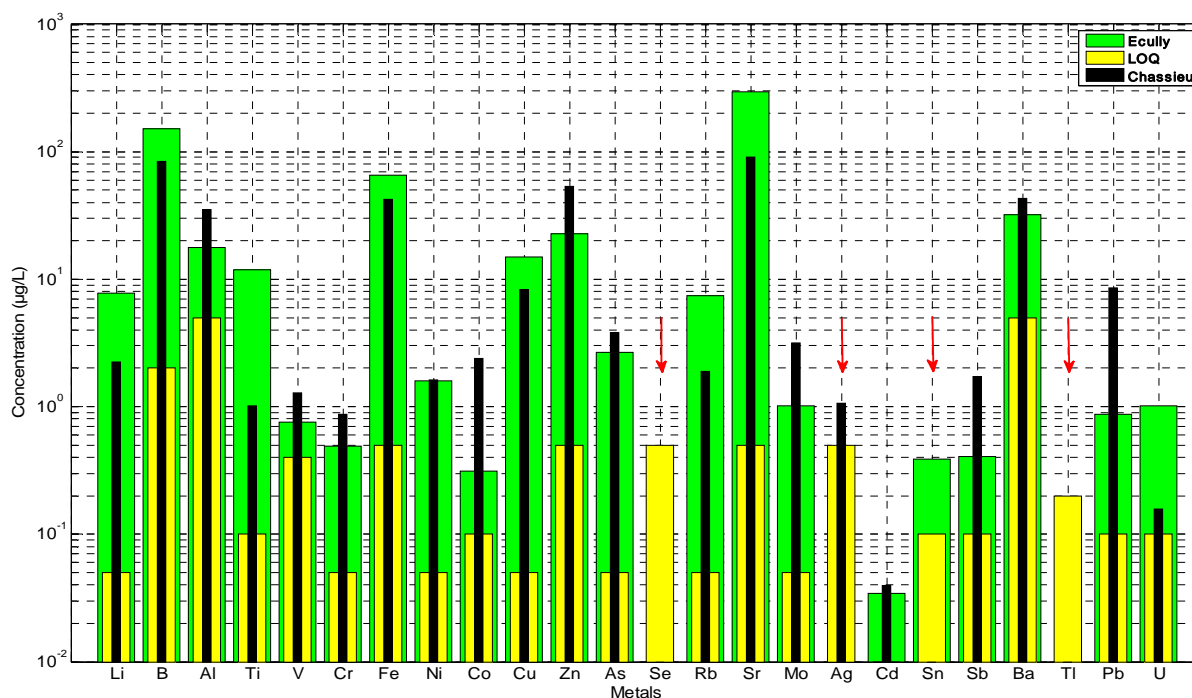


Figure 7. Results of preliminary screening of dissolved metals for both sites. LOQ = limit of quantification. Arrows above some bars indicate concentration lower than LOQ.

Preliminary screening analyses have been carried out in 2007, to check if expected substances are effectively present in wet weather effluents in both catchments. Figure 7 shows the results obtained for dissolved metals for one EMC in Chassieu and one DMC in Ecully.

Most metals are present at both sites with concentrations higher than LOQs. However, some metals were absent or present with concentrations lower than their LOQ: selenium (Se) and titanium (Ti) in both sites, silver (Ag) in Ecully and tin (Sn) in Chassieu. These are only preliminary results that should not be used to draw general conclusions.

CONCLUSION

The ESPRIT project started in March 2007. All sampling equipments are installed since February 2008 on two sites in Ecully (combined sewer system) and Chassieu (separate sewer system) in Lyon, France. Sampling and analytical protocols for a list of 41 priority substances have been validated. Effective monitoring campaigns have started in 2008: their results will be shown and discussed on the poster to be presented during the 11th International Conference on Urban Drainage.

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More information

ESPRIT website at <http://esprit-rhodanos.fr>

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