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## URBAN RUNOFF IMPACT ON COMPOSITION AND CONCENTRATION OF HYDROCARBONS IN RIVER SEINE SUSPENDED SOLIDS

Hacène Boudries<sup>1,3</sup>, Cécile Broguet<sup>1,3</sup>, Jean-Marie Mouchel<sup>2,3</sup> and Daniel R. Thévenot<sup>1,3</sup>

<sup>1</sup> Laboratoire de Bioélectrochimie et d'Analyse du Milieu (LABAM), Université Paris XII-Val de Marne, Avenue du Général de Gaulle, 94010 Créteil Cedex, France,

<sup>2</sup> CERGRENE, ENPC-ENGREF, La Courtine, 93167 Noisy-le-Grand Cedex, France,

<sup>3</sup> PIREN-Seine, CNRS GDR 1067, Laboratoire de Géologie Appliquée, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France.

**KEYWORDS** : Urban runoff, suspended solids, hydrocarbons, carbon preference index.

### INTRODUCTION

It is now well established that hydrocarbons are recognised like hazardous compounds, especially polynuclear aromatic hydrocarbon (PAH) [Bomboi and Hernandez, 1991; Hermann R., 1981]. Urban runoff is a non negligible source of hydrocarbon that may damage the quality of receiving river.

In this report, we present the first results of a study of the impact of combined sewer overflows (CSOs), during summer 1995, on the distribution of n-alkanes (C<sub>11</sub>-C<sub>37</sub>) in the Seine river. Figure 1 shows the site of Chatou, where suspended solids (SS) were sampled just before and during a week period following the moderate CSO event of September 7, 1995.

### EXPERIMENTAL

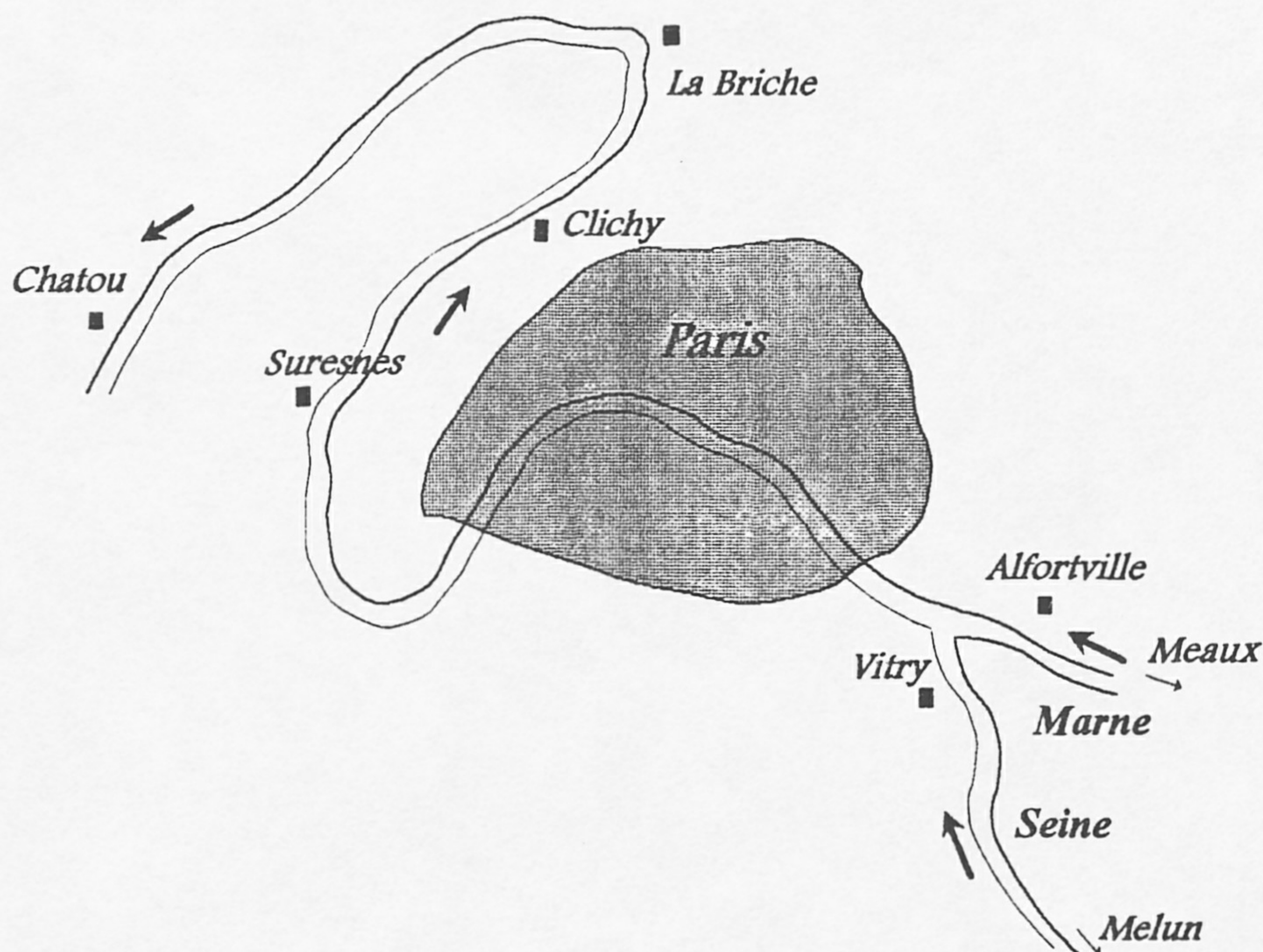
#### Sampling site

SS were collected at Chatou, a site located 35 km downstream Paris and 20 km downstream the 2 main CSOs of Paris region, namely Clichy and La Briche (Fig. 1). Just before and after a CSO event of Paris region on September 7, 1995, samples were collected daily between September 7 to September 12, 1995.

A settling trap (50 cm depth, and 30 cm internal diameter), equipped with a honeycomb filling, was used to collect SS samples. The trap is placed 40 cm below the water surface and 1,5 m from the bank of the river Seine. It allowed us to collect 15 to 70 g dry SS

necessary to identify and quantify aliphatic and PAHs. Table 1 shows the concentration of SS matter collected between September 5 and 12 1995, and the flow of the river Seine.

The samples were collected from the bottom of traps into 2.5 l glass bottles and transported rapidly (2 to 3 h) to the laboratory for centrifugation (3700 rpm, 20 min) and drying at 60°C. This treatment stabilises the composition of hydrocarbons in the sample before analysis and was shown to be as efficient as lyophilisation for solvent extraction. No significant losses of the lower hydrocarbons have been observed.



*Fig. 1: Site sampling downstream and upstream the Paris district during summer 1995*

### **Analysis of hydrocarbons**

About 4 g of dry SS were extracted for 24 h under subdued light with a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  (5:1, v/v) in a Soxhlet apparatus with internal standard hydrocarbons added (Phenanthrene- $\text{D}_{10}$  and Pyrene- $\text{D}_{10}$  as aromatic standard and Tetracosane- $\text{D}_{50}$  as the aliphatic hydrocarbon standard). The extract was dried by  $\text{Na}_2\text{SO}_4$  and concentrated down to 5 ml, using rotary evaporation. All solvents or chemical product used were distilled or extracted in Soxhlet apparatus.

The extracts were evaporated under a flux of pure nitrogen down to 1 ml and separated by adsorption chromatography using glass micro-column filled with 2 g of deactivated Silica gel and elution with a series of solvents of increasing polarity. Two fractions were obtained by elution with n-hexane (5 ml) and 20% of dichloromethane in n-hexane (3 ml), corresponding, respectively to the aliphatic and poly-aromatic hydrocarbons. Both fractions were then further evaporated to 0.25 ml under a flow of pure nitrogen.

The analysis of each column eluting fraction was carried out with Hewlett-Packard GCD, gas chromatography-mass spectrometer (GC/MS) system equipped with PONA capillary column (Hewlett Packard, 95% methyl silicone, 50 m length, 0.20 mm i.d., 0.45  $\mu\text{m}$  film thickness) coupled directly to the mass spectrometer. The oven temperature was programmed from 70 to 300°C at 2°C.min<sup>-1</sup>. Hydrogen was used as a carrier gas at constant flow (1 ml.min<sup>-1</sup>). The mass spectrometer scanned repeatedly from 10 to 450 Da at one scan per second and the ionisation electron energy was 70 eV.

Sampling date	Sept. 5-6 1995	Sept. 7 1995	Sept. 8 1995	Sept. 9 1995	Sept. 10 1995	Sept. 11 1995	Sept. 12 1995
Instantaneous SS concentration (mg l <sup>-1</sup> )	16.1	31.1	18.1	12.5	10.7	11.8	11.3
SS weight in settling trap (g)	68.5	37.6	15.2	15.9	16.3	18.7	17.1
Seine river flow (m <sup>3</sup> s <sup>-1</sup> )	149	180	188	174	165	174	201
$\Sigma_{\text{n-alkanes}}$ ( $\mu\text{g g}^{-1}$ )	75.7	131.9	162.3	149.0	123.4	144.2	148.0
$\Sigma_{\text{aromatic}}$ ( $\mu\text{g g}^{-1}$ )	7.56	10.3	9.6	11.6	14.3	12.0	11.2
UCM ( $\mu\text{g g}^{-1}$ )	1741	3003	2133	3854	2139	4172	2946
Global CPI	1.96	1.59	1.44	1.55	1.88	1.71	1.17
CPI (< C <sub>20</sub> )	2.13	1.18	0.98	0.96	1.07	0.97	0.78
CPI (> C <sub>20</sub> )	1.87	2.65	2.76	2.29	3.95	4.96	3.01

Table 1: Concentration and hydrocarbon composition of Seine river SS at Chatou (5-12 September 1995)

## RESULTS AND DISCUSSION

The impact of September 7 CSO event appears clearly on variation of SS concentrations which increase from 16 to 31 mg.l<sup>-1</sup> before returning, within 24 h, to 11-12 mg.l<sup>-1</sup> (Table 1). During that wet period, river Seine flow, at Austerlitz bridge in Paris, increases gradually from 150 to 200 m<sup>3</sup>.s<sup>-1</sup> with a small peak at 190 m<sup>3</sup>.s<sup>-1</sup> 2 days after the CSO event, i.e. when the Clichy and La Briche CSOs reach Chatou.

We observe on chromatograms of SS extracts more than 20 aliphatic (C<sub>11</sub>-C<sub>36</sub>) and 15 polycyclic aromatic well identified and quantified hydrocarbons but also an unresolved

complex mixture (UCM). Table 1 shows that, during this one week sampling period including a CSO impact, concentrations of aliphatic hydrocarbons increased from 75 to 162  $\mu\text{g g}^{-1}$  dry SS whereas PAHs concentrations increased from 7 to 14  $\mu\text{g g}^{-1}$  dry SS. This factor 2 increase of concentrations of both types of hydrocarbons is similar, in amplitude, to the heavy metal concentration increase in SS after a CSO event (Estèbe *et al.* this conference). However, the fate of hydrocarbons seems significantly different from that of metals. The increase of hydrocarbon concentrations lasts several days after the overflow event although the water transfer time between Clichy urban runoff site and Chatou is limited to 2 days. This different behaviour may indicate a difference of mechanism of pollution transport by CSO SS which have been shown to rapidly settle and then slowly migrate on the bottom of river Seine (Estèbe *et al.*, this conference).

### Distribution of n-alkanes

Figure 2 shows the distribution of particulate  $\text{C}_{11}$ - $\text{C}_{36}$  n-alkanes from September 5 to 12, 1995. We can observe two maximum concentrations, respectively for  $\text{C}_{17}$  and  $\text{C}_{29}$ , and a minimum concentration corresponding to  $\text{C}_{20}$ - $\text{C}_{21}$  together with, in general, an odd carbon-numbered predominance. If we consider now two classes of aliphatic hydrocarbons, the first one corresponding to lighter n-alkanes  $\text{C}_{11}$ - $\text{C}_{20}$  and the second class to heavier ones, i.e.  $\text{C}_{21}$ - $\text{C}_{36}$ , we can observe a difference in the distribution of aliphatic hydrocarbons from one day to another. Before the CSO event of September 7, the sample taken on September 5, shows high concentrations of heavier hydrocarbons ( $\text{C}_{21}$ - $\text{C}_{36}$ ) and very low level concentrations for lighter hydrocarbons, except  $\text{C}_{17}$ . An opposite distribution is observed for the September 7 and 8 samples, which correspond to the period of CSO event: we observe higher level of concentration for the  $\text{C}_{11}$ - $\text{C}_{20}$  n-alkanes.

### Carbon preference index (CPI)

The CPI represent the ratio between the odd and even-carbon aliphatic hydrocarbons. We have calculated 3 different CPIs: the first one, correspond to all hydrocarbons measured ( $\text{C}_{11}$ - $\text{C}_{36}$ ), the second and the third one correspond, respectively, to the lighter hydrocarbons, i.e.  $\text{C}_{11}$ - $\text{C}_{20}$ , and to the heavier ones, i.e.  $\text{C}_{21}$ - $\text{C}_{36}$ . We observe that for the first group, i.e.  $\text{C}_{11}$ - $\text{C}_{20}$ , the CPI decrease from 2.13 to below 1 after the CSO impact. This suggests a significant predominance of even-carbon numbered aliphatic hydrocarbons and might indicate a recent petrogenic contamination [Readman J. W. *et al.*, 1986]. Several study [Broman D. *et al.*, 1987,] have already shown that fuel oil product exhibit similar low range n-alkanes distribution. In the higher carbon-number range, i.e.  $\text{C}_{21}$ - $\text{C}_{36}$ , we observe an increase of the concentration level with always odd-carbon numbered predominance after the overflow (September 8): it is very difficult to distinguish between the natural and anthropic sources, due the value of CPI between 2-5, in spite of dominant n- $\text{C}_{27}$ , n- $\text{C}_{29}$  and n- $\text{C}_{31}$ , which are indicative of a natural higher plant input [Readman *et al.*, 1986].

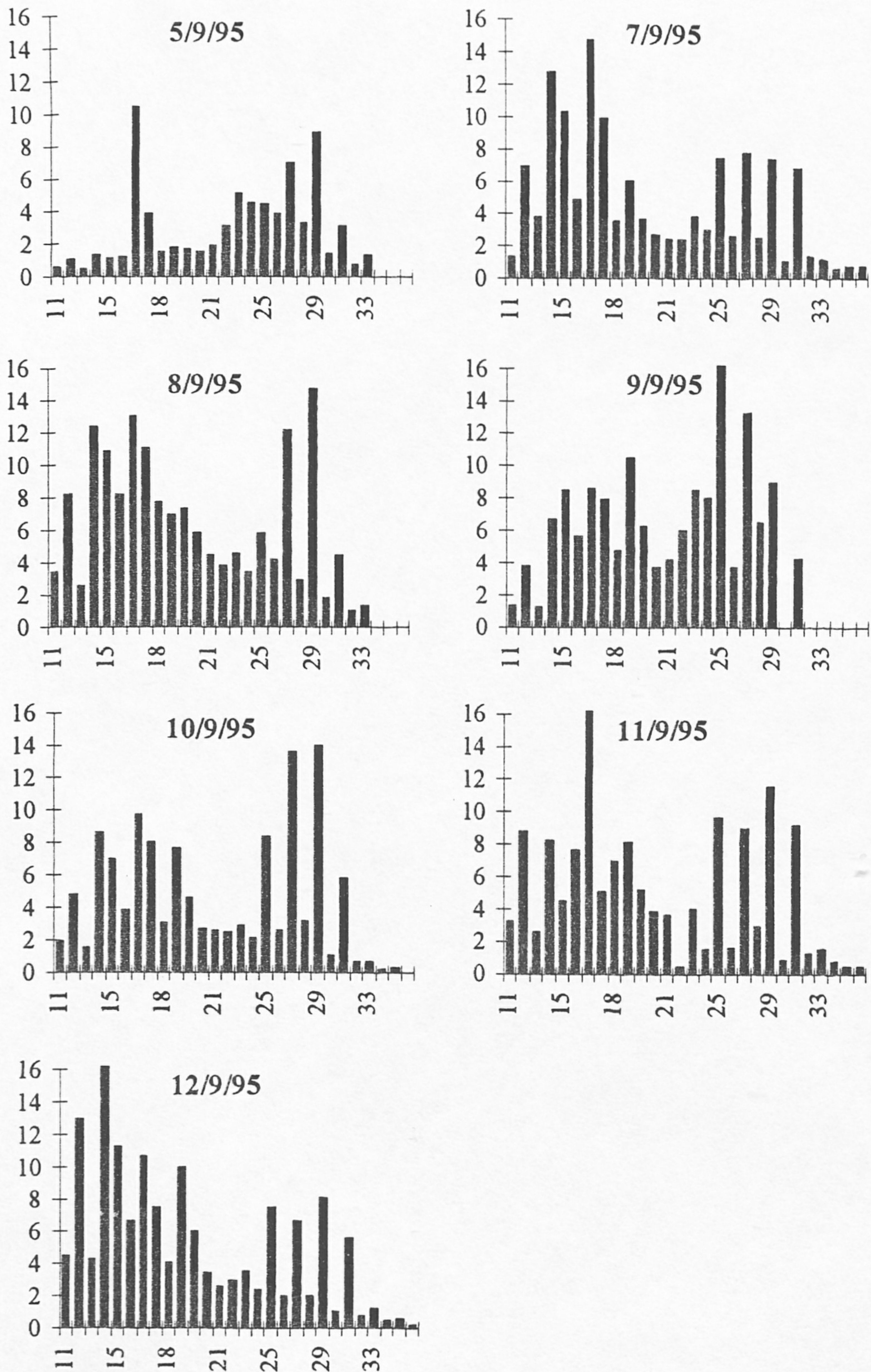


Figure 2: Distribution of n-alkanes, in  $\mu\text{g g}^{-1}$  dry SS, according to their number of C atoms, between September 5 and 12, 1995 in Seine River, at Chatou.

## CONCLUSION

A significant impact of Paris CSO has been demonstrated on the basis of total aliphatic and aromatic hydrocarbons linked to SS present in Seine river (Table 1). During this CSO event contribution of hydrocarbons is observed with a significant concentration of lighter n-alkanes, i.e. C<sub>11</sub>-C<sub>21</sub>, with even-carbon numbered predominance: these hydrocarbons are typically anthropic (CPI <1).

This study is a part of a larger ongoing research programme named « PIREN-Seine »: it will be completed with comparison of other site sampling sites either upstream (Alfortville on River Marne and Vitry-sur-Seine) or downstream Paris region (Chatou and Suresnes) including a site situated upstream the 2 main Paris CSO sites (Suresnes) (Figure 1). Samples have been collected during one year, both during dry and wet periods and during low and high flow periods, in order to confirm the results presented in this report and to determine particulate hydrocarbon transport mechanism in Paris district.

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