A QUANTITATIVE ANALYSIS OF THE SURFACE REMOVAL OF POLLUTANTS IN A SEPARATIVE URBAN CATCHMENT

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Abstract
The aim of this paper is to present the results of the fieldwork conducted in the catchment "Fontiñas" located in the city of Santiago de Compostela (Northwest Spain). The aim of this fieldwork is twofold: firstly, to carry out a hydraulic analysis and evaluate the contamination discharged by the occurrence of the rainfall events, and secondly to know the behaviour of the pollutants in terms of the lag between the time to peak of the hydrograph and the pollutographs. 8 events have been analysed. The first flush phenomenon of urban wet weather discharges is a controversial theme. In this paper, the L(V) curves have been used as an analysis tool. Each curve L(V) can be fitted by a function like $Y=X^a$. The "a" values have been presented for suspended solids (SS), dissolved solids (DS), copper, lead, zinc, mercury, chromium, nickel, cadmium, iron and manganese.

Keywords
Heavy metals, suspended solids, dissolved solids, separative sewered basin, load distribution, first flush, peak concentrations, EMC, urban stormwater pollution.

Introduction

Urban wet weather discharges are recognized as significant sources of pollution to receiving waters. These discharges can cause different types of effects according to the type of discharged pollutants (organic matter, solids, toxicants or nutrients) and according to the time scale of the degradation processes occurring in the receiving waters. Then, a rapid oxygen depletion, over a period of several hours or several days, are linked to shock effects. Whereas, discharges of pollutants like toxicants, solids and nutrients, during a period of several months, are linked to cumulative effects.

The "Nationwide Urban Runoff Program" (US-EPA, 1983) involved monitoring 120 "priority pollutants" in stormwater discharges. The study detected 77 priority pollutants in samples of stormwater discharges from the study sites, including 14 inorganics and 63 organic substances. Representative detection frequencies included lead (94%), zinc (94%), copper (91%), chromium (58%), arsenic (52%), cadmium (48%) and nickel (43%).

Thus, in view of the negative effects of urban wet weather discharges on receiving waters, we are interested in 3 kind of discharges:

- Annual loads to estimate the cumulative effect over a long period;
- Loads per event to estimate the shock effect which appear during several hours;
- Inside the events to study the variation in small time intervals.

The third type is also important to define treatment strategy. Pollutants are normally removed from surface waters through some combination of structural BMPs through the basic mechanisms: physical removal and settling, filtering, chemical reaction, and biochemical transformation.

First-flush conditions result in relatively high pollution concentrations during the initial stages of storm water runoff. This can induce shock-loading and short term degradation of the water quality of receiving waters.

First flush effects are attributed primarily to the washoff of particles from impervious area. It is very important to know if pollutants are in a dissolved or particulate structure, and their associations, mostly if talking about heavy metals, with are ussually considered to be associated among them and with the particulate fraction of pollution.

In this study, the concentrations of Cu, Pb, Zn, Hg, Cr, Ni, Cd, Fe, Mn and As have been analysed, as well as the concentrations of the different fractions of solids.

Morphology of the studied catchment

Santiago de Compostela has a typical atlantic climate with a rainfall profile near to 1500 mm/year. The catchment here studied has a separative urban sewer network. The surface area covers around 45 hectares having an imperviousness of 75%. This is a commercial and residential area exhibiting the characteristics typical of an urban zone with a medium population density and medium traffic flow. The catchment's slope average is about 6.5%. This fact is highly relevant to the hydrological and the pollutant behaviour. Catchment concentration time is approximately 15-20minutes (Cagiao et al., 1999). The figures below show the catchment studied with its sewer network and control section (Figure 1).

At the low point of the catchment a control section was set up where, to date, a total of 10 rainfall events have been sampled, having collected information on total flows and pollutant parameters, including solids, heavy metals and organic carbon among others. A rainfall meter was installed at the catchment to provide reliable data on rainfall.

It has been noticed a constant base flow of about 5 L/s, whose origin can be the infiltration or some parasit intakes. This base flow hase been measured in order to make a proper analysis of the mass corresponding to runoff.

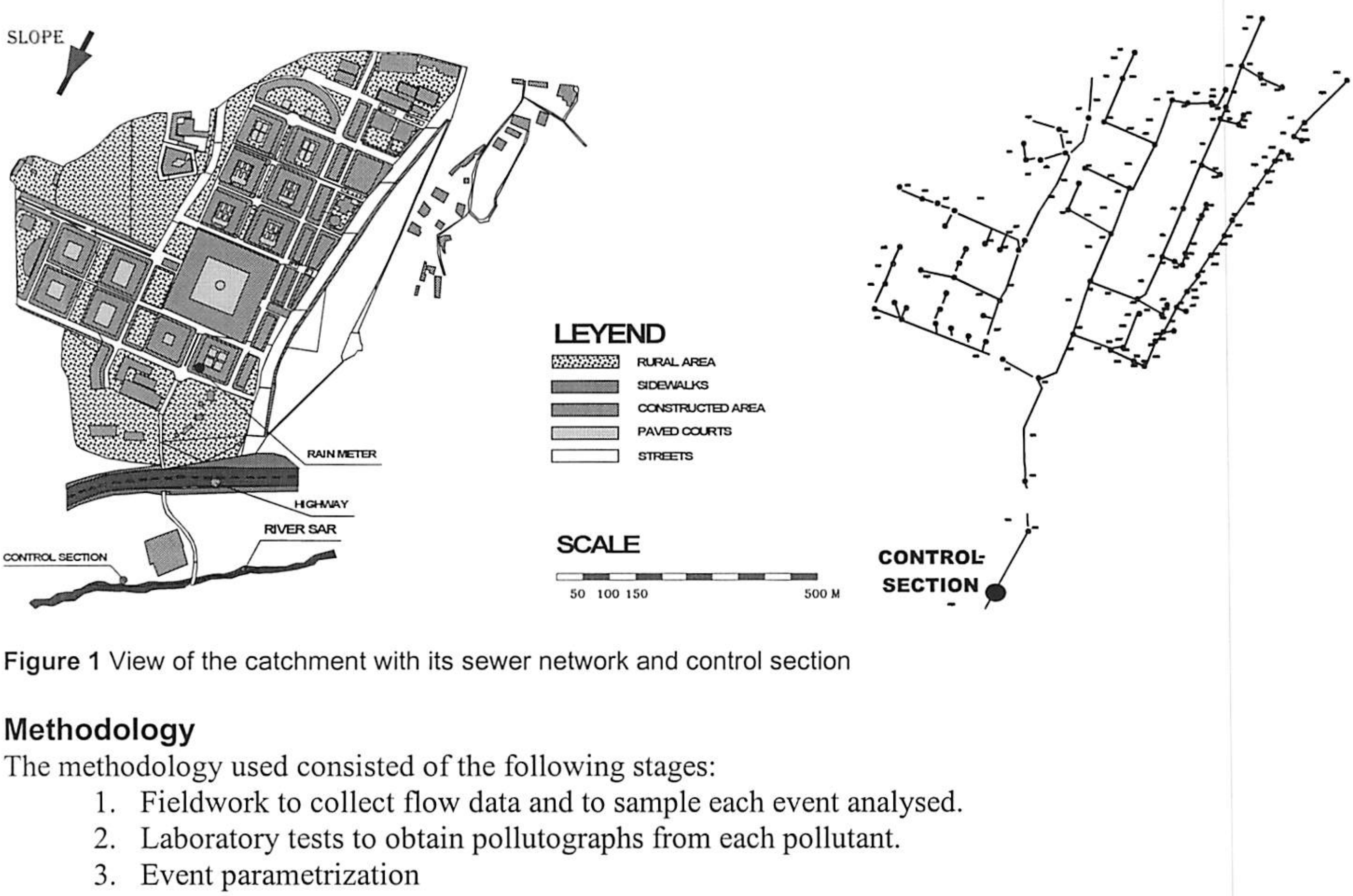

Figure 1 View of the catchment with its sewer network and control section

Methodology

The methodology used consisted of the following stages:

1. Fieldwork to collect flow data and to sample each event analysed.
2. Laboratory tests to obtain pollutographs from each pollutant.
3. Event parametrization
4. L(V) curves analysis.

Based on all of the information gathered from 1 and 2, we were able to draw up a number of parameters, which are summarised below (Table 1).

Table 1 Parameters used for the study of the runoff pollution at Fontiñas catchment.

Pluviometric parameters:	Hydrological parameters:
PDW: duration of previous dry weather (days).	Q_{max}: maximum flow (m^3/s).
P: total precipitation height (mm).	Q_{mean}: mean flow (m^3/s).
D: total duration of the storm event (hours).	***Vw***: total volume per surface unit (L/m^2).
I_{max}: maximum rainfall intensity (mm/h).	
I_{mean}: mean rainfall intensity (mm/h) or *P/D*.	

Pollutant Parameters:	
M_{ss}: total mass of SS mobilized per surface unit (g/m^2).	EMC_{Zn}: event mean concentration of Zn (mg/L).
Qss_{mean}: mean mass flux of SS (mg/s).	EMC_{Cu}: event mean concentration of Cu (mg/L).
Qss_{max}: maximum mass flux of SS (mg/s).	EMC_{Pb}: event mean concentration of Pb (mg/L).
EMC_{SS}: event mean concentration of SS (mg/l), or *Mss/Vw*.	EMC_{Hg}: event mean concentration of Hg (mg/L).
EMC_{DS}: event mean concentration of DS (mg/l).	EMC_{Cr}: event mean concentration of Cr (mg/L).
SS_{max}: maximum concentration of SS (mg/l).	EMC_{Ni}: event mean concentration of Ni (mg/L).
$Cond_{max}$: maximum conductivity (µS/cm)	EMC_{Cd}: event mean concentration of Cd (mg/L).
	EMC_{Fe}: event mean concentration of Fe (mg/L).
	EMC_{Mn}: event mean concentration of Mn (mg/L).
	Cmean: mean conductivity (µS/cm).
	Cmax: maximum conductivity (µS/cm).

The variation of the pollutant concentration during an event is described by the pollutograph. To compare different events a non-dimensional curve is more pertinent (Saget et al, 1996). It is the reason why to study the pollution load distribution, we use for each event and each pollutant, the cumulative load divided by the total pollution load versus the cumulative volume divided by the total volume of the event. Each curve can be fitted by a function like $Y=X^a$. "Y" is the fraction of the discharges pollution load and "X" is the corresponding fraction of volume. The value of the parameter "a" characterizes the deviation of the curve from the diagonal. These curves permit an analysis of the existence of first flush.

The first flush of pollutants has been identified as relatively high proportion of the total storm pollution load that ocurrs in the initial part of the combined sewer runoff. Thornton and Saul (1986) and Pearson et al. (1986), mentioned by Gupta and Soul (1996), defined the first flush as the initial period of storm flow during which the concentration of pollutants was significantly higher than those observed during the latter stages of the storm event. Previous studies have highlighted that the time of the day, the antecedent dry weather conditions, the length of antecedent dry weather period, the magnitude and pollutant characteristics of the dry wheather and the storm flows, together with the characteristics of the sewer system and the layout and side of the catchment area, all influence the temporal variability in the concentration and the load of the pollutants. Saget et al. (1996) defined the first flush when at least 80% of the pollution load is transferred in the first 30% of the volume

General description of the events sampled

The following tables (Table 1, 2 and 3) present a summary of the minimum, mean and maximum values and the standard deviation of the different parameters mentioned in the above section pertaining to the 10 events analysed:

Table 2 Hydrologic and hydraulic parameters

Parameter	Values MIN	MEAN	MAX	Standard Deviation
PDW (days)	0.02	6.21	30	8.8 (10)
P (mm)	0.8	2.34	6.70	1.9 (7)
I_{max} (mm/h)	1.2	2.63	6.0	1.6 (8)
I_{med} (mm/h)	0.73	1.52	3.70	0.94 (8)
D (h)	0.42	1.27	3	0.75 (10)
V_w (L/m^2)	0.61	1.21	3.91	0.95 (10)
Q_{max} (m^3/s)	0.05	0.17	0.42	0.10 (10)
Q_{med} (m^3/s)	0.05	0.16	0.26	0.06 (10)

( ): no. of samples

Table 3 Parameters of solids

Parameter	Values MIN	MEAN	MAX	Standard Deviation
M_{ss} (g/m^2)	0.06	0.26	0.70	0.23 (10)
SS_{max} (mg/L)	84	744	3526	972.1 (10)
Qss_{max} (g/s)	21	77.76	235	69.4 (10)
Qss_{med} (g/s)	7.29	226.43	66	22.5 (10)
EMC_{SS} (mg/L)	64	216	581	160.7 (10)
EMC_{DS} (mg/L)	67	111.25	199.7	44.9 (10)
$Cond_{max}$ (µS/cm)	79	251	344	70.51 (9)

( ): no. of samples

Table 4 Event mean concentrations

Parameter	Values MIN	MEAN	MAX	Standard Deviation
EMC_{Cu} (µg/L)	14.3	25.6	54	11.7 (9)
EMC_{Zn} (µg/L)	136	225.2	442	97.5 (10)
EMC_{Pb} (µg/L)	12.9	32.3	77.2	19.4 (8)
EMC_{Hg} (µg/L)	0.4	0.65	0.9	0.4 (10)
EMC_{Cd} (µg/L)	0.29	0.4	0.6	0.1 (5)
EMC_{Ni} (µg/L)	13	24	46	10.9 (10)
EMC_{Fe} (mg/L)	4	12.9	40	11.1 (10)
EMC_{Al} (µg/L)	3	8	21	5.9 (10)
EMC_{Cr} (µg/L)	8	36	167	53 (8)
EMC_{Mn} (µg/L)	109	299	752	208 (10)
EMC_{As} (µg/L)	0.1	16	97	38 (6)

( ): no. of samples

We have estimated the parameters for each event available event for suspended solids (SS), dissolved solids, (DS) and several heavy metals. We have given the range of values for the parameters, and try to link then to some particular characteristics.

Eight events have been selected to be analysed in order to know a patters for pollution removing. The sampling process started using the discharge as a flag: a minimum value for the discharge acts as a signal which starts sampling. Sampling interval has been set as 5 minutes. Automated samples have 24 bottles, so the sampling total time has been about 2 hours. The number of valid samples has varied between 7 and 24, with a mean value of 15 bottles for the eight events considered.

Figure 2 presents the hydrograms and pollutograms for the eight events considered. It is very noticeable that the pollution mass is almost totally removed from the catchment in every event, if considering the low concentrations in the tails of the pollutographs. That can be clearly appreciated in figure 3, corresponding to an event registered during may 4th, 1999.

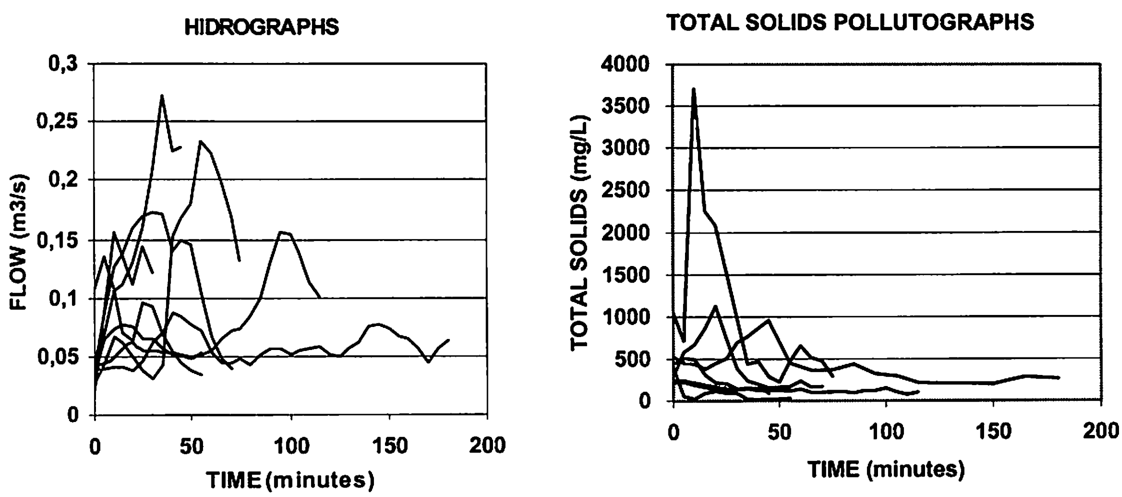

Figure 2 Hydrographs and pollutographs of eight selected event.

Table 2 shows the mass of pollutant removed by runoff processes. Water volumes measured during the event are also shown. The mean values are 103.8 Kg for total solids, 6.4 g Pb, 25.5 g Cu and 49.4 g Zn.

Table 5 Volumes and pollutant load of the selected events

No.	Date	Volume (m^3)	TS (Kg)	DS (Kg)	SS (Kg)	Al (Kg)	Cr (g)	Mn (g)	Fe (Kg)	Ni (g)	Zn (g)	Cu (g)	Cd (g)	Hg (g)	Pb (g)	As (g)
1	09-02-99	127,5	52,10	32,68	19,41	0,84	2,21	24,91	1,05	2,66	35,64	10,44	0,05	0,02	5,66	--------
2	04-05-99	198,0	150,21	54,13	96,07	2,26	5,97	0,04	3,83	6,26	0,04	11,30	0,06	0,03	5,80	--------
3	27-06-99	473,8	237,91	41,31	196,59	6,58	4,21	196,19	9,55	10,85	86,14	83,00	0,12	0,11	4,17	7,39
4	05-08-99	70,3	190,86	14,69	176,17	7,13	15,98	227,12	13,71	12,69	122,52	23,15	0,14	0,03	10,78	9,31
5	19-12-99	427,7	69,69	40,97	28,72	1,31	6,96	57,32	1,82	6,70	59,63	15,51	0,11	0,39	7,43	1,00
6	01-02-00	209,3	72,38	21,69	50,69	2,27	6,49	92,98	2,75	7,69	61,35	23,80	0,15	0,09	12,60	2,13
7	10-02-00	160,5	29,22	18,71	10,47	0,68	3,21	18,91	1,05	2,60	25,45	9,56	0,03	0,01	5,23	0,77
8	22-02-00	144,3	28,50	16,95	11,55	0,62	2,77	12,56	0,92	1,82	4,48	27,13	0,27	0,02	0,02	0,03

As the aim of this paper is to analyse the initial mass removal, in order to know if first flush occurs, and considering that the mass of pollution in the catchment is removed during the first time intervals of the events, as it have been shown in figure 2, the tails of the hydrographs have not been taken into account in the analysis. If considering the event shown in Figure 3, (may 4th, 1999), which have been recorded with 22 samples, only the first 13 have been considered for the analysis, as the others give no relevant pollutants concentration and the pollutant concentrations variation with the discharge is nearly nil.

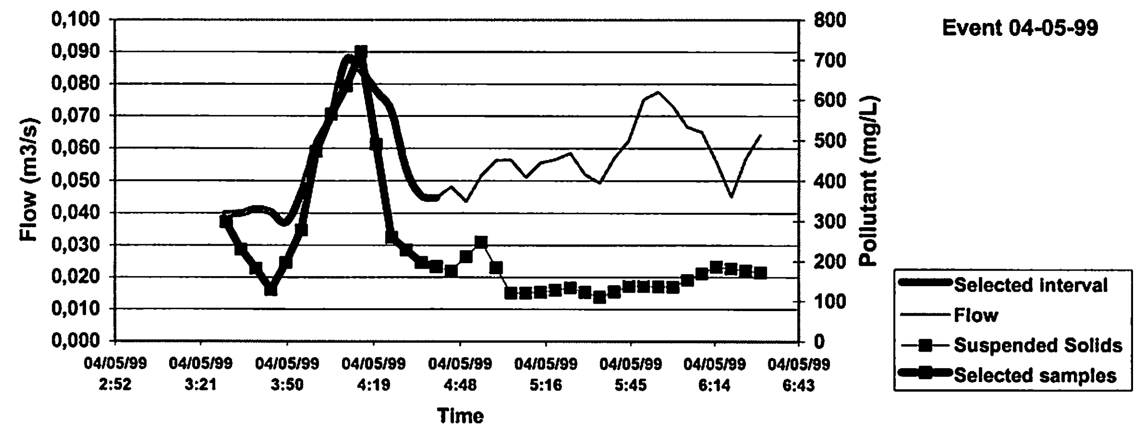

Figure 3 Event 04/05/99 Fontiñas Catchment

Shown next is other of the events analysed (event 27-06-99) with their respective graphs (Figure 3) in addition to two standardised graphs showing the event that give an idea of the phenomenon of the first flush in the catchment (Figures 5-6). The first flush phenomenon of urban wet weather discharges is presently a controversial subject.

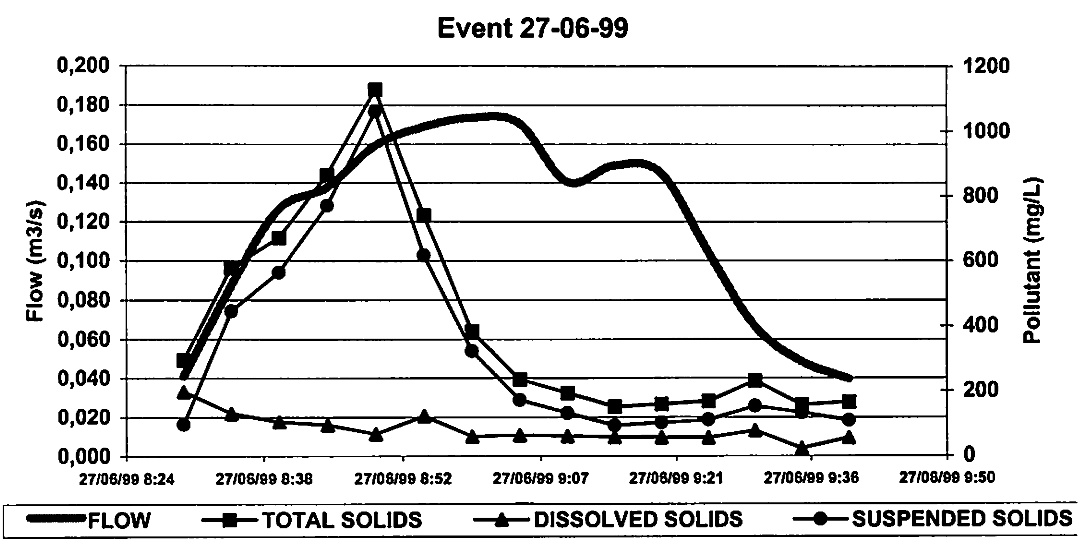

Figure 4 Event 27/06/99 Fontiñas Catchment: SS, DS and TS

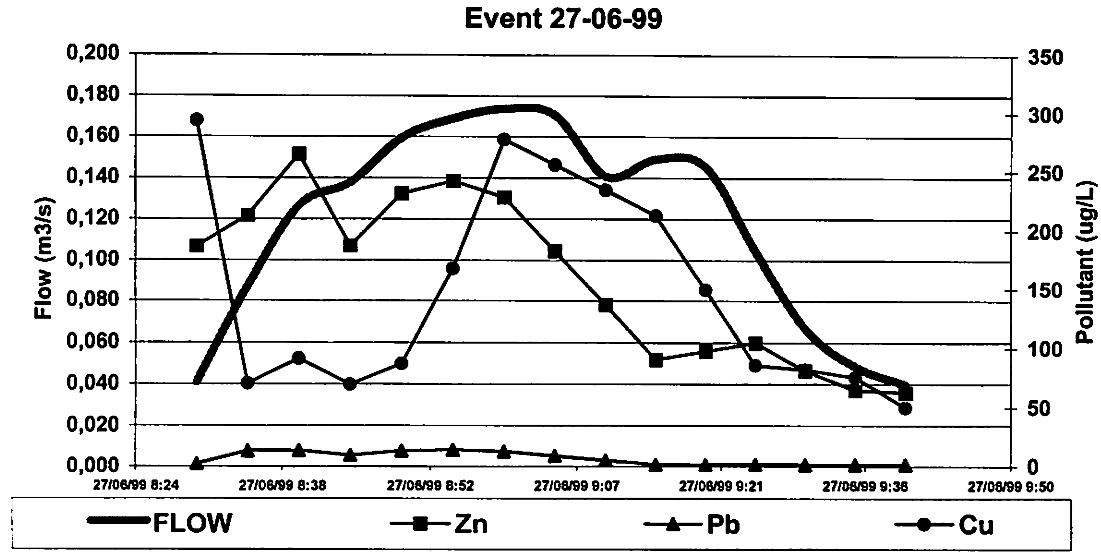

Figure 5 Event 27/06/99 Fontiñas Catchment: Zn, Pb and Cu

Figure 6 shows L(v) curves for SS, DS, Cu and Pb

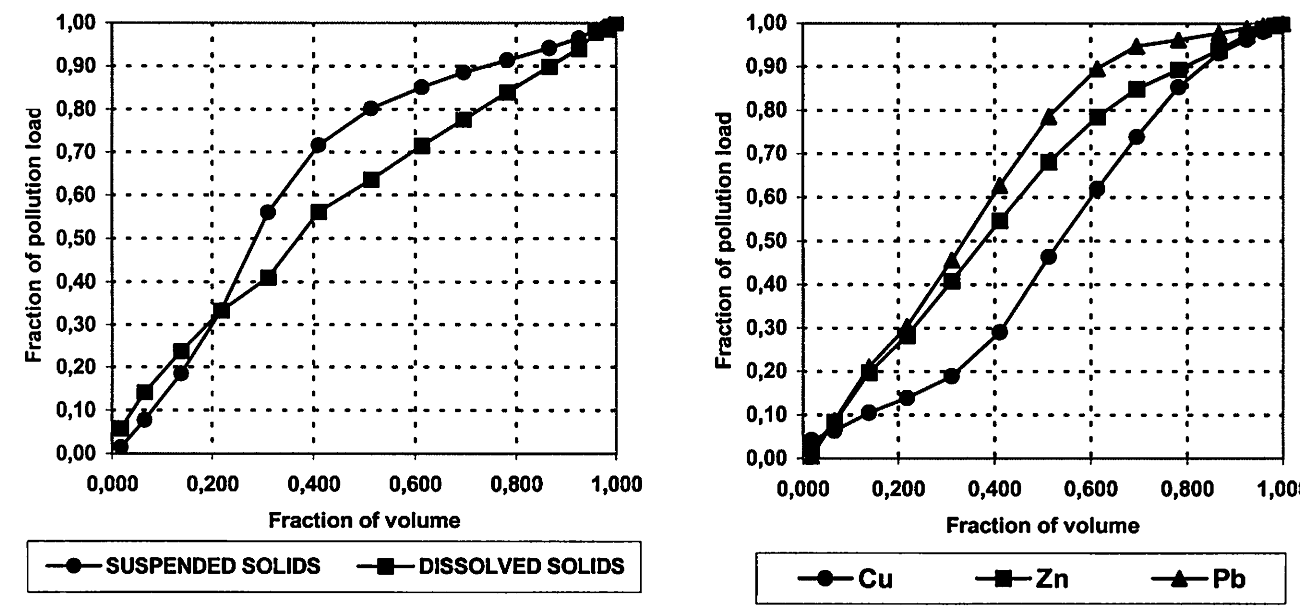

Figure 6 Event 27/06/99 Fontiñas Catchment: Analysis of first flush

The "a" coefficients for this event (june 27th, 1999) are 0.566 for SS, 0.709 for DS, 1.124 for Cu, 0.711 for Zn and 0.610 for Pb. The full table of "a" coefficients for every event and pollutant is shown in table 6, including the mean value and the standard deviations for every pollutant.

Table 6 "a" coefficient of L(v) curves; all events.

EVENT N°	DATE	TS	DS	SS	Al	Cr	Mn	Fe	Ni	Zn	Cu	Cd	Hg	Pb	As
1	**09/02/99**	0,627	0,807	0,351	0,443	0,408	0,391	0,573	0,602	0,639	0,630	0,602	0,751	0,556	—
2	**04/05/99**	0,999	0,865	1,078	1,005	1,048	1,138	0,987	0,895	0,752	0,994	0,761	0,766	1,113	—
3	**27/06/99**	0,586	0,709	0,566	0,689	0,720	0,697	0,697	0,685	0,711	1,124	0,734	0,856	0,610	0,757
4	**05/08/99**	0,992	0,768	1,015	1,000	1,014	1,002	1,030	0,939	0,635	0,842	0,757	0,625	0,977	1,069
5	**19/12/99**	0,755	0,667	0,907	0,906	0,954	0,886	0,971	0,694	0,694	0,718	1,520	2,239	0,830	0,982
6	**01/02/00**	0,597	0,777	0,540	0,497	0,523	0,488	0,486	0,490	0,510	0,495	0,502	0,657	0,541	0,501
7	**10/02/00**	0,793	0,889	0,646	0,719	0,898	0,678	0,717	0,652	0,579	0,626	0,868	0,984	0,598	0,739
8	**22/02/00**	0,769	0,898	0,617	0,967	1,055	1,065	1,010	0,779	0,578	0,838	3,421	0,880	1,386	0,673
	MEAN	**0,765**	**0,798**	**0,715**	**0,778**	**0,828**	**0,793**	**0,809**	**0,717**	**0,637**	**0,783**	**1,146**	**0,970**	**0,826**	**0,787**
	STAND.DEV.	0,16	0,08	0,26	0,23	0,25	0,27	0,22	0,15	0,08	0,21	0,97	0,53	0,31	0,21

Figure 7 shows DS and SS L(v) curves for the full range of sampled events. A slight first flush-like trend can be noticed in both cases. The difference among curves is more important in SS curves, being the area covered by DS curves quite narrow. The mean values for "a" coefficients are 0.798 for dissolved solids and 0.715 for suspended solids, which is nearly the same value, as can be appreciated in figure 8.

There is an event in which a 80% of pollution (SS) removal corresponds with a 50% of water volume. That can be considered as a real first flush, but it is an isolate event, showing the general trend much more equilibrium between pollution removal and water release.

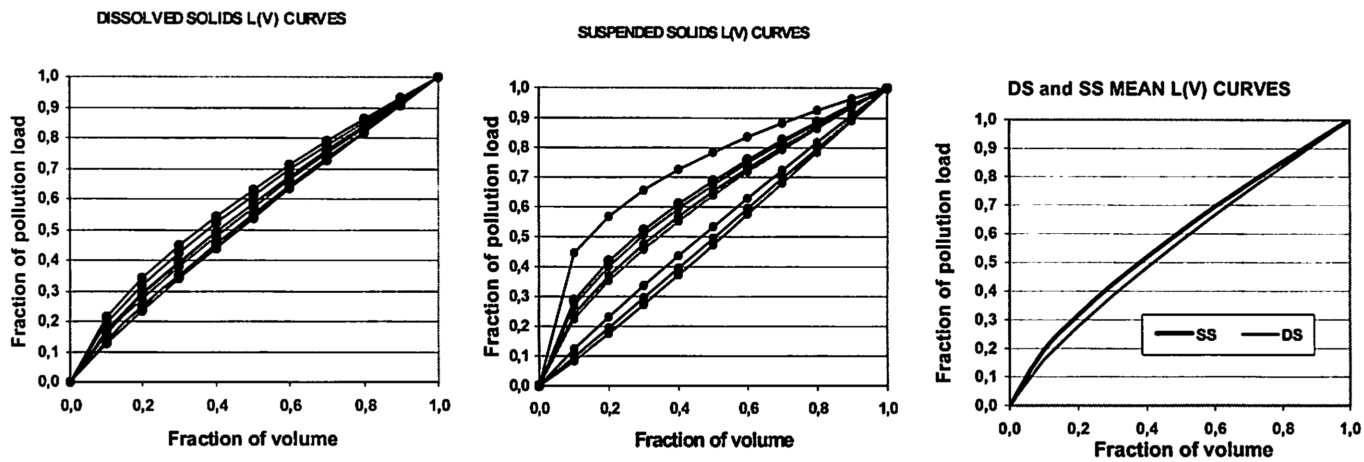

Figure 7 All events of Fontiñas Catchment. L(V) curves, and Dissolved solids and Suspended Solids mean L(V) curves.

Results

Tables 2 and 3 show EMC and maximum values for some stormwater runoff pollutants. If comparing with the literature, the SS values recorded in Fontiñas catchment are in the same range of some others (i.e Germany and Great Britain). Heavy metal values have much more dispersion between authors, and our values fit Ellis (1989) values but are cleary below the ones proposed by german researchers.

Table 7 Stormwater pollution values. Mean values and ranges for EMC( )*

Water Quality parameters	*FONTIÑAS*	GERMANY [1]	GERMANY [1]	ONTARIO MARSALEK [2]	GRAN BRETAÑA ELLIS (1989) [3]	USA - NURP (1983) [4]	NOVOTNY (1994) [5]	METCALF-EDDY (1991) [6]	ELLIS (1986) [7]
SOIL USE	*RESIDENTIAL*	*RESIDENTIAL*	*HIGHWAYS*	*MIXED*	*MIXED*	*MIXED*			
SS (mg/L)	***216***	134	140 - 250	----	21 - 2582 (190)	100 *[1.0 - 2.0]*	3 - 11000 (650)	67 - 101	3 - 11000
LEAD (mg/L)	***0.032***	0.27	0.16 - 0.62	0.146	0.01 - 3.1 (0.21)	0.14 *[0.5 - 1.0]*	0.03 - 3.1 (0.3)	0.27 - 0.33	0.4
ZINC (mg/L)	***0.025***	—	0.36 - 0.62	0.490	0.01 - 3.68 (0.30)	0.16 *[0.5 - 1.0]*	—	0.135 - 0.226	—
COPPER (mg/L)	***0.225***	----	----	----	----	0.043	----	----	----

*( ) Mean values [ ] Variation coefficients.
[1] GERMANY, several references: Goettle (1978), Paulsen (1984), Klein (1982), Grottker (1987), Durchschlag (1987), Grottker (1989), referred in MARSALEK, J. *et al* (1993); [2] MARSALEK, J.; SCHROETER, H.O.; (1989); [3] ELLIS, J.B. (1989); [4] NURP, (1983); [5] NOVOTNY, V.; OLEM,,H. (1994); [6] METCALF & EDDY, (1991); [7] ELLIS, J.B. (1986).

The main sources for heavy metals pollution are the traffic and the metal-made roofs. In our catchment the traffic level is moderate and the roffs are made on ceramic (arabig-like) tiles. High Mn concentrations have been noticed, whose origin is not known until now.

Our "a" coefficient values can be compared with the ones by Saget et al (1996) (table 8). Our SS coefficient fits quite well the mean value proposed by Saget, but so does our DS value, as well.

Table 8 Range of values of the parameter obtained by Saget et al.(1996) in storm water

Pollutant	Minimun	Average	Maximum	Standard deviation
SS	0.152	0.769	2.023	0.307
COD	0.282	0.681	1.375	0.215
BOD_5	0.271	0.669	1.379	0.238

Saget et al state that the study of the "a" parameter values show that they can be very different from one event to another, and gathering the events of storm water, it is difficult find any difference between the curves of SS, COD or BOD_5. They conclude that no pollutant can be properly represented by a single characteristic curve.

These conclusion are more or less the same that we have obtained by analysing "Fontiñas" data.

Conclusions

EMC values in "Fontiñas" catchment fit quite well the ones shown in the literature.
Low concentrations have been measured for Pb and Zn, but high values have been registered for Cu.
The use of "a" coefficients to study pollution removal in a catchment is useful to obtain general trends.
A very slight first flush trend can be noticed both in SS and DS, with no significant differences between them, and also in heavy metals.
A single L(V) curve gives not the real behaviour of the pollution removal in a catchment. The differences from one event to another are very noticeable.

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