DIFFUSE AND POINT SOURCE POLLUTIONS AT CATCHMENT SCALE : A STATISTICAL QUANTIFYING TOOL

C. Salles[1], M. G. Tournoud[1], B. Picot[2], Y. Chu[1] and C. Rodier[1]

[1] *HYDROSCIENCES (UMR 5569 CNRS-IRD-UM2), Université Montpellier II, Maison des Sciences de l'Eau, F-34095 Montpellier Cedex 5, France (e-mail address: salles@msem.univ-montp2.fr)*
[2] *Département Sciences de l'Environnement et Santé Publique, Université Montpellier 1, Faculté de Pharmacie, BP 14491, F-34093 Montpellier Cedex 5, France*

ABSTRACT.
Determination of input loading rates from tributaries is an essential component of nutrients mass balance studies on lagoon coastal waters. Small Mediterranean catchments are subject to short duration flood events which flow the main part of the annual loads. This paper describes a statistical modelling approach based on data collected at flood scale. The objective is to predict particulate phosphorus (PP), soluble reactive phosphorus (SRP) and total suspended sediment (TSS) loads during floods.
Flash floods have been monitored in three small Mediterranean catchments located near the sea coast in the south of France. The three catchments differs from geological aspects, land-use and land covers patterns. The temporal evolutions of nutrients concentrations (total phosphorus, phosphate, nitrate, nitrite, ammonium, …) have been measured. Continuous rainfall and discharge data are also available for each event. The nutrients loads have been calculated for twenty one sampled floods.
The statistical analysis investigating relationships between flood descriptors, hydrological conditions, basin characteristics and phosphorus and sediment flood exports demonstrates that the maximum flood discharge appears as the best explicative factor for soluble reactive phosphorus, particulate phosphorus and total suspended sediments. Nevertheless, since the available dataset is small, the main explicative factor is largely dependent on the calibration dataset used.

Keywords. Flash flood, Mediterranean rivers, phosphorus load, quantification, suspended sediment.

INTRODUCTION
Constituents loading of coastal lagoon tributaries is a concern for lagoon end-users from a multitude of perspectives. Suspended sediments interfere with oyster breeding activity by impacting lagoon biological integrity along with recreational opportunities. Phosphorus loading is another concern. The increased availability of nutrients in the lagoon will create eutrophic conditions. Phosphorus, rather than nitrogen, is usually the limiting nutrient for growth of aquatic plants.
River discharges are a prime source of materials for the lagoon receiving waters. There are evidences that the main part of river load occurs in very short period of the year. House et al. (1997) observed that the majority of river load is transported in autumn winter storms. This observation applies very well to basins located in Mediterranean area. Small Mediterranean catchments are subject to intense short duration flood events which flow the main part of the annual loads of suspended solids, nutrients and other pollutants. Cherifi and Loudiki (1999) reported that in Moroccan basins more than 90 % of the total matter was transported during floods. Letcher et al. (1999) observed that 86 % of the annual total phosphorus load in the South Pine catchment, is transported in 2.8 % of time. Meybeck et al. (1992) noticed that the annual load of the small Mediterranean rivers transits in less than 20 % of time.
These flash floods require careful attention in a twofold manner, i) they are heavy polluted and therefore potentially harmful for the receiving waters. ii) the flood load is a significant part of the river annual load budget.
The flood load can be estimated from observed discharge and pollutant concentration in rivers. An adapted monitoring for high flow events would require important task forces and quickly become very time consuming. Existing tools are unsuitable for the Mediterranean rivers. Hanrahan et al. (2001) reports that monthly loads of TP calculated using the export coefficient model agreed well with monthly observed loads except in months of variable discharge.
The objective of this study is to provide a simple tool to predict particulate phosphorus (PP), phosphate (i.e. soluble reactive phosphorus :SRP) and total suspended sediment loads during floods in three small Mediterranean basins. The tool has been elaborated using forward stepwise regression analysis on the available data. These data consist of continuous rainfall and discharge monitoring plus water sampling during some floods at the outlet of the three basins. The study sought for relationships between phosphorus and suspended solid load during flood events with easily available hydrological descriptors. Characteristics of the flood event (mean discharge and peak flow), the rain event (rain depth and maximum intensity) and the antecedent hydrological conditions in the basin (base flow, cumulate rainfall, dry period duration) are chosen as descriptors.

MATERIALS AND METHOD
Description of the basins
The studied rivers are located on the French Mediterranean coast (see Fig. 1). The Vène and the Pallas rivers are tributaries of the Thau lagoon renowned for its mussel and oyster farming. The Salaison river flows into the Or lagoon.
The Vène river drains a 67 km^2 basin, that consists mainly of tertiary or secondary limestone blocks highly karstified and overlain in the central part by Miocene clays (Ben Othman et al., 1997). Occasionally, during the wet season, two karstic sources feed the Vène river. The Pallas river is a typical small Mediterranean ephemeral river. Its 52 km^2 basin is

essentially composed of Eocene and Miocene marl-clay, partly filling karstic areas in the upper part. The Salaison river drains a 53 km^2 area. The geology of the basin consists of alluvial deposits in the southern part and marns and calcareous rocks in the northern part (Diop, 1980).
Because of a spatial annual rainfall gradient from East to West (Ascencio 1984), the annual rainfall decreases from about 750 mm over the Salaison basin to less than 600 mm over the top of the Pallas basin. Annual rainfall is bi-seasonnal, occurring primarily from September through December and in a lesser extent from March through May. Precipitations occur mainly as short duration and intense storms - a feature of Mediterranean climate - generating flash floods on the small basins.

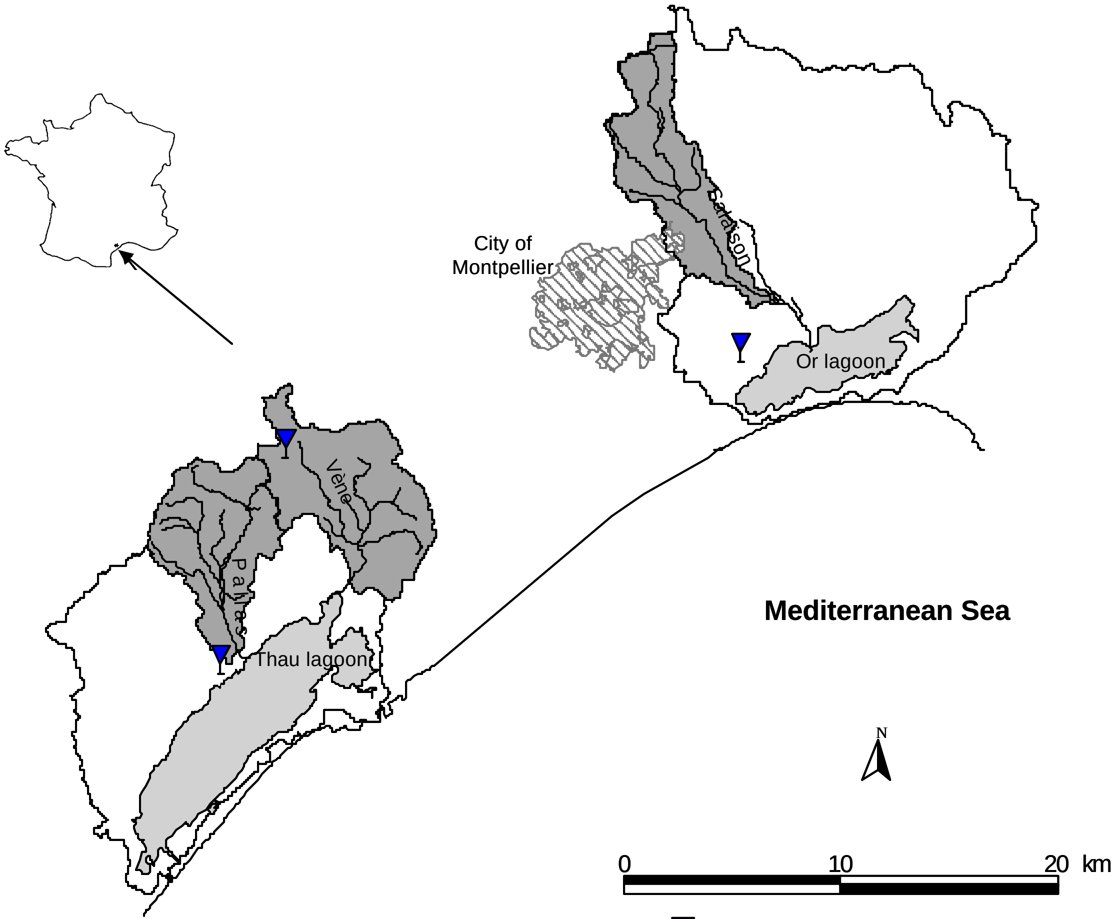

Figure 1 : *Location of the study areas (from Payraudeau, 2002).( ) marks indicate the location of raingauge stations.( ) marks indicate the location of flow recording stations.*

Flood monitoring and chemical analysis
The locations of the rain and stream gauges are represented in Figure 1. Rainfall data were collected by typing bucket rain gauges, with a 0.1 mm accuracy. Water level were continuously monitored, upstream of a weir. Water level was converted into flow using rating curves established by carrying out in-situ discharge measurements. Discharge data are available on a five minute basis.

Sampling was carried out at the stream gauges. Samples were collected on a two hour basis during the rising flow. After the peak flow, the sampling interval was modified and varied from four hours when the flow decreased rapidly to one day when the recession curves were slow.
The water samples were analysed for their total suspended solid (TSS), soluble reactive phosphorus (SRP) and total phosphorus (TP) contents. All the analysis were done following the Standard Methods requirements (APHA, 1992). The TSS concentrations were determined on GFF Whatman filters ; from 50 mL up to 2 L of water have been filtered depending on the solid loads. The soluble reactive phosphorus (SRP) was determined on filtered samples by reaction with ammonium molybdate and reduction with ascorbic acid. The TP concentrations were determined on unfiltered samples, after mineralization of phosphorus into phosphates. The P associated with solids, i.e. particulate phosphorus (PP) was calculated by substracting SRP and dissolved organic phosphorus (when concentration was above detection threshold) to TP.
Flood loads were estimated using the linear interpolation method. It combines (Q_i), the measured flow on a five minute time step and (c_i) the linearly interpolated concentration between two consecutive samples. This method was identified by Kronvang and Bruhn (1996) as the best and most reproducible for estimating annual transport of total nitrogen and total phosphorus. Elsewhere, the linear method was believed to be accurate and unbiased by Letcher et al. (1999).

The descriptors selected as explicative variables are divided into three categories. The peak flow (Q_{max}) and the baseflow (Q_b) before the event characterize the flood event. The rain event is described by the total rain depth (H), the mean intensity (I) and the maximum value of the intensity on a five minute time step (I_{max}). The duration of the dry period and the rain depth recorded the last 3 (P_{3d}) and 30 days (P_{30d}) before the rain event are indicative of the basin antecedent hydrological conditions.

RESULTS AND DISCUSSION

Floods main characteristics, timing and load estimate normalised by the basin area (i.e. loads obtained using the linear interpolation method) are reported table 1.

Flood data analysis

Twenty one floods were sampled. Flood durations extend from 6 hours to 9 days, but are shorter for the Salaison and Pallas rivers than for the Vène river. Some events present a very low mean specific discharge, especially during spring.
The runoff coefficients show great differences within and between basins. For the Pallas river, the coefficients range between 0.1 and 42.2 %, three events out of five being less than 5 %. Runoff coefficients from the Salaison river have a lesser extended range, from 1.5 to 8 %, except for the latter events (14.1 %) that corresponds to the highest rain event. The runoff coefficients of the Vène basin are quite exceptional, ranging from 0.1 to 87.9 %, these especially high values resulting from the outbasin feeding by the two karstic springs.

Total Phosphorus (TP) concentrations, that combines particulate phosphorus and dissolved phosphorus are quite low in the Pallas and the Vène rivers (ranging from 0.03 to 2.3 mg-P L^{-1}) compared to the Salaison river (up to 7.7 mg-P L^{-1}). The highest level of SRP concentration is observed in the Salaison river. Nevertheless, in the three observed rivers, SRP concentrations are decreasing with discharge increase. This behaviour is indicative of dilution of point sources effluent. Figure 2a reports log of SRP concentration versus log of discharge. log(SRP) shows a slope of -0.28 significantly different from 0 at a level of 0.01%.

For the three sampled rivers, PP concentrations are mainly in the range 0.1 to 1 mg-P L^{-1}.The slope of log(PP) vs. log(discharge) is different from zero only at a level of 2%. The ratio of SRP to TP was quite variable from sample to sample and flood to flood. Globally, none of the P fraction (i.e. SRP and PP) dominates the P concentration even when splitting of samples between the rising and the falling period of the flood.

The Pallas river has the highest TSS loads. The range of TSS concentration is more than 3 order of magnitude, from 1 to 1672 mg.L^{-1}. The TSS concentrations display the highest values during the first flash floods occurring after a long period of low flow.

SRP and PP and SRP and TSS concentration present a low correlation. The coefficient of determination between the logarithm of concentration are respectively 0.052 and lower than 10^{-3} ; but PP and TP concentration reveals a slight correlation(r^2= 0.398). PP versus TSS on the three basins is plotted fig. 2b. The strongest correlation is obtained in the Pallas river (r^2=0.869) while the correlation for Salaison (r^2= 0.465) and Vène (r^2= 0.164) are less.
Rating curves linking concentration to discharge are traditionally applied for annual load estimation (e.g. Walling, 1977). At the flood event time scale and for the studied catchment, an attempt to link concentrations to specific discharges with a classical power law does not give satisfactory results. The fitted laws only account for 30 %, 2% and 8 % of respectively the SRP, PP and TSS variances. Therefore no significant concentration vs. discharge relations can be inferred from our dataset. Despite, the PP-TSS correlation, PP is less dependent on discharge than is TSS.

Regression analysis

Loads are inferred from the measurements of TSS, SRP and PP concentrations and water discharges as explained above, and normalised with respect to the catchment scale (kg km^{-2}). The numerical values shows that there is more than 3 orders of magnitude between the maximum (16308 kg/km2) and the minimum(0.3 kg/km2) TSS load. Altogether, loads are lower in the Salaison than in the Vène and Pallas river. For the Salaison and Vène rivers the fraction of dissolved and particulate phosphorus loads are approximately equal. In the Pallas river four out of the five events are PP load in the majority.

The data set has been split in two subsets : the first subset contains eighteen randomly chosen floods and is used to calibrate the regression models ; the remaining floods are used for validation. For calibration purposes, nineteen forward stepwise regression were processed. The first one uses the entire calibration subset, the followings consider the calibration subset from which one flood event was removed (see the results in table 2).

When applying the regression to the entire calibration subset and considering a single explicative factor all the three categories are present. Flood event, rain event and hydrological antecedent contribute towards respectively PP, SRP and TSS loads quantification. PP loads variance is explained at 54 % by the flood maximum discharge (Q_{max}). The variable that explains the largest part of the SRP variance (61%) is the rainfall depth (H) although rainfall is ultimately the source of water that flushes nutrient from the catchment. The TSS variance is explained (at 72%) by the cumulative rainfall depth in the 30 days preceding the event (P_{30d}).

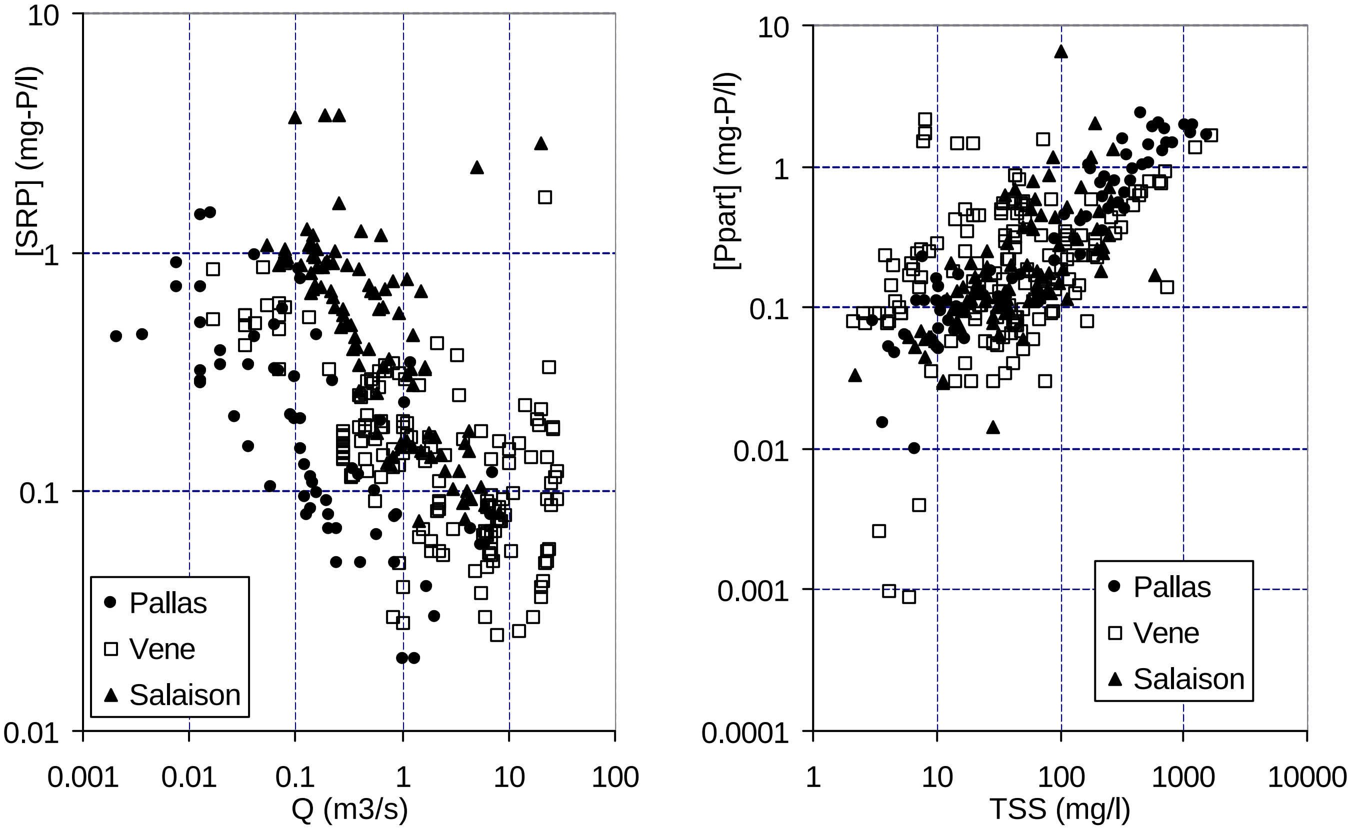

***Figure 2 : (a)** Soluble reactive phosphorus concentration versus discharge and **(b)** Particulate phosphorus (PP) versus total suspended sediment concentration (TSS).*

Table 1 : Characteristics of the twenty one sampled floods.

Event name	Rain event characteristics		Flood characteristics			Loads		
	Depth (mm)	Duration (day)	Peak discharge (L s^{-1}km^{-2})	Mean discharge (L s^{-1}km^{-2})	Volume (10^3 m^3)	PP (kg km^{-2})	PO_4 (kg km^{-2})	TSS (kg km^{-2})
Calibration set								
Salaison 4/99	39.2	0.5	33.9	14.52	33.23	0.68	0.36	66
Salaison 5/99	85.2	2.0	79.9	25.16	230	1.8	0.68	540
Salaison 9/99	50.6	1.2	106.0	31.31	41.87	0.48	1.36	88
Salaison 10/99	48.6	0.7	78.3	36.44	234	0.78	0.91	611
Salaison 11/99	130.2	3.0	78.3	42.33	1066	3.1	2.72	1745
Salaison 4/00	34.4	1.0	36.3	5.81	66.55	0.74	0.91	57
Vène 9/94	70	2.9	18.3	6.70	155	0.72	0.40	65
Vène 10/94	160	1.8	365.8	217.34	10065	47	7.35	16308
Vène 4/95	32	1.3	0.6	0.26	2.97	0.02	0.07	0.53
Vène 4/96	25.2	5.2	34.4	21.09	1099	0.92	1.40	55
Vène 5/99	115.2	1.6	161.4	92.98	807	3.3	1.07	1717
Vène 9/99	72.6	1.2	398.4	188.15	545	10	1.78	9081
Vène 10/99	105.2	2.5	125.2	83.09	3367	5.5	2.81	2791
Vène 11/02	18	0.5	11.0	5.71	13.22	0.05	0.05	14
Pallas 10/94	119	1.7	155.8	85.42	1343	16	1.99	11946
Pallas 4/95	22.2	1.3	0.4	0.15	1.32	0.003	0.03	0.33
Pallas 3/96	67.2	2.3	130.4	54.22	1340	9.5	1.18	4562
Pallas 4/96	25.2	5.2	17.3	7.48	22.41	0.10	0.04	44
Validation set								
Salaison 3/99	21	0.8	20.7	6.44	27.03	0.33	0.77	56
Vène 11/99	167.2	3.0	433.5	207.84	7219	21	5.97	14712
Pallas 9/94	69.8	1.9	22.8	4.96	24.52	0.70	0.15	287

Table 2 : Forward stepwise regression analysis results. The table report the results of the most significant regression. The regression is obtained from the entire calibration except a removed event is specified

SRP				PP				TSS			
Model	removed event	r^2	Factors	Model	removed event	r^2	Factors	Model	removed event	r^2	Factors
SRP1	none	0.611	H	PP1	none	0.611	Q_{max}	TSS1	none	0.724	P_{30d}
SRP2	Vène 9/99	0.799	Q_{max}	PP2	Vène 9/99	0.813	Q_{max}	TSS2	Pallas 10/94	0.805	Q_{max}
				PP3	Salaison 11/99	0.595	H	TSS3	none	0.699	Q_{max}

H : event rain depth – Qmax : peak flow – P_{30d} : cumulate rainfall recorded during the last 30 days

The regression runs on the reduced calibration subsets let appear different explicative factor. From 14 out of the 18 runs the maximum discharge (Q_{max}) is the first factor that explains PP load. The remaining runs give P_{30d} (2 out of 18 runs) and H (1 out of the 18 runs) as the first explicative factor. The best coefficient of determination (81%) was obtained when removing the Vène 9/99 event from the calibration subset. This latter event was the first after along dry period and is associated with the highest rainfall intensity of the 21 events..
The first explicative factor of SRP is H for 17 out of the 18 runs (r^2 ranges from 57 to 70%). Still, when the Vene 9/99 event is not considered, Q_{max} became the first explicative factor and the coefficient of determination increased significantly(r^2=80%).
With TSS load as dependent variable, from 15 out of 18 runs, P_{30d} explains more than 70% of the TSS variance. The 3 remaining runs gave Q_{max} as the first explicative factor. When the second higher TSS load event is removed (Pallas 10/94) the explained variance (80%) is the highest.

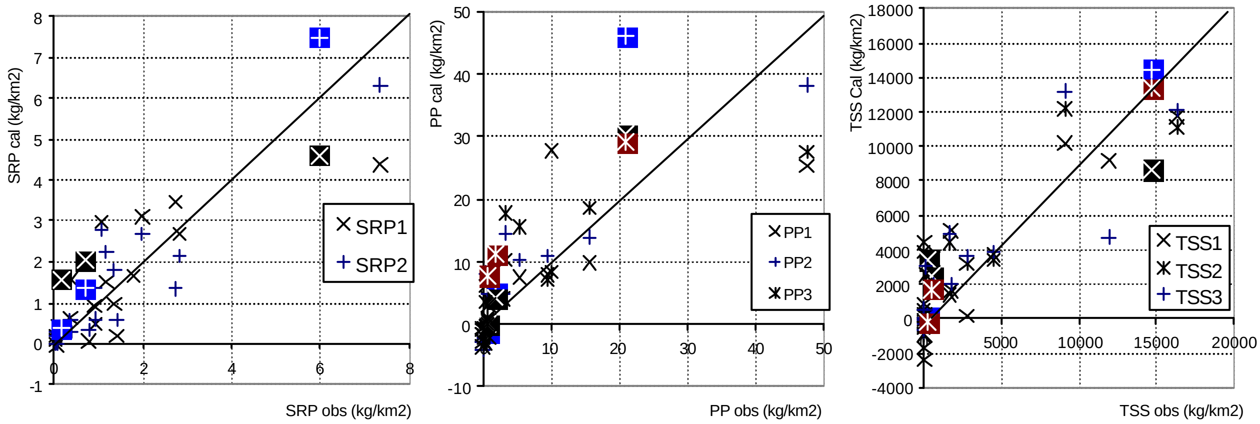

***Figure. 3** : Regression models : SRP, PP and TSS calculated (cal) versus observed (obs) loads. Calibration and validation points. Reverse video pictograms identify the validation events.*

The validation results are plotted on Fig. 3. For SRP, the prediction obtained by SRP2 model stay under an acceptable range (from 25% to 141%) and are better than SRP1 model for the lower load values. For PP, even if the coefficient of determination of PP1 model (0.611) is significantly less than PP2 model (0.813), validations results are better with PP1 model. For, TSS, Q_{max} as explicative factor give significantly better validation results than P_{30d}.

CONCLUSION

In three Mediterranean catchments, flash floods have been monitored in order to characterize phosphorus and suspended solid loads. Analysis of concentration bring to the fore the decrease of SRP with increasing discharge and the obvious PP-TSS light correlation. Concentration versus discharge relationships are not suitable for load estimation. In the best the discharge explains no more than 30 % of the concentration variances.

Stepwise forward regression investigate for relationships between loads and descriptors that characterise the flood event, the rain event and the antecedent hydrological condition in the basin. One explicative factor regression models have been tested on different data subset.

The models explain from 60% to 80% of the load variance. The various conducted regressions demonstrate the dependence of the main explicative factor to the considered data subset. The factor that fit best the calibration and the validation tests is the maximum discharge for the three considered loads: phosphate, particulate phosphorus and total suspended sediments.

At this point deeper investigations at the basin scale are needed to clearly identify nutrient and suspended solid sources and transport processes.

REFERENCES

APHA, 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association/ American Water Works Association/ Water Environment Federation, Washington DC, USA.

Ascencio, E., 1984. Aspect climatologique des départements de la région Languedoc-Roussillon. Monographie Volume 4. Bureau Climatique Régional du Sud Est. Ministère des transports Direction de la Météorologie., Aix en Provence.

Ben Othman, D., Luck, J.M., Tournoud, M.G., 1997. Geochemistry and water dynamics : application to short-time scale flood phenomena in a small Mediterranean catchment : I- alkalis, alkali-earths and Sr isotopes. Chem. Geol., 140 : 9-28.

Cherifi, O. and Loudiki, M., 1999. Flood transport of dissolved and suspended matter in the El Abid river basin (Morocco). Hydrobiologia, 410: 287-294.

Diop, M., 1980. Contribution à l'étude des systèmes aquifères de plaine littorale (Lez et Vidourle, France). Modèle de simulation mathématique., Doctorat Université des Sciences et Techniques du Languedoc, Montpellier, 138 pp.

House, W.A., Leach D;, Warwick M.S., Whitton, B.A., Pattinson, S.N., Ryland G., Pinder A;, Lishman J.P., Smith S.M., Rigg E. and Denison F.H., 1997. Nutrient trasnport in the Humber rivers. THe science of the Total Environment194:303-320.

Hanrahan G., Gledhill M., House, W.A., and Worsfold P, 2001. Phosphorus load in the Frome catchment, UK : Seasonal refinment of the coefficient modelling approach. J. Environ. Qual. 30(5): 1738-1746

Kronvang, B. and Bruhn, A.J., 1996. Choice of sampling strategy and estimation method for caclulating nitrogen and phosphorus transport in small lowland streams. Hydrological Processes, 10: 1483-1501.

Letcher, R.A., Jakeman, A.J., Merritt, W.S., McKee, L.J., Eyre, B.D. and Baginska, B., 1999. Review of techniques to estimate catchment exports. Report EPA 99/73, Environment Prtection Authority, Sydney.

Meybeck, M., Bouloubassi, I., Huang Wei Wen, Hubert, P., Pasco, A., Ragu, A. and Toma, A., 1992. Etablissement des flux polluants, Rapport Inter-Agences, Laboratoire de Géologie appliquée, Naturalia Biologia 9, 500p.

Payraudeau, S., 2002. Modélisation distribuée des flux d'azote sur des petits bassins versants Méditerranéens, Doctorat ENGREF Montpellier, Montpellier, 424 pp.

Walling, D.E., 1977. Assessing the accuracy of suspended sediment rating curves for a small basin. Water Resour. Res., 13(3): 531-538.