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Contribution of small mountainous rivers to particulate organic carbon input in the Bay of Biscay

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Abstract. The Nivelle River, a typical Pyrenean mountainous watershed reaching the Bay of Biscay (Atlantic Ocean), was sampled with high resolution during 1996. The particulate organic carbon (POC) contents during successive floods shows that there is a graduated impoverishment of the organic fraction of suspended particulate matter (SPM) from the first flood to the next ones, reaching a threshold value (3%) attributed to allochtonous fraction (soil). On the basis of the high frequency data of water discharge and POC concentration, an annual POC flux was established: 845 tons, corresponding to a specific POC flux of 5.3 tC km^{-2} yr^{-1}. This value was obtained during a dry period and must be considered as a minimum value for longer time scale. The POC originated mostly from soil (55%) and riparian/litter (~40%) with a very minor (<5%) contribution of autochthonous POC. Thirty-two percent of the annual POC flux was carried in 1% of time and 66% in 10% of time. The specific POC yield, 5.3 tC km^{-2} yr^{-1}, if extended to the whole mountainous area of the southern coast of the Bay of Biscay (19,000 km^2), leads to an estimated POC flux around 100,000 t yr^{-1}. Although small Cantabrian mountainous rivers contributed to only 28% of the freshwater discharge in the Bay of Biscay, their POC load was estimated to account for 70% of the total POC inputs in the Bay.

Introduction

In the context of a better understanding of the global carbon cycle, there has been an increasing concern over the quantification of sediment and carbon transport by rivers to the ocean (Milliman and Syvitski 1992; Meybeck et al. 1993; Ludwig and Probst 1998). The erosion of carbon from land and its subsequent transport to sea via rivers represent a major pathway in the global carbon cycle (Kempe 1979; Degens et al. 1984). Among the total flux of carbon carried by world rivers (1 Gt yr^{-1}), the contribution of organic carbon is estimated to represent ~40% (Meybeck 1993).

Over 25 years, investigations of the SCOPE/CARBON program (Degens 1982) have substantially improved our knowledge on fluvial carbon fluxes (Lewis and Saunders 1989; Richey et al. 1990; Degens et al. 1991; Kempe et al. 1993). Even if the global figures are more precise today, important gaps persist, mainly due to the scarcity of river data. Little data take into account the temporal variability of fluvial carbon fluxes because of the requirement of time-extensive researches. The precision of the riverine flux estimates suffers from the temporal variability of water and sediment discharges. This implies that flux estimations require suitable hydrological monitoring and sampling frequency (De Vries and Klavers 1994; Meybeck 2001). Furthermore, only most of the world's largest rivers are taken into account in the global fluvial organic carbon transport to the ocean. However, small mountainous rivers may contribute much more sediment than previously estimated (Milliman and Syvitsky 1992). For example, Maneux et al. (1999) showed that suspended particulate matter (SPM) fluxes by small mountainous rivers can be the primary source of suspended matter to the Bay of Biscay.

Using high resolution of water discharges, SPM and particulate organic carbon (POC) concentrations, the present paper provides high frequency data (every 2 h during floods) of POC fluxes in a small mountainous river within an hydrological and geochemical observation network in the Southwest of France: the Nivelle River in 1996.

The aims of this study are:

1. To describe temporal variability of POC concentrations during high frequency sampling, and discuss POC origins (soil, litter or autochthonous production);
2. To produce a reliable annual POC flux based on this extensive database;
3. To assess the contribution of small mountainous rivers to the regional POC budget of the southern part of the Bay of Biscay.

Sampling area: the Nivelle River watershed

The Nivelle River drains a typical Pyrenean mountainous watershed, reaching the Bay of Biscay (Atlantic Ocean) in the Saint Jean-de-Luz Bay (Figure 1a). The main channel (mean channel slope: 2.5%) of the Nivelle River is 39 km long and drains 238 km^2 of the Western Pyrenean mountains coast (Maneux et al. 1999). Water discharges and SPM concentrations were measured at Saint Pée-sur-Nivelle (downstream gauging station). Consequently, the drainage area sampled in this work (160 km^2) represents 68% of the total basin area. A vegetation map is shown in Figure 1b. Outcrop areas in the watershed are composed of Carboniferous Black Schist (16%), Devonian Schist (23%), Trias Sandstone (16%), Albian Schist/Sandstone (6%) and Cretaceous Flyschs (40%). Morphological characteristics of the Nivelle Basin are characterized by a 24 km-main channel length at the sampling station, maximum and minimum

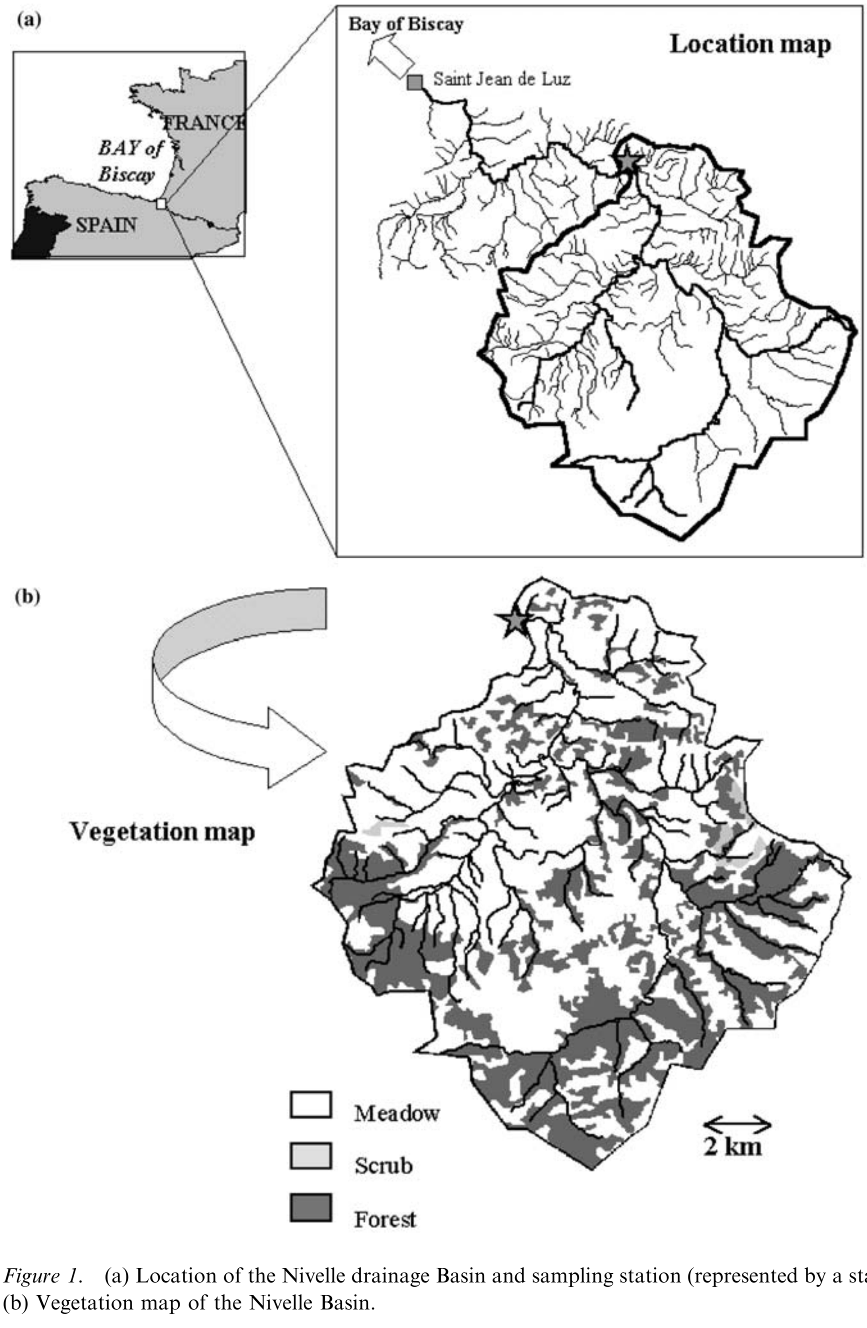


Figure 1. (a) Location of the Nivelle drainage Basin and sampling station (represented by a star). (b) Vegetation map of the Nivelle Basin.

heights respectively of 660 and 17 m, and mean slope channel 27 m km^{-1}. The high drainage density (sum of all streams length in km divided by the watershed area in km^2) of the Nivelle River at the sampling station (3.7 km^{-1})

is responsible for high temporal variability of water and SPM transport (Coynel et al. 2004). The Nivelle Basin is influenced by temperate oceanic climate with annual mean precipitations ~1476 mm (mean between 1951 and 1980). The average annual discharge for the period 1969–2002 is 5.2 $m^3 s^{-1}$. However, intense rainfall events occasionally cause 'flash' floods with discharge temporary exceeding 100 $m^3 s^{-1}$.

Materials and methods

In this study, we present a dataset of water discharges, SPM and POC concentrations in the Nivelle River acquired during 1996 (Figure 2 and Table 1).

Sampling frequency

At the Nivelle River station (Saint Pée-sur-Nivelle), one litre samples were pumped at 1 m from the riverbank and at 0.5 m distance from the sediment–water interface with an automatic river sampler (SIGMA 800SL) every 2 h during the 1996-year. Water samples were filtered through pre-combusted and pre-weighed Whatman GF/F glassfibers. Then, the filters were dried in an oven at 50 °C during 24 h and weighted to determine SPM concentrations. Thus, during floods, 30 min-water discharge data and 2 h-SPM concentration data allowed us to estimate the instantaneous SPM fluxes over the entire flood time period. The spatial reproducibility of SPM values during different hydrological

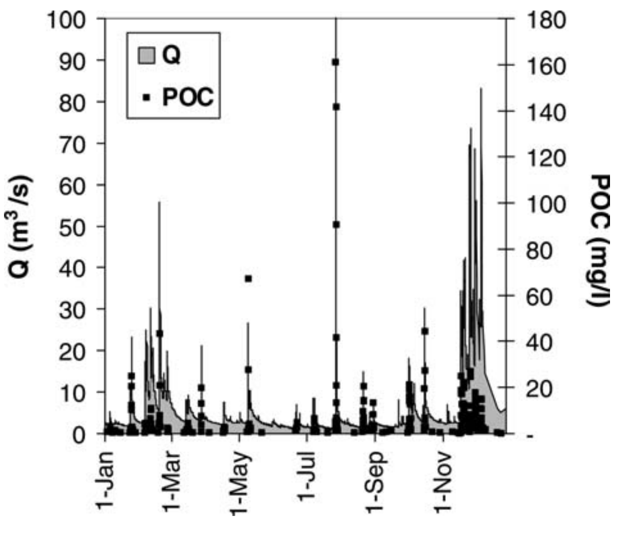


Figure 2. Discharges and POC concentrations in the Nivelle River during 1996.

Table 1. Data bank at Saint Pée-sur-Nivelle in 1996: POC concentrations (expressed in % and in mg l^{-1}) and corresponding water discharges (Q in $m^3 s^{-1}$) and suspended particulate matter concentrations (SPM in mg l^{-1}).

Date	Q	SPM	POC%	POC
12/20/95 15:30	1.7	0.7	30.0	0.3
12/24/95 11:00	1.8	0.4	30.0	0.3
12/25/95 11:00	2.8	2.0	28.7	0.6
12/26/95 9:00	3.2	4.4	16.1	0.7
12/29/95 9:00	2.6	1.5	26.0	0.4
01/03/96 8:30	2.1	2.3	23.4	0.5
01/05/96 15:00	2.8	19.5	14.7	2.9
01/05/96 17:00	4.4	33.3	8.5	2.8
01/06/96 0:00	3.7	26.5	11.4	3.0
01/06/96 20:00	2.8	3.4	16.6	0.6
01/08/96 9:00	2.4	2.9	15.9	0.5
01/10/96 13:00	2.8	9.7	15.5	1.5
01/11/96 11:00	2.7	6.9	9.7	0.7
01/15/96 9:00	2.2	1.5	15.9	0.2
01/23/96 9:00	1.8	1.9	21.7	0.4
01/24/96 15:00	1.8	21.8	7.7	1.7
01/24/96 18:00	2.2	38.3	7.5	2.9
01/25/96 2:00	12.5	134	7.6	10.2
01/25/96 6:00	17.4	466	5.3	24.8
01/25/96 8:00	23.3	361	5.7	20.5
01/25/96 10:00	17.0	188	6.6	12.4
01/25/96 18:00	10.1	37.2	7.4	2.8
01/26/96 8:00	6.3	13.8	9.1	1.3
01/28/96 8:00	3.7	2.5	11.3	0.3
02/06/96 2:00	3.1	3.2	15.0	0.5
02/06/96 4:00	5.7	62.4	6.8	4.2
02/07/96 0:00	10.4	17.5	7.2	1.7
02/07/96 12:00	14.6	58.8	7.4	4.3
02/08/96 12:00	16.0	25.2	10.2	2.6
02/11/96 4:00	8.7	7.6	11.3	0.9
02/11/96 8:00	22.5	103	6.4	6.6
02/11/96 12:00	17.7	34.9	7.7	2.7
02/11/96 16:00	19.5	57.7	7.0	4.0
02/11/96 18:00	27.8	197	5.2	10.3
02/11/96 20:00	29.4	186	5.8	10.8
02/12/96 2:00	21.2	37.7	8.4	3.1
02/12/96 20:00	13.5	17.7	8.9	1.6
02/13/96 0:00	19.8	25.2	7.4	1.9
02/13/96 12:00	14.6	13.4	8.6	1.1
02/18/96 12:00	5.7	2.7	14.1	0.4
02/19/96 3:00	7.6	63.5	7.1	4.5
02/19/96 6:00	13.2	72.5	4.9	3.5
02/19/96 10:00	14.6	66.1	7.6	5.0
02/19/96 18:00	32.7	136	5.7	7.7
02/19/96 20:00	46.8	745	6.6	43.2
02/19/96 22:00	36.5	298	7.0	20.9
02/20/96 6:00	19.5	32.7	8.3	2.7

Table 1. Continued

Date	Q	SPM	POC%	POC
02/26/96 10:00	7.9	5.5	12.4	0.7
02/26/96 16:00	12.8	34.1	6.5	2.2
02/26/96 20:00	19.8	39.8	6.2	2.4
02/27/96 2:00	14.2	31.0	5.8	1.8
02/27/96 16:00	10.7	6.6	10.1	0.6
03/12/96 12:00	3.1	1.0	30.0	0.5
03/14/96 16:00	4.9	3.8	15.0	0.6
03/15/96 0:00	8.2	13.9	10.6	1.5
03/15/96 6:00	6.3	16.5	11.2	1.9
03/16/96 2:00	4.9	20.8	12.0	2.5
03/16/96 6:00	6.1	12.3	9.1	1.1
03/16/96 10:00	9.3	59.2	7.7	4.6
03/16/96 20:00	8.2	22.7	8.8	2.0
03/17/96 12:00	7.6	6.9	11.1	0.8
03/20/96 12:00	4.9	2.4	13.1	0.3
03/27/96 20:00	2.9	5.5	13.3	0.7
03/28/96 2:00	5.7	68.2	5.7	3.9
03/28/96 4:00	21.2	252	5.2	13.1
03/28/96 6:00	14.2	319	6.2	19.9
03/28/96 10:00	7.9	89.1	8.4	7.5
04/04/96 12:00	3.1	3.9	12.7	0.5
04/16/96 20:00	2.2	2.8	17.6	0.5
04/17/96 6:00	5.9	7.0	13.3	0.9
04/17/96 10:00	6.1	18.5	10.2	1.9
04/17/96 16:00	6.8	25.2	8.8	2.2
04/17/96 20:00	7.6	35.2	7.3	2.6
04/18/96 4:00	7.6	27.4	8.3	2.3
04/18/96 12:00	5.7	16.0	10.4	1.7
05/08/96 12:00	2.4	3.4	17.9	0.6
05/09/96 12:00	3.4	6.4	12.2	0.8
05/09/96 14:00	17.0	19.0	10.4	2.0
05/09/96 16:00	24.5	1038	6.5	67.1
05/09/96 18:00	16.7	395.0	7.0	27.4
05/10/96 2:00	8.2	47.0	8.5	4.0
05/10/96 12:00	7.9	24.8	9.4	2.3
05/11/96 12:00	10.4	30.1	8.4	2.5
05/11/96 14:00	9.9	25.2	9.2	2.3
05/11/96 20:00	7.9	17.4	9.6	1.7
05/21/96 12:00	2.8	1.5	18.9	0.3
06/21/96 4:00	1.7	9.1	10.1	0.9
06/21/96 12:00	5.1	11.9	9.5	1.1
06/21/96 22:00	2.3	25.3	6.0	1.5
06/22/96 4:00	7.1	28.5	8.3	2.4
06/22/96 6:00	6.3	66.3	7.0	4.6
06/22/96 10:00	5.3	86.3	5.2	4.5
06/22/96 18:00	2.8	38.4	7.0	2.7
07/07/96 6:00	1.6	6.6	10.4	0.7
07/07/96 22:00	5.1	25.8	8.1	2.1
07/08/96 2:00	7.1	91.0	7.3	6.6

Table 1. Continued

Date	Q	SPM	POC%	POC
07/08/96 6:00	5.1	64.0	7.6	5.0
07/09/96 0:00	3.1	13.0	9.1	1.2
07/10/96 12:00	2.3	7.9	10.1	0.8
07/20/96 12:00	1.4	2.7	14.6	0.4
07/27/96 2:00	1.8	8.3	12.8	1.1
07/27/96 4:00	2.4	9.7	9.8	0.9
07/27/96 6:00	5.1	15.7	8.0	1.3
07/27/96 8:00	6.5	41.6	6.8	2.8
07/27/96 10:00	6.8	75.1	6.6	5.0
07/27/96 12:00	23.3	76.0	6.7	5.1
07/27/96 14:00	72.6	2215	7.3	160.8
07/27/96 16:00	98.2	2726	5.2	141.5
07/27/96 18:00	56.6	2190	4.1	90.6
07/27/96 20:00	36.0	1260	3.3	41.6
07/27/96 22:00	27.4	547	3.8	20.9
07/28/96 0:00	22.1	311	4.3	13.2
07/28/96 4:00	16.3	158	4.3	6.8
07/28/96 8:00	13.2	85.8	4.4	3.7
07/28/96 12:00	10.7	87.6	5.2	4.5
07/28/96 18:00	8.7	57.4	4.8	2.7
07/29/96 0:00	7.3	36.2	6.0	2.2
07/29/96 12:00	6.1	26.4	5.6	1.5
08/13/96 12:00	1.8	2.2	18.9	0.4
08/20/96 10:00	1.8	7.4	9.5	0.7
08/20/96 18:00	2.3	14.5	9.5	1.4
08/21/96 0:00	3.4	83.8	4.7	3.9
08/21/96 4:00	3.4	51.0	6.0	3.1
08/21/96 6:00	2.9	56.7	6.2	3.5
08/21/96 8:00	2.7	85.0	6.9	5.9
08/21/96 10:00	2.7	209	4.5	9.4
08/21/96 12:00	5.9	281	5.1	14.2
08/21/96 14:00	14.2	475	4.3	20.3
08/21/96 16:00	9.6	274	5.1	13.9
08/21/96 18:00	7.6	138	4.9	6.7
08/21/96 20:00	5.9	73.5	5.7	4.2
08/22/96 0:00	4.1	33.5	6.1	2.1
08/22/96 12:00	2.8	16.4	8.3	1.4
08/24/96 12:00	2.2	5.5	16.7	0.9
08/26/96 12:00	2.6	11.3	15.6	1.8
08/29/96 12:00	2.7	7.8	15.3	1.2
08/30/96 0:00	2.7	9.6	15.3	1.5
08/30/96 4:00	3.5	24.4	13.7	3.3
08/30/96 8:00	5.5	116	11.4	13.2
08/30/96 12:00	4.6	65.9	12.2	8.0
08/31/96 0:00	3.4	16.8	13.9	2.3
09/07/96 12:00	2.1	2.9	17.1	0.5
09/11/96 12:00	1.7	3.8	18.4	0.7
09/15/96 12:00	1.6	7.1	19.0	1.3
09/30/96 12:00	2.0	2.5	16.9	0.4

Table 1. Continued

Date	Q	SPM	POC%	POC
10/01/96 8:00	6.1	14.7	10.9	1.6
10/01/96 10:00	6.3	27.4	10.7	2.9
10/01/96 14.00	5.0	51.4	11.8	6.0
10/01/96 16:00	5.3	46.8	11.6	5.4
10/01/96 18:00	10.4	159	8.7	13.8
10/01/96 20:00	13.5	244	7.8	19.0
10/01/96 22:00	9.9	238	8.9	21.2
10/02/96 0:00	9.0	175	9.2	16.1
10/02/96 8:00	9.0	42.6	9.2	3.9
10/02/96 12:00	7.9	30.0	9.8	2.9
10/02/96 16:00	9.3	30.8	9.1	2.8
10/02/96 20:00	15.3	171	7.4	12.7
10/03/96 0:00	10.4	74.8	8.7	6.5
10/03/96 8:00	8.7	19.4	9.4	1.8
10/15/96 0:00	3.7	20.2	13.4	2.7
10/15/96 10:00	4.1	11.2	12.9	1.4
10/15/96 12:00	6.3	182	10.7	19.5
10/15/96 18:00	24.5	727	6.1	44.3
10/15/96 20:00	16.3	378	7.2	27.3
10/15/96 22:00	13.9	87.5	7.7	6.8
10/16/96 0:00	17.0	83.2	7.1	5.9
10/16/96 12:00	9.6	29.2	9.0	2.6
10/22/96 12:00	3.9	4.2	13.1	0.6
10/29/96 12:00	2.9	2.6	14.7	0.4
11/09/96 12:00	2.7	4.2	15.3	0.6
11/14/96 12:00	2.7	2.8	15.3	0.4
11/16/96 12:00	2.7	0.8	15.3	0.1
11/17/96 8:00	2.6	2.8	15.6	0.4
11/17/96 10:00	2.7	3.3	15.3	0.5
11/17/96 14:00	5.9	31.4	11.0	3.5
11/17/96 16:00	11.1	90.7	8.5	7.7
11/17/96 18:00	15.3	254	7.4	18.8
11/17/96 20:00	28.2	303	5.7	17.4
11/17/96 22:00	33.9	469	5.3	24.9
11/18/96 0:00	30.3	304	5.6	16.9
11/18/96 2:00	27.8	221	5.8	12.8
11/18/96 4:00	26.2	121	5.9	7.1
11/18/96 6:00	26.2	117	5.9	6.9
11/18/96 8:00	26.6	115	5.9	6.8
11/18/96 10:00	23.3	114	6.2	7.1
11/18/96 12:00	22.1	36.1	6.4	2.3
11/18/96 16:00	18.4	38.9	6.9	2.7
11/18/96 20:00	20.5	42.9	6.6	2.8
11/19/96 0:00	24.1	63.3	6.1	3.9
11/19/96 22:00	32.3	204	5.4	11.1
11/20/96 0:00	33.1	241	5.4	12.9
11/20/96 2:00	27.0	174	5.9	10.2
11/20/96 4:00	27.4	382	5.8	22.2
11/20/96 6:00	33.5	222	5.3	11.9

Table 1. Continued

Date	Q	SPM	POC%	POC
11/20/96 8:00	38.3	244	5.1	12.3
11/20/96 10:00	38.7	394	5.0	19.8
11/20/96 12:00	35.6	215	5.2	11.2
11/20/96 14.00	38.7	178	5.0	9.0
11/20/96 16:00	38.7	203	5.0	10.2
11/20/96 18:00	36.0	185	5.2	9.6
11/20/96 20:00	35.2	145	5.2	7.6
11/20/96 22:00	36.0	88.7	5.2	4.6
11/21/96 0:00	36.9	125	5.1	6.4
11/21/96 2:00	42.3	123	4.9	6.0
11/21/96 4:00	38.3	129	5.1	6.5
11/21/96 8:00	31.5	67.9	5.5	3.7
11/21/96 12:00	28.6	48.4	5.7	2.8
11/21/96 16:00	26.6	34.7	5.9	2.0
11/21/96 20:00	23.7	27.4	6.2	1.7
11/22/96 8:00	18.8	26.1	6.8	1.8
11/22/96 12:00	18.1	31.1	6.9	2.1
11/25/96 14:00	10.7	9.7	8.6	0.8
11/25/96 18:00	11.4	13.3	8.4	1.1
11/25/96 20:00	15.3	51.1	7.4	3.8
11/25/96 22:00	40.9	166	4.9	8.2
11/26/96 0:00	66.5	668	4.0	26.8
11/26/96 2:00	59.0	577	4.2	24.4
11/26/96 4:00	43.6	251	4.8	12.0
11/26/96 6:00	37.4	117	5.1	6.0
11/26/96 8:00	32.3	80.3	5.4	4.4
11/26/96 10:00	29.4	118.3	5.6	6.7
11/26/96 14:00	37.9	68.2	5.1	3.5
11/30/96 6:00	16.3	27.4	7.2	2.0
11/30/96 10:00	45.9	236	4.7	11.0
11/30/96 12:00	63.5	428	4.1	17.5
11/30/96 14:00	65.5	396	4.0	16.0
11/30/96 16:00	65.5	352	4.0	14.2
11/30/96 18:00	54.0	300	4.4	13.2
11/30/96 20:00	51.7	219	4.5	9.8
11/30/96 22:00	46.8	194	4.7	9.0
12/01/96 0:00	46.3	157	3.2	5.0
12/01/96 2:00	42.7	132	3.3	4.4
12/01/96 4:00	40.9	119	3.4	4.1
12/01/96 6:00	45.0	111	3.4	3.8
12/01/96 8:00	56.2	194	3.1	6.0
12/01/96 10:00	53.1	238	3.7	8.8
12/01/96 12:00	48.1	216	2.6	5.6
12/02/96 10:00	36.9	164	2.8	4.6
12/02/96 12:00	34.8	58.6	3.7	2.2
12/02/96 14:00	33.1	69.0	3.5	2.4
12/02/96 20:00	29.4	51.1	3.5	1.8
12/03/96 6:00	25.3	43.2	3.8	1.6
12/04/96 12:00	17.7	56.8	3.2	1.8

Table 1. Continued

Date	Q	SPM	POC%	POC
12/04/96 16:00	29.8	101	4.9	5.0
12/04/96 18:00	32.3	124	4.7	5.8
12/04/96 20:00	31.1	102	4.6	4.7
12/04/96 22:00	26.6	62.1	5.8	3.6
12/05/96 0:00	25.7	85.3	5.5	4.7
12/05/96 2:00	32.7	79.5	5.2	4.1
12/05/96 4:00	39.2	124	4.4	5.4
12/05/96 6:00	40.9	122	4.1	5.0
12/05/96 8:00	38.7	97.9	4.4	4.3
12/05/96 10:00	38.3	112	3.5	3.9
12/05/96 12:00	43.2	113	3.7	4.2
12/05/96 14:00	47.2	153	4.3	6.6
12/05/96 16:00	61.0	280	3.9	10.9
12/05/96 18:00	73.6	406	3.6	14.6
12/05/96 20:00	83.1	401	3.7	14.8
12/05/96 22:00	69.1	330	3.2	10.6
12/06/96 0:00	61.0	217	3.2	7.0
12/06/96 2:00	51.7	148	3.2	4.7
12/06/96 4:00	45.9	139	3.0	4.2
12/06/96 8:00	39.6	93.8	3.0	2.8
12/06/96 12:00	34.8	74.4	3.3	2.5
12/06/96 16:00	31.5	55.0	3.6	2.0
12/06/96 20:00	29.0	46.0	3.9	1.8
12/07/96 0:00	27.0	32.0	5.0	1.6
12/07/96 4:00	25.7	35.4	4.2	1.5
12/07/96 8:00	29.4	53.6	4.3	2.3
12/07/96 12:00	26.6	44.2	4.6	2.0
12/08/96 4:00	20.2	25.4	5.1	1.3
12/09/96 15:00	14.6	30.7	5.0	1.5
12/20/96 12:00	6.1	2.8	15.0	0.4
12/23/96 12:00	5.1	4.5	3.7	0.2
12/28/96 12:00	6.1	16.1	12.6	2.0

conditions (left and right banks, middle of the river) was very good (less than 15% rsd.). During low water levels, one sample per week was analysed for POC. To complete the database, POC was interpolated between POC measurements. During floods, POC was analysed every 2 h.

Analyses

The filters for POC analysis were acidified with HCl 2N to remove carbonates and dried at 60 °C for 24 h and POC analyses were made with a LECO CS 125 analyzer (Etcheber et al. 1999; Veyssy et al. 1999). POC contents are expressed in percentage of dry weight of SPM, abbreviated POC%, and POC concentrations are expressed in mg l^{-1}. Precision was better than ±5%.

Results and discussion

Temporal variability and origin of POC

Data records

The data of discharge, SPM and POC are listed in Table 1. During the 1996-year monitoring, SPM concentrations ranged from 1 mg l^{-1} up to 2730 mg l^{-1}. POC concentrations (n = 275 samples) varied between 0.12 and 160 mg l^{-1} and followed the same pattern as the water discharge and the SPM concentrations with maximum concentrations during floods (Table 1 and Figure 2).

Discharge-weighted POC concentration ($\sum QiCi/\sum Qi$) was 4.45 mg l^{-1} during 1996-year, where Ci is the POC concentration (mg l^{-1}) in a sample i and Qi is the instantaneous river water flow measured at the time when the sample i was collected.

The POC concentrations are similar to the Brazos River (4.32 mg l^{-1}) and the Nile River (3.85 mg l^{-1}), higher than in major world equatorial rivers (Amazon, 2.83 mg l^{-1}; Zaïre, 2.00 mg l^{-1}), and much lower than in very turbid Chinese Rivers such the Changjiang or Huanghe with 13.36 and 190.63 mg l^{-1}, respectively (Ludwig et al. 1996).

Global trends of POC contents in SPM

The percentage of organic carbon of the SPM (POC%) showed very important variations: average 6%, maximum 30% at low discharge in December 1995 and March 1996 and minimum 2.6% during a flood in December 1996.

Generally, POC% decreased when SPM increased, following an hyperbolic relationship (Figure 3). This is a very typical trend as reported for other world rivers (Meybeck 1982) and is thought to be due to changes of organic matter sources during the hydrograph (Ittekkot and Laane 1991).

Two non-exclusive processes can explain this trend. During low water stages, only small amount of terrigeneous SPM is transported by the river and the main portion of the organic material is due to phytoplankton, as described in the Gironde and the Loire rivers and several other world rivers (Ittekkot 1988; Meybeck et al. 1988; Veyssy et al. 1999). At these times, the average POC concentration in the Nivelle River was ~0.60 mg l^{-1} (POC% = 15.6; n = 55), and never exceeded 1.5 mg l^{-1} (POC% = 15.5). During high water stages, abundant silt and clay fractions, originating from soil and/or bank erosion and characterized by low organic carbon content, become dominant. Simultaneously, aquatic primary production is inhibited by high turbidity, so the autochthonous organic material becomes minor in comparison to the terrigeneous organic fraction (Meybeck 1982).

Seasonal trend of POC contents: impact of successive floods

The evolution of POC contents was studied during a series of eight autumnal successive floods (Figure 4). This clearly showed that there was a gradual

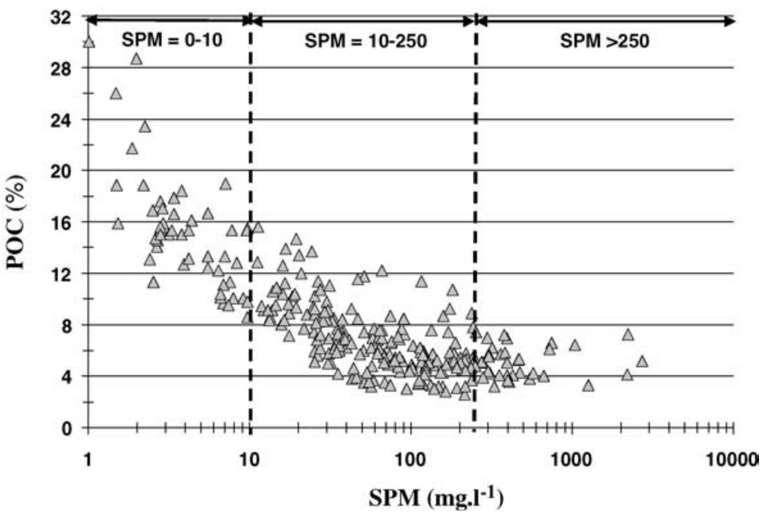


Figure 3. Relationship between POC contents (% of dry weight) and SPM concentrations from the Nivelle River at Saint Pée-sur-Nivelle.

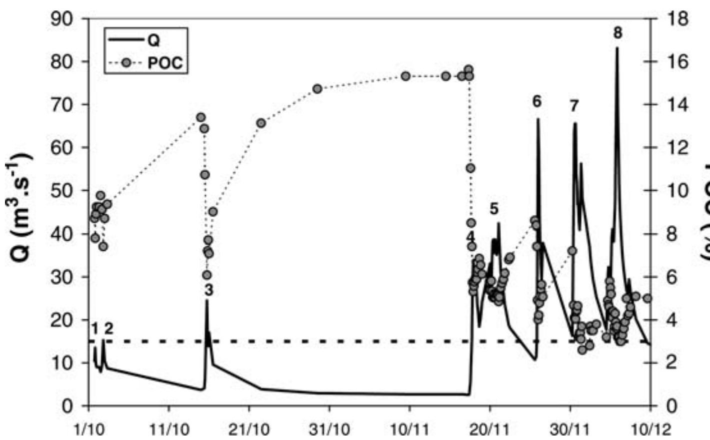


Figure 4. Water discharges and POC contents (%) during successive floods in autumn 1996. After eight floods, a POC threshold is observed, marked by a dashed line (POC = 3%).

impoverishment of the organic content from the first floods (1st October 1996; POC = 7.8%) to the last ones (5th December 1996; POC = 3%). Because the autochthonous organic fraction is negligible during all these flood events, it appears that successive eroded materials became poorer and poorer in organic matter.

The same conceptual model of continental organic carbon transport by rivers, as the one used by Veyssy et al. (1999) in the Garonne River, can be proposed here. Riparian matter, associated with litter standing crop and very rich in organic carbon, and soil materials are transported during the first floods. Later, as the litter fraction is depleted, organic matter linked to the mineral matrix of soil particulate matter becomes more important. A POC threshold value of 3% (average of the lowest values) was obtained in December 1996 and could be attributed to the basic organic fraction of soils. A similar trend is observed during the entire 1996-year record when considering the average POC concentrations during each flood peak (Figure 5). The POC% decrease during three different periods (Figure 5) was caused by successive floods, as discussed previously in Figure 4. The presence of low water stages during weeks between the three floods periods induced the recharging of riparian/litter organic fraction of surface layers: two POC recharges are observed (Figure 5), when POC contents increased from 5.7% in April to 9.7% in May and from 4.2% in August 1996 to 8.4% in October 1996. Such processes can be attributed to several causes. These include snow melting and liberation of POC stock; the leaching by rain of the material from 'the prescribed burning', local techniques used in Winter for pastoral activities (controlled burns in limited areas in order to well defined management objectives, e.g. to provide a better access in mountains and improve pastoral activities and ecosystems; Palu, personal communication), the spring flowering and the autumnal leaf falling, as already reported by Veyssy et al. (1999) in the Garonne River.

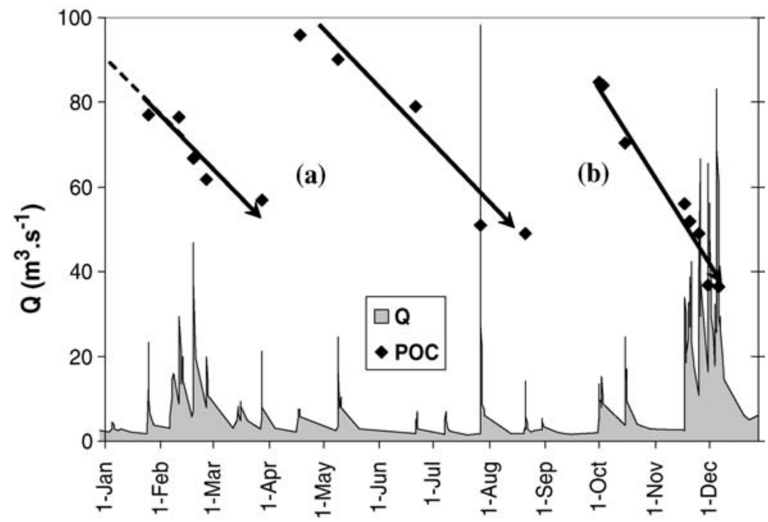


Figure 5. Seasonal evolution of mean POC contents (%) at different flood peaks in 1996. Two POC recharges (a and b) are observed.

Evolution of POC concentrations during individual and successive floods

The highest POC concentrations were measured when the Nivelle River was flowing at an extremely high discharge in July 1996 (water discharge: 100 $m^3\ s^{-1}$). During this summer flood, the relationships between POC concentrations and water discharge showed a counterclockwise loop (Figure 6a): at a similar discharge, POC values on the falling limb were greater than the ones on the rising limb. Two processes can explain this loop type: (1) a relatively long travel time of the flood wave and the POC flux between the flood

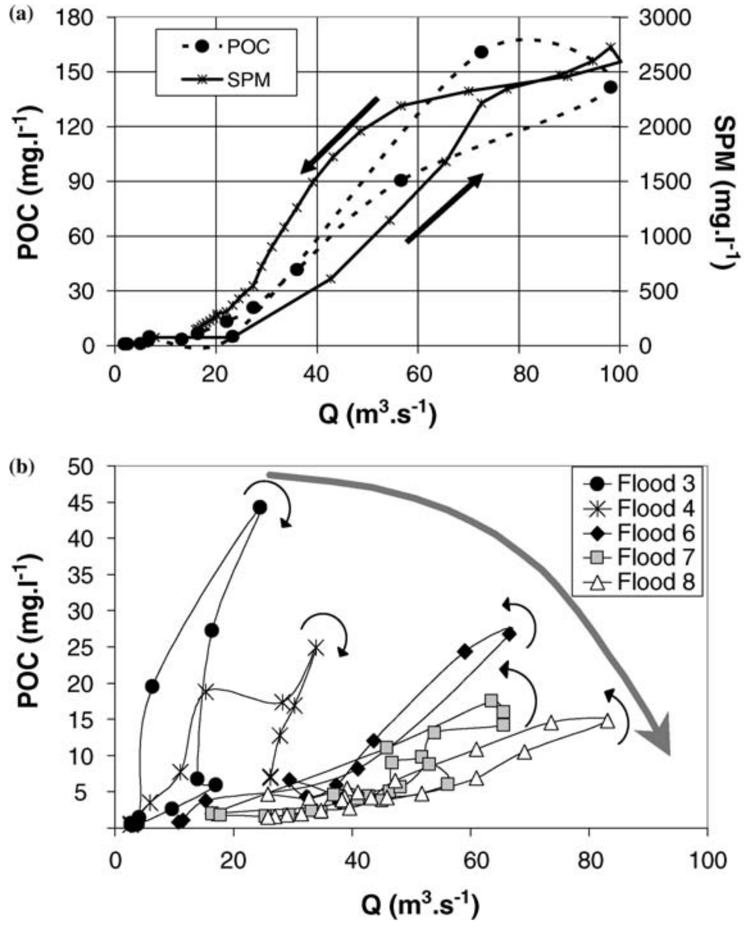


Figure 6. (a) Relationship between POC and SPM concentrations (in mg l^{-1}) vs. water discharges (m^3/s) during the 27 July 1996 flood event showing hysteresis. (b) Relationship between POC concentrations (mg l^{-1}) and water discharges from the first floods (the third flood: the first major flood event) to the last one recorded in December 1996. The black arrow directions indicate the evolution of POC during flood and the long grey arrow displays the decrease of POC concentrations during successive floods.

source and the measuring station; (2) a high soil erodibility in conjunction with prolonged erosion during the flood (Williams 1989). This counterclockwise pattern also has been observed for SPM in the Nivelle River (Maneux et al. 1999).

However, clockwise loops can also occur as shown in Figure 6b. This was the case for the autumn floods (Figure 6b). We suggest that this pattern could be due to the following reasons.

First, from the third to the eight flood, at a same order of SPM concentrations, POC concentrations decreased when water discharges increased, highlighting the impoverishment in organic carbon of eroded material. This phenomenon is consistent with the decrease of POC% in Figure 4.

Second, the POC vs. discharge loops change from clockwise during the 3rd and 4th floods to counterclockwise during the 5th to 8th floods. This suggests that, during the first floods (# 3 and 4), POC is primarily riparian litter/ resuspended river bed material, rich in POC content, easily erodible layer and/ or originating from a source close to the sampling station (Williams 1989). During the last floods (# 5–8), POC is constituted of more compacted soil relatively resistant to mechanical erosion and poorer in POC.

POC fluxes

On the basis of the high resolutions of water discharges measurements and POC concentrations data, an annual flux was established at Saint Pée-sur-Nivelle as follows:

$$F_{\mathrm{POC}} = \sum (F_{\mathrm{SPM}} \times \mathrm{POC}\%),$$

where F_{POC} is the annual POC flux, F_{SPM} is the instantaneous SPM flux with a 2-h frequency and POC% is the POC content in SPM (either measured during floods or extrapolated to correspond to 2-h SPM fluxes, considering that POC% is a constant between each weekly sampling during low waters).

The Nivelle River exported 845 tons of POC during the 1996-year which corresponds to a specific POC yield of 5.30 tC km^{-2} yr^{-1}. Such a value has been obtained during a dry year (discharge = 4.6 m^3 s^{-1} compared to the interannual average of 5.2 m^3 s^{-1}) and must be considered as a minimum value of annual POC fluxes over a longer time scale.

Nevertheless, this specific POC yield is much higher than for the Garonne River (France) with a value of 1.47 tC km^{-2} yr^{-1} (Veyssy et al. 1999) and rivers in the Europe with a mean of 1.10 tC km^{-2} yr^{-1} (Ludwig et al. 1996) or even the Amazon River (2.83 tC km^{-2} yr^{-1}; Richey et al. 1990). However, this specific yield is at least one order of magnitude lower than values for Huanghe River (14.7 tC km^{-2} yr^{-1}; Zhang et al. 1992) due to high organic carbon content in the loess covering the basin (Meybeck 1993), or high-standing islands of the Southwest Pacific (43–222 tC km^{-2} yr^{-1}, but for a sediment yield ~15,000 t km^{-2} yr^{-1}) for equivalent drainage areas (Lyons et al. 2002).

Maneux et al. (1999) highlighted the high variability of SPM outputs in the Nivelle River during 1996 with instantaneous SPM fluxes, which ranged from 10 tons up to 4540 tons for floods events of a 12–48 h-duration. All flood events exported ~82% of the annual SPM flux. The SPM flux of the largest 1996 flood (07/27/96; less than 1% of time) was 4540 t, i.e. 33% of the total annual flux. During the spring flood in July 1996, 30% of annual POC export was carried, i.e. an equivalent percentage that for the SPM flux. We used the duration curve of SPM and POC inputs which was expressed as the percent of annual SPM and POC flux (fluxes are listed from the highest SPM and POC concentrations) carried during a given percentage of time (Figure 7). We found that SPM and POC variability were similar with 32% of annual POC flux carried in 1% of time.

Using the same approach as Veyssy et al. (1999), we have estimated the relative importance of different organic pools during the 1996-year: the autochthonous organic material; the organic fraction due to riparian or soil litter; the organic material associated with the mineral matrix of soils, mainly refractory, quantitatively assimilated here to the constant POC threshold value of 3%.

As shown in Figure 3, SPM concentrations can be divided in three different classes corresponding to different degrees of SPM mobilization intensity. For each of them, we assume that an organo-mineral matrix from soil exists and is enriched by phytoplankton for the first class (0–10 mg l^{-1}) and by litter for the two other ones.

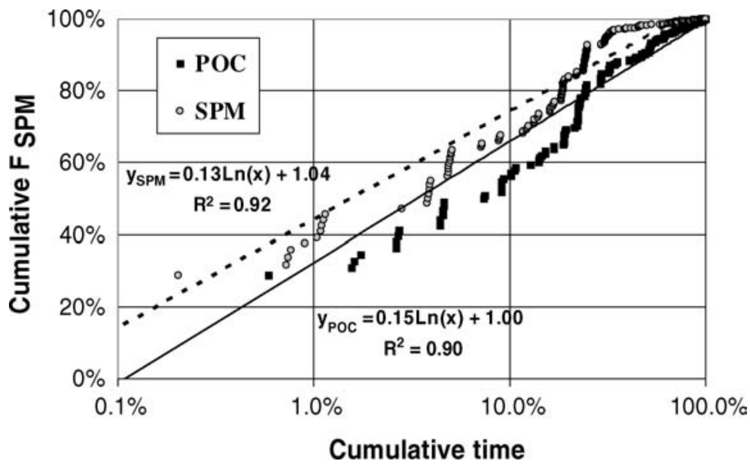


Figure 7. Temporal variability of SPM and POC fluxes expressed by the relation between cumulative SPM and POC fluxes (listed from the highest fluxes) and cumulative time.

During low water stages (water discharges lower than 20% of mean annual discharge, i.e. 4.2 $m^3 s^{-1}$: 275 days in 1996), SPM concentrations are low (< 10 mg l^{-1}) and waters are very clear, allowing for the development of phytoplankton blooms as evidenced by a high POC%. When assuming all this POC is autochthonous, and its contribution to the annual POC budget is less than 5%. When we subtract the part of POC due to soil material, autochthonous material is about 3%. In order to estimate litter organic fraction, we subtract the POC threshold of 3% in the second and third classes and multiply by corresponding SPM fluxes. This results in a contribution of litter to the annual POC flux of 42%. By difference, 55% of the total POC flux is related to soil organic contribution. We confirm this latter estimate by multiplying the POC threshold by the annual SPM flux in the three classes. The equations for the calculation of the different organic matter pools, based on the technique of Veyssy et al. (1999), are specified below:

Flux of autochthonous POC pool:

$$F = \sum (\mathrm{F_{SPM}}\ \mathrm{class1} \times (\mathrm{POC\%}\ \mathrm{class1} - \%\ \mathrm{threshold}));$$

Flux of litter/riparian POC pool:

$$F = \sum (\mathrm{F_{SPM}}\ \mathrm{class2} \times (\mathrm{POC\%}\ \mathrm{class2} - \%\ \mathrm{threshold})) + \sum (\mathrm{F_{SPM}}\ \mathrm{class3} \times (\mathrm{POC\%}\ \mathrm{class3} - \%\ \mathrm{threshold}));$$

Flux of soil POC pool:

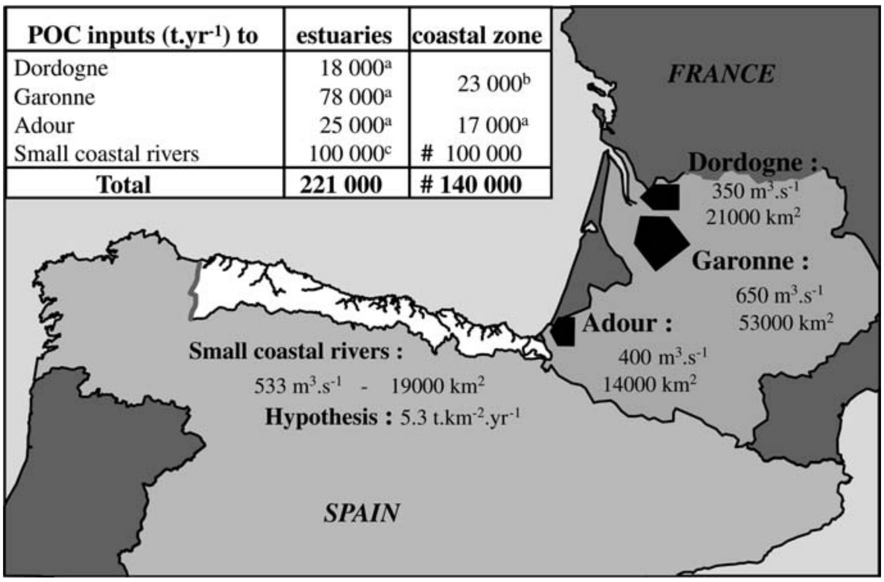
$$\begin{aligned} F &= (\%\ \mathrm{threshold} \times F_{\mathrm{SPM}}\ \mathrm{class1} + \%\ \mathrm{threshold} \times F_{\mathrm{SPM}}\ \mathrm{class2} + \%\ \mathrm{threshold} \times F_{\mathrm{SPM}}\ \mathrm{class3}) \\ &= 3\% \times F_{\mathrm{SPM}}\ \mathrm{total}. \end{aligned}$$

These results are in the same order as the ones obtained for the Garonne River where 54, 38 and 8% were evaluated respectively for soil, riparian/litter and autochthonous organic pools (Veyssy et al. 1999).

Contribution of small Pyrenean and Cantabrian rivers to the continental organic carbon inputs to the Bay of Biscay

At a global scale, Milliman and Syvitski (1992) demonstrated the importance of small mountainous river basins in the transfer of suspended material from the continent to the ocean. At a regional scale, recent studies (Uriarte 1992, 1995; Maneux et al. 1999, 2001) confirmed high specific yields for the Nivelle River and all the other Pyrenean and Cantabrian mountainous rivers. The Nivelle Basin can be considered as representative of the Northern Spanish rivers because of similar geomorphologic and hydrological features (Prego and Vergara 1998; Maneux et al. 1999). The global export rate from the Nivelle basin (5.3 tC km^{-2} yr^{-1}), extended to the whole area of the southern coast of the Bay of Biscay (19,000 km^2), leads to an estimated POC flux around 100,000 t yr^{-1}. This flux is close to the one entering from the Gironde system (96,000 t yr^{-1}; Veyssy et al. 1996), but for a water discharge two times lower.

In addition, in the Gironde, residence time of POC in the estuary is very long (1–2 years), which allows the mineralization and sedimentation of a large fraction of the riverine POC, leading to CO_2 emissions in the estuary (Frankignoulle et al. 1998; Abril et al. 1999, 2002;). Consequently, 75% of this organic load is lost inside the estuary itself and only 23,000 t yr^{-1} of POC reach the coastal zone. In the Adour Estuary, 25,000 t yr^{-1} of POC is entering the estuarine area and nearly 17,000 t yr^{-1} (70%) reaches the open ocean, because of neatly shorter residence time of the suspended material inside the estuary (a few weeks) than in the Gironde Estuary (Veyssy et al. 1998). By contrast, Pyrenean and Cantabrian mountainous rivers have torrential characteristics and the POC loads are directly transported to the Bay of Biscay where they probably rapidly settle in the coastal area. Our estimate of carbon fluxes from small mountainous watersheds to ocean allowed us to propose a general scheme of POC inputs in the Bay of Biscay (Figure 8) and to show that small mountainous rivers contributed to ~70% of the total POC input.



POC inputs ($t.yr^{-1}$) to	estuaries	coastal zone
Dordogne	18 000[a]	23 000[b]
Garonne	78 000[a]	
Adour	25 000[a]	17 000[a]
Small coastal rivers	100 000[c]	# 100 000
Total	**221 000**	**# 140 000**

Figure 8. Particulate Organic Carbon inputs to coastal zones by rivers of the Southern Bay of Biscay (References: [(a)] data from Veyssy 1998 and Veyssy et al. 1999; [(b)] data calculated from Abril et al. 2002 and [(c)] our study). Water discharges (m^3 s^{-1}) and areas (km^2) of different watersheds are given for information.

Conclusion

Small mountainous river basins tend to erode faster than larger basins. Because of the high temporal variability of sediment fluxes their contribution to global terrigeneous inputs to coastal areas has been underestimated. The lack of data limits our ability to quantify the POC from these systems. On the basis of high resolution SPM and POC data of a typical small mountainous river in France, we have:

(1) described the evolution of POC contents (expressed in %) during successive floods and a threshold value (3%) attributed to allochtonous fraction (soil);

(2) established the annual POC flux (845 tons) which mainly originates from soil and riparian/litter environments (~55% and 40% of the annual load, respectively); the autochthonous organic fraction does not exceed 5% of the annual load; temporal variability of POC inputs shows that 32% of annual POC flux carried in 1% of time;

(3) by applying the specific POC yield (5.3 tC km^{-2} yr^{-1}) to the whole area of the Southern coast of the Bay of Biscay (19,000 km^2) showed that small mountainous rivers contributed to ~70% of the total POC inputs in the Bay of Biscay.

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