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Effect of flood events on transport of suspended sediments, organic matter and particulate metals in a forest watershed in the Basque Country (Northern Spain)

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HIGHLIGHTS

- Fluxes of SPM, DOC, POC and particulate metal during flood events and at annual scale were estimated.
- From good regressions between SPM and particulate metal concentrationobtained during floods, it is possible to calculate the metal annual load.
- A methodology to classify floods according to their intensity and export capability of particulate metal was established.
- High intensity-flood events are the largest contributors to the export of SPM, organic carbon and particulate metal load.
- Variability of particulate metal load is related with suspended particulate matter (SPM), precipitation and discharge.

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ABSTRACT

An understanding of the processes controlling sediment, organic matter and metal export is critical to assessing and anticipating risk situations in water systems. Concentrations of suspended particulate matter (SPM), dissolved (DOC) and particulate (POC) organic carbon and metals (Cu, Ni, Pb, Cr, Zn, Mn, Fe) in dissolved and particulate phases were monitored in a forest watershed in the Basque Country (Northern Spain) (31.5 km^2) over three hydrological years (2009–2012), to evaluate the effect of flood events on the transport of these materials. Good regression was found between SPM and particulate metal concentration, making it possible to compute the load during the twenty five flood events that occurred during the study period at an annual scale. Particulate metals were exported in the following order: Fe > Mn > Zn > Cr > Pb > Cu > Ni. Annual mean loads of SPM, DOC and POC were estimated at 2267 t, 104 t and 57 t, respectively, and the load (kg) of particulate metals at 76 (Ni), 83 (Cu), 135 (Pb), 256 (Cr), 532 (Zn), 1783 (Mn) and 95170 (Fe). Flood events constituted 91%-SPM, 65%-DOC, 71%-POC, 80%-Cu, 85%-Ni, 72%-Pb, 84%-Cr, 74%-Zn, 87%-Mn and 88%-Fe of total load exported during the three years studied. Flood events were classified into three categories according to their capacity for transporting organic carbon and particulate metals. High intensity flood events are those with high transport capacity of SPM, organic carbon and particulate metals. Most of the SPM, DOC, POC and particulate metal load was exported by this type of flood event, which contributed 59% of SPM, 45% of organic carbon and 54% of metals.

1. Introduction

An understanding of the processes controlling sediment, organic matter and metal export is critical to assess and anticipate risk situations in water systems. Catchment characteristics such as geology, slope, drainage and land use are all factors controlling the form and quantity of sediments and metals transported into rivers (Miller et al., 2003; Kang et al., 2009). Contamination from non-point sources is difficult to determine due to the varied origin of natural and anthropogenic sources. In agroforestry catchments, possible sources of metal pollution include domestic wastewater, atmospheric deposition, soil erosion and agricultural and livestock activities. Runoff from agricultural soils is a relevant factor in metal transfer to watercourses where fertilization is commonly practiced because metals are present in agrochemical products (Xue et al., 2003; Taboada-Castro et al., 2012).

In surface water, metals are transported in dissolved form or bound to suspended sediments, which are basically composed of iron oxyhydroxides, natural organic matter and clay minerals (Viers et al., 2009). Although sediment-associated metals accumulate in the river

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during periods of low discharge, they are re-suspended and a major part of element transport in small catchments takes place during high-magnitude floods (Ciszewski, 2001), when the risk of metal mobilization increases. Floods are fundamental events in the transfer of freshwater, sediments, organic carbon and contaminants from the hinterland to the coastal zone. Great attention should therefore be paid to the hydrological processes and transport of sediment-associated metals during flood events (Garneau et al., 2015). The increase in discharge is quite often accompanied by marked changes in the concentration of suspended sediments, resulting in a noticeable increase in the loads of particulate-associated pollutants. This relevant variation may in turn affect the annual budget of large and minor rivers.

Time series of dissolved and particulate metals in rivers are important for making flux calculations, understanding the mechanisms controlling the concentrations of these elements and designing research and monitoring programs (Ollivier et al., 2011).

Oeurng et al. (2011) state that total precipitation, flood discharge and total water are the main factors controlling the suspended particulate matter (SPM), dissolved organic carbon (DOC) and particulate organic carbon (POC) load. Transport of metals in fluvial systems is controlled by a variety of geochemical processes, including mineral weathering, pH, amount and characteristics of both DOC and SPM and redox cycling, precipitation/dissolution and adsorption/desorption reactions. The influence of each factor varies for each element (Kerr et al., 2008).

Knowledge of the dynamics of suspended sediments, organic matter and metals in the Oka River watershed is important because it runs out into the Urdaibai estuary and is the main contributor of continental water and sediment to the estuary. In 1984, due to its ecological wealth, the estuary was designated a biosphere reserve by UNESCO (the Urdaibai Biosphere Reserve).

This research provides a very important data set for developing semi-empirical models. Such models could be used to predict the catchment's metal exportation for routine programs of water-quality monitoring and to design strategies for catchment management focusing on protection and sustainable management of water resources. For the basin under study, Peraza-Castro et al. (2015) used the semi-distributed, physically-based SWAT model to estimate the SPM and Ni load from simulated SPM. They conclude that the basin has a high annual variability due to hydrological variations. This approach allows long-term predictions with a reduced sampling time and cost.

The impact of individual, short-duration, high-magnitude discharge events on mean annual metal load is poorly known. This paper therefore aims: (*i*) to identify the processes controlling sediment, organic matter and metal export; (*ii*) to establish a classification of flood events based on export of SPM, POC, DOC and metals in particulate phase; and (*iii*) to estimate the contribution of SPM, organic carbon and particulate metals by flood event type and annual scale in the Oka catchment (Basque country, Northern Spain) during three hydrological years (2009–2012).

2. Material and methods

2.1. Study area

The study area is located in the Oka Hydrographic Unit. This hydrographic unit is divided into five watersheds: Oka, Golako, Mape, Artigas and Laga (www.uragentzia.euskadi.net).

This study was conducted in the upper part (31.5 km^2) of the Oka river catchment (178 km^2) in the Urdaibai Biosphere Reserve in the province of Bizkaia, Basque Country (Fig. 1). The elevation of this catchment ranges from 20 m at the Muxika gauging station to 607 m at the highest peak (Garoño).

The catchment has steep slopes of 26%. The main bedrock in the southern part of this catchment is an alternation of Tertiary sandy limestones, sandstones and lutites, whereas in the north part it is Upper Cretaceous calcareous flysch with alternation of marl and sandy limestone layers. Both Tertiary and Cretaceous formations are characterized by low permeability (EVE, 1996). The main soils in the upper catchment are Humic Cambisols (90%) and Eutric Fluvisols in the near-stream areas. This head catchment has been mostly (75%) reforested for industrial purposes with *Pinus radiata* and *Eucalyptus sp.*; autochthonous vegetation (*Quercus ilex*) occupies around 12%, and farmlands only 7%. Important for our study in trace metal, the pH recorded between 2009-2012 shows a mean value of 7.63 (neutral to alkaline). The waters of the Oka stream are bicarbonate calcic.

The climate is temperate and humid. Annual mean temperature is 14 °C, with a minimum mean in January (8 °C) and a maximum mean in August (20 °C). Annual mean rainfall is 1205 mm (from 1999 to 2012) mainly falling in autumn and winter. The dry season is from June to September, although exceptionally high rainfall can occur. The hydrological regime is principally pluvial, with maximum water volume in November and low discharge during summer (August and September) (www.bizkaia.net).

Mean recorded discharge at Muxika gauging station from 1999 to 2012 was 0.64 m^3 s^{-1} and 0.61 m^3 s^{-1} for this study period.

2.2. Field methodology

Discharge (Q, m^3 s^{-1}), precipitation (P, mm), turbidity (NTU), Electrical Conductivity (EC) and pH were monitored continuously at the Muxika gauging station, which is owned by Bizkaia Provincial Council (www.bizkaia.net). The station comprises a crump profile single-crest weir. These variables are electronically logged at ten-minute intervals. Turbidity was measured directly in the river course using a Solitax infrared backscattering turbidimeter with an expected range of 0–1000 NTU.

An automatic water sampler (SIGMA 900) was installed at the gauging station and programmed to start pumping 24 water samples of 800 mL when turbidity in the stream reached 100 NTU to ensure monitoring of flood events. Pumping frequency was every two hours in all flood events. Thus, samples were obtained on the rising and falling limb of the hydrograph to give representative values of metal concentration during the flood events studied. Metal data used for this study covers eight flood events during the period 2009 to 2012, as shown in Fig. 2.

Water samples were taken in polyethylene bottles and brought immediately to the Chemical and Environmental Engineering Laboratory (University of the Basque Country) for determination of suspended particulate matter (SPM), total organic carbon (TOC), dissolved organic carbon (DOC) and dissolved and particulate metal (Cu, Ni, Pb, Cr, Zn, Mn, Fe). These samples were treated immediately after arrival to laboratory to avoid potential alterations, according the protocol indicated in APHA-AWWA-WPCF (1998).

Clean procedures were employed to avoid contamination, all polyethylene samples bottles were acid washed (10% HNO_3 for 24 h) and rinsed with distilled water four times. This procedure was repeated for each sampling series.

2.3. Laboratory methodology

Chemical analyses were performed on water samples in the Chemical and Environmental Engineering laboratory (University of the Basque Country).

Samples taken during flood events were taken to the laboratory for suspended particulate matter concentration (mg L^{-1}) measurements. SPM was measured by filtration of the samples through previously weighted 0.45 μm filters and subsequent drying and weighting. A relationship was established between turbidity, optically measured in the field, and suspended particulate matter, physically measured in the laboratory ($SPM = 0.9708 * NTU$, $R^2 = 0.97$). This relationship was used to obtain continuous SPM (mg L^{-1}) data from the continuous turbidity (NTU) series measured in the field. Turbidimeters are commonly used