



# ASSESSMENT OF HEAVY METAL FLUXES IN A FOREST WATERSHED IN BASQUE COUNTRY (NORTHERN SPAIN) USING SWAT MODEL

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**Scientific context:** Nowadays, the main threat to the water body's damage comes from non-point sources of pollution, as result of intensive agriculture and urban development (Boskidis et al., 2012). All of these sources, sediment represents the highest volume for weight of material transported to the sea. Metals can be transported in association with the sediment (adsorbed) or in solution (soluble contaminants) (FAO, 1993, Boithias et al., 2012). The fine sediment is an important vector for pollutants transport such as heavy metals (Ankers et al., 2003), since it is a material highly enriched. During flood events, a significant proportion of heavy metal content from bottom sediments may be resuspended and transported to coastal zones, affecting negatively on the environment. In this sense, modeling is useful in assessing the impact of agricultural management and land use changes on water, sediment yield and pollutants as metals without altering the physical environment in the catchments.

**Objective:** To quantify annual particulate metal fluxes associated to suspended particulate matter (SPM) from a small forestry catchment to the Bay of Biscay (Northern Spain) during eleven hydrological years (2001-2012).

## Study area and data

The Oka River is located in the Basque Country-northern Spain, within Urdaibai Biosphere Reserve (declared in 1984 by UNESCO).

Drainage basin: 31 km<sup>2</sup>

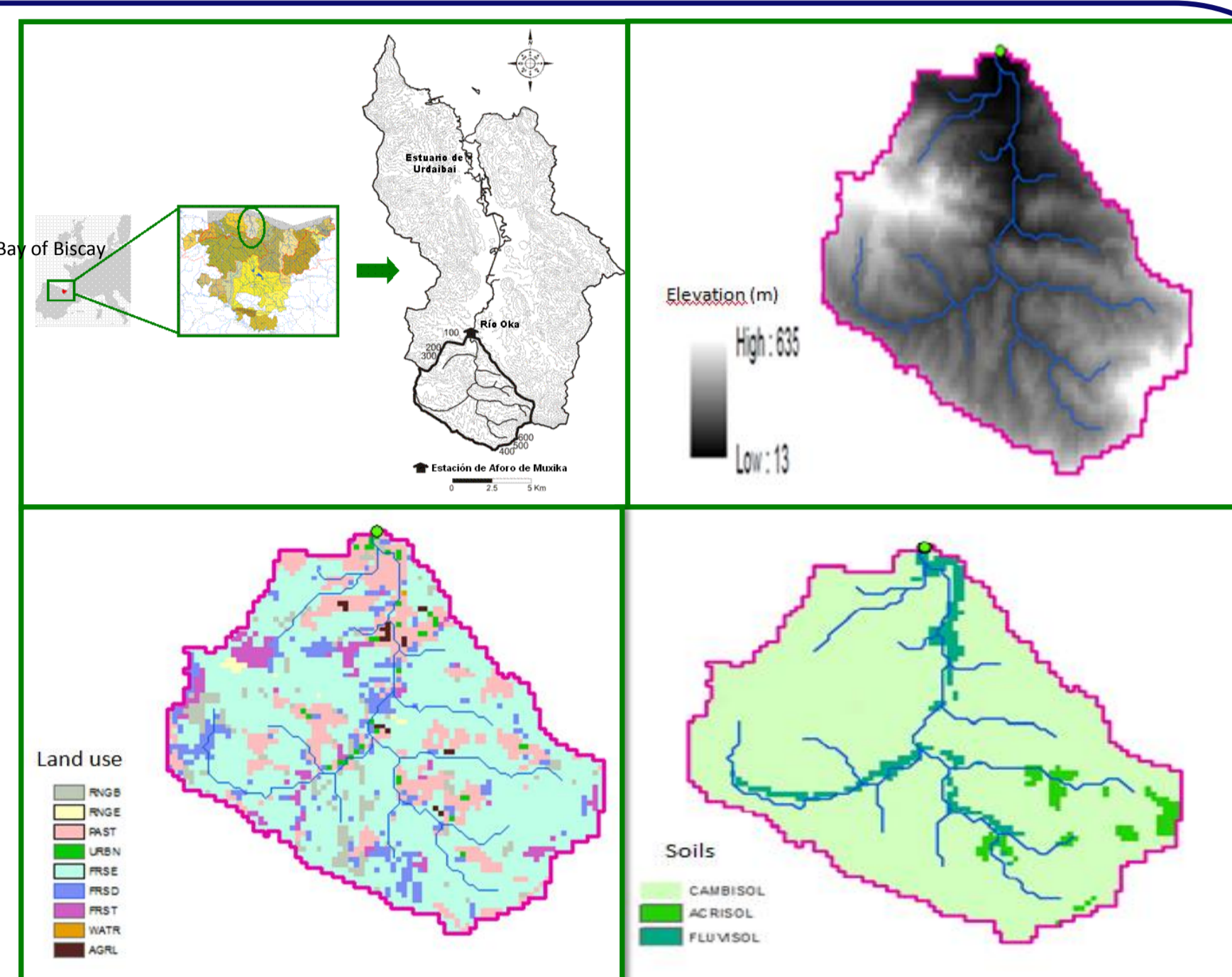
Elevation: 13 m to 605 m

Average precipitation: 1205 mm

Average discharge: 0.64 m<sup>3</sup> s<sup>-1</sup>

Vegetation: pasture, pinus, eucalyptus

Main bedrock: Calcareous Flysch



## Methodology

- Gauging station } Flow (m<sup>3</sup> s<sup>-1</sup>) 10 min  
Turbidity (NTU) 10 min  
SPM(mg l<sup>-1</sup>) 10 min

- Annual fluxes of particulate metals were estimated using Waling and Webb method (Waling and Webb, 1985):

$$F = V * \sum_{i=1}^n (Q_i * C_i) / \sum_{i=1}^n Q_i$$

- V (m<sup>3</sup>): annual water discharge,
- C<sub>i</sub> (μg l<sup>-1</sup>): particulate metals concentration,
- Q<sub>i</sub> (m<sup>3</sup> s<sup>-1</sup>): instantaneous river water flow and
- n: number of measures.

- Water samples collected manually during eight flood events occurred in 2009-2012 were carried to Chemical and Environmental Engineering Laboratory (UPV/EHU) to determinate particulate metal concentration (Cu, Ni, Pb, Cr, Zn, Al, Fe, Mn).

## Modelling approach

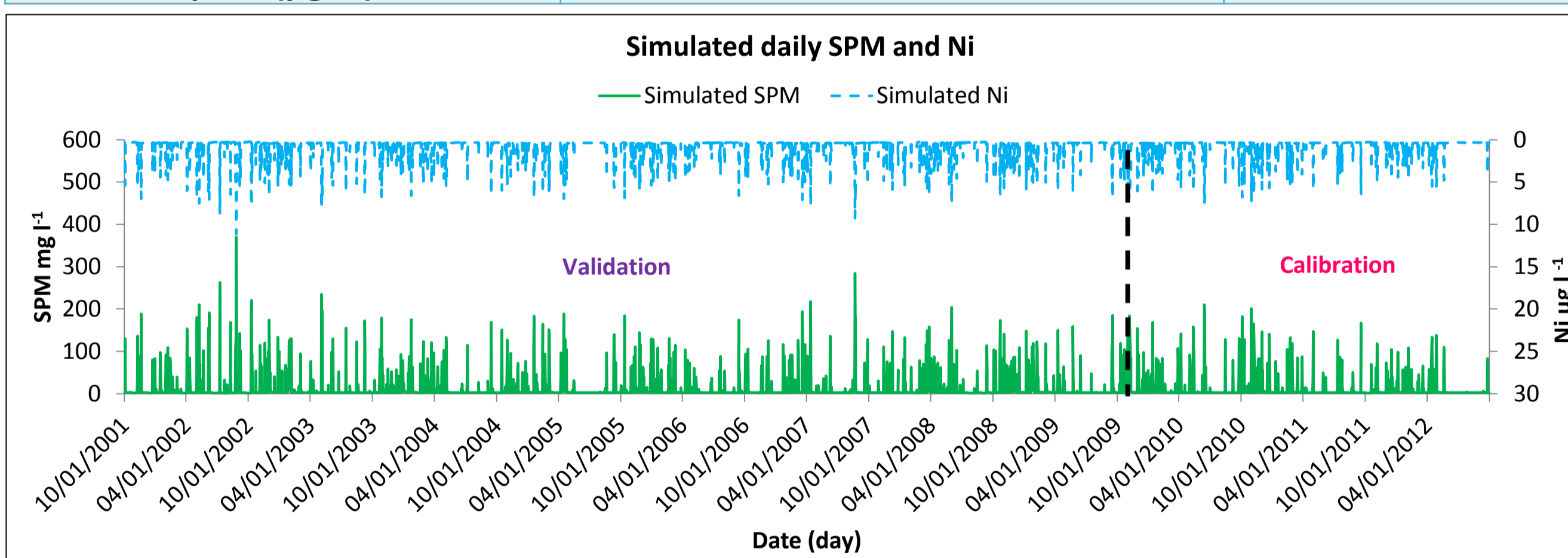
- SWAT model was applied to assess the temporal variability of discharge, SPM and Ni during 2001–2012 at daily scale in Oka catchment. The details of calibration and validation can be consulted in our earlier paper Peraza-Castro et al., 2014.
- To evaluate the model performance between simulated and observed annual metal fluxes the following efficiency criteria were used: coefficient of determination (R<sup>2</sup>), volumetric efficiency (VE) and index of agreement (d). VE represents the fraction delivered at the proper time; its complement represents the fractional volumetric mismatch (Crisis et al., 2008). d represents the ratio of the mean square error and the potential error (Willmot, 1982). Both VE and d, were proposed to overcome the insensitivity of R<sup>2</sup> and Nash-Sutcliffe Efficiency.

## Results and discussion

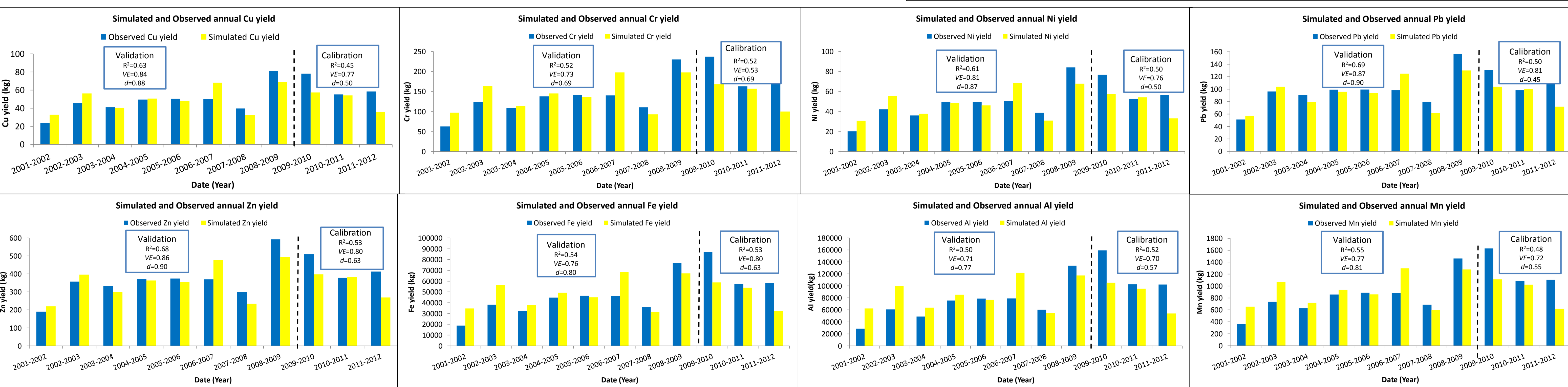
- With SPM and particulate metal concentrations obtained in eight flood events at the outlet, linear regression model were employed to express its relationships.
- It was found that SPM correlated well with metals (R<sup>2</sup>>0.62).
- Based on these relationships, the long term observed and simulated metal concentrations could be computed from SPM.

Particulate metal concentration (pMe)	Regression equations	R <sup>2</sup>
pCu (μg l <sup>-1</sup> )	0.0268*SPM + 1.1826	0.84
pNi (μg l <sup>-1</sup> )	0.1843*SPM <sup>0.6935</sup>	0.83
pPb (μg l <sup>-1</sup> )	0.0317*SPM + 3.3149	0.62
pCr (μg l <sup>-1</sup> )	0.0909*SPM + 2.5897	0.92
pZn (μg l <sup>-1</sup> )	0.135*SPM + 11.753	0.70
pAl (mg l <sup>-1</sup> )	0.0988*SPM <sup>0.9557</sup>	0.97
pFe (mg l <sup>-1</sup> )	0.038*SPM + 0.4693	0.92
pMn (μg l <sup>-1</sup> )	0.7004*SPM + 10.168	0.90

- Ni and other metal concentrations follows the SPM trend. In this example, simulated Ni ranged between 0.2-11.1 μg l<sup>-1</sup>, with a mean of 0.8 μg l<sup>-1</sup> comparable with the observed mean of 0.9 μg l<sup>-1</sup>.



## Particulate metal annual fluxes



- Exportation order of particulate metal yield: Al>Fe>Mn>Zn>Cr>Pb>Cu>Ni.
- The years 2008/09-2009/10 produced the highest metal load while 2001/02 generated the lowest.

Mean specific (kg km <sup>-2</sup> y <sup>-1</sup> ) metal yield during total period								
	Cu	Cr	Ni	Pb	Zn	Fe	Mn	Al
Observed	1.6	4.7	1.6	3.2	12.8	1562	29.8	2682
Simulated	1.5	4.5	1.5	2.9	11.2	1544	29.3	2702

- The mean specific annual of particulate metal export was compared with other European and American rivers with similar land use and the results are very similar each other; except for Pb and Zn that are slightly higher, which is attributed to the slight industrial and agricultural activity in the area.
- Al, Fe and Mn are more similar to the basins with agricultural landuse. These metals are major compounds soil.

Specific particulate metal fluxes (kg km <sup>-2</sup> y <sup>-1</sup> ) of other catchments										
River	Author	Country	Land use	Cu	Cr	Ni	Zn	Fe	Mn	Al
Mero	Palleiro et al., 2014	Spain	Agroforestry	0.3			1.6	361	15.4	319
Corbeira	Soto-Varela et al., 2014	Spain	Agroforestry	0.3			1.6	260	8.3	205
Chester Branch	Miller et al., 2003	EEUU	Agricultural	0.4	1.8	1	0.7	3.3	1090	1550
Montoussé	Roussiez et al., 2013	France	Agricultural	1.6	4.1	2.6	1.1	7	1692	40

## Conclusions

- With a good relationships between metal and SPM measured in field and a satisfactory SPM calibration by SWAT, is possible to compute the long term metal concentrations at daily time step.
- The statistical criteria indicate a fair and satisfactory annual metal fluxes simulation.
- Swat model is useful to estimate annual fluxes of pollutants which have punctual measures.
- Oka catchment showed a high annual metal fluxes variability during period study, which is related with sediment load.
- Annual simulated metal fluxes (kg) ranged from: 32.5-69 for Cu, 93.2-198 for Cr, 30.7-68.4 for Ni, 57-130 for Pb, 220-494 for Zn, 31525-68464 for Fe, 600-1297 for Mn and 53994-121724 for Al.

## References

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