Geophysical Research Abstracts, Vol. 7, 09633, 2005 SRef-ID: 1607-7962/gra/EGU05-A-09633 © European Geosciences Union 2005



1 Spectroscopic surface water characteristics in the Vouga river basin, central Portugal, under dry and wet antecedent weather conditions

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The present work concerns a preliminary spectroscopic characterisation of the spatiotemporal variation in composition of dissolved organic matter in the lower part of the Vouga river basin, central Portugal. Over the past three decades, this part of the Vouga river basin has undergone a dramatic change in land cover/use. The formerly prevailing Maritime Pine stands have now been replaced at a grand scale by eucalypt plantations. In order to address the impact of this land-cover change on the organic matter composition of the surface water, this investigation includes: i) sampling of surface water along a 35-km stretch from the middle section of the Alfusqueiro river to the lagoon area of lower Vouga river; *ii*) sampling at the outlets of four small experimental catchments dominated by a single of the two forest types; *iii*) collecting stemflow, throughfall and overland flow samples in both eucalypt and pine stands; *iv*) gathering extracts from eucalypt and pine litter, leaf/needle and bark material (by submersion in distilled water for 36 hours). The temporal variation in surface water composition is addressed by sampling at three occasions with contrasting antecedent weather conditions, i.e. following a dry spell late in August 2003 and following rainfall in the preceding 24 hours in December 2003 and April 2004.

The samples were analysed by UV-VIS and molecular fluorescence spectroscopy. Prior studies have found ultraviolet and fluorescence spectra to allow estimating organic matter content, degree of aromaticity, and features related with molecular size that can be used as fingerprint of origin of dissolved organic matter. Here, UV-VIS spectra were registered in the range of 200-500 nm on an UV-VIS spectrophotometer Shimadzu (Düsseldorf, Kent, Germany) Model UV 2101PC in 10 cm path length quartz cells. Fluorescence spectra were obtained with a spectrophotometer JASCO (Tokyo, Japan) Model FP-770. Using a scan speed of 1000 nm min⁻¹ and excitation and emission slit bandwidths of 10 nm, all samples were scanned with $\lambda_{excitation}$ varying from 200 to 600 nm and with $\Delta\lambda$ ($\lambda_{emission} - \lambda_{excitation}$) varying from 18 to 230 nm, giving a grand total of 7825 readings per three-dimentional spectrum.

The spectra of the dry-season samples showed very promising results in that the 3-dimensional fluorescence spectra of the small pine-dominated catchments differed considerably from those of the small eucalypt-dominated catchments. The former spectra lacked the noticeable peaks in fluorescence intensity in the $\lambda_{excitation}/\lambda_{emission}$ range of 200-300/400-500 nm that were present in the latter spectra. The December-spectra equally revealed clear differences between the two types of catchments but in distinct $\lambda_{excitation}/\lambda_{emission}$ ranges. Data analysis is currently focussing on how to explain the observed differences from the spectra of the hydrological flow components and/or plant material.