Nutrient availability (P, K, S) changing red-ox condition in freshwater sediments of Reno river Basin (North Italy)

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Introduction: Rivers and canals play an important role as nutrient and pollution sink since they are often the final collectors of municipal, agricultural and industrial wastewaters (Yi et al, 2011). In urban basins, waterways management can result problematic due to a large amount of sediments which are transported through the flow, and dragging operations are needed to assure the hydraulic security. Therefore the monitoring of sediments quality and the study of the behaviour of nutrient availability during oxidizing processes are very important in order to assure a correct way to manage dragged materials. Usually dragged sediments are added to agricultural soils but they could also be considered special waste as a function of their contamination degree. The change of red-ox characteristics in wet and dry sediments can deeply influence both metal and nutrients availability (Wilson and Chang, 2000) decreasing their quality. The aim of this work was to evaluate the seasonal variability of nutrients in sediments focusing on their availability in wet and dry condition.

Methods: Sediment samples were collected from rivers and reclamation canals in Reno river basin, North Italy (Ferronato et al, 2013) during four seasons in 2012-2013. Total organic carbon (TOC) and total nitrogen (TN) were detected by an CHN Elemental Analyzer (EA 1110, Thermo Fisher) after a pre-treatment with HCl for eliminating inorganic carbon. The total concentration of nutrients (TK, TP, TS) were determined in dry sediment sample though digestion with Aqua Regia (HCl and HNO_3 3:1 w:w) in a microwave oven (Spectro Arcos) and then the supernatant measured with ICP-OES equipment. Concentration of soluble P, K and S (SP, SK, SS) in wet and dry sediments were quantified after extraction with MilliQ water (1:10 v:w) for 16h and then measured by ICP-OES (Vittori Antisari, 2010).

Results: TOC, TN and total nutrients concentration in reclamation canals was statistically higher than those of rivers ($p<0.05$). Nutrients recovery showed a seasonal variability and higher values in June in both rivers and canals samples were detected. TP and TK concentration were from 0.19 to 3.09 g kg^{-1} and 2.26 and 17.28 g kg^{-1} for March and June sampling respectively. No trends was found for TS and its values are ranged from 0.51 to 1.61 g kg^{-1}.
Solubility of elements are presented in Table 1. Generally, SP, SK and SS concentration were statistically higher ($p<0.05$) in dry sediment than that in wet one and the same trend was found for seasonal variability: the soluble nutrients amount was higher in summer than in winter.

	Rivers				Canals			
	Winter		Summer		Winter		Summer	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
				P				
Mean	0,08	5,70	7,35	6,95	0,10	10,72	10,26	11,28
RSD	0,21	0,14	0,39	0,69	0,16	0,31	0,26	0,71
				K				
Mean	15,53	25,82	26,09	46,66	68,73	77,00	78,44	90,66
RSD	0,42	0,46	0,72	0,46	0,56	0,47	0,62	0,44
				S				
Mean	34,03	114,81	85,33	103,07	339,13	728,14	626,17	877,92
RSD	0,39	0,44	0,16	0,49	0,04	0,07	2,27	3,27

Table 1. Mean (mg kg^{-1}) and Relative Standard Deviation (RSD) of SP, SK, SS in wet and dry sediments.

Discussion: The correlation between P/TOC ($r^2=0.41$) and P/NT ($r^2=0.53$) suggests that P concentration is linked to organic content as the result of both erosion and run off processes from the agricultural lands and discharge by wastewater plants. TP accumulation during summer period may also be linked to the impact of domestic wastewater which increase in water during summer when there is the minimum flow condition. One of the problems of these water courses is the eutrophication issue due to a high P concentration in summers. The comparison between air-dried and wet sediment manipulation, as also reported by Hartley et al (2010), rises profound changing in nutrients availability due to a different chemistry speciation which bring to a different equilibrium in sorption/desorption and precipitation/dissolution cycles. This way of studying the element behaviour, simulating aeration of dragged materials is of great interest for assessing the potentiality of sediments for soil reuse.
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References: [1] Yi et al, (2011) *Env.Pollution* **159**:2575–2585; [2] Wilson and Chang (2000) *Env.Geochem*. **31**: 493-502; [3] Ferronato et al (2013) *J.Water Reources Protection* **5**:458-468; [4] Vittori Antisari et al, *W.Quality Expo Heath* **2**:1-13; [5] Hartley et al (2010) *Env. Pollution* **158**:649-657.