

Natural and anthropogenic contributions of heavy metals from surface waters and suspended solids from the Valdinievole sub-basin (Tuscany, Central Italy)

Maccelli C.^{*1}, Natali C.², Nisi B.³, Casalini M.², Vaselli O.²⁻³, Venturi S.² & Avanzinelli R.²

¹ Dipartimento di Scienze della Terra, Università di Pisa. ² Dipartimento di Scienze della Terra, Università degli Studi di Firenze. ³ CNR-Istituto di Geoscienze e Georisorse, Firenze.

Corresponding author e-mail: chiara.maccelli@phd.unipi.it

Keywords: water geochemistry, heavy metals, isotopes, Valdinievole.

The Padule di Fucecchio (Tuscany, Central Italy) is a protected swampy zone that has an important role in the migratory routes of several bird species. It is located in the lower reaches of the Valdinievole sub-basin and is fed by a relatively complex riverine network mainly consisting of the Nievole, Pescia di Collodi, and Pescia di Pescia rivers as well as numerous artificial canals that collect urban and industrial wastewaters from the densely inhabited and industrialized surroundings. The Usciana River represents the only emissary of the Padule di Fucecchio and, after 25 km, it flows into the right bank of the Arno River. Many relevant anthropic activities and small-medium enterprises, such as paper mill industries, flora-nursery farms, thermal spas, and one of the most productive Italian tanning districts, are present in the investigated area, making this zone one of the most polluted districts of the Arno River. In order to evaluate the presence of anthropogenic and natural contributions in the surface waters and suspended solids load of the Valdinievole sub-basin, this study is aimed at determining the seasonal variations in terms of main, minor, and trace elements by the analysis of 36 sampling points, distributed along an area of about 320 km² by Ionic Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Department of Earth Sciences (University of Florence). Furthermore, the Sr and Pb isotopic ratios on water and suspended solid load samples by Thermal Ionization Mass Spectrometer (TIMS) to discriminate natural and anthropic sources are presently in progress. According to the geochemical survey carried out in March 2021, the water chemistry showed a relatively wide compositional variability, being comprised from Ca²⁺(Mg²⁺)-HCO₃⁻ to Na⁺-Cl(SO₄²⁻). The concentrations of the N-bearing species were up to 36 (NO₃⁻), 2.4 (NO₂⁻) and 11.5 (NH₄⁺) mg/L while the contents of Mn, Fe, and Cs were up to 595, 432, and 36.7 mg/L, respectively. As far as the concentrations of metals in the suspended solids, Cr and Zn presented the highest values, being up to 429 and 409 mg/kg, respectively. Nickel, V, Pb, Cs, and As showed contents up to 120, 149, 83, 46, and 25 mg/kg, respectively. It is mentioned that Cr shows a positive correlation with V and Ni, although enrichments in Cr were recorded in those samples close to the tanning district. The preliminary chemical data are clearly suggesting, as expected, the strong anthropogenic pressure acting on the Valdinievole sub-basin, which is in its turn reflecting into the Arno River water.