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Anthropogenic and geogenic Cd, Hg, Pb and Se sources of contamination in a brackish aquifer below agricultural fields

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Groundwater quality is often threatened by industrial, agricultural and land use practices (anthropogenic input). In deltaic areas is however difficult to distinguish between geogenic and anthropogenic inorganic contaminants pollution, since these phenomena can influence each other and often display a seasonal cycling. The effect of geogenic groundwater ionic strength (>10 g/l) on the mobility of trace elements like Cd, Hg, Pb and Se was studied in combination with the anthropogenic sources of these elements (fertilizers) in a shallow aquifer. The site is located in the Po river plain (Northern Italy) in an agricultural field belonging to a reclaimed deltaic environment, near Codigoro town. It is 6 ha wide and is drained by a subsurface drainage system made of PVC tile drains with a slope of 3‰ which provides gravity drainage towards two ditches that in turn discharge in a main channel. The whole area has been intensively cultivated with cereal rotation since 1960, mainly using synthetic urea as nitrogen fertilizer at an average rate of 180 kg-N/ha/y and pig slurry at an average rate of 60 kg-N/ha/y. The sediments were analyzed for major and trace elements via XRF, while major ions in groundwater were analyzed via IC and trace elements via ICP-MS. Three monitoring wells, with an inner diameter of 2 cm and screened down to 4 m below ground level, were set up in the field and sampled every four month from 2012 to 2014. The use of intensive depth profiles with resolution of 0.5 m in three different locations, gave insights into groundwater and sediment matrix interactions. To characterize the anthropogenic inputs synthetic urea and pig slurry were analyzed for trace elements via ICP-MS. The synthetic urea is a weak source of Cd and Hg (∼1 ppb), while Se and Pb are found below detection limits. The pig slurry is a much stronger source of Se (∼19 ppb) and Pb (∼23 ppb) and a weak source of Cd (∼3 ppb) and Hg (∼2 ppb). Although, the mass loading rate pig slurry is three times lower than the synthetic urea on yearly basis. In general Cd, Hg, Pb and Se concentrations were found lower in sandy sediments, since usually these elements concentrate in the clay fraction. Hg, Pb and Se groundwater concentrations generally increased with the ionic strength of the solution witnessing a geogenic origin, while Cd groundwater concentrations were not clearly related to saline groundwater. Most probably, the latter was released both by fertilizers and by sediments during shifts between oxic and reducing conditions. In addition, the elevated soil organic carbon induced reducing conditions throughout the saturated aquifer profile (usually below the tile drains), which further promoted Hg, Pb and Se dissolution. The combined use of high-resolution sediment profiles, seasonal groundwater sampling and end-member analyses seems to be a promising procedure to distinguish between anthropogenic inorganic contaminants input and geogenic contribution in reclaimed deltaic environments.