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Geochemical fingerprints and controls in the sediments of an urban river: River Manzanares, Madrid (Spain)

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Abstract

The geochemical fingerprint of sediment retrieved from the banks of the River Manzanares as it passes through the City of Madrid is presented here. The river collects the effluent water from several Waste Water Treatment (WWT) plants in and around the city, such that, at low flows, up to 60% of the flow has been treated. A total of 18 bank-sediment cores were collected along the course of the river, down to its confluence with the Jarama river, to the south–east of Madrid. Trace and major elements in each sample were extracted following a double protocol: (a) "Total" digestion with HNO_3, $HClO_4$ and HF; (b) "Weak" digestion with sodium acetate buffered to pH=5 with acetic acid, under constant stirring. The digests thus obtained were subsequently analysed by ICP-AES, except for Hg which was extracted with aqua regia and sodium chloride-hydroxylamine sulfate, and analysed by Cold Vapour-AAS. X-ray diffraction was additionally employed to determine the mineralogical composition of the samples. Uni- and multivariate analyses of the chemical data reveal the influence of Madrid on the geochemistry of Manzanares' sediments, clearly manifested by a marked increase in the concentration of typically "urban" elements Ag, Cr, Cu, Pb and Zn, downstream of the intersection of the river with the city's perimeter. The highest concentrations of these elements appear to be associated with illegal or accidental dumping of waste materials, and with the uncontrolled incorporation of untreated urban runoff to the river. The natural matrix of the sediment is characterised by fairly constant concentrations of Ce, La and Y, whereas changes in the lithology intersected by the river cause corresponding variations in Ca–Mg and Al–Na contents. In the final stretch of the river, the presence of carbonate materials seems to exert a strong geochemical control on the amount of Zn and, to a lesser extent, Cu immobilised in the sediments. This fact suggests that a variable but significant proportion of both elements may be susceptible to reincorporation in the aqueous phase under realistic environmental conditions.

Keywords: Urban; Sediments; River; Trace elements; Pollution; Multivariate; Manzanares; Madrid

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1. Introduction

The need to gain a better understanding of the behaviour of urban environments and the consequences of living within or close to a city's boundaries is clearly justified by the fact that cities have become the habitat where 2.7 billion people, or 47% of the total world population are currently housed. Furthermore, the (U.N. Population Division (UNPD) (2001)) estimates that nearly all the population growth in the next 30 years will be concentrated in the urban areas of the world. If this projection is accurate, 5.1 billion people will live in cities in 2030 and the percentage of urban population will accordingly increase to 60% of the world's total. If the statistical analysis is restricted to the more developed regions, it is estimated that the percentage of urban population in 2030 will reach 83.5%, up from 76% in 2000 (U.N. Population Division (UNPD), 1996, 2001; World Bank, 2000).

With the growing interest in the rules that govern the fate of pollutants in urban environments, the sediments of urban rivers pose a particularly challenging scientific problem. As in natural environments, urban river sediments have a high potential for storage of trace elements. Unlike natural rivers, however, a large proportion of the trace element load contained in urban sediments is not associated with the original geologic parent material, but with the steady supply of trace elements, both dissolved and in particulate form, carried by treated and untreated urban waters. Changes in the aqueous environment to which urban sediments are exposed could result in the release of these trace elements that have accumulated over long periods of time. The linkage between the concentration of toxic elements in the sediment and ecosystem health explain the growing interest and the—consequent—rapid increase in scientific publications dealing with metals in fluvial sediments (Sutherland, 2000).

A further complication in the study of urban rivers arises from the fact that their hydrodynamic behaviour is sometimes profoundly altered as they run through a city. Urban rivers are often canalised, the flow of water is regulated, some sections of the river can be isolated and the water in them removed for cleaning operations, during which sediments are dredged and/or exposed to the atmosphere, etc. All these factors combine to make predictions about deposition and geochemical behaviour of urban sediments quite uncertain. Within this context, River Manzanares constitutes an excellent example of an urban river with a strong anthropic control on its hydrodynamic behaviour and the geochemistry of its sediments. After passing through the city of Madrid, a large proportion of the water carried by River Manzanares is of urban origin and has entered the stream as discharge from five Waste Water Treatment (WWT) Plants that collect and treat the street runoff and domestic waste water (combined sewer system) of Madrid and a few nearby smaller towns. The river receives approximately 5.3×10^8 m^3 of treated water from Madrid every year. The percentage of treated urban water in River Manzanares varies from approximately 20% in wet years to 60% in years with low precipitation.

1.1. Description of River Manzanares

The river rises at an altitude of 2160 m in the granite mountains of Sierra de Guadarrama, north of Madrid. For 90 km, River Manzanares follows a southeast direction (Fig. 1), until it meets with the Jarama river shortly after exiting the urban perimeter of Madrid (pop. 3 million). Between the granitic Sierra and the city of Madrid, the Manzanares crosses Quaternary detrital materials, primarily gravel, sand and silt. Two major dams in the northern-most section of the river (Embalse de Santillana and El Pardo) control the flow of water arriving at the first of several weirs operated by Madrid's municipality. Four small streams between the first dam and Madrid and three downstream of the city—some of which flow only intermittently—contribute minor amounts of water to the River Manzanares. As it flows through the central part of the city, the river is canalised. Before and after this culverted section, small sections of the river banks are stabilised with large, angular boulders or rip-rap. South of Madrid, the River Manzanares flows through a landscape dominated by gypsiferous marls, clays and gypsum, intercalated with lenses of limestone.

2. Methods and materials

Eighteen sampling stations were positioned along the course of the River Manzanares (Fig. 1). The first four were located between the river's source and the