ASSESSMENT OF ANTHROPOGENIC TRACE METALS AND RARE EARTH ELEMENTS IN A SUBTROPICAL URBAN AREA (THE DANSHUI SYSTEM, TAIWAN)

Antoine Lerat[(1)], Alexandra Coynel[(1)], R.S.W. Yam[(2)], F-J. Chang[(2)], A. Legeay[(1)], M. Baudrimont[(1)], A. Feurtet-Mazel[(1)], L. Gorse[(1)], L. Dutruch[(1)], C. Bossy[(1)], G. Blanc[(1)] & G. Vachaud[(3)]

(1)Université de Bordeaux, UMR EPOC 5805, Pessac, France
(2)National Taiwan University, Department of Bioenvironmental Systems Engineering, Taipei, Taiwan
(3)Université Joseph Fourier, UMR LTHE 5564, Grenoble, France
antoine.lerat@etu.u-bordeaux.fr; alexandra.coynel@u-bordeaux.fr

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Introduction

The identification of urban pollutant sources is a major issue to restore estuarine and coastal water quality. Moreover, it is a useful tool to minimize future contamination as worldwide urban populations are projected to increase from ~3.1 to 6.7 billion in 2050, particularly in East Asian countries with high economic development. The Danshui River (L=159 km and S=2,726 km²) is the major system in North Taiwan. It is a quite undisturbed section upstream and it drains the Taipei-Keelung-Taoyuan Metropolitan area downstream with roughly 9.1 million inhabitants. This study aims at determining the distribution of trace metals (V, Cr, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Th, U and Hg) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) within the Danshui system in order to i) identify geochemical anomalies using local geochemical background (LGB); ii) determine anthropogenic sources, and/or physicochemical processes (Figure 1.A).

Methods

A sampling campaign was performed in March 2015 in 16 strategic sites along the Danshui System and its major tributaries (Xindian, Dahan and Keelung) in order to determine the spatial distribution of trace metal and REE concentrations in water (i.e. unfiltered (UF), < 0.2 µm and < 0.02 µm fractions) and in river sediments. River sediments were treated with a tri-acid digestion with HNO_3, HCl and HF. Trace metal and REE concentrations were determined by ICP-MS (Thermo SCIENTIFIC X-Series 2) with external calibration under standard conditions. The applied analytical methods were continuously quality checked by analysis of international certified reference materials.

Results

Enrichment factors (EF) were calculated using Th-normalized concentrations in river sediments compared with LGB values (determined at PRP station) (e.g. Cu, Figure 1.B). The sequence for mean EF values is: 9.5 > Sn > Hg > Cu > Ag > Zn > Cd > As > Mo > Pb > Sb > Ni > Sr > V > Co > Cr > U > Ba ~1. High EF for Sn (EFmax=28), Cu (EFmax=9; Figure 1.B) and Ag (EFmax=7) in river sediments are concomitant with significant Gadolinium (Gd) anomalies in < 0.2µm waters (until 32 ng/l); both are observed in urban areas which are surrounded by several hospitals and industrial centers (Figure 1.A). Trace metal concentrations in water increase from upstream (mainly on < 0.2 µm or < 0.02 µm fractions) to downstream (mainly on unfiltered fractions) (Figure 1.C). However this increase is not only due to anthropogenic urban sources. The increase of unfiltered fractions in the Danshui system can be explained by sediment resuspension (tide effect). Different geochemical behaviors along the salinity gradient are reported such as conservative

behavior (e.g. Cd) and not conservative behavior (addition or subtraction). For example, Cu showed an addition in the dissolved phase at DS1 which could be related to organic matter degradation.

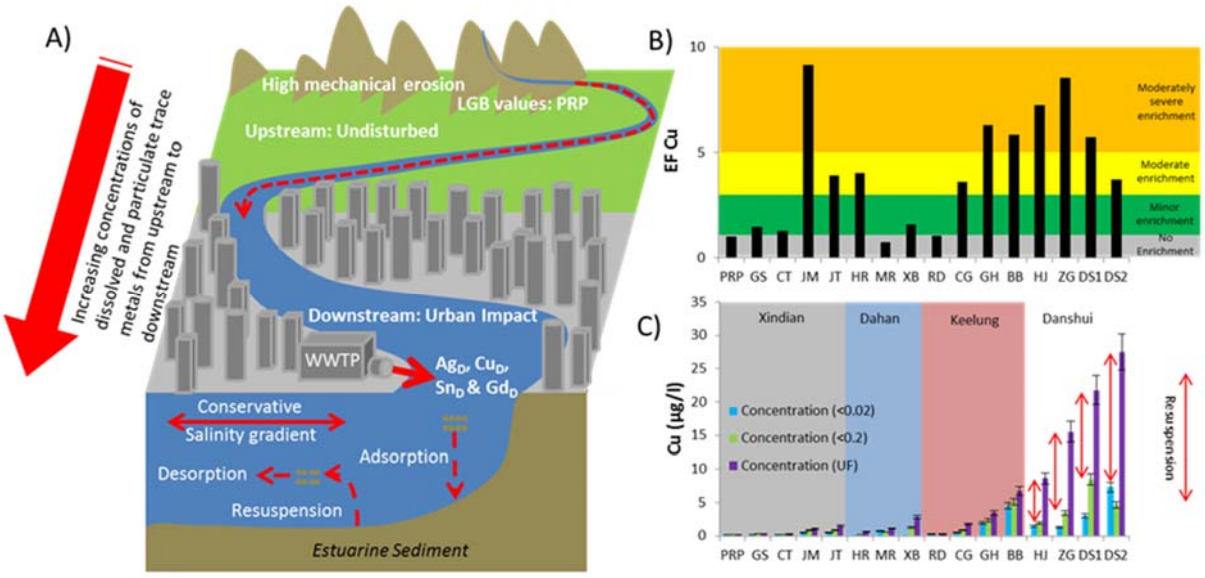

Figure 1. A) Hydrogeochemical cycle of trace metals in the Danshui System. B) Enrichment factors for Cu in river sediment. C) Trace metal concentrations in water in dissolved (<0.02 and <0.2 µm) and unfiltered (UF) phases.

Conclusion

Our results suggest that anthropogenic urban activities may contribute to additional sources of both dissolved and particulate Ag, Sn, Cu and Gd in the Danshui System and these elements could be used as tracers of wastewater discharges. Despite of significant anomalies, the fluvial-estuarine Danshui System can be considered as less polluted than other urban systems. High mechanical erosion and unpolluted sediment supply entering in the estuary may diminish this impact during extreme rainy events (e.g. typhoons).