Topic/Special Session
1. Urban Hydrologic Processes

Subtopic
1.4 Sources, accumulation, wash-off and transport of pollutants

Metal water-sediment interactions and impacts on an urban ecosystem

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Keywords: metals; sediment quality; water quality; sediment/water interactions; environmental quality guidelines

Summary

The metal loadings and distributions are determined in water and sediment samples collected from 11 sites within the Lower Lee catchment (London, UK). Total concentrations of Cd, Cu, Pb, Hg, Ni, Sn and Zn indicate exceedances of relevant environmental water quality standards/sediment quality guidelines. Mean metal sediment concentrations were found to be highest for Zn (499.9±264.7 µg/g), Pb (175.7±83.0 µg/g) and Cu (141.1±111.0 µg/g) with Zn demonstrating elevated mean water concentrations (17.2±13.8 µg/l) followed by Ni (15.6±11.4 µg/l) and Cu(11.1±17.8 µg/l). Dynamic relationships between water and sediment phases influence metal distributions throughout the catchment.

Introduction

The EU Water Framework Directive aims to ensure that all European surface waters achieve good chemical and ecological status by 2027. Although sediment quality is not included directly, its importance is acknowledged in terms of the impact that accumulated pollutants may have on both the overlying water and associated biota. Progressive urbanisation can lead to acute contamination of sediments with the potential to be mobilised to the overlying water column through both natural river processes (e.g. storm events, influx from groundwater and bio-turbation) and/or human activities (e.g. dredging and permitted and unpermitted discharges of effluents and runoff). These factors are examined in the Lower Lee catchment, in North-East London (UK), which has a long history of water quality problems caused by increasing urbanisation including the development of the Olympic site in the lower reaches.

Methods and Materials

Surficial bottom sediments, collected using an Ekman grab, were dried overnight at 105 °C and ground to particle sizes ≤ 1 mm. Extraction was achieved by microwave digestion in the presence of a mixture of concentrated nitric and hydrochloric acids. Subsequently, metal concentrations were determined using ICP-OES (Thermo Scientific iCAP 6000). Collected surface water samples were immediately transferred to acid washed plastic bottles and stored at 4 °C prior to extraction. Following acid assisted microwave digestion, the water samples were analysed for metals using ICP-MS (Thermo Scientific X-Series 2). Multi-element calibration standards of 0.1, 0.5, 0.75 and 1 mg/l were prepared for sediment analyses with the six standards for water analyses covering the concentration range of 2 to 20 µg/l. All analyses were carried out in triplicate and the analytical method was validated against certified reference materials.

Results and Discussion

The mean concentrations of selected metals in the surface waters within the Lower Lee catchment increase in the order Hg<Cd< Sn<Pb<Cu<Ni<Zn, with the wide ranges and high

standard deviations (Table 1) identifying the influences exerted by factors such as the extent and type of urbanization, weather conditions immediately prior to sampling and land use. A similar trend is observed for metals in the sediments (Hg<Cd<Sn<Ni<Cu<Pb<Zn) except for an interchanging of the positions of Ni, Cu and Pb (Table 2). Sediments typically provide a site for metal accumulation but there is still a considerable, although less pronounced, variation throughout the catchment and on different sampling dates as indicated by the ranges and standard deviations (Table 2). In view of the reduced temporal variation, sediments are the preferred medium for monitoring the environmental pollution of aquatic systems. However, it is important to sample both water and sediment compartments to obtain a more complete understanding of contamination patterns in an urban river. The metal concentrations in sediment samples are considerably higher than those determined in the overlying waters when rationalised to comparable units. This behaviour is supported by the pH values (8.23±0.45) which encourage metals to come out of solution and be incorporated in the deposited sediment. However, it is also possible for metals to be remobilised from sediment and resuspension experiments show that over 3% of the Cd, Cu, Ni and Zn present in the sediment can be transferred to the overlying waters during turbulent conditions. Thus the interaction between metals in sediments and the aqueous phase is a dynamic system with correlation analysis identifying the tendency for an inverse relationship although this is not at a statistically significant level.

Table 1. Maximum, minimum and mean surface water metal concentrations from the River Lee Catchment and comparison with relevant standards.

Metal	Range in concentration	Mean concentration (± SD)	UK TAG* Standards (µg/l)	EU EQS** (µg/l)	
				Annual Average	Maximum Allowable Concentration
Cd	0.01 – 2.78	0.19 (± 0.38)	---	0.25[c]	1.50[c]
Cu	1.04 – 117.71	11.13 (± 17.78)	1.00[a]	---	---
Hg	0.01 – 3.56	0.17 (± 0.41)	---	---	0.07[d]
Ni	0.11 – 55.05	15.64 (± 11.40)	---	4.00[a]	34.00
Pb	0.02 – 13.25	2.39 (± 2.42)	---	1.20[a]	14.00
Sn	0.01 – 13.90	0.73 (± 1.58)	---	---	---
Zn	0.55 – 62.68	17.16 (± 13.76)	14.20[b]	---	---

* UK TAG (2013)
** EU (2008)
[a] Bioavailable fraction
[b] Bioavailable fraction 10.90 µg/l + Ambient Background Concentration 3.3 µg/l dissolved Zn for River Lee.
[c] For Cd and its compounds the EQS values here are for Class 5 (≥ 200 mg $CaCO_3$ /l) as per hardness of water in the Lower Lee catchment
[d] Value for Hg and its compounds

Table 2. Maximum, minimum and mean sediment metal concentrations from the River Lee catchment and comparison with relevant standards/guidelines.

Metal	Range in concentration (µg/g)	Mean concentration (± SD)	Dutch guidelines* (µg/g)		Canadian guidelines** (µg/g)	
			TV[a]	IV[b]	ISQG[c]	PEL[d]
Cd	0.18 – 22.53	2.33 (± 2.79)	0.80	12.00	0.60	3.50
Cu	32.59 – 642.11	141.07 (± 111.00)	36.00	190.00	35.70	197.00
Hg	0.01 – 1.68	0.53 (± 0.45)	0.30	10.00	0.17	0.48
Ni	0.01 – 121.74	22.72 (± 17.20)	35.00	210.00	---	---
Pb	49.98 – 350.95	175.70 (± 82.96)	85.00	530.00	35.00	91.30
Sn	0.53 – 73.95	18.88 (± 15.99)	---	---	---	---
Zn	94.12 – 1017.49	499.92 (± 264.66)	140.00	720.00	123.00	315.00

* Ministry of Housing, Spatial Planning and the Environment (2000)
** Canadian Council of Ministers of the Environment (2002)
[a] Target Value - level from which full recovery of human, plant and animal life is possible
[b] Intervention Value – level at which human, plant and animal life will be seriously impaired or threatened
[c] Interim Sediment Quality Guideline - concentration below which adverse biological effects are expected to occur rarely
[d] Probable effect level - level above which adverse biological effects are expected to occur frequently.

The comparisons provided in Table 1 between the measured aqueous metal concentrations and the existing water quality standards (where available) need to take into account that the former are for total aqueous metals whereas the latter are for dissolved concentrations only. Therefore it is not surprising that exceedances are observed, particularly of the long term standards, although the higher than expected Hg levels demonstrate the potential to considerably exceed the short term standard. The sediment quality data are compared to the Dutch (2000) and Canadian (2002) sediment guideline values, which are designed to protect aquatic life. The mean concentrations of Cd, Cu, Hg, Pb and Zn exceed both the Dutch target values (TV) and the Canadian Interim Sediment Quality Guideline (ISQG) and the maximum measured levels of Cd, Cu and Zn can exceed the Dutch intervention values (IV) and the Canadian probable effect levels (PEL) indicating that adverse biological effects would exist.

Conclusions

An investigation of metal distributions within an urban catchment identifies the importance of measuring concentrations in both the overlying river water and sediment in order to fully understand the potential threats to the ecological status of the system. Sedimentary concentrations of Cd, Cu and Zn are shown to pose the greatest threats to exceeding guidelines designed to protect the river environment against adverse biological effects.

References

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