MERCURY CONTAMINATION AND BACTERIAL ACTIVITY DOWNSTREAM OF A CHLOR-ALKALI PLANT IN THE OLT RIVER

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Introduction

Chlor-alkali plants using mercury-cell technology are major point sources of mercury (Hg) pollution in the aquatic environment. Moreover, some of the emitted Hg can be transformed to neurotoxic methyl-Hg (MeHg). While there have been recent efforts to reduce the use of Hg-cells, our global understanding of the biotically mediated Hg methylation, and the quantitative importance of such processes at the ecosystem level is only emerging. Here, we aimed to study (i) the dispersion of Hg emitted by the chlor-alkali plant in downstream reservoirs along the Olt River, (ii) to determine the amount of Hg which is methylated in sediments of these reservoirs and (iii) to elucidate whether bacterial activity was related to the MeHg concentration and/or formation in environmental samples.

Methods

Water, sediments, and biota (seston and the macrophyte *Elodea nuttallii*) where sampled in September 2014 in five reservoirs: Babeni, Ionesti, Zavideni, Dragasani (downstream) and Valcea (upstream, used as a reference). Depth, temperature, specific conductivity, pH, and dissolved oxygen were measured *in situ* (water quality probe). Major cations and anions in water (ion chromatography), sediment organic matter (CHN Elemental Analyser and Loss on Ignition; LOI), grain size distribution (Coulter), Hg (AMA, Merx and GC-ICP-MS), the expression level of genes for Hg resistance and methylation in Bacteria (RNA extraction and RT-qPCR) in sediments were measured.

Results

Total Hg (THg) concentrations in water, sediments, and seston decreased successively from Babeni to Dragasani (Table 1). THg concentrations in all compartments of ecosystem were lower than those measured during a field campaign in 2009 (Bravo et al., 2014), due to the reduced production of the chlor-alkali plant after the financial crisis. Nonetheless, the particularly high MeHg concentration found in the Babeni Reservoir in 2014 (Table 1) is comparable with that measured in 2009 (Bravo et al., 2014) and highlights the long-term legacy impact of the chlor-alkali plant discharge.

Table 1. THg contents measured in water, sediments, seston and *Elodea nuttalii* in September 2014 (n = 3 ± s.d.).

	Water	Sediments (0-1 cm)		Seston ≥65 µm	*E. nuttallii*
Reservoir	THg (ng/L)	THg (µg/g)	MeHg (ng/g)	THg (µg/g)	THg (µg/g)
Valcea	1.53 ± 0.27	0.8	4.9	0.042 ± 0.008	0.051 ± 0.001
Babeni	2.36 ± 0.23	1.7	18.6	0.080 ± 0.007	0.095 ± 0.005
Ionesti	0.90 ± 0.06	1.0	5.5	0.083 ± 0.008	0.035 ± 0.001
Zavideni	0.70 ± 0.13	1.0	3.1	0.059 ± 0.001	0.055 ± 0.004
Dragasani	0.52± 0.07	1.5	4.1	0.055 ± 0.004	0.035 ± 0.001

Principal Component Analysis (PCA) of parameters measured suggests that (i) THg concentration was bound to fine grains and hence that THg reaches sediments through transport of suspended particles, and (ii) MeHg concentration in sediments was linked to THg concentration in water.

The microbial activity in sediments assessed with the *rRNA 16S* gene was similar in all reservoirs. The same order of *dsrA* (targeting sulfate reducing bacteria; SRB) and *GCS* (targeting *Geobacteraceae*) activity was found, while *mcrA* (targeting methanogens) activity was less abundant and close/below detection limit. Pearson correlation analysis showed a strong positive correlation between *rRNA 16S* activity and ratio of MeHg to THg (0.79, *p*-value <0.001) in sediments and between *GCS* and *merA* (Hg resistance gene; 0.91), supporting the link between bacterial activity and Hg net methylation, and that somehow *Geobacteraceae* were linked to Hg resistance. The abundance of *hgcA* (Hg methylating gene) transcript was also inversely correlated to LOI (-0.85) in sediments and to Cl^- concentration in water (-0.76). Redundancy analysis (RDA) analysis further suggests that *hgcA* activity is correlated with *dsrA*, pointing to SRB as the main methylators.

Conclusion

The quality of the Olt River ecosystem was strongly impacted by releases from the chemical platform despite a reduced activity, and pointed to a gradual quality improvement with distance from the Chlor-alkali plant effluent. Suspended fine size particles and seston appeared to be responsible for the transport of THg in downstream reservoirs, while macrophytes reflected the local bioavailability of Hg. In sediments, the concentration and proportion of MeHg was correlated with THg, and with *rRNA 16S* activity. Nonetheless, the abundance of *hgcA* transcript correlated with organic matter and Cl^- concentration, indicating the importance of Hg bioavailability in sediments for Hg methylation. Sediments acted as a sink for Hg, and as a source for MeHg. Our data clearly highlights the importance of considering Hg contamination as a legacy pollutant since there is a high risk of continued Hg accumulation in food webs long after the Hg-cells phase out.

References

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