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Relating nautical traffic and copper concentration in coastal waters: a case-study in the Krka River estuary (Croatia)

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Abstract:

Copper (Cu) is essential metal needed for the growth of aquatic organisms. However, above certain level, it behaves as toxicant. Hence, the monitoring of its level in natural waters is of primary interest. Copper is used as a biocide in anti-biofouling Cu-based paints, and as such it is released in the water as contaminant. Previous studies carried out in the Krka River estuary in last several years, have showed that during summer season concentrations of Cu are up to 20 times higher compared to winter season. It was presumed that such increase is due to Cu leaching from the boat-paints, enhanced during touristic season. However this relation was not fully confirmed, because the traffic intensity in Estuary was unknown. To evaluate impact of nautical traffic on Cu concentrations in surface layer of the Krka River estuary, one-year monitoring study was undertaken. Monitoring program consisted of two main activities: 1) counting vessels by video observing system and 2) measuring copper content in water. It was shown that the number of vessels are dramatically increased in summer season, when compared to winter season: the average number of boats passes was ~50/day in winter, and in summer it increased over 1000/day. Similar trend of Cu concentration increase was recorded, with $\sim 5 \times$ higher concentrations in summer season. The conducted research confirmed strong relation between nautical traffic and Cu content in water. However, it was found that at selected monitoring location not only number of vessels is factor on which Cu concentrations are linked, but also other variables are having influence: salinity, the Krka River flow, intensity and direction of the wind and rainfall.

Keywords:

Nautical tourism, Trace elements, Central Adriatic Sea, Estuary.

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1. Introduction

Copper (Cu) is a micronutrient required in a number of cellular processes that are key for phytoplankton growth. As phytoplankton is the first level of the food chain, therefore deficiency in copper can lead to numerous unfavourable biological conditions in the sea ecosystem. At physiologically high concentrations, copper is toxic and may affect both planktonic abundance and diversity in coastal waters. Range of copper concentrations between these two extremes is relatively narrow (DONAT & DRYDEN, 2001; SUNDA et al., 1987; TESSIER & TURNER, 1996). Copper contaminates coastal waters due to anthropogenic input. It is used as an anti-biofouling agent with Cu-based paint covering the hull of boats, releasing considerable quantity in coastal waters. The areas which are potentially endangered are those with high variations of copper concentration and small water exchange rate. One of these potentially endangered areas is the Krka River estuary protected as NATURA 2000 site. Preliminary studies carried out in Krka River estuary in last several years, have showed that during summer season concentrations of copper are up to 20 times higher compared to winter season (CINDRIĆ et al., 2015). Unfortunately, the number of vessels (per day/month/year) in the Estuary was unknown. Thus, monitoring program has been established to evaluate relation between copper contents in water, the number of vessels during one-year period and other parameters such are salinity, Krka River flow, rainfall, wind strength and direction.

2. Methodology

Monitoring program was based on the two main activities: (1) video surveillance/observing system for vessels counting, (2) monitoring of copper content in water. Video surveillance system consisted of video camera that was monitoring the entrance to the estuary and software which provided continuous information about entrance/exit and statistics of the vessels (hour, day, month, year). As a part of a second monitoring activity, surface water samples have been collected every 2-3 days at selected location within the Šibenik Bay. Concentration of Cu was measured by electrochemical technique (anodic stripping voltammetry, ASV) using fully automated system. Furthermore, salinity was measured in each sample and meteorological and hydrological data were collected.

3. Results

Results of counting vessels system have shown significant differences between number of boat passes during winter and summer season (~50/day to ~1100/day; figure 1A). Moreover, obtained copper concentrations demonstrate clear distinction between winter and summer values (min/max: 3.8/19.2 nM of Cu). Low concentrations of Cu during

winter season, with more rainy days, indicate that contribution of Cu caused by the process of soil weathering is negligible.

The established monitoring has confirmed strong relation between the nautical tourism and concentrations of copper in surface layer (figure 1A).



Figure 1. Salinity, boat passes and total Cu concentrations (A) and environmental conditions - river flow and wind speed (B) over 1-year period.

Additionally, the influence of other factors to Cu concentrations were established, such as salinity, the Krka River flow, wind strength and particularly, its direction. Aside of the boats traffic intensity, it is also clear from the figure 1A that concentration of Cu is related to salinity, which in turn depends on other mentioned parameters. However, the influence of each of these parameters on the final Cu spatio-temporal distribution within the bay would require confirmation by using circulation modelling tools. Monitoring study showed that pleasure boats (small boats, yachts and sailing boats: 3 to 15 m) are the most frequent in traffic within the estuary. However, as the amount of Cu released depends on the exposed area of the vessel, an additional analysis of numerical results (passage of the boat is peak shaped) should be undertaken in order to classify boats according to their size. Research study performed over several years at the same site over vertical profile (CINDRIĆ et al., 2015) showed that concentration of Cu in bottom seawater layer is relatively stable (~5 nM), whereas in the surface layer it is season and weather conditions dependent, as shown also in this monitoring study (ranging from 4 to 20 nM). The results from this case-study can be used as support in planning sustainable tourism in this area, as well as in other protected areas. However, the influence of each of these parameters on the final Cu distribution on the bay would require using water circulation modelling.

4. References

CINDRIĆ A. M., GARNIER C., OURSEL B., PIŽETA I., OMANOVIĆ D. (2015). *Evidencing the natural and anthropogenic processes controlling trace metals dynamic in a highly stratified estuary: The Krka River estuary (Adriatic, Croatia).* Mar. Pollut. Bull., Vol. 94, pp. 199-216. https://doi.org/10.1016/j.marpolbul.2015.02.029

DONAT J., DRYDEN C. (2001). *Transition metals and heavy metal speciation*. In: Steele J. H., Thorpe S. A., Turekian, K. K. (eds.). Marine Chemistry and Geochemistry. Academic press, London, pp. 72-81.

SUNDA W. G., TESTER P. A., HUNTSMAN S. A. (1987). *Effects of cupric and zinc ion activities on the survival and reproduction of marine copepods*. Mar. Biol., Vol. 94, pp. 203-210. https://doi.org/10.1007/BF00392932

TESSIER A., TURNER D. R. (1996). *Metal speciation and bioavailability in aquatic systems*. John Wiley & Sons, Chichester, UK.