Coastal groundwater stable isotope composition as predictor and measure of marine pollution

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Introduction

There are numerous health hazards arising from recreational exposures to microbiologically polluted marine environments. Microbial contaminants from catchment areas of coastal and submarine springs (due to leakages of private septic tanks and/or faults in sewage systems) could be a cause of microbial marine quality worsening after heavy rainfalls. Before testing this hypothesis groundwater dynamics should be known. Stable isotopes of water have been proven to be a very useful tool in karst hydrology and we used them as a mediator variable in predicting marine coastal water microbial contamination.

We refer to the problem of the pollution from the position of environmental economics and economic institutional mechanism design, where such ecological problems are described as either stock or flow problems. Stock pollution is strongly dependent on the concentration potentials of the pollutant in the medium. Flow pollution depends on the speed of emission of the pollutant in the medium, as well as on the rate of its depletion by natural causes. On the example of fecal indicator bacteria (FIB) Escherichia coli and enterococci propagating through karstic underground and finally ending in seawater we show how stable isotope composition of coastal springs' water can be used to differentiate marine pollution into stock or flow.

Coastal groundwater stable isotope composition as predictor of marine pollution (Mance et al. 2018a)

We tested the approach on two close coastal locations Bakar Bay and Pećine located at the Kvarner Bay (the Northern part of the Croatian part of the Adriatic Sea). Locations differ in terms of the open and closed sea as well as anthropogenic pressure (Fig.1). Three springs: Dobra (DB), Dobrica (DBC), and Perilo (PER) were chosen as representative of springs that discharge in the Bakar Bay. Zvir (ZV) and one of the Martinšćica wells (MB) are representative groundwater outlets for Pećine.

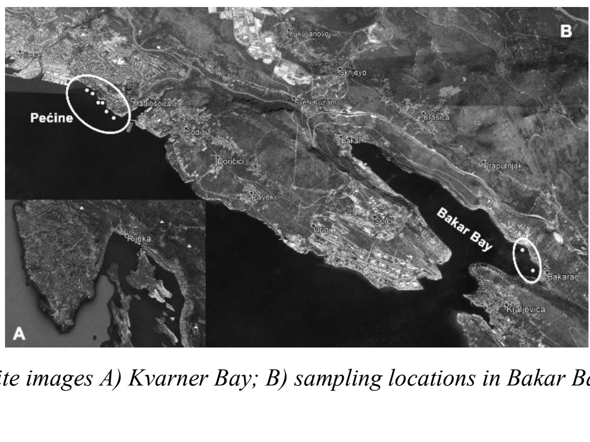

Fig. 1. Satellite images A) Kvarner Bay; B) sampling locations in Bakar Bay and Pećine

Groundwater and marine samples were collected during two consecutive bathing seasons Fig.2-Fig.5.

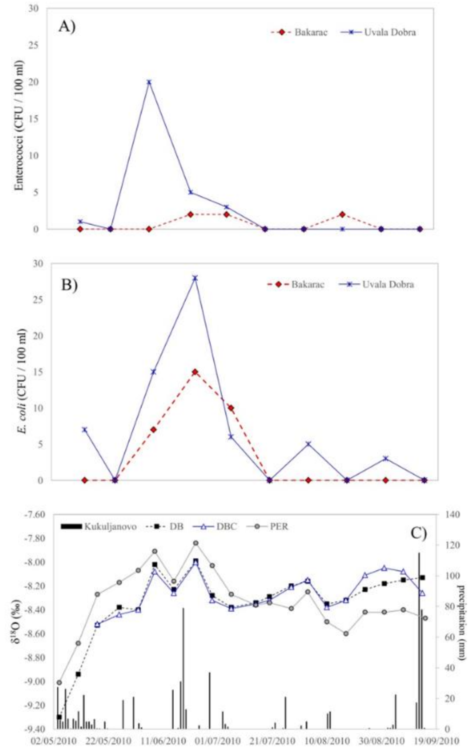

Fig. 2. Bakar Bay, bathing season 2010: A) enterococci; B) E. coli; C) daily precipitation amount at station Kukuljanovo and $\delta^{18}O$ time series

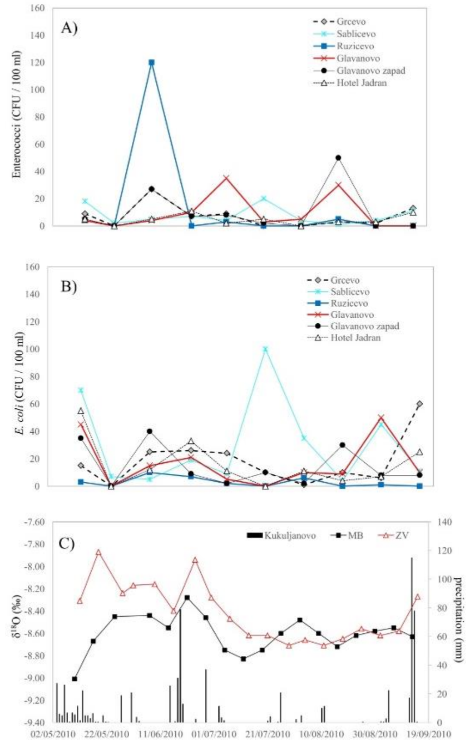

Fig. 3. Pećine, bathing season 2010: A) enterococci; B) E. coli; C) daily precipitation amount at station Kukuljanovo and $\delta^{18}O$ time series.

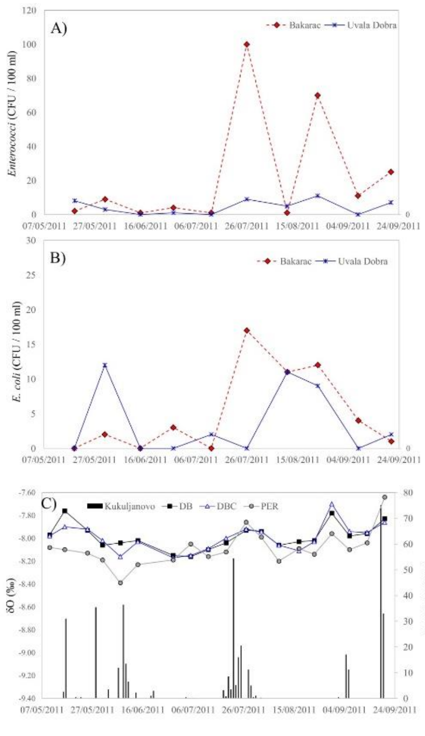

Fig. 4. Bakar Bay, bathing season 2011: A) enterococci; B) E. coli; C) daily precipitation amount at station Kukuljanovo and $\delta^{18}O$ time series

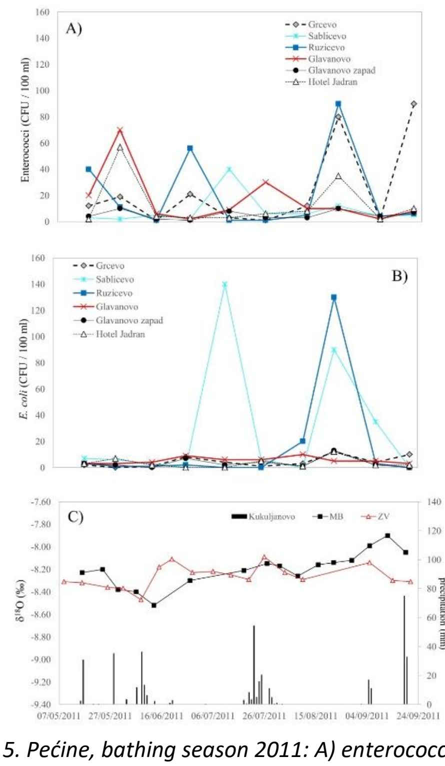

Fig. 5. Pećine, bathing season 2011: A) enterococci; B) E. coli; C) daily precipitation amount at station Kukuljanovo and $\delta^{18}O$ time series.

The Panel Data Pairwise Granger Causality test was used to test for statistical associations. The example of Bakar Bay (Table1) shows that by introducing $\delta^{18}O$ as an intermediate indicator variable between rainfall and marine microbial pollution, we introduced the missing link that might enable us to predict the occurrence of microbiological pollution of the sea and to organise timely interventions to protect public health. The values shown in Table 1 are the highest results achieved by our calculations and show $\delta^{18}O$ and bacteria stock retention times of around 4 weeks (lag = 2 for the non-differenced variables) with stockpiling / depletion times of around 2 weeks (lag = 1 for the differenced variable). Because of the biweekly sampling dynamics, we leave room for values representing shorter periods.

Table 1. Panel Data Pairwise Granger Causality Tests for Bakar Bay

Variable		**Non-differenced (lag=2)**		**Differenced (lag=1)**	
Independent (*X*)	**Dependent (*Y*)**	***F*-Stat.**	***P***	***F*-Stat.**	***P***
total rainfall	enterococci	0.87	0.43	0.51	0.48
total rainfall	*E. coli*	0.54	0.59	0.08	0.77
total rainfall	$\delta^{18}O$ PER	**4.02**	**0.03***	**4.80**	**0.04***
total rainfall	$\delta^{18}O$ DB	**7.07**	**0.002***	**12.91**	**0.001***
total rainfall	$\delta^{18}O$ DBC	**8.78**	**0.001***	**6.46**	**0.02***
$\delta^{18}O$ PER	enterococci	0.08	0.92	0.24	0.63
$\delta^{18}O$ PER	*E. coli*	**4.81**	**0.02***	**10.80**	**0.002***
$\delta^{18}O$ DB	enterococci	0.2	0.82	0.58	0.45
$\delta^{18}O$ DB	*E. coli*	**6.48**	**0.004***	**19.74**	**< 0.001***
$\delta^{18}O$ DBC	enterococci	0.09	0.9	0.12	0.73
$\delta^{18}O$ DBC	*E. coli*	**4.26**	**0.02***	**9.97**	**0.003***

*Note: For $X \rightarrow Y$, H_0: X does not cause Y. * denotes rejection of the H_0. Total rainfall – amount of rain between two consecutive marine water samplings; PER – Perilo; DB –Dobra; DBC – Dobrica.*

Coastal groundwater stable isotope composition as differentiator of marine pollution **(Mance et al. 2018b)**

Since, the groundwater $\delta^{18}O$ value has been recognised as a possible predictor of marine microbial pollution in karstic coastal environments, we take a step further and use the $\delta^{18}O$ as one of the components in statistical modelling of the marine microbial pollution. In such way $\delta^{18}O$ helps determine the type of pollution. We analyse the two locations in Kvarner Bay that differ in anthropogenic pressure and in terms of open and closed sea. As a closed bay location, we chose the Bakar Bay and for the open sea, we chose the Kantrida district of the City of Rijeka (Fig.6). Both locations are known for their fresh water inflows from numerous coastal and bottom wells.

Fig. 6. Satellite images of Kvarner Bay and sampling locations in Bakar Bay and Kantrida

Groundwater and marine samples were collected during two consecutive bathing seasons Fig.2&4 and Fig.7&8.

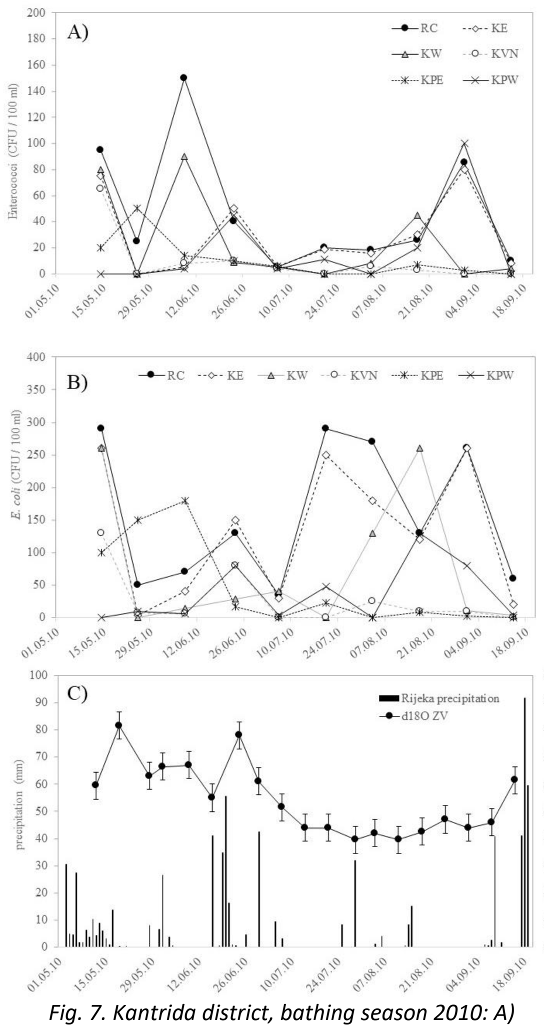

Fig. 7. Kantrida district, bathing season 2010: A) enterococci; B) E. coli; C) daily precipitation amount at station Rijeka and spring water $\delta^{18}O$ time series

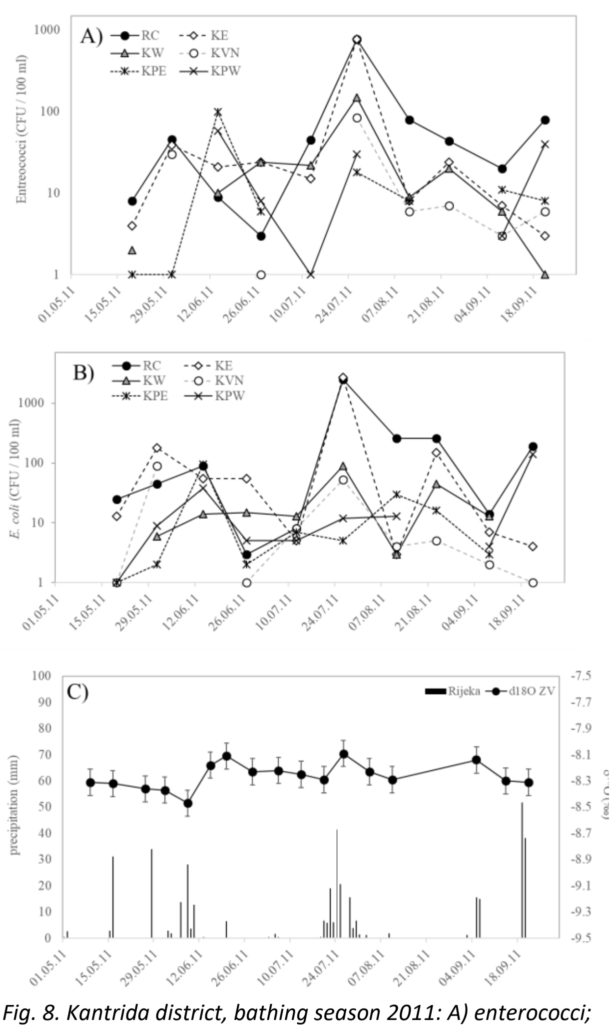

Fig. 8. Kantrida district, bathing season 2011: A) enterococci; B) E. coli; C) daily precipitation amount at station Rijeka and spring water $\delta^{18}O$ time series

Static (EGLS) and dynamic Generalised Method of Moments (GMM) statistical methods were used to distinguish between stock and flow pollution. The results of models' estimations show significant differences between the two locations. Static EGLS modelling at a closed bay Bakar location shows acceptable results of $\delta^{18}O$ values predominantly explaining the FIB variation. Static EGLS modelling could not explain the *E. coli* variation at open sea location at Kantrida. Dynamic GMM FD modelling with $\Delta(\delta^{18}O)$ had to be used instead. Static modelling and static (non-differenced) $\delta^{18}O$ values indicate that FIB in closed bay waters behave like a stock pollutant. Dynamic modelling and $\delta^{18}O$ first differences suggest that FIB in an open sea environment behave like a flow pollutant.

Conclusions

The commonly presumed connection between rainfall occurrence and an increase of faecal bacteria concentrations could easily be rejected by using standard statistical methods (e.g. correlation). We upgraded the usual black box (rainfall − bacteria) model into a grey box model by adding an intermediate step: isotope content of groundwater discharging into the sea. We tested the proposed model with the Panel Granger test. At examined sites, we established the existence of a hypothetical predicted statistical relationship between rain, groundwater $\delta^{18}O$ values and bacteria concentrations. Accordingly, stable isotopes, which often serve as indicators of the functioning of karstic systems, could potentially be predictors of faecal contamination of bathing waters in karst littoral areas, as well.

An efficient institutional pollution allocation and abatement mechanism design for water pollution is based on stock or flow pollutant differentiation. This differentiation is as much based on the medium as on the pollutant itself. We present $\delta^{18}O$ content of karst groundwater discharging into the sea as a new possible indicator for marine pollution differentiation. In a relatively closed bay, the microbial pollution variations are well modelled by static statistical models that include $\delta^{18}O$ values. We understand this to be a characteristic of a stock pollution. At an open sea location, the results of static microbial pollution modelling were not as good as dynamic modelling that included first differences of $\delta^{18}O$ values. Dynamic modelling and changes of $\delta^{18}O$ values indicate we are dealing with flow pollution.

References

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