

Marine Pollution Differentiation with Stable Isotopes of Groundwater

Mance, Diana; Mance, Davor; Vukić Lušić, Darija

Source / Izvornik: **Pomorstvo**, 2018, 32, 80 - 87

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:184:403918>

Rights / Prava: [Attribution 3.0 Unported](#)/[Imenovanje 3.0](#)

Download date / Datum preuzimanja: **2024-07-15**



Repository / Repozitorij:

[Repository of the University of Rijeka, Faculty of Medicine - FMRI Repository](#)



Multidisciplinary
SCIENTIFIC JOURNAL OF
MARITIME RESEARCH



University of Rijeka
Faculty of Maritime
Studies Rijeka

Multidisciplinarni
znanstveni časopis
POMORSTVO

Marine Pollution Differentiation with Stable Isotopes of Groundwater

Diana Mance¹, Davor Mance², Darija Vukić Lušić³

¹ University of Rijeka, Department of Physics, Trg braće Mažuranića 10, 51000 Rijeka, Croatia, e-mail: diana.mance@uniri.hr

² University of Rijeka, Faculty of Economics, Ul. Ivana Filipovića 4, 51000 Rijeka, Croatia, e-mail: davor.mance@efri.hr

³ Teaching Institute of Public Health of Primorje-Gorski Kotar County, Department of Environmental Health, Krešimirova 52 a, 51000 Rijeka, Croatia, and University of Rijeka, Faculty of Medicine, Department of Environmental Health, Braće Branchetta 20, 51000 Rijeka, Croatia, e-mail: darija.vukic-lusic@zzjzpgz.hr

ABSTRACT

Stock and flow pollution differentiation is the basis for efficient pollution-abatement mechanism designs. The focus of our research has been marine pollution from land-based sources. Stable isotope analysis of groundwater is an acknowledged method for karst aquifer characterisation. We have tested whether stable isotopes of water, when used as a proxy for groundwater dynamics in the karst, could also be used as an indicator of marine pollution differentiation in terms of flow and stock pollution. The focus has been on two close coastal locations characterized by differences in terms of open and closed sea as well as anthropogenic pressure. A static Estimated General Least Squares (EGLS) statistical model described the closed bay location suggesting stock pollution. For a good description of the open sea location, we have had to resort to dynamic Generalised Method of Moments (GMM) statistical modelling, indicating flow pollution. Stable isotopes of groundwater together with appropriate statistical tools have proved to be a useful tool of marine pollution differentiation into stock or flow.

ARTICLE INFO

Original scientific paper
Received 15 May 2018
Accepted 4 June 2018

Key words:

Microbial marine pollution
Natural physical tracers
Oxygen stable isotopes
Pollution abatement institutional mechanism design

1 Introduction

Ecological problems, as dealt in environmental economics and economic institutional mechanism design, are described as stock and flow problems [21, 25]. A stock is an entity that accumulates or depletes over time. A flow is the rate of change in a stock. Mathematically, it is its first difference. Rates of pollution emission and depletion finally determine the system's sustainability [15].

Stock pollution measures are highly dependent on concentration potentials of the pollutant in the medium. Flow pollution is dependent on the speed of emission of the pollutant into the medium and rates of the pollution depletion by natural causes from the medium. In economics, stock pollutants deplete a "Common Good" and flow pollutants deplete a "Common Pool Resource" [21].

For any reasonable institutional mechanism design of pollution control, we need to know the critical concentrations of pollutants as well as the factors and determinants of their accumulation and depletion, and when these are not known directly, indicator variables may serve as proxies.

The starting point of our research is the assumption that whether pollution is a stock or a flow depends mainly on the pollutant itself and the conditions of the media the pollutant is propagating through. As the pollutant variables, we chose the Faecal Indicator Bacteria (FIB): *Escherichia coli* (*E. coli*) and enterococci propagating through the karstic littoral and ending in seawater.

The conditions at sea have been represented at two locations in the Kvarner Bay, Croatia. The bathing waters in the Kvarner Bay are, in general, of a good bacteriological quality, but there is evidence of temporary faecal bacterial pollution at certain locations conditioned by the sewage and septic tanks faults, vicinity of sewage disposal systems and/or certain times conditioned by the total rainfall [24].

The total rainfall as a determinant of marine bacteriological faecal pollution and salinity as a determinant of its decay are known from literature [8, 11, 13]. We have added an additional variable: groundwater $\delta^{18}\text{O}$ as a proxy for the dynamics of the groundwater discharging microbiological pollution into the sea. The groundwater $\delta^{18}\text{O}$ value has already been recognised as a possible predictor of ma-

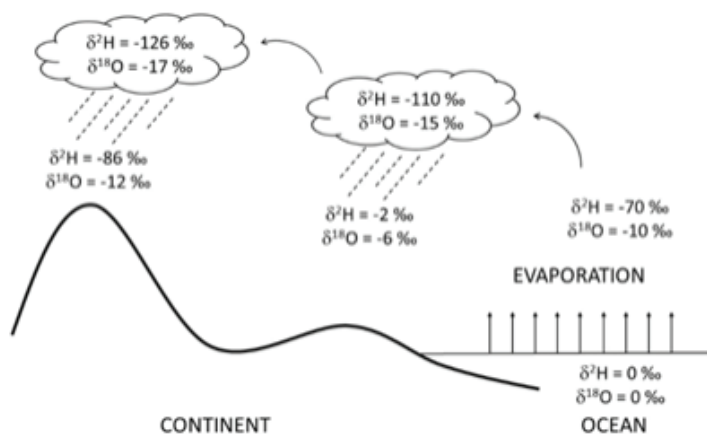


Figure 1 Illustration of the Atmospheric Hydrologic Cycle with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Changes (modified after [5])

rine microbial pollution in karstic coastal environments [18]. In this paper, we have taken a step further and have used the $\delta^{18}\text{O}$ as one of the components in statistical modelling of the marine microbial pollution and in such way help determine the type of pollution according to the stock and flow classification.

2 Stable Isotopes of Water

Isotopes of an element have the same number of protons but differ in the number of neutrons in the atomic nuclei. Based on their abundance variations, stable isotopes of water (^2H , ^{18}O) have successfully been used as natural hydrological tracers determining water origin, hydrograph separation, mean residence time determination, etc. [4, 10, 22, 23].

Hydrogen has two stable isotopes: ^1H and ^2H . The lighter isotope: ^1H constitutes $\approx 99.985\%$ of the total stable hydrogen, while the remaining $\approx 0.015\%$ is the heavier isotope ^2H [20]. Oxygen has three stable forms: ^{16}O , ^{17}O and ^{18}O . The most abundant among them is the lightest one ^{16}O ($\approx 99.76\%$), while ^{17}O and ^{18}O are less commonly

found in nature ($\approx 0.035\%$ and $\approx 0.204\%$, respectively) [20]. According to the number of stable hydrogen and oxygen species, there are nine different stable water configurations, and the most commonly occurring in nature are $^1\text{H}^1\text{H}^{16}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$ and $^1\text{H}^1\text{H}^{18}\text{O}$. Various stable water configurations have different masses and consequently different physical and chemical properties. Those differences cause isotopic fractionation i.e. differences of stable isotopes' abundances at the beginning and at the end of physical, chemical or biological processes.

The results of stable isotope measurements have been expressed in terms of δ -values. δ -value is defined as a relative difference of heavier to lighter isotope abundance ratio in the sample (R_{sample}) and the standard (R_{standard}): $\delta (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}}) - 1$. Hydrogen and oxygen δ -values ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of water are expressed according to the international VSMOW (Vienna Standard Mean Ocean Water) standard. Fresh water δ -values are commonly negative, indicating the depletion in ^2H and ^{18}O in comparison to the standard.

The most important changes in water isotope abundances occur in the atmospheric part of the hydrological circle (Fig. 1). Water vapour depletes in heavy isotopes in

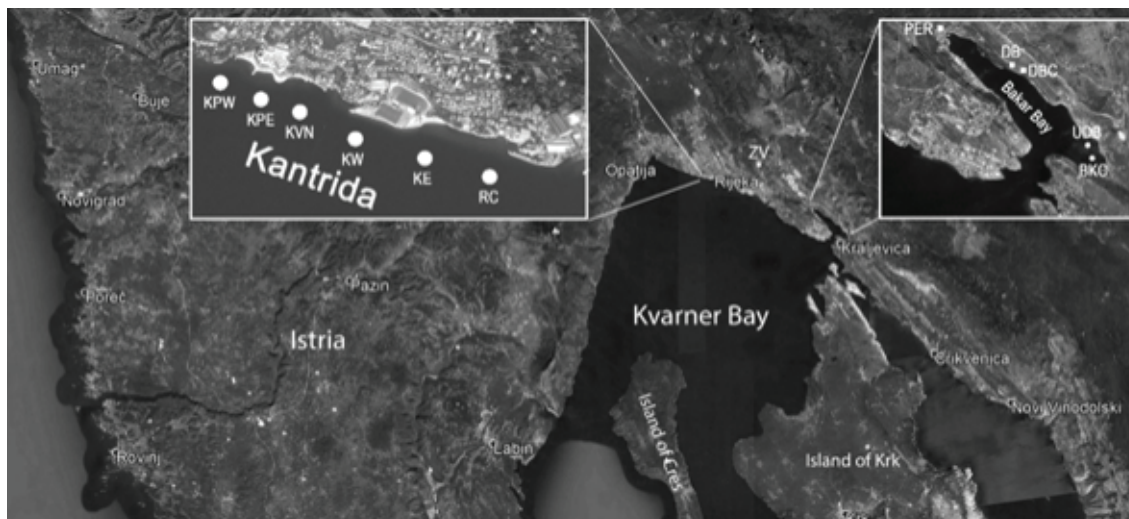


Figure 2 Macro Area, Two Study Areas, Marine Sampling Locations (Circles), and Discharging Springs (Squares)

comparison to the evaporating body. On the other hand, rain is enriched in heavy isotopes compared to residual vapour [6, 20]. Commonly, once the precipitation enters the underground, its isotopic composition remains unaltered [1]. Nevertheless, there are changes in the groundwater stable isotope composition as a consequence of water mixing [19]. Strong influence of air temperature on isotope composition of the precipitation results in seasonal isotopic effects: higher values in summer and lower values in winter [20].

In natural waters that are not under the influence of evaporation, there is a linear correlation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values [7]. The existence of this correlation in the Kvarner Bay area has already been confirmed [14, 17], and, therefore, in this paper, we have focused only on $\delta^{18}\text{O}$ of groundwater.

3 Study Area, Data and Measurement

We have analysed the two locations in the Kvarner Bay that differ in anthropogenic pressure and in terms of open and closed sea. As a closed bay location, we have chosen the Bakar Bay and for the open sea, we have chosen the Kantrida area of the City of Rijeka (Fig. 2). The Bakar Bay is 4.6 km long, 1.1 km wide and 40 m deep. Approximately 1,500 people live in the Bakar Bay area, with some 6,000 more in its approximate hinterland. Kantrida is the City of Rijeka area with popular beaches. There are some 7,000 inhabitants in Kantrida, and some 35,000 more in the nearby surroundings.

Marine water samples have been collected at two beaches in the Bakar Bay: Bakarac (BKC) and Uvala Dobra (UDB), and on six Kantrida area beaches: Kantrida recreational centre (RC), Kantrida east (KE), Kantrida west (KW), Kantrida Villa Nora (KVN), Kantrida pool east (KPE) and Kantrida pool west (KPW) as shown in Fig. 2. Marine water samples have been regularly collected, during the bathing seasons 2010 and 2011, as part of the national bathing water quality-monitoring programme. Biweekly based marine water sampling has resulted in 160 samples for *E. coli* and enterococci analysis. While sampling, sea temperature, air temperature and salinity have been recorded.

Both micro-locations are known for their fresh water inflows from numerous coastal and bottom wells. The fresh water inflow is most intensive during winter that is the consequence of high precipitation in that period of the year. As representatives of springs that discharge in the Bakar Bay, Dobra (DB), Dobrica (DBC), and Perilo (PER), have been chosen as shown in Fig. 2. Spring Zvir (ZV) is a representative groundwater outlet for Kantrida. ZV does not discharge into the sea on the Kantrida area, but is the closest spring that could be regularly sampled and analysed. Spring water samples were collected on a weekly basis from April 2010 to March 2012, but only samples that coincided with the collecting of the marine samples for microbiological analysis have been presented in this study ($N = 80$).

From the systematic stable isotope study of the area [14], we know the following. The springs of the area are dominantly fed by winter precipitation. A dual porosity model consisting of a fissure-porous aquifer (baseflow) and a karstic channels (quick flow) best describe the examined springs dynamics. The baseflow has lower isotopic values in comparison to the quick flow and, at heavy rain, the water of the examined spring experiences positive isotopic shifts. The Croatian Meteorological and Hydrological Service have provided data on daily precipitation amounts from meteorological stations at Kukuljanovo and Rijeka.

To analyse the stable isotope oxygen composition of water, we have used the Standard $\text{H}_2\text{O}-\text{CO}_2$ equilibration method [12]. We have performed the stable isotope measurements on a Delta plusXP (Thermo Finnigan) isotope ratio mass spectrometer (IRMS) coupled with HDO eq48/24 (IsoCal) equilibration unit and a Dual Inlet (Thermo Finnigan) peripheral unit. Precision for $\delta^{18}\text{O}$ has been better than 0.1 ‰ ($\pm 1\sigma$). We have conducted the normalization and the analysis of the measurement results using the United States Geological Survey (USGS) Laboratory Information Management System (LIMS).

As for traditional bacterial-based cultures, we have used a membrane filtration technique and reference methods. To analyse *E. coli*, we have used the Rapid EN ISO 9308-1:2000 test, while for intestinal enterococci, we have used the EN ISO 7899-2:2000 method. Further details may be found in literature [18]. The results of the FIB analysis have been expressed as a number of colony forming units (CFU) in 100 mL of seawater.

4 Statistical Analysis and Modelling

For the description of the variability of *E. coli* and enterococci, we have used descriptive statistics (min, max, median, upper and lower quartiles) in package Statistica 13.0 (StatSoft Inc., USA). Statistical significance of spatial differences for *E. coli* and enterococci have been tested using Kruskal-Wallis test supplemented by the Nemenyi post-hoc test in PMCMR package of the R statistical software (R Development Core Team). The data have been in form of longitudinal data enveloping the locational cross-section data over several time units. We have used two forms of panel data analysis. Firstly, we have used a static approach in form of an Estimated Generalised Least Squares (EGLS) model testing to account for the heteroscedasticity present in the residuals and to incorporate spatial-temporal effects. Secondly, we have run a dynamic panel data modelling in form of a General Method of Moments (GMM) with First Differences (FD) transformation to control for the unobserved time-invariant individual effect heterogeneity. We have used a lag of the dependent variable as a regressor where needed. The GMM estimators are consistent, asymptotically normal, and efficient, as they do not use any extra information aside from that contained in the moment conditions. The process of differencing removes non-stationarity from the data, controls for momentum

and inertia, removes the problem of locational fixed effects, autocorrelation, and other time invariant components [3, 9]. Panel GMM FD is thus a good supplement for EGLS estimation. We have tested the residuals for autoregression using the Arellano-Bond estimator [2]. EGLS and GMM FD testing has carried out using the statistical package E-Views 9 (IHS Global Inc).

5 Results and Discussion

A summary of the descriptive statistics regarding FIB on the examined sites has been presented in Table 1. In the Kantrida area, specifically at the RC location, enterococci and *E. coli* have had positive values in every measurement (Table 1). The highest recorded FIB values have been at RC and KE locations: 780 CFU / 100 ml in case of

enterococci and higher than 2500 CFU / 100 ml for *E. coli* (Table 1). Based on the Kruskal-Wallis and on the Nemenyi post-hoc test (Table 1 and 2), we have concluded the RC and KE locations at Kantrida are of worse microbiological quality than both marine-sampling locations in the Bakar Bay. Considering the Kantrida area alone, the RC location has had a worse microbiological quality than KVN, KPE and KPW (Table 2).

The findings about $\delta^{18}O$ at PER DB and DBC have been described in [18]. Here, we have used the Bakar Bay location primarily because of its feature as a closed bay contrary to the Kantrida relatively open sea location. The isotopic composition of the groundwater discharged into the sea in the Bakar Bay and in the Rijeka Bay has exhibited similar behaviour [16]. We have attributed their relatively constant isotopic composition to the baseflow.

Table 1 Descriptive Statistics of Enterococci and *E. coli* in Marine Samples Collected in the Bakar Bay and at Kantrida. Note the Significant Differences between Sampling Sites based on Kruskal-Wallis ANOVA.

| | | Bakar | | Kantrida | | | | | | Kruskal-Wallis ANOVA H (p) |
|-------------------------------|--------|-------|-----|----------|-------|-------|-------|-------|------|----------------------------|
| | | BKC | UDB | RC | KE | KW | KVN | KPE | KPW | |
| enterococci (CFU / 100 ml) | Min | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 | 39.52 (< 0.001) |
| | LQ | 0 | 0 | 16 | 6.75 | 1.75 | 0 | 0.75 | 0 | |
| | Median | 1.5 | 1 | 33 | 17.5 | 8.5 | 3.5 | 6.5 | 3.5 | |
| | UQ | 5.25 | 5.5 | 80 | 32.25 | 22.5 | 7.25 | 11.75 | 22.5 | |
| | Max | 100 | 20 | 780 | 780 | 150 | 85 | 100 | 100 | |
| <i>E. coli</i> (CFU / 100 ml) | Min | 0 | 0 | 3 | 3 | 0 | 0 | 0 | 0 | 56.3 (< 0.001) |
| | LQ | 0 | 0 | 42.25 | 11.5 | 3 | 1 | 1.75 | 4 | |
| | Median | 0.5 | 2 | 110 | 55 | 13.5 | 5.5 | 6 | 7.5 | |
| | UQ | 7.75 | 7.5 | 260 | 180 | 41.25 | 13.75 | 24.75 | 40.5 | |
| | Max | 17 | 28 | 2500 | 2700 | 260 | 130 | 180 | 140 | |

LQ – lower quartile; UQ – upper quartile; BKC – Bakarac, UDB – Uvala Dobra, RC – Kantrida recreational center, KE – Kantrida east, KW – Kantrida west, KVN – Kantrida Villa Nora, KPE – Kantrida pool east, KPW – Kantrida pool west.

Table 2 Results of the Post-hoc Nemenyi Test (p-values). Statistically Significant Results are in Emphasis and Denoted with *.

| | | Bakar | | Kantrida | | | | | |
|----------------|-----|----------|----------|----------|-------|------|------|------|--|
| | | BKC | UDB | RC | KE | KW | KVN | KPE | |
| Entreococci | UDB | 0.99 | - | - | - | - | - | - | |
| | RC | < 0.001* | < 0.001* | - | - | - | - | - | |
| | KE | 0.034* | 0.006* | 0.92 | - | - | - | - | |
| | KW | 0.56 | 0.24 | 0.19 | 0.91 | - | - | - | |
| | KVN | 0.99 | 0.98 | 0.002* | 0.11 | 0.82 | - | - | |
| | KPE | 0.95 | 0.73 | 0.023* | 0.45 | 0.99 | 0.99 | - | |
| | KPW | 0.99 | 0.91 | 0.007* | 0.24 | 0.95 | 1.00 | 1.00 | |
| <i>E. coli</i> | UDB | 1.00 | - | - | - | - | - | - | |
| | RC | < 0.001* | < 0.001* | - | - | - | - | - | |
| | KE | < 0.001* | < 0.001* | 0.98 | - | - | - | - | |
| | KW | 0.095 | 0.17 | 0.075 | 0.51 | - | - | - | |
| | KVN | 0.77 | 0.89 | 0.001* | 0.03* | 0.92 | - | - | |
| | KPE | 0.50 | 0.66 | 0.005* | 0.1 | 0.99 | 0.99 | - | |
| | KPW | 0.30 | 0.44 | 0.016* | 0.21 | 0.99 | 0.99 | 0.99 | |

BKC – Bakarac, UDB – Uvala Dobra, RC – Kantrida recreational center, KE – Kantrida east, KW – Kantrida west, KVN – Kantrida Villa Nora, KPE – Kantrida pool east, KPW – Kantrida pool west.

Positive $\delta^{18}\text{O}$ shifts occurring after heavy rainfalls are probably consequences of precipitation fast infiltration and activation of the quick flows [17].

Figures 3 and 4 show how some of the jumps in ZV $\delta^{18}\text{O}$ coincide with the rise of FIB levels. This was visible in the June 2010 and 2011, as well as in the July 2011 data (Fig. 4). In July 2010, the rise of the *E. coli* levels occurred during the ZV baseflow regime (Fig. 3B). These *E. coli* elevations were probably due to some factors, such as sewage faults, we did not consider in our modelling.

To study possible determinants related to FIB levels, we have carried out the EGLS modelling using enterococci and *E. coli* as dependent variables. Many different independent variables have been tested ($\delta^{18}\text{O}$, total rainfall between two samplings, rainfall before the sampling day,

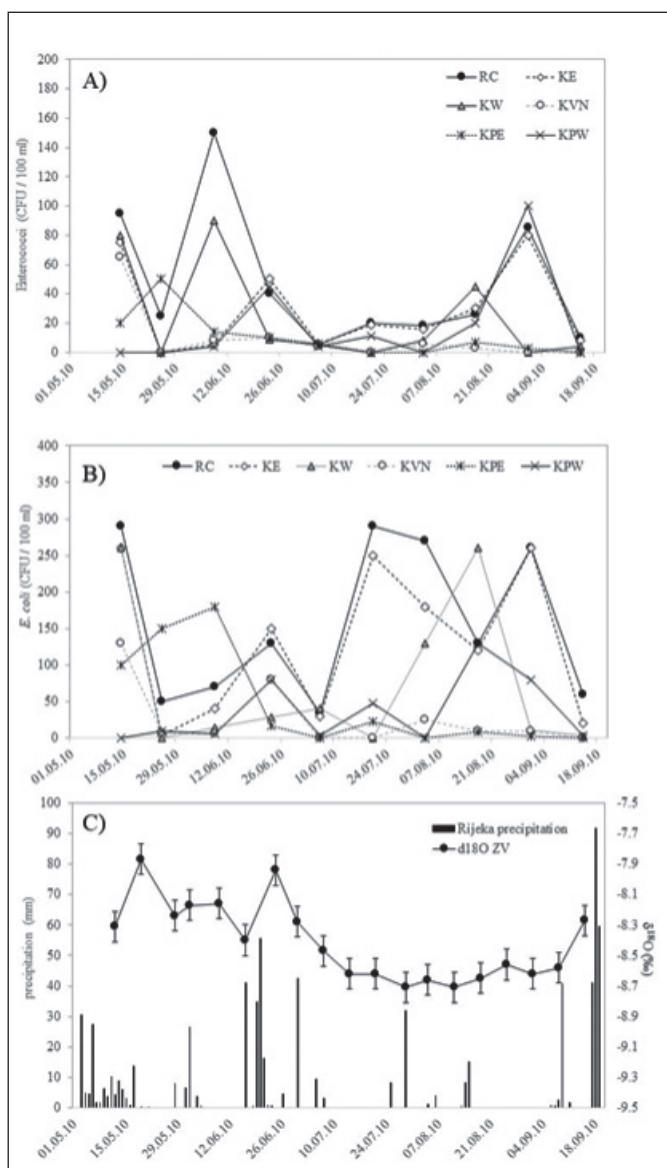


Figure 3 Kantrida area, bathing season 2010: A) enterococci; B) *E. coli*; C) daily precipitation amount at station Rijeka and spring water $\delta^{18}\text{O}$ time series. RC – Kantrida recreational center, KE – Kantrida east, KW – Kantrida west, KVN – Kantrida Villa Nora, KPE – Kantrida pool east, KPW – Kantrida pool west, ZV – Zvir.

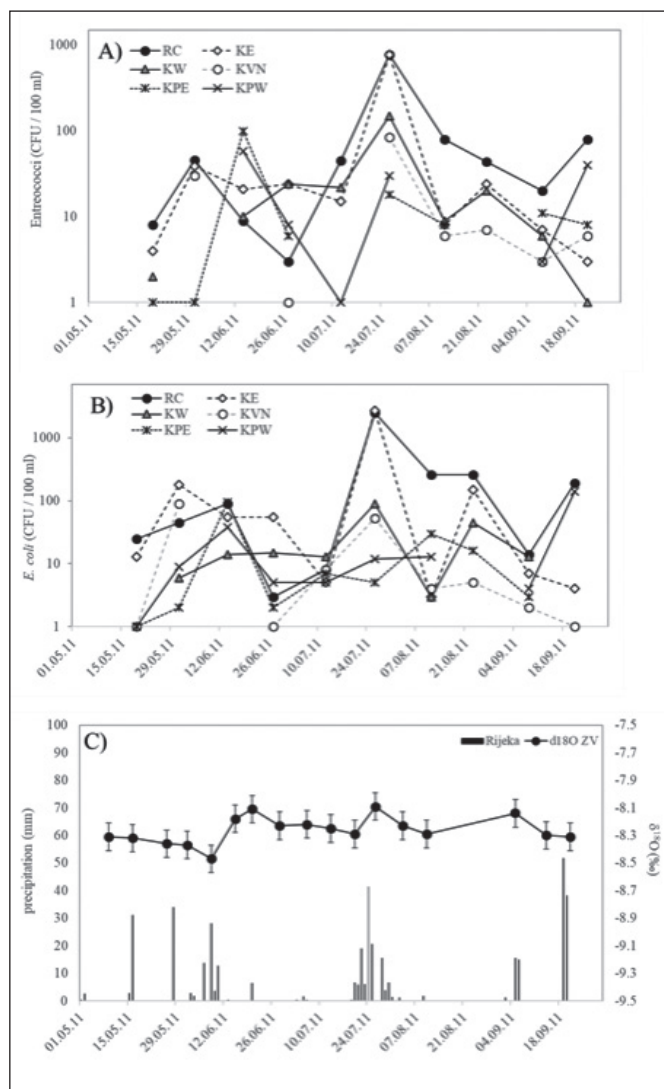


Figure 4 Kantrida area, bathing season 2011: A) enterococci; B) *E. coli*; C) daily precipitation amount at station Rijeka and spring water $\delta^{18}\text{O}$ time series. RC – Kantrida recreational center, KE – Kantrida east, KW – Kantrida west, KVN – Kantrida Villa Nora, KPE – Kantrida pool east, KPW – Kantrida pool west, ZV – Zvir.

rainfall at the day of sampling, sea temperature, air temperature, salinity), and variables being statistically significant only, are shown in Tables 3 and 4.

Although rainfall is instrumental in explaining the direction of change in the FIB quantity, in the Bakar Bay the $\delta^{18}\text{O}$ has been a better predictor (Table 3). The $\delta^{18}\text{O}$ alone has explained 30.9 % ($p < 0.001$) of the observed *E. coli* variations. The cumulative model, including $\delta^{18}\text{O}$ and salinity, has had a better predictor of *E. coli* variations than any other combination of the variables we have tested ($R^2 = 0.525$; $p < 0.001$). In case of enterococci, $\delta^{18}\text{O}$ has explained 42.6 % ($p < 0.001$) of its variations. No other variable, or combination thereof, has been subsequently added as it has neither been statistically significant (for salinity $p = 0.45$), nor has increased the coefficient of determination, or has not increased the adjusted R-squared even when it has increased the R-squared.

Table 3 Panel EGLS Modelling Results for the Bakar Bay

| Dep. Var. | Independent variable | Coeff. | S. E. | p | R ² |
|----------------|----------------------------------|--------|-------|--------|----------------|
| <i>E. coli</i> | Total rainfall | 0.044 | 0.003 | <0.001 | 0.128 |
| | δ ¹⁸ O oxygen isotope | 7.473 | 0.449 | <0.001 | 0.309 |
| | Salinity | -0.244 | 0.031 | <0.001 | 0.377 |
| | δ ¹⁸ O oxygen isotope | 7.919 | 1.355 | <0.001 | 0.525 |
| | Salinity | -0.233 | 0.049 | <0.001 | |
| Enterococci | Total rainfall | 0.059 | 0.005 | <0.001 | 0.122 |
| | δ ¹⁸ O oxygen isotope | 11.890 | 1.395 | <0.001 | 0.426 |

Table 4 Panel EGLS Modelling Results for Kantrida

| Dep. Var. | Independent variable | Coeff. | S. E. | p | R ² |
|-------------|----------------------------------|--------|--------|--------|----------------|
| Enterococci | Total rainfall | 0.195 | 0.037 | <0.001 | 0.059 |
| | δ ¹⁸ O oxygen isotope | 22.250 | 6.691 | 0.001 | 0.048 |
| | Salinity | -3.218 | 0.177 | <0.001 | 0.542 |
| | δ ¹⁸ O oxygen isotope | 22.800 | 10.547 | 0.033 | 0.695 |
| | Total rainfall | 0.091 | 0.0227 | <0.001 | |
| | Salinity | -3.366 | 0.292 | <0.001 | |

Table 5 Panel GMM FD Modelling Results for *E. coli* at the Bakar Bay

| Dep. Var. | Independent variable | Coeff. | S. E. | p | J-stat. | AR(1) p | AR(2) p |
|----------------|---------------------------|--------|-------|--------|---------|------------|------------|
| <i>E. coli</i> | δ ¹⁸ O isotope | 12.51 | 1.19 | <0.001 | 26.38 | 0.22 | 0.088 |
| | Salinity | -0.50 | 0.10 | <0.001 | 17.29 | 0.04 | 0.567 |
| | δ ¹⁸ O isotope | 5.16 | 0.32 | <0.001 | 19.14 | 0.05 | 0.796 |
| | Salinity | -0.46 | 0.11 | <0.001 | | | |

Note: Difference Specification Instrument Weighting Matrix. White Period Standard Errors & Covariance (d.f. corrected). Instrument Specification: @DYN(ESCHERICHIA, 0, 0).

No examined variable or variable combination at Kantrida has proved to be a statistically significant predictor of *E. coli* variations ($p > 0.05$) in our EGLS modelling. In case of enterococci at Kantrida, δ¹⁸O, total rainfall, and salinity have been the only statistically significant independent variables (Table 4). Although statistically significant, the total rainfall and δ¹⁸O isotopes taken separately fall short of gaining significant statistical association in terms of the coefficient of determination: 0.059 and 0.048 respectively (Table 4). Salinity, as the sole independent variable has described 54.2 % of enterococci variations ($p < 0.001$). The results of the cumulative model estimation, taking into account all three statistically significant variables from previous individual tests (oxygen isotope, total rainfall, and salinity), has also been statistically significant at 5 % significance level with $R^2 = 0.695$ (Table 4).

To summarize, we can see that in EGLS models, the Bakar Bay’s FIB behaviour is predominantly explained by δ¹⁸O values. The δ¹⁸O has indicated the difference between the base flow and the quick flow carrying bacterial contamination to the seashore at peaking rainfalls. Salinity has directly explained the depletion effects on bacterial contamination. Since, *E. coli* is more sensitive to salinity than enterococci; the model for *E. coli* incorporates salinity

as an explanatory variable, whereas the enterococci model has to exclude it as it has not been statistically significant. Kantrida is the location with the highest FIB levels, most probably due to a higher degree of anthropogenic pressure. The location differs from the Bakar Bay as it is more open and, therefore, under stronger influence of sea currents. Considering this, it is not surprising that the EGLS model has not explained the short-lived *E. coli* variations in an open sea environment. EGLS modelling has been possible for enterococci, but the predicting power of the δ¹⁸O has been lower than in the Bakar Bay. Therefore, no long-term bacteriological modelling has been feasible at open sea locations by using static models only. In continuation, we have shown the results of the dynamic modelling using Panel GMM with FD. In case of *E. coli*, the results for the Bakar Bay have been comparable to the ones obtained using the EGLS, and the best cumulative model has included δ¹⁸O as well as salinity (Table 5). GMM FD modelling with enterococci as a dependent variable in the Bakar Bay, has shown that the enterococci autoregressive (-1) component is statistically significant (Table 6). The latter is a strong argument in favour of the Bakar Bay stock pollution conjecture.

In the Kantrida case, for GMM FD modelling, we have had to use a first difference Δ(δ¹⁸O) of the oxygen isotope

Table 6 Panel GMM FD Modelling Results for Enterococci at the Bakar Bay

| Dep. Var. | Independent variable | Coeff. | S. E. | p | J-stat. | AR(1) p | AR(2) p |
|-------------|-------------------------------|--------|-------|--------|---------|------------|------------|
| Enterococci | Enterococci (-1) | -0.39 | 0.01 | <0.001 | 35.46 | 0.01 | 0.159 |
| | $\delta^{18}\text{O}$ isotope | 41.43 | 12.12 | 0.002 | 26.28 | 0.001 | 0.024 |
| | Salinity | -0.50 | 0.10 | <0.001 | 17.29 | 0.041 | 0.567 |
| | Enterococci (-1) | -0.49 | 0.01 | <0.001 | 40.34 | 0.061 | 0.538 |
| | $\delta^{18}\text{O}$ isotope | 26.54 | 4.38 | <0.001 | | | |
| | Salinity | -0.26 | 0.02 | <0.001 | | | |

Note: Difference Specification Instrument Weighting Matrix. White Period Standard Errors & Covariance (d.f. corrected).
Instrument Specification: @DYN(ENTEROCOCCI, 0, 0).

Table 7 Panel GMM FD Modelling Results for *Escherichia coli* at Kantrida

| Dep. Var. | Independent variable | Coeff. | S. E. | p | J-stat. | AR(1) p | AR(2) p |
|----------------|---------------------------------------|--------|--------|--------|---------|------------|------------|
| <i>E. coli</i> | $\Delta(\delta^{18}\text{O})$ isotope | 495.75 | 157.79 | 0.002 | 62.62 | < 0.001 | 0.721 |
| | Rain day before | 12.78 | 5.11 | 0.014 | 68.99 | < 0.001 | 0.670 |
| | Salinity | -28.40 | 6.20 | <0.001 | 57.62 | < 0.001 | 0.684 |
| | $\Delta(\delta^{18}\text{O})$ isotope | 344.36 | 129.08 | 0.009 | 47.82 | < 0.001 | 0.654 |
| | Rain day before | 17.05 | 7.89 | 0.033 | | | |
| | Salinity | -30.49 | 8.01 | <0.001 | | | |

Note: Difference Specification Instrument Weighting Matrix. White Period Standard Errors & Covariance (d.f. corrected).
Instrument Specification: @DYN(ESCHERICHIA,-1, -1). Constant Added to Instrument List.

Table 8 Panel GMM FD Modelling results for Enterococci at Kantrida

| Dep. Var. | Independent variable | Coeff. | S. E. | p | J-stat. | AR(1) p | AR(2) p |
|-------------|---------------------------------------|--------|-------|--------|---------|------------|------------|
| Enterococci | $\Delta(\delta^{18}\text{O})$ isotope | 156.21 | 50.11 | 0.002 | 72.73 | < 0.001 | 0.968 |
| | Rain day before | 4.89 | 1.54 | 0.002 | 80.18 | < 0.001 | 0.965 |
| | Salinity | -8.50 | 1.86 | <0.001 | 69.05 | < 0.001 | 0.844 |
| | $\Delta(\delta^{18}\text{O})$ isotope | 164.45 | 43.11 | <0.001 | 54.71 | < 0.001 | 0.785 |
| | Rain day before | 7.14 | 2.00 | <0.001 | | | |
| | Salinity | -8.25 | 2.30 | <0.001 | | | |

Note: Difference Specification Instrument Weighting Matrix. White Period Standard Errors & Covariance (d.f. corrected).
Instrument Specification: @DYN(ENTEROCOCCI, -1, -1). Constant Added to Instrument List.

as well as the rainfall one day before the sampling day (Tables 7 & 8). This has resulted in an acceptable model even for *E. coli* (Table 7), indicating that the dynamic modelling is better suited for open sea locations.

The notable difference between the Bakar Bay and Kantrida has been found in the enterococci GMM FD modelling whereby an autoregressive (-1) lagged variable had to be inserted into the model for the Bakar Bay indicating its more static character.

To conclude, we can say that the results of models' estimations have shown significant differences between the two locations. Static EGLS modelling at the closed Bakar Bay location has shown acceptable results of $\delta^{18}\text{O}$ values predominantly explaining the FIB variation. Static EGLS modelling could not explain the *E. coli* variation at the open sea location at Kantrida. Dynamic GMM FD modelling with $\Delta(\delta^{18}\text{O})$ had to be used instead. Static modelling

and static (non-differenced) $\delta^{18}\text{O}$ values have indicated that FIB in closed bay waters behaves like a stock pollutant. Dynamic modelling and $\delta^{18}\text{O}$ first differences have suggested that FIB in an open sea environment behaves like a flow pollutant.

6 Conclusion

Efficient institutional pollution allocation and abatement mechanism designs for water pollution need to be based on stock or flow differentiation. This differentiation is as much based on the medium as on the pollutant itself. We have presented $\delta^{18}\text{O}$ content of karst groundwater discharging into the sea as a new possible indicator for marine pollution differentiation.

The data about the rainfall have not been enough by its own to give us consistent information about anthropogen-

ic pollution originating from the land. Pollution has been carried out to the sea mainly by the quick-flow. We have used the $\delta^{18}\text{O}$ oxygen isotope to differentiate the quick-flow from the base-flow. Peak $\delta^{18}\text{O}$ values, indicating the quick-flow, have been statistically well associated with the FIB pollution.

In a relatively closed bay, the microbial pollution variations have been well modelled by static statistical models that include $\delta^{18}\text{O}$ values. We have understood this to be a characteristic of a stock pollution. At an open sea location, the results of static microbial pollution modelling have not been as good as the dynamic models. Dynamic modelling using the changes of $\delta^{18}\text{O}$ values has indicated that we are dealing with flow pollution. The most significant piece of evidence in favour of the hypothesis that in case of the Bakar Bay we are dealing with a stock pollution is the presence of a statistically significant enterococci autoregression parameter.

References

- [1] Araguas-Araguas, L., Froehlich, K., Rozanski, K. (2000) Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture, *Hydrological Processes*, 14(8), pp. 1341–1355.
- [2] Arellano, M.; Bond, S. (1991) Some tests of specification for panel data: Monte Carlo evidence and an application to employment equations, *Review of Economic Studies*, 58, pp. 277–297.
- [3] Baltagi, B. H. (2005) *Econometric analysis of panel data*. 3rd edn. Chichester: John Wiley & Sons Ltd.
- [4] Binet, S., Joigneaux E., Pauwels, H., Albéric, P., Fléhoc, Ch., Bruand, A. (2017) Water exchange, mixing and transient storage between a saturated karstic conduit and the surrounding aquifer: Groundwater flow modeling and inputs from stable water isotopes, *Journal of Hydrology*, 544, pp. 278–289.
- [5] Brand, W.A., Coplen, T.B. (2012) Stable isotope deltas: tiny, yet robust signatures in nature, *Isotopes in Environmental and Health Studies*, 48(3), pp. 393–409.
- [6] Clark, I., Fritz, P. (1997) *Environmental isotopes in hydrogeology*. 1st edn. Boca Raton: CRC Press/Lewis Publishers.
- [7] Craig, H. (1961) Isotopic Variations in Meteoric Waters, *Science*, 133(3465), pp. 1702–1703.
- [8] Dwight, R. H., Caplan, J. S., Brinks, M. V., Mitchell, V., Catlin, S. N., Buescher, G., Semenza, J. C. (2011) Influence of Variable Precipitation on Coastal Water Quality in Southern California, *Water Environment Research*, 83(12), pp. 2121–2130.
- [9] Elhorst, J. P. (2003) Specification and Estimation Of Spatial Panel Data Models, *International Regional Science Review*, 26(3), pp. 244–268.
- [10] Ford, D., Williams, P. (2007) *Karst hydrogeology and geomorphology*. Chichester (UK): Wiley & sons.
- [11] Haramoto, E., Katayama, H., Oguma, K., Koibuchi, Y., Furumai, H., Ohgaki, S. (2006) Effects of rainfall on the occurrence of human adenoviruses, total coliforms, and Escherichia coli in seawater, *Water Science and Technology*, 54(3), pp. 225–230.
- [12] Horita, J., Kendall, C. (2004) 'Stable Isotope Analysis of Water and Aqueous Solutions by Conventional Dual-Inlet Mass Spectrometry' in: de Groot P.A. (ed.) *Handbook of Stable Isotope Analytical Techniques*. Elsevier, pp. 1–37.
- [13] Kashefipour, S. M., Lin B., Falconer R. A. (2006) Modelling the fate of faecal indicators in a coastal basin, *Water Research*, 40(7), pp. 1413–1425.
- [14] Mance, D. (2014) *Karakterizacija krškog vodonosnika temeljena na prostornim i vremenskim promjenama stabilnih izotopa vodika i kisika (Characterization of a karst aquifer based on the spatial and temporal variations of hydrogen and oxygen stable isotopes)* PhD. University of Zagreb.
- [15] Mance, D. (2015) *Upravljanje zajedničkim dobrima na tržištu emisija u okoliš Europske unije (Management of Common Goods in the European Union Emissions' Trading Scheme)*. PhD. University of Rijeka.
- [16] Mance, D., Hunjak, T., Lenac, D., Rubinić, J., Roller-Lutz, Z. (2014) Stable Isotope Analysis of the Karst Hydrological Systems in the Bay of Kvarner (Croatia), *Applied Radiation and Isotopes*, 90, pp. 23–34.
- [17] Mance, D., Lenac, D., Rubinić, J. (2017) Isotope studies of karst springs included in the water supply system of the City of Rijeka (Croatia), *Southeastern European Medical Journal*, 1(2) pp. 46–54.
- [18] Mance, D., Mance, D., Vukić Lušić, D. (2018) Environmental isotope ^{18}O in coastal karst spring waters as a possible predictor of marine microbial pollution, *Acta Adriatica*, 59(1), accepted for publication.
- [19] McGuire, K., McDonnell, J.J. (2006) A review and evaluation of catchment transit time modelling, *Journal of Hydrology*, 330, pp. 543–563.
- [20] Mook, W.G. (ed.) (2001) *Environmental Isotopes in the Hydrological Cycle: Principles and applications*. Paris: UNESCO/IAEA.
- [21] Ostrom, E. (1990) *Governing the Commons: The Evolution of Institutions for Collective Action*. 1st edn. New York: Cambridge University Press.
- [22] Ozyurt, N.N., Lutz, H.O., Hunjak, T., Mance, D., Roller-Lutz, Z. (2014) Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times, *Science of the total environment*, 487, pp. 245–254.
- [23] Palmer, A.N. (2010) Understanding the hydrology of karst, *Geologia Croatica*, 63(2), pp. 143–148.
- [24] Vukić Lušić, D., Kranjčević, L., Maćešić, S., Lušić, D., Jozić, S., Linšak, Ž., Bilajac, L., Grbčić, L., Bilajac, N. (2017) Temporal variations analyses and predictive modeling of microbiological seawater quality, *Water research*, 119, pp. 160–170.
- [25] Weitzman, M. L. (1974) Prices vs. Quantities, *The Review of Economic Studies*, 41(4), pp. 477–491.