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»Kisanje« severnega Jadrana

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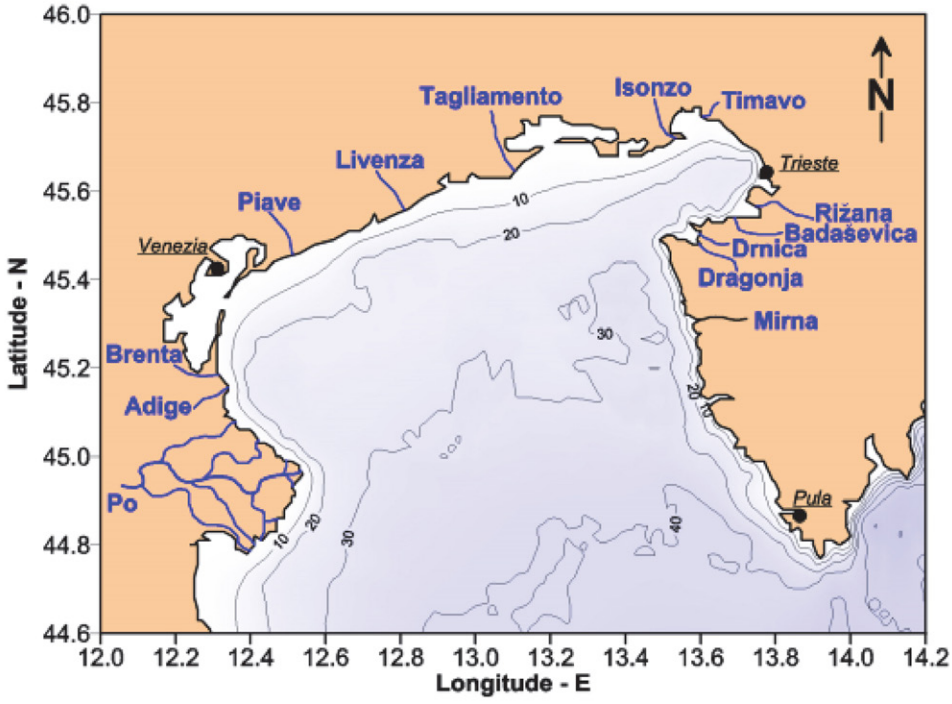
Povzetek

Prikazan je kratek pregled dosedanjega znanja o karbonatnem ravnotežju severnega Jadrana, ki je dobro pufran zaradi dotoka karbonata z rekami alpskega in kraškega izvora in s tem omejenemu »kisanju«. V prihodnosti napovedujemo še vedno uravnoteženost s povečanim raztapljanjem CO_2. V plitvih evtrofnih obalnih vodah bo lahko povezan vpliv povečanja atmosferskega CO_2, naraščajoče temperatutre in rečnega vnosa antropogenega CO_2 ter zmanjšane puferske kapacitete povečal »kisanje« morja in pomembno vplival na karbonatne organizme.

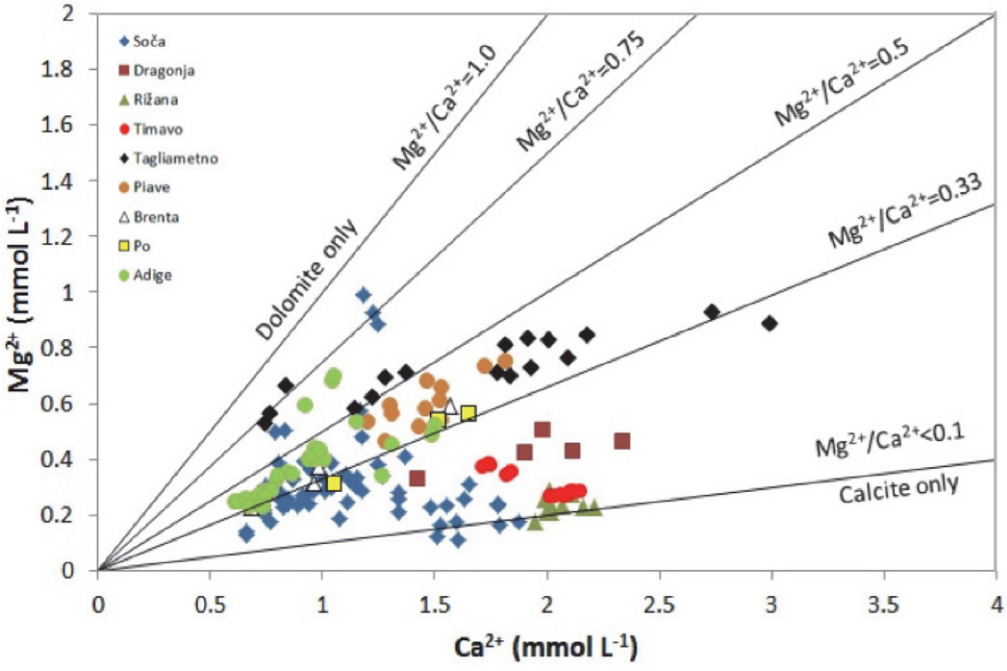
Ključne besede: karbonatno ravnotežje; tok CO_2; kisanje morja; severni Jadran

Danes se karbonatno ravnotežje v morju spreminja zaradi raztapljanja naraščajočega CO_2 (v obalnih predelih tudi dušikovih in žveplovih oksidov) v atmosferi (najmanj četrtina) kot posledica človekove dejavnosti.[1] V morskem karbonatnem ravnotežju, ki ga opredeljujejo alkalnost (TA, A_T ali T_A), raztopljeni anorganski ogljik (ang. Dissolved Inorganic Carbon – DIC), parcialni tlak (fugativnost) CO_2 (pCO_2, fCO_2) in pH (dovolj dve spremenljivki, najbolje najtežje merljivi DIC in pCO_2, z uporabo konstant ravnotežij različnih avtorjev v odvisnosti od temperature, tlaka in slanosti), sta hitrejši reakciji fotosinteza in respiracija ter disociacija ogljikove kisline (ionski reakciji) kot pa vzpostavitev ravnotežja med atmosferskim CO_2 in morsko vodo.[2] Posledica je znižanje pH, danes približno 0,1, glede na predindustrijsko dobo. Pojav je znan kot »kisanje morja« (»acidifikacija«). Površinska plast oceana je še vedno prenasičena glede na aragonit (prisoten v koralah in mehkužcih) in kalcit (prisoten v kokolitoforidih in foraminiferah). V estuarijih vodi absorpcija CO_2 do znižanja pH, v odvisnosti od lokalnega pufranja (puferske kapacitete) vode, tudi zaradi evtrofikacije.[3,4]

Tudi Jadransko morje je ponor CO_2 in privzema približno 1–3 mol C m^{-2} $leto^{-1}$.[5] Večji ponor je v zimskem in vetrovnem obdobju in vpliv temperature (»topnostna črpalka«) presega porabo v primarni produkciji (»biološka črpalka«). Ponor CO_2 v Jadranu je primerljiv z Lyonskim zalivom v SZ Sredozemlju (4–5 mol C m^{-2} $leto^{-1}$).[6,7] Primerjava podatkov z dveh zimskih križarjenj v severnem Jadranu leta 1983 in 2008 je pokazala padec pH 0,063[8], kar ustreza letnemu padcu (»kisanju«) pH 0,003, in je primerljivo s Sredozemljem: med 0,003 in 0,004 pH v odprtih in obalnih vodah.[8,9,10] Pri navajanju trendov in primerjav moramo upoštevati, na žalost ne vedno, različne uporabljene analizne metode (potenciometrično ali kolorimetrično določanje pH, merjeni ali izračunani pCO_2) in natančnost meritev v karbonatnem ravnotežju v morju (pH ± 0.002, TA ± 1 μmol/kg, DIC ± 1 μmol/kg, pCO_2 ± 0.5 μbar (± 0.05 Pa)[11], kar večkrat vodi do ocen, ki jih ni mogoče eksperimentalno preveriti in primerjati. Ker je pufranost (izračunani Revellov faktor[2] kot indikator puferske kapacitete približno 10) Jadranskega morja razmeroma visoka, le-to ni izdatno podvrženo »kisanju«.[12] Izmerjena TA (2,6–2,7 mmol l^{-1}) v Jadranskem morju je med najvišjimi v Sredozemlju[12,13,14] zaradi rečnega vnosa (slika 1) karbonata s preperevanjem apnenca in dolomita v Apeninih, Alpah, Krasu in Dinarskem pogorju (slika 2).[15,16] Jadransko morje (319 Gmol $leto^{-1}$) je, takoj za Egejskim morjem z vnosom iz Črnega morja, najpomembnejši rečni vnos alkalnosti v Sredozemlje.[14] Približno 60 % vnosa alkalnosti izvira iz Pada.[17] V severnem Jadranu alkalnost pada z naraščanjem slanosti[18] (slika 3). Vode Jadranskega morja so prenasičene glede na kalcit in aragonit v celem letu.[19] Pri dnu je nasičenost sicer manjša zaradi bentoške respiracije in remineralizacije predvsem v poletnem obdobju gostotne razslojenosti vodnega stolpa.

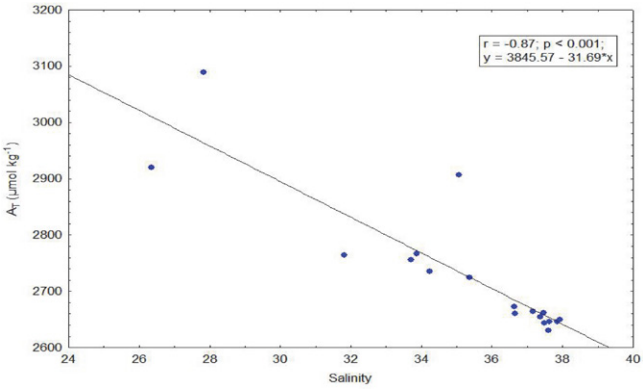


Slika 1. Severni Jadran z rečnimi pritoki.



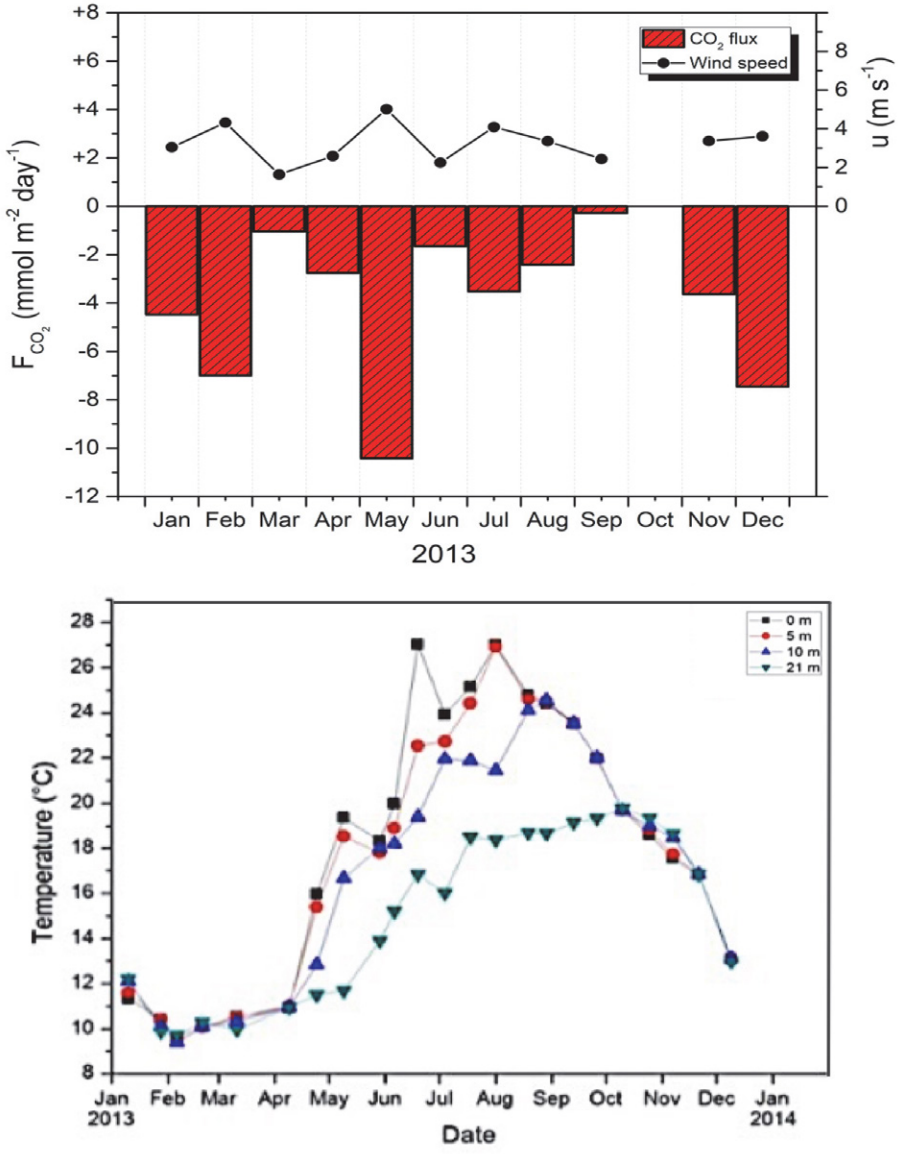
Slika 2. Ca^{2+} in Mg^{2+} v severnojadranskih rekah. Razmerje $Mg^{2+}/Ca^{2+} < 0{,}1$ kaže raztapljanje čistega kalcita, razmerje $Mg^{2+}/Ca^{2+} = 0{,}33$ ponazarja vode, ki raztapljajao enake molske deleže kalcita in dolomita, razmerje Mg^{2+}/Ca^{2+} približno 1 pa raztapljanje čistega dolomita.[25]

Tudi Tržaški zaliv deluje na letni ravni kot ponor CO_2 (približno 1,5 mol m^{-2} $leto^{-1}$) in je bolj izrazit pozimi s prevladujočim vplivom temperature in vetra (slika 4).[16,20,21,22] Poleti lahko obstoji šibek nasprotni tok v smeri atmosfere, posebej še v izlivu (estuariju) Soče.[22,23] Reke (predvsem Soča), ki se stekajo v Tržaški zaliv, izpirajo karbonatna področja (Julijske Alpe, Kras) podvržena intenzivnemu preperevanju.[24] Zato sta alkalnost in koncentracija DIC v rečnih vodah in posledično v obalnem morju višje (slika 5). Na osnovi masne bilance in izotopske sestave $^{13}C_{DIC}$ smo ocenili, da reke prispevajo približno do 15% k DIC v površinski plasti morja v

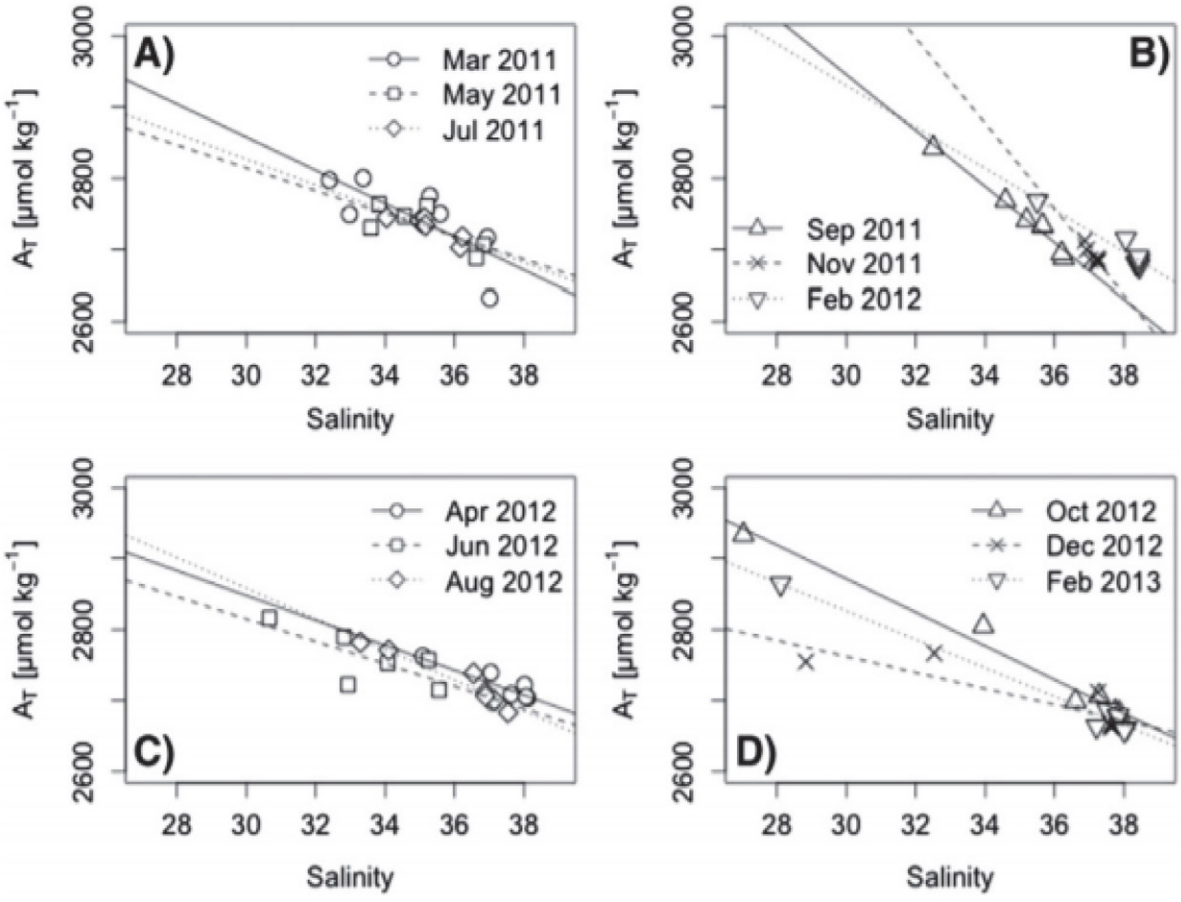


Slika 3. Alkalnost (A_T) v odvisnosti od slanosti v severozahodnem Jadranu pod vplivom izliva reke Pad v obdobju gostotne razslojenosti vodnega stolpa[17]

zalivu.[25] Povečane koncentracije DIC in hranil se nato zmanjšajo zaradi bioprodukcije predvsem v času povečanega zadrževalnega časa vode v zalivu.[22] Vpliv posameznih procesov na alkalnost in DIC je nazorno prikazan v nomogramu (slika 6). Vpliv temperature (»termični«) na (izračunani) pCO_2 ($pCO_{2,NT}$) prevladuje nad biološkim (»netermičnim«) vplivom ($pCO_{2,T}$) (slika 6) v celotnem letnem obdobju v zalivu[16], v severnem Jadranu pa je »termični« vpliv izrazit poleti in biološki vpliv prevladuje v ostalih sezonah.[18] Meritve pH v zalivu kažejo višje vrednosti pozimi in nižje poleti v plasti pri dnu (slika 7). Karbonatno ravnotežje v plasti pri dnu uravnavajo procesi na meji sediment-voda in v pornih vodah površinskega sedimenta. Študij bentoških tokov DIC in njihove izotopske sestave ^{13}C ($d^{13}C_{J\text{-}DIC}$) ter tokov Ca in Mg je pokazal, da prihaja na meji sediment-voda do



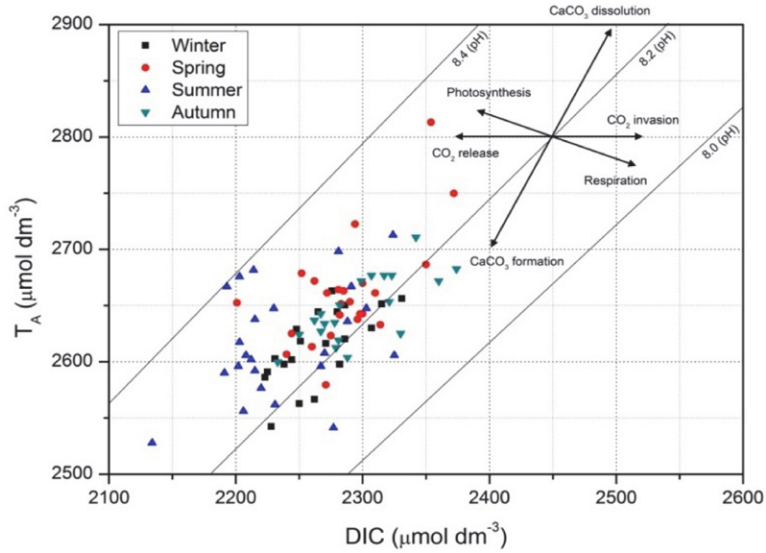
Slika 4. Tok CO_2 med zrakom in vodo (F), povprečna dnevna hitrost vetra 5 m and morsko gladino (u) in temperature morja v Tržaškem zalivu (oceanografska boja »VIDA«). Negativne vrednosti predstavljajo tok CO_2 iz atmosfere v morje.[25]



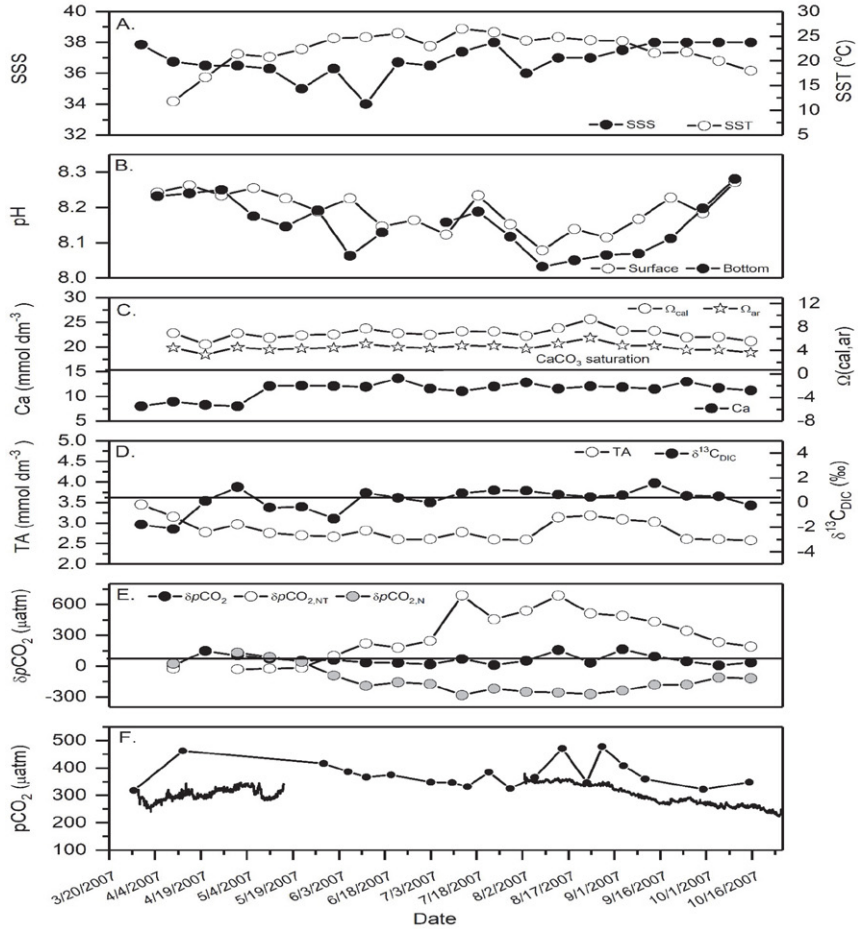
Slika 5. Alkalnost (A_T) in slanost v površinski plasti morja v Tržaškem zalivu[22]

obarjanja karbonatov in obsežnih intenzivnih izmenjav ter adsorpcije Ca in Mg na (in v) glinene minerale.[26] Izotopska sestava $^{13}C_{DIC}$ kaže, da je bentoški tok DIC večinoma organskega izvora in sicer v toplejšem (poletnem) obdobju izvira iz razgradnje razgradljivega organskega C sedimentiranega fitoplanktona in bentoških mikroalg, v hladnejšem (zimskem) obdobju pa iz razgradnje bolj odpornega (tudi kopenskega) sedimentiranega organskega C. V poletnem obdobju gostotne razslojenosti vodnega stolpa prihaja do intenzivne remineralizacije na meji sediment-voda, posebno v anoksičnih razmerah[27], in oksidacije sulfida v H_2SO_4.[28] Takrat poteka omejeno raztapljanje karbonatov, ki prispeva približno 10% k toku DIC (slika 8). Podobne vrednosti (5%) so zasledili tudi ob obali italijanske dežele Emilia-Romagna.[29] Tudi v pornih vodah v površinskem sedimentu izvira nastali DIC s pretežno razgradnjo organske snovi. Delež z izvorom v raztapljanju karbonatov je višji kot na meji sediment-voda in je pomemben v hladnejših obdobjih, ko je razgradnja organske snovi upočasnjena.[30] Zmanjšano raztapljanje (ali povečano obarjanje) ponazarjajo tudi nižje koncentracije Ca in Mg v pornih vodah v anoksičnih razmerah nad sedimentom v primerjavi z oksičnimi razmerami (slika 9). Na pH morske vode vpliva tudi kinetika heterogenih reakcij v sedimentih, saj je reakcija H^+ s karbonati hitrejša kot s silikati. Ker je morje v Tržaškem zalivu prenasičeno glede na kalcit in aragonit (slika 7) in je njegova pufranost visoka, zaliv ni podvržen občutnemu »kisanju«.[16]

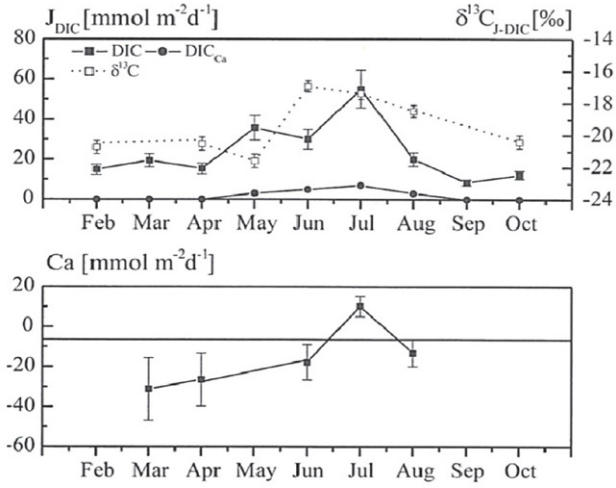
V prihodnosti lahko pričakujemo (napovedovanje z modeli) še vedno prenasičenost morja glede na kalcit in aragonit, vendar moramo upoštevati, da organizmi potrebujejo izdatno nasičenje s karbonatnimi minerali. Prognoze (Ocean Carbon Cycle Model Intercomparison Project – OCMIP-3, 1994–2020) kažejo, da bo pufranost morja v severnem Jadranu v prihodnosti verjetno še vedno uravnotežena s povečanim raztapljanjem CO_2. V plitvih evtrofnih obalnih vodah (npr. ob obali dežele Emilia-Romagna, Italija) bo lahko povezan vpliv povečanja atmosferskega CO_2, naraščajoče temperatutre in rečnega vnosa antropogenega CO_2 ter zmanjšane pufranosti povečal »kisanje« morja.[18,25] Pričakujemo lahko pomemben negativen (povečano raztapljanje) vpliv na karbonatne organizme[33], vpliv na mikrobne procese pa zaenkrat ostaja neznanka. Večina študij je pokazala, da sprememba pH vpliva bolj na biogeokemijske procese (kroženje N) kot na mikrobno biodiverziteto.[34,35,36] Morske bakterije vzdržujejo znotrajcelično alkalno homeostazo pH[37], ki je odvisna od pH medija (sinteza znotrajceličnih kislin in baz ali ekspresija genov, ki kodirajo procese protonske čr-



Slika 6. Nomogram med alkalnostjo (T_A) in raztopljenim anorganskim ogljikom (DIC)[32] v Tržaškem zalivu (Oceanografska boja »VIDA«): zima (črno), pomlad (rdeče), poletje (modro) in jesen (zeleno).[17] Premice ponazarjajo konstantni pH kot funkcijo DIC in TA, puščice ponazarjajo vpliv procesov na porazdelitev TA in DIC: fotosinteza, respiracija, raztapljanje karbonata ($CaCO_3$), obarjanje karbonata ($CaCO_3$), raztapljanje atmosferskega CO_2, sproščanje CO_2 v atmosfero



Slika 7. Sezonske spremembe povprečnih dnevnih rečnih pritokov v Tržaškem zalivu (A), alkalnosti (TA) and $\delta^{13}C_{DIC}$ (B), koncentracije Ca in nasičenost glede na kalcit in aragonit (C), slanost in temperatura (D), normalizirane vrednosti pCO_2 glede na slanost in temperaturo (δpCO_2) ter »termični« ($\delta pCO_{2,T}$) in »netermični« ($\delta pCO_{2,NT}$) vplivi na morski pCO2 v južnem delu Tržaškega zaliva (E) in pCO_2 (F) • – iz TA in pH,[16] – *in situ* v globini 3 m.[22] Razlike med izračunanimi in merjenimi *in situ* pCO_2 pripisujemo predvsem izbiri disociacijskih konstant ogljikove kisline v morski vodi, vpliv raztopljenih organskih baz (ang. Dissolved Organic Carbon – DOC) pa je majhen.[16]



Slika 8. Bentoški tokovi celotnega raztopljenega anorganskega ogljika (J_{DIC}) in kot posledica raztapljanja karbonatov (J_{DICCa}), njihova izotopska sestava ^{13}C (vrednosti $\delta^{13}C_{DIC}$) in bentoški tokovi Ca v Tržaškem zalivu[26]

Zahvala

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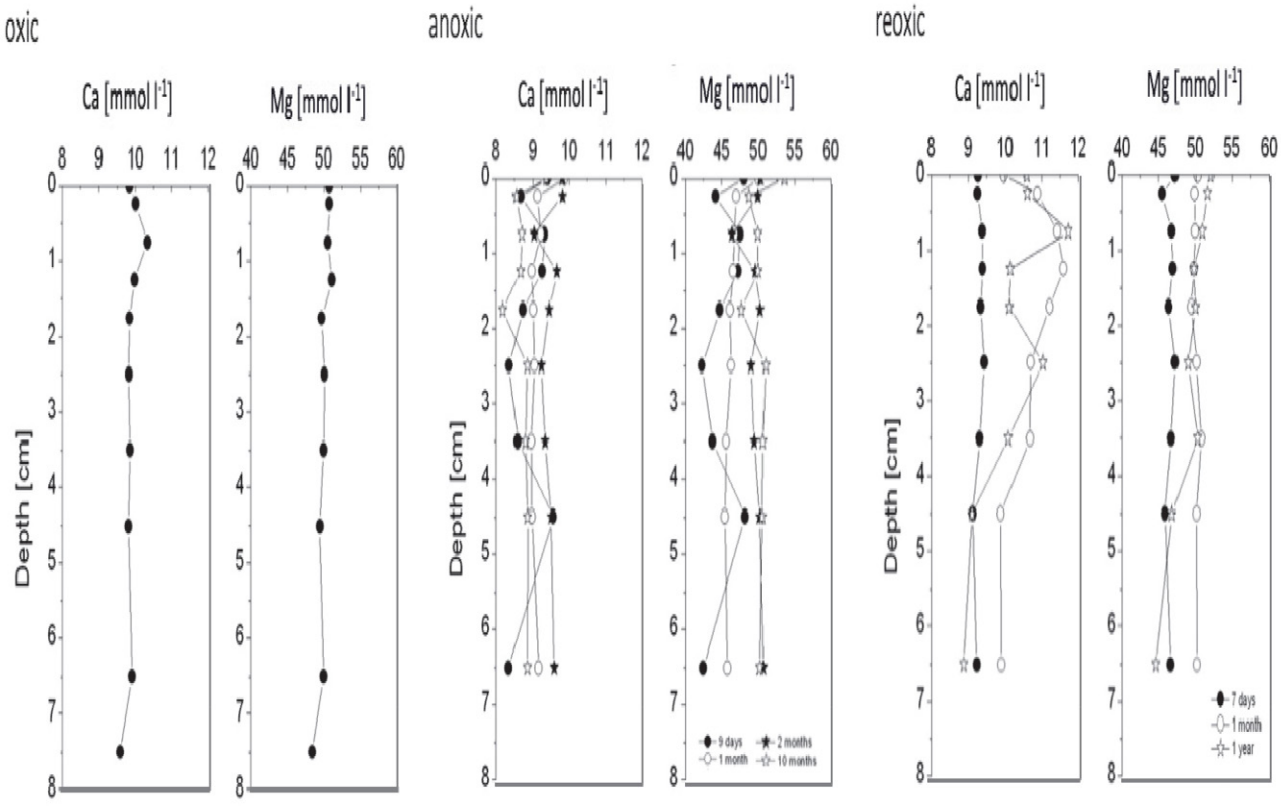

Slika 9. Koncentracije Ca in Mg v pornih vodah sedimenta Tržaškega zaliva z oksično, anoksično in ponovno oksično plastjo vode and sedimentom[31]

palke). Temperatura, slanost in anorganska ter organska hranila vplivajo na številčnost in produktivnost mikrobov in s tem na trofično stanje morja. Negativni vplivi »kisanja« lahko povzročajo spremembe v prehranjevalnih verigah in s tem posledično vplivajo na ribolov in marikulturo.

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Abstract

The present knowledge of the carbonate system in the northern Adriatic is described in this short overview. Its buffer capacity is rather high, due to riverine input of carbonates dissolved from Alpine and Karstic watersheds, and the waters should have a higher resilience to acidification. In the shallow eutrophic areas, the combined effect of rising atmospheric CO_2, warming and river-induced anthropogenic CO_2 with the associated decrease in buffer capacity could act to acidification process. Significant effect on calcifying organisms is expected in the future.

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5. J. Szegezdi, F. Csizmadia, Prediction of dissociation constant using microconstants, http://www. chemaxon.com/conf/Prediction_of_dissociation _constant_using_microco nstants.pdf, (assessed: March 31, 2008)

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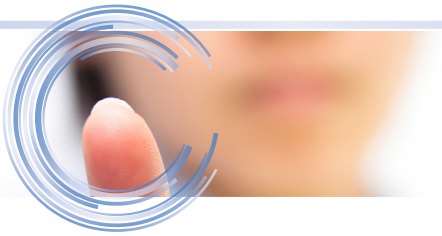

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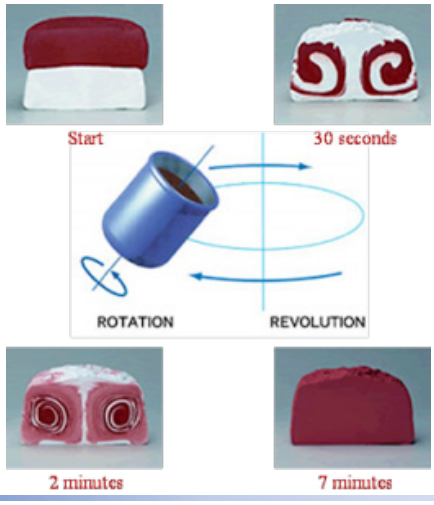

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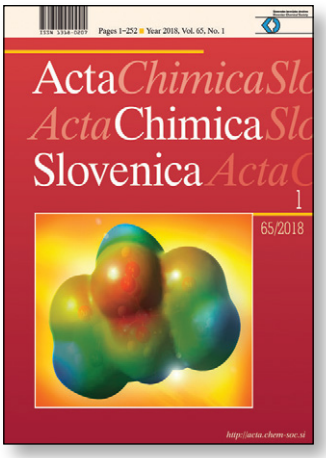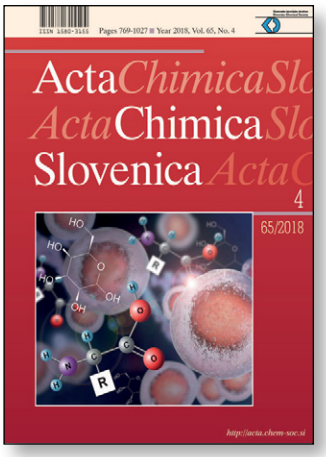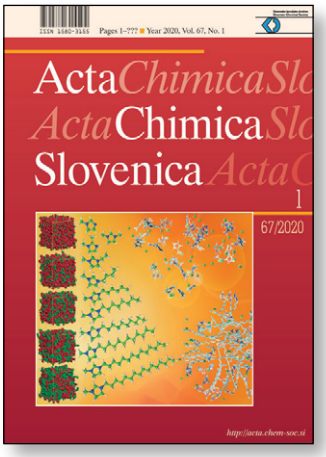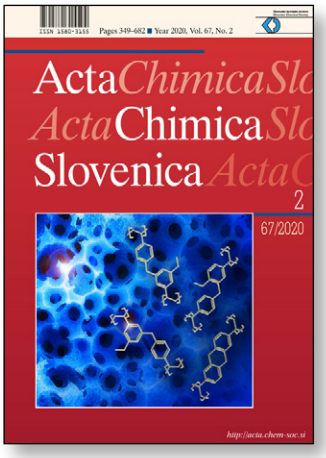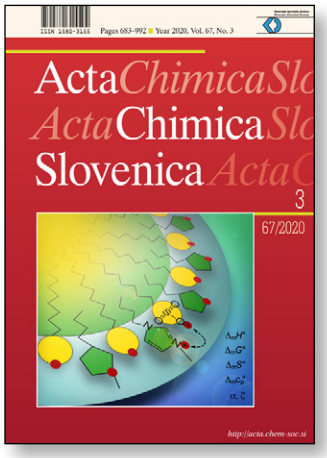
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