Svojstva i dinamika promjena organske tvari u Jadranu

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SVOJSTVA I DINAMIKA PROMJENA ORGANSKE TVARI U JADRANU

DOKTORSKI RAD

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Zagreb, 2019

University of Zagreb

FACULTY OF SCIENCE

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PROPERTIES AND DYNAMICS OF ORGANIC MATTER CHANGES IN THE ADRIATIC

DOCTORAL THESIS

Supervisor: Vjeročka Vojvodić, PhD.

Zagreb, 2019

Ova doktorska disertacija izrađena je u Laboratoriju za fiziku mora i kemiju vodenih sustava, Zavod za istraživanje mora i okoliša Instituta Ruđer Bošković u Zagrebu, pod vodstvom dr.sc. Vjeročke Vojvodić, kao dio aktivnosti unutar HRZZ projekata „Sulphur and carbon dynamics in the marine and freshwater environment“ (IP-11-2013-1205, SPHERE) te „Rogozničko jezero kao odziv ekosustava na promjene u okolišu“ (IP-2018-01-1717, MARRES).

Dugoročna istraživanja unutar ovog doktorata bila su financirana mnogim nacionalnim i međunarodnim projektima. Posebno ističem:

- Hrvatski nacionalni monitoring program: Sustavno istraživanje Jadranskog mora kao osnova održivog razvitka Republike Hrvatske – Projekt Jadran, 1998-2010 (financirala hrvatska vlada)
- Norwegian Cooperation Program on Research and Higher Education with the countries of the western Balkan – Marine Science and Coastal Management in the Adriatic, Western Balkans, 2006-2010 (financirala norveška vlada)
- MAT Project – Mucilages in the Adriatic and Tyrrhenian seas, 1999-2002 (financirale talijanska i hrvatska vlada)

Zahvaljujem mentorici i voditeljima projekata/laboratorija što su mi omogućili korištenje podataka dugoročnih istraživanja u izradi ove disertacije.

Disertacija je izrađena u sklopu Interdisciplinarnog doktorskog studija Oceanologije na Prirodoslovno-matematičkom fakultetu Sveučilišta u Zagrebu.

ZAHVALA

Veliko hvala mojoj mentorici dr.sc. Vjeročki Vojvodić na pomoći, usmjeravanju, predloženoj temi, vođenju eksperimentalnoga dijela doktorskoga rada, na svim objašnjenjima, savjetima, sugestijama, diskusijama, na velikom strpljenju, entuzijazmu i prijateljskoj podršci tijekom izrade ove disertacije.

Hvala dr.sc. Ireni Ciglenečki-Jušić na podršci i pruženoj prilici da se bavim znanstvenim radom, napredujem i usavršavam se, na mnogim korisnim savjetima, sugestijama i diskusijama kroz pripremanje zajedničkih publikacija.

Hvala dr.sc. Boženi Ćosović na podršci tokom cijelog doktorskog studija, mnogim korisnim savjetima i diskusijama kroz koje sam zaista puno naučila.

Hvala dr.sc. Ivici Vilibiću na diskusijama vezanim za utjecaj BiOS-a na Jadran.

Zahvaljujem Nataši Tepić na velikoj pomoći u statistici.

Zahvaljujem terenskoj ekipi istraživačkog broda Vila Velebita na pomoći kod prikupljanja uzoraka te prilikom rada na terenu.

Hvala Zdeslavu Zovku na pomoći kod uzorkovanja i obrade uzoraka te u svakodnevnom laboratorijskom radu, na podršci i strpljenju kroz sve ove godine.

Hvala Nataši Cesarec, prof. za jezične i gramatičke savjete.

Zahvaljujem svim članovima bivšeg Laboratorija za fizičku kemiju vodenih sustava koji su tijekom godina na razne načine doprinosili izradi ovog rada.

Veliko hvala dr.sc. Kristini Pikelj – na svemu.

Hvala dr.sc. Željki Fiket koja je izradu ovog doktorskog rada učinila lakšom i puno zabavnijom. Hvala na entuzijazmu, nesebičnoj pomoći i podršci.

Veliko hvala mojoj obitelji bez čijeg razumijevanja i neizmjerne podrške ovaj rad ne bi mogao biti napisan. Hvala vam na beskrajnom strpljenju.

TEMELJNA DOKUMENTACIJSKA KARTICA

Sveučilište u Zagrebu
Prirodoslovno-matematički fakultet
Geološki odsjek

Doktorska disertacija

SVOJSTVA I DINAMIKA PROMJENA ORGANSKE TVARI U JADRANU

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Sažetak: Organski ugljik važan je indikator globalnih promjena te sudjeluje u mnogim biogeokemijskim procesima u moru. Ovaj rad dokumentira dinamiku promjena sadržaja i svojstava otopljene organske tvari/ugljika, u odabranim područjima Jadrana koja su pod jakim utjecajem unosa slatke vode kao i različitih vodenih masa: sjeverni Jadran (SJ) na profilu Rovinj – rijeka Po, Boka kotorska i albanski šelf. Ispitivani su sadržaj i svojstva otopljenog organskog ugljika (eng. DOC), partikularnog organskog ugljika (eng. POC) te površinski aktivnih tvari (PAT). Varijabilnost i trendovi u promjeni sadržaja i svojstava organske tvari u SJ u vremenskom razdoblju od 28 godina ukazuju na vrlo dinamičan sustav na prostornoj, a posebno na vremenskoj skali. Rezultati također pokazuju da je područje SJ dominantno oligotrofno, s kraćim, vrlo izraženim eutrofnim/mezotrofnim epizodama. Svojstva i sadržaj organske tvari u sjevernom Jadranu pod jakim su utjecajem promjenjivog unosa slatke vode rijekom Po te pod utjecajem advekcije vodenih masa koje ulaze u Jadransko more iz Mediterana tijekom različitih tipova cirkulacija u sjevernom Jonskom moru uvjetovanih Jadransko-jonskom bimodalnom oscilacijom (BiOS). U vremenskom razdoblju u kojem su istraživana sva tri područja (03/2008-05/2009), najadsorbabilniji, to jest najreaktivniji organski materijal nađen je u području Boke kotorske (ali bez naznaka eutrofnosti), po svojstvima bliži adsorbabilnijim modelnim spojevima dekstranu T-500 i fulvičnoj kiselini. Slično je pokazano i u jednokratnoj proljetnoj analizi tada oligotrofnog albanskog šelfa.

Varijabilnost reaktivnosti otopljene organske tvari u SJ tijekom ovog dugogodišnjeg ispitivanja je bila izraženija nego u ostala dva istraživana sustava. Svojstva organske tvari mijenjala su se od reaktivnijeg, adsorbabilnijeg materijala sličnog fulvičnoj kiselini i dektranu T-500, do slabije adsorbabilnog, odnosno manje reaktivnog organskog materijala predstavljenog modelom visokokomolekularnog polisaharida ksantana.

Ključne riječi: otopljeni organski ugljik (DOC), partikularni organski ugljik (POC), površinski aktivne tvari (PAT), normalizirana površinska aktivnost (NPA), morska voda, utjecaj slatke vode, Jadransko-jonska bimodalna oscilacija (BiOS), sjeverni Jadran, Boka kotorska, albanski šelf

Rad sadrži: 54 stranice, 11 slika, 1 tablicu, 73 literaturnih navoda

Jezik izvornika: hrvatski

Rad je pohranjen u: Nacionalnoj i sveučilišnoj knjižnici u Zagrebu, Hrvatske bratske zajednice 4, Zagreb

Mentor: Dr.sc. Vjeročka Vojvodić, viša znanstvena suradnica

Ocjenjivači: Dr.sc. Irena Ciglenečki, znanstvena savjetnica u trajnom zvanju
Dr.sc. Božena Ćosović, profesor emeritus
Dr.sc. Ivica Vilibić, znanstveni savjetnik u trajnom zvanju
Dr.sc. Tamara Đakovac, viša znanstvena suradnica (zamjena)

Rad prihvaćen: 8.2.2019.

BASIC DOCUMENTATION CARD

University of Zagreb
Faculty of Science
Department of Geology

Doctoral Thesis

PROPERTIES AND DYNAMICS OF ORGANIC MATTER CHANGES IN THE ADRIATIC

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Abstract: Organic carbon is an important indicator of global change and is a constituent of many biogeochemical processes in the sea. In this thesis organic matter/carbon properties, variability and dynamics in selected areas of the Adriatic (which differ in freshwater influence as well as advected water masses) are shown: transect Rovinj – Po in the northern Adriatic (NA), Boka Kotorska Bay and Albanian shelf. Organic matter in selected areas was monitored regarding its concentration (dissolved organic carbon, DOC; particulate organic carbon, POC) and properties (surface active substances, SAS). The NA was investigated for a period of 28 years. Through investigations of 28-years long time series, it is shown that the NA organic matter has high temporal and spatial variability. Oligotrophic conditions are common in the NA, yet with short but very strong eutrophication episodes. Properties and concentration of organic matter in the NA appears to be under strong local influence of the Po River load, but also under the influence of different water masses entering the Adriatic from the Mediterranean caused by the Adriatic-Ionian Bimodal Oscillating System (BiOS). During the period when all three areas were investigated (03/2008-05/2009), the most adsorbable (hence the most reactive) organic material was found in the Boka Kotorska Bay (with no signs of eutrophication), whose properties are close to more adsorbable model substances such as dextran T-500 and fulvic acid (FA). Similar finding was documented for the single analysis carried out on the oligotrophic Albanian shelf.

Reactivity of the dissolved organic matter in the NA during this long-term investigation is shown to be the most variable of all investigated areas. Organic matter properties changed from more reactive/adsorbable material, close to FA and dextrane T-500 in properties, to less adsorbable/reactive organic material close to high molecular polysaccharide xanthan in properties.

Keywords: dissolved organic carbon (DOC), particulate organic carbon (POC), surface active substances (SAS), normalized surfactant activity (NSA), seawater, freshwater influence, Adriatic-Ionian Bimodal Oscillating System (BiOS), northern Adriatic, Boka Kotorska Bay, Albanian shelf

Thesis contains: 54 pages, 11 figures, 1 table, 73 references

Original in: Croatian

Thesis deposited in: National and University Library of Zagreb, Hrvatske bratske zajednice 4, Zagreb

Supervisor: Vjeročka Vojvodić, PhD, senior research associate

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Thesis accepted: 8.2.2019

Sadržaj

1. Uvod

1.1. Hipoteze istraživanja

1. Dugoročna istraživanja organske tvari (otopljeni organski ugljik, eng. DOC, partikularni organski ugljik, eng. POC, i površinski aktivna frakcija organske tvari PAT, eng. SAS, kao grube mjere reaktivnosti) u poluzatvorenom, produktivnom plitkom bazenu sjevernog Jadrana (SJ) pokazuju vrlo izražene promjene u količini i svojstvima organske tvari.
2. Količina i svojstva organske tvari u sjevernom Jadranu uvjetovane su a) unosom slatke vode, uglavnom rijekom Po, i b) cirkulacijom vodenih masa u Jadranu kontroliranom Jadransko-jonskom bimodalnom oscilacijom (eng. BiOS, dekadska jadransko-jonska oscilacija koja dovodi do advekcije različitih vodenih masa u Jadran).
3. Promjene u sadržaju i svojstvima (reaktivnosti) organske tvari u sjevernom Jadranu (na dugoročnoj skali) podudaraju se s drugim istraživanjima koja ističu značajne promjene u ekosustavu SJ (količina nutrijenata, sastav i vrsta fitoplanktonskih zajednica)
4. Organska tvar u obalnom sustavu južnog Jadrana (Boka kotorska i obalni pojas albanskog dijela Jadrana) pod utjecajem su donosa različitih tipova slatkih voda: podzemne vode u Boki kotorskoj te lokalni unosi rijekama (Bojana, Drim), kao i dotoka različitih tipova vodenih masa (Levantinska intermedijarna voda, eng. LIW, Modificirana atlantska voda, eng. MAW) iz Mediterana.

1.2. Cilj i svrha rada

Cilj ovog istraživanja je karakterizacija organske tvari, odnosno organskog ugljika u otopljenom obliku (eng. DOC) kao dominantne frakcije organske tvari u moru te karakterizacija reaktivne komponente otopljene organske tvari s površinski aktivnim svojstvima (površinski aktivne tvari, PAT) i partikularnog organskog ugljika (eng. POC) u području sjevernog Jadrana, te Boki kotorskoj i priobalnom moru Albanije u južnom Jadranu, kao sustavima koji su pod različitim utjecajem slatkih voda i strujanja vodenih masa. Posebna pažnja posvetiti će se analizi promjena sadržaja i svojstava otopljene organske tvari u sjevernom Jadranu u dugom razdoblju ispitivanja od 28 godina (1989.-2017.). Kako bi se utvrdila moguća povezanost tzv. daljinski uzrokovanih promjena i kolebanja sastava i sadržaja organske tvari u sjevernom Jadranu, dobiveni rezultati iz ovog istraživanja usporediti će se i diskutirati s poznatim literaturnim podacima dugoročnih istraživanja hidrografskih prilika i bioloških parametara u SJ i Jadranu općenito. Na taj način će se objasniti opažena izrazita varijabilnost, od razdoblja visoke akumulacije (eutrofikacija) do iscrpljivanja (oligotrofikacija) sadržaja organske tvari. Rezultati kratkoročnih ispitivanja DOC i PAT u preostala dva sustava u južnom Jadranu, Boki kotorskoj i priobalnom moru Albanije, usporediti će se s podacima iz sjevernog Jadrana te će poslužiti za dobivanje šire slike o organskoj tvari u području Jadranskog mora.

1.3. Organska tvar u moru

Istraživanja organske tvari (OT) u ekosustavima mora dijele se u dvije kategorije:

- Holistički pristup fokusiran je na određivanje ukupne koncentracije te kolektivno ponašanje kompleksne smjese organskih tvari, s ciljem određivanja njenih reprezentativnih karakteristika u prirodnim vodama. Primjeri za to su ispitivanja otopljenog organskog ugljika DOC, partikularnog organskog ugljika POC, površinski aktivnih tvari PAT, ukupnog otopljenog organskog dušika DON, promjene sadržaja kisika i hranjivih soli vezane uz mikrobiološku razgradnju organske tvari.
- Redukcionistički pristup usmjeren je na detaljne analize svojstava specifičnih organskih spojeva ili grupa spojeva frakcioniranih iz smjese. Analize na molekularnom nivou vrlo su selektivne za pojedine biokemijske klase ili podklase koje čine mali, ne nužno reprezentativni dio ukupnog sustava. Primjeri za to su ispitivanja specifičnih organskih spojeva, organske tvari raznih veličina molekula, hidrofobne i hidrofilne organske tvari.

Organska tvar u prirodnim vodama kompleksna je smjesa spojeva koji se međusobno razlikuju po porijeklu, sastavu te fizičko-kemijskim svojstvima (kao na primjer hidrofobnost-hidrofilnost). Smatra se da je između 20-30% ukupne otopljene organske tvari u morskoj vodi dobro karakterizirano (Hansell i Carlson, 2002).

Organska tvar u moru može biti autohtona, nastala unutar sustava procesima primarne produkcije, bakterijske razgradnje, autolizom mrtvih organizama ili alohtona, tj. ona koja u sustav dospijeva iz okoline (unos rijekama, otpadnim vodama, iz atmosfere). Prema porijeklu OT se može podijeliti i na akvagenu, pedogenu i antropogenu organsku tvar. Akvagena organska tvar produkt je metabolizma i razgradnje bioloških organizama u moru i tu kategoriju čine ugljikohidrati, proteini i lipidi koji imaju značajnu ulogu u mnogobrojnim biogeokemijskim procesima u moru. U kompleksnoj smjesi organskih spojeva u moru ove grupe spojeva najbolje su definirane. Pedogena organska tvar dospijeva u more ispiranjem okolnog tla, a nastaje mikrobiološkom razgradnjom viših biljaka. Antropogena organska tvar nastaje kao posljedica ljudske djelatnosti, te nerijetko doprinosi zagađenju prirodnih vodenih sustava.

Organska tvar u moru nalazi se u otopljenoj i partikularnoj formi. Za odvajanje partikularne od otopljene frakcije koriste se filteri veličine pora 0,2 – 1 μm (Hansell i Carlson, 2002), ovisno o ciljevima istraživanja. Najčešće se koriste filteri veličine pora 0,2 μm (bakterije zaostaju na filteru) i 0,7 μm (GF/F).

1.3.1. Otopljena i partikularna organska tvar

Otopljena organska tvar

Organska tvar u moru jedan je od najvećih spremnika ugljika na Zemlji – ukupna količina ugljika u moru (~ 700 Pg, 1 Pg = 10^{15} g) približno je jednaka količini ugljika prisutnog u atmosferi u obliku CO_2 (~ 750 Pg). Više od 97% organskog ugljika u morima i oceanima nalazi se u otopljenom obliku (Hansell i Carlson, 2002).

Otopljeni organski ugljik predstavlja dinamičnu komponentu globalnog ciklusa ugljika i mogući je pokazatelj globalnih promjena. U moru daje podlogu za život, ishodište je regeneracije hranjivih tvari, ionske izmjene, apsorpcije svjetla i topline, te utječe na specijaciju metala i zagađivala itd.

Otopljena organska tvar dominantna je frakcija OT u prirodnim morskim sustavima. Unutar otopljene frakcije sadržani su i koloidi koji se smatraju vrlo značajnima u morskim sustavima zbog svoje reaktivnosti. Oni sudjeluju u raznim procesima kao što je uklanjanje organske tvari iz vodenog stupca te imaju ulogu u stvaranju agregata prilikom prekomjernog cvjetanja mora (Dafner i Wangersky, 2002b; Giani i sur., 2005).

Kemijske karakteristike otopljene organske tvari razlikuju se u površinskom, eufotičkom sloju mora od one u dubljim slojevima. U gornjem, eufotičkom dijelu vodenog stupca dominira uglavnom svježe proizvedena, najreaktivnija frakcija otopljene organske tvari nastala procesima primarne proizvodnje kontrolirane nizom internih faktora poput temperature, hidrografskih uvjeta te dostupnosti hranjivih soli (uglavnom dušik i fosfor te silikati). U dubljim slojevima mora prevladava starija tzv. refraktorna otopljena organska tvar, otpornija na biološku razgradnju.

Prva istraživanja otopljene organske tvari (DOC i DON) proveli su Krogh i Keys 1934. godine – koncentracije DOC određivane su u vodenom stupcu u oceanu nedaleko od Bermude metodom mokre oksidacije u kromatnoj kiselini. Pronađene su uniformne koncentracije DOC u vodenom stupcu, te je zaključeno da je otopljena organska tvar u morskoj vodi kronološki gledano stara, kemijski i biokemijski inertna te beznačajna kao izvor hrane za organizme u dubokim morima.

Visokotemperaturna katalitička oksidacija (HTCO) donijela je visoku preciznost mjerenja niskih koncentracija te omogućila određivanje vremenskih i prostornih koncentracijskih gradijenata kao i varijabilnosti DOC u moru (Sugimura i Suzuki, 1988; Dafner i Wangersky, 2002a). Na taj način je pridonijela stvaranju sasvim nove slike o važnosti otopljenog organskog ugljika u moru.

Partikularna organska tvar

Partikularna organska tvar (POC) zbog svoje reaktivnosti značajni je dio ukupne organske tvari u moru, sudjeluje u brojnim biogeokemijskim procesima i važni je indikator produktivnosti određenog vodenog sustava.

Vernadsky (1934) je u dvadesetim i tridesetim godinama prošlog stoljeća proučavao partikularnu organsku tvar i ukazao na važnost procjenjivanja ukupne količine partikularnog ugljika u oceanima kao jedne od „planetarnih konstanti“.

U partikularnoj frakciji nalaze se (a) živući planktonski organizmi, fito-, zoo- i bakterioplankton, jajašca, larvae, morski snijeg nastao agregacijom polisaharidnih fitoplanktonskih izlučevina, važan jer brzo tone i prenosi hranu bentosu (b) ostaci različitih organizama i njihovih fekalnih peleta, (c) organska tvar iz skeletnih struktura te ona terigenog i eolskog unosa, (d) organska tvar koja se adsorbirala iz vodenog stupca, agregirala ili koprecipitirala. Dakle, partikularnu tvar čini živa i neživa organska tvar. Živa organska tvar značajna je za ekosustave mora, premda je poznato da sadrže samo 2% ukupne organske tvari u morima i oceanima (Duursma i Dawson, 1981).

Glavnina partikularne organske tvari nastaje *in situ*, primarnom proizvodnjom živih organizama. Živi organizmi (uglavnom fitoplankton) u okolno more izlučuju tvari poput ugljikohidrata, bilo da se radi o jednostavnim šećerima ili kompleksnijim polisaharidima, zatim organske kiseline, lipide, proteine, aminokiseline, polifenolne supstance, organske fosfate, toksine i drugo. Više je faktora koji utječu na vanstanično izlučivanje organskih tvari: ona je viša u površinskom sloju gdje je fotosinteza uvjetovana količinom svjetla, viša je u eutrofnim vodama, viša je kad su stanice u stacionarnoj fazi rasta u odnosu na stanice koje su u eksponencijalnoj fazi rasta, i tako dalje.

Neživi partikularni organski materijal (detritus) kompleksan je i dinamičan materijal koji se pojavljuje u 5 puta većoj količini nego ukupna biomasa fitoplanktona te 10 puta manjoj količini od otopljenog organskog ugljika. Ima ga 10 puta više u eufotičkoj zoni, što je razlog da se upravo u toj zoni najintenzivnije istraživao kroz povijest (Duursma i Dawson, 1981).

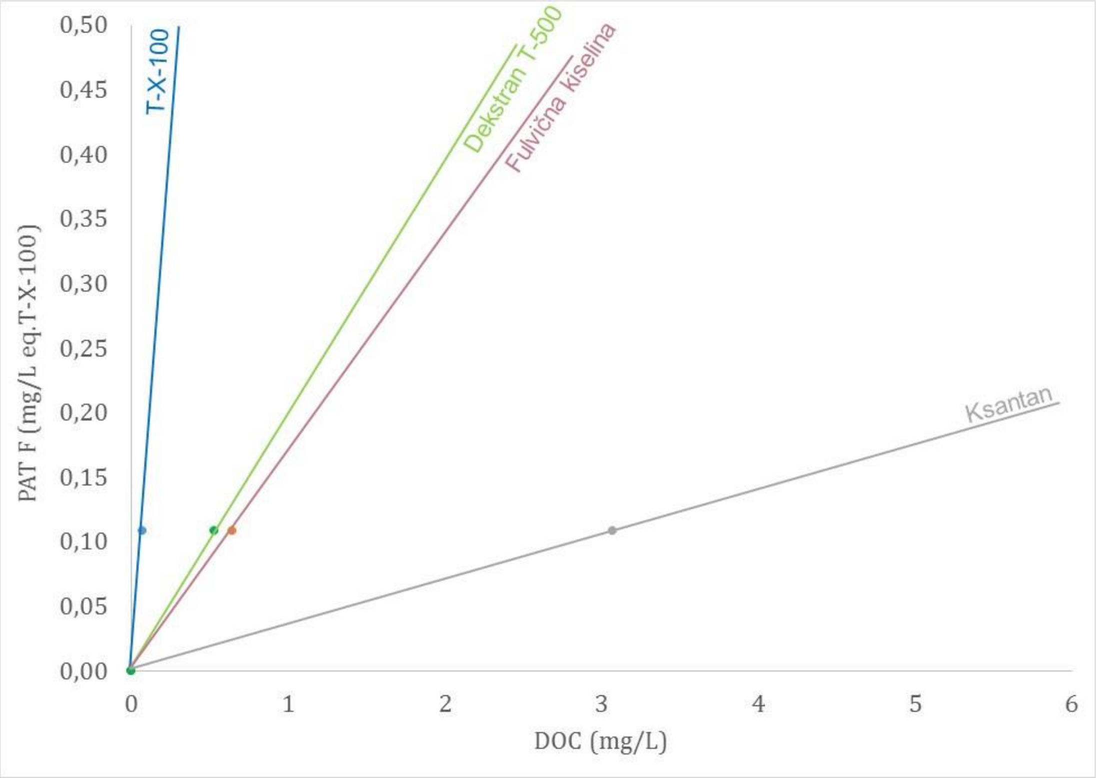
Razvojem analitičkih metoda (ranije spomenuta HTCO metoda) pokazano je da je i partikularni organski ugljik dinamična komponenta organskog ugljika u vodenom stupcu, iako značajno manje zastupljena od otopljene frakcije, te da je izuzetno važna za mnoge biogeokemijske procese (agregiranje organskih molekula, flokulacija ili adsorpcija otopljene frakcije na mineralne čestice).

U eufotičkoj zoni sadržaj i ravnoteža između akvagene otopljene i partikularne frakcije značajno varira. U dubljim slojevima sadržaj i sastav obiju frakcija je stabilniji. S vremenom se dio otopljene frakcije pretvara u partikularnu te konačno procesima sedimentacije dospjeva u morski sediment.

1.3.2. Površinski aktivne tvari

Od fizikalno-kemijskih karakteristika spojeva u kompleksnoj smjesi organske tvari u moru, značajna su površinski aktivna svojstva. Površinski aktivne tvari, prisutne u nefiltriranoj (PAT NF) i filtiranoj frakciji (PAT F) organske tvari (uzorka) reaktivne su i igraju važnu ulogu u ciklusu ugljika u moru, jer se adsorpcijskim procesima nakupljaju na prirodnim granicama faza (zrak/površina mora, more/sediment, more/živi i neživi suspenidrani materijal), gdje utječu na procese prijenosa tvari i energije i važni su za sve biogokemijske procese (Ćosović i Vojvodić, 1982; Ćosović i Vojvodić, 1987; Vojvodić i Ćosović, 1996; Ćosović i Ciglenečki, 1997; Gašparović i Ćosović, 2001).

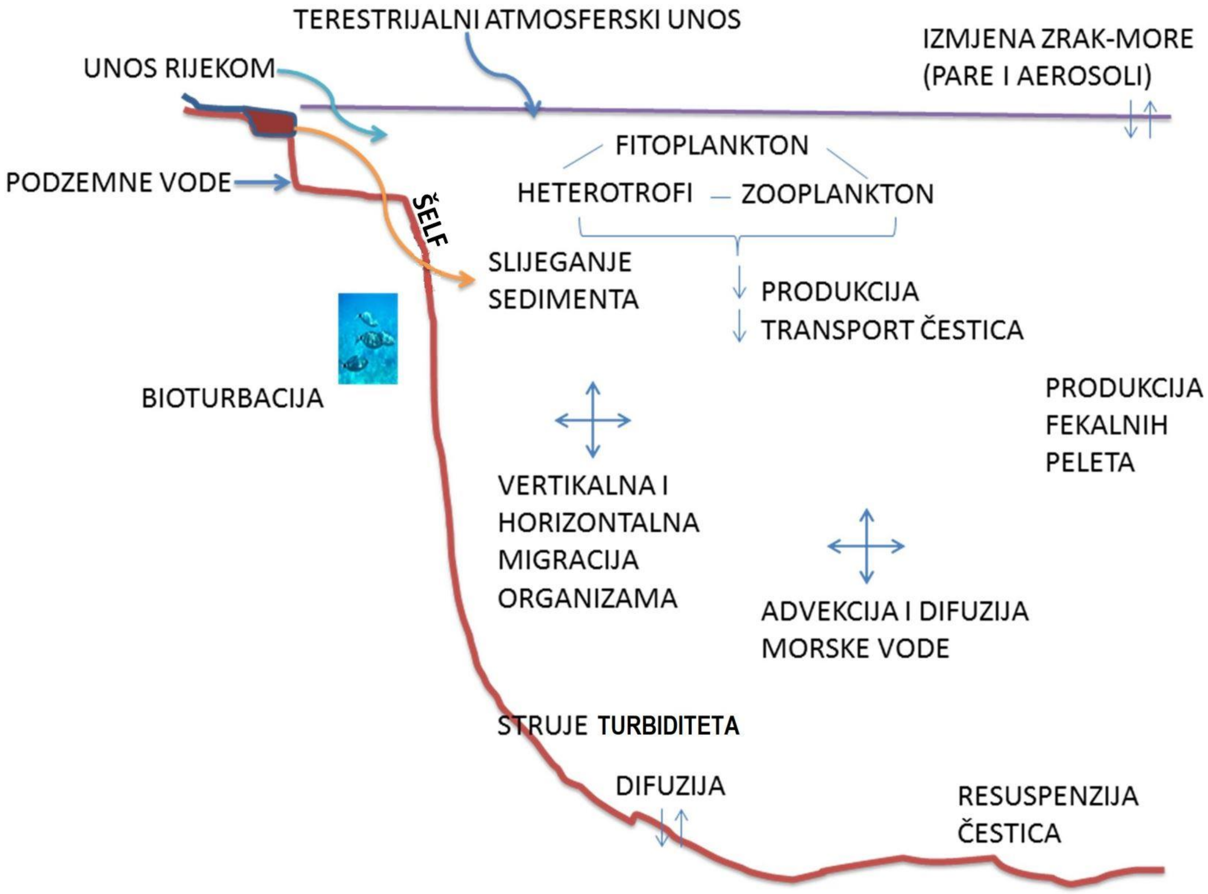
Komparativnim pristupom, rezultatima mjerenja PAT F i DOC u otopljenoj frakciji OT, normalizirana je površinska aktivnost (NPA, eng. NSA) kao omjer sadržaja PAT F (filtrirana frakcija) i sadržaja DOC (NPA=PAT F/DOC). Vrijednosti NPA morskih uzoraka uspoređivane su s različitim modelima površinski aktivnih tvari (T-X-100, dekstran T-500, fulvična kiselina, ksantan) također normaliziranim za njihov sadržaj organskog ugljika (Ćosović i Vojvodić, 1998). Odabrane modelne PAT karakteristične su za adsorpcijska svojstva prirodno prisutne organske tvari u moru (Slika 1). Takvim je pristupom omogućena dodatna karakterizacija nepoznate smjese organske tvari u moru (Ćosović i Vojvodić, 1998).



Slika 1. Normalizirana površinska aktivnost odabranih modelnih tvari relevantnih za tip materijala koji nalazimo u moru (triton X-100, dekstran T-500, fulvična kiselina, ksantan); modificirano iz Ćosović i Vojvodić (1998); NPA vrijednosti modelnih tvari: 1,54 T-X-100; 0,20 dekstran T-500; 0,17 fulvična kiselina; 0,04 ksantan

1.3.3. Utjecaj slatke vode na organsku tvar u moru

Slika 2. pokazuje kojim sve procesima transporta slatka voda ulazi u more, što sve donosi, kako utječe na procese u obalnom moru te koja je dinamika unesene organske tvari.



Slika 2. Procesi transporta koji kontroliraju distribuciju organske tvari u moru (modificirano iz Duursma i Dawson, 1981, poglavlje 5)

Slatka voda u more dospijeva na različite načine: riječnim donosima, oborinama, otapanjem leda, podzemnim vodama, remineralizacijom, itd. (Slika 2).

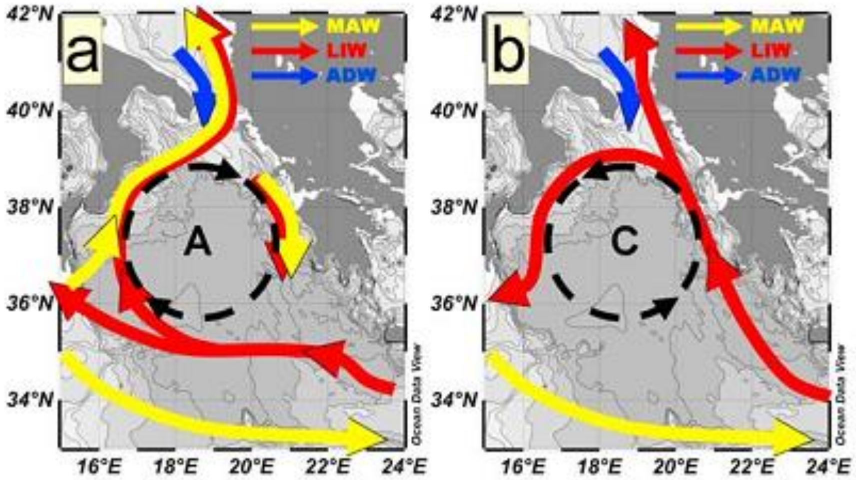
Slatka voda sa sobom donosi nutrijente, ali i organsku tvar koju direktno koriste morske bakterije ili koja se fotokemijski transformira i time postaje biodostupnija. Organski ugljik koji dolazi s kopna u velikom se postotku (i do 50%) može ponovo iskoristiti u obalnim morskim područjima (Duursma i Dawson, 1981).

Rijeke se razlikuju po protocima, tj. količini unosa slatke vode te sadržaju nutrijenata i organske tvari koju donose (Vojvodić i Ćosović, 1992; Sempere i Cauwet, 1995). Podzemne vode uglavnom su siromašne organskom tvari, posebno u krškim područjima (Ćosović i Vojvodić, 1989; Cauwet, 1991; Korlević i sur., 2016; Strmečki i sur., 2018), dok unos nutrijenta ovim tipom slatke vode može biti značajan (Ciglenečki i sur., 2012 i 2015; Krivokapić i sur., 2015).

Rijeka Po ima dominantan utjecaj na salinitet u sjevernom Jadranu (Supić i sur., 2004). U sjevernom se Jadranu pojavljuje površinska, anticiklonalna istarska obalna protustruja (eng.

ICCC), u nekim godinama jako u drugima slabije izražena, koja slatku vodu sniženog saliniteta približava prema istarskoj obali (Supić i sur., 2000). U razdoblju 2000.-2009. istarska obalna protustruja rjeđe se uspostavljala (Djakovac i sur., 2012).

Gačić i suradnici pokazali su kako su Jadransko i Jonsko more usko povezani BiOS mehanizmom (eng. Adriatic-Ionian Bimodal Oscillating System). Naime, u Jonskom se moru izmjenjuju dva tipa cirkulacije, ciklonalna i anticiklonalna (Slika 3). Ciklonalna cirkulacija u Jadran donosi levantinsku vodu (LIW, eng. Levantine Intermediate Water) visokog saliniteta, a anticiklonalna atlantsku vodu (MAW, eng. Modified Atlantic Water) niskog saliniteta bogatiju nutrijentima (Gačić i sur., 2010). Ciklonalna cirkulacija dovodi do smanjenog unosa nutrijanata kroz Otrantska vrata (Civitarese i sur., 2010; Vilibić i sur., 2012) i obratno.



Slika 3. Cirkulacija u Jonskom moru (BiOS); preuzeto iz Gačić i sur. (2010).

Rezultati istraživanja u rijekama Bojana i Drim (Plavšić i sur., 2013, koji je dio ove disertacije) rijetki su dostupni objavljeni podaci o organskoj tvari u tom području Jadrana.

Prekomjerno stvaranje sluzavih nakupina (cvjetanje mora; „mucilage aggregates“)

Kompleksna kombinacija meteoroloških i oceanoloških uvjeta kao što su riječni donos nutrijenata, anorganskog dušika i fosfora u visokom omjeru, nagle promjene temperature mora, složeno raslojavanje vodenog stupca, mirno more, povoljna cirkulacija (izraženo poluzatvorena tj. vrtložna), manjak ravnoteže između biološke produkcije i akumulacije organskog materijala te njegove bakterijske razgradnje može epizodno dovesti do fenomena cvjetanja mora (Degobbis i sur., 1999, 2005; Precali i sur., 2005).

U području Mediterana, pojava stvaranja sluzavih nakupina u povijesti je zabilježena u Jadranu, Tirenskom moru, uz obalu Sicilije, u Jonskom moru i u Grčkoj. Fenomen je prvi puta zabilježen u Jadranu 1729. godine i od tad se periodički pojavljuje (Vollenweider i sur., 1995). Vrlo izražen cvat s pojavom sluzavih nakupina organskog materijala („mucilage aggregates“) zabilježen je 1983., 1988., 1991., 1997., 2000.-2004. godine, dajući eutrofna svojstva inače oligotrofnom području. Na svjetskoj razini, fenomen je zabilježen i na Novom Zelandu (MacKenzie i sur., 2002).

Polisaharidi su glavni sastavni dio ovih nakupina (Marchetti i sur., 1989; Murano i sur., 1993; Faganelli i sur., 1995; Baldi i sur., 1997). Fizičko-kemijska svojstva organske tvari u makroagregatima podudaraju se sa svojstvima polisaharida, uglavnom sulfopolisaharida vrlo visoke molekularne mase (Ciglenečki i sur., 2000; Ciglenečki i sur., 2003). Smatra se da su ovi događaji povezani s promjenom TIN/PO_4^{3-} omjera u sustavu (Volf i sur., 2013).

Nakupljanjem organskog i anorganskog materijala u gornjim slojevima vodenog stupca procesima geliranja i polimerizacije izlučevina fitoplanktona stvaraju se trodimenzionalne nakupine, koje mogu biti veličine od nekoliko centimetara do nekoliko metara. U procesu agregiranja sudjeluje OT nastala produkcijom dijatomeja i dinoflagelata te drugih rodova fito- i bakterioplanktona, u priobalju i makroalga (Degobbis i sur., 1995; Najdek i sur., 2005). Nakon formiranja agregati postaju svojevrstan *mikrokozmos* kojeg onda mogu kolonizirati cijanobakterije i druge prisutne vrste fitoplanktona, bakterije i virusi. U takvim agregatima potvrđeni su i anoksični uvjeti s izraženom produkcijom sulfida (Ciglenečki i sur., 2000 i 2003).

Makroagregati se najčešće pojavljuju u kasno proljeće ili rano ljeto kad započne razgradnja materijala proizašlog iz proljetnih cvatova fitoplanktona u uvjetima stratifikacije vodenog stupca te vrlo slabe izmjene vode između sjevernog i srednjeg Jadrana, povezano s razvojem istarske obalne protustruje (Djakovac i sur., 2012). Izmješavanje vodenog stupca npr. kao posljedica oluja, u kombinaciji s različitim hidrografskim, biokemijskim i mikrobiološkim procesima, na kraju ljeta razbijaju stratifikaciju te razbijaju nastale nakupine organskog materijala (Degobbis i sur., 1999).

1.4.Metode određivanja i karakterizacije organske tvari u prirodnim vodama

1.4.1. Visokotemperaturna katalitička oksidacija (HTCO)

Metode određivanja otopljenog i partikularnog organskog ugljika su se kroz povijest razvijale (metode mokre oksidacije, metode suhog izgaranja), dok se danas koristi visoko osjetljiva metoda visokotemperaturne katalitičke oksidacije uz nedispernu infracrvenu detekciju oksidacijom nastalog CO_2 (Sugimura i Suzuki, 1988; Dafner i Wangersky, 2002a; Dafner i Wangersky, 2002b).

Morska voda može predstavljati problematičan medij/matricu za oksidaciju organske tvari, pri čemu na preciznost analitičke metode utječe: niska koncentracija organskog ugljika u moru, visoka koncentracija anorganskog ugljika u moru (10 i više puta veća od organskog ugljika), kontaminacija tijekom uzorkovanja, pohrane uzoraka, pripreme za mjerenje te samog mjerenja, problemi prilikom određivanja slijepih proba postupka te nepotpuna oksidacija.

Prilikom određivanja organskog ugljika u morskoj vodi povoljniji katalizator platina na siliki zamijenio je prvotno korišten katalizator platinu na alumini. Cauwet (1994) je pokazao da Pt/alumina i Pt/silika imaju jednaku efikasnost oksidacije, ali se s katalizatorom na siliki dobivaju niže vrijednosti slijepe probe (Cauwet, 1994), zbog toga jer je silika kiseli oksid koji ima puno manji kapacitet adsorpcije CO_2, dok amfoterna alumina adsorbira znatno više oksidacijom nastalog CO_2, što stvara probleme u postizanju zadovoljavajuće vrijednosti slijepe probe (Dafner i Wangersky, 2002a).

Metodom visokotemperaturne katalitičke oksidacije moguće je postići nisku granicu detekcije organskog ugljika, no potrebna je izuzetna pažnja vezana uz čistoću svih koraka, od posuđa koje je potrebno prati u krom sumpornoj kiselini kako bi se efikasno uklonile sve organske nečistoće, preko filtracije na žarenim filterima.

1.4.2. Elektrokemijska metoda fazno osjetljive ac. voltametrije

Jedna od metoda kojom se može pratiti prisutnost površinski aktivnih tvari u moru je elektrokemijska tehnika fazno osjetljive voltametrije izmjenične struje.

Voltametrija je grana elektrokemije koja se razvila početkom 20. stoljeća, točnije 1922. godine. Češki kemičar Jaroslav Heyrovsky za to je otkriće 1959. godine dobio Nobelovu nagradu (Komorsky-Lovrić i Lovrić, 2007.). Opća karakteristika svih voltametrijskih tehnika jest da se informacije o količini i vrsti analita dobivaju mjerenjem struje kao funkcije potencijala narinutog na živinu kap kao elektrodu.

Općenito, prednosti voltametrijskih tehnika očituju se u relativno visokoj osjetljivosti određivanja koncentracija, relativno širokom linearnom rasponu koncentracija, brzini i jednostavnosti analize, istovremenom određivanju više različitih analita, te mogućnosti direktnog određivanja analita u uzorku bez prethodne pripreme ili obrade (Scholz, 2002).

Osnova za provođenje elektrokemijskog mjerenja je elektrokemijska ćelija koja se sastoji od radne, referentne i pomoćne elektrode. Kao radna elektroda obično se koristi sferična stacionarna eletroda viseća živina kap, kao referentna Ag/AgCl elektroda i platina kao pomoćna elektroda.

Živina elektroda je univerzalna radna elektroda zbog slijedećih fizičko-kemijskih karakteristika:

- u tekućem je stanju pri sobnoj temperaturi, te
- posjeduje veliku površinsku napetost i hidrofobnost površine elektrode.

Živa prolazi iz rezervoara kroz kapilaru na čijem se kraju zbog velike površinske napetosti stvaraju kapi. Glavna prednost kapajuće i viseće živine kapi elektrode je kontinuirano obnavljanje kapi i čista, uvijek nova površina elektrode. Reproducibilan nastanak čiste površine elektrode osnova je za pouzdano praćenje procesa adsorpcije površinski aktivnih spojeva kao i oksido-redukcijske procese.

Mjerenjem metodom fazno osjetljive voltametrije izmjeničnom strujom mogu se odrediti kapacitetna i faradejska struja (Ćosović, 1994). Kapacitetna struja je struja potrebna da se uspostavi određeni potencijal na elektrodi, a faradejska struja je struja potrebna za prijenos elektrona u oksido-redukcijskom procesu. Procesi adsorpcije organske tvari prate se kao sniženje kapacitetne struje koje se preko kalibracijske krivulje dovodi u vezu s koncentracijom prisutnih adsorbiranih površinski aktivnih tvari (Ćosović, 1994; Strmečki i sur., 2014).

Kod ove se tehnike elektroda polarizira na način da je izmjenični potencijal male amplitude najčešće sinusoidnog oblika superponiran na istosmjerni potencijal, a mjeri se nastala izmjenična struja u ovisnosti o istosmjernom potencijalu koji se linearno mijenja. Ova se eksperimentalna tehnika uspješno primjenjuje za praćenje adsorpcije površinski aktivnih tvari na površini elektrode koje izazivaju promjene kapaciteta električnog dvosloja dajući kao odziv izmjeničnu struju. Obzirom na nepolaran i hidrofoban karakter živine elektrode na granici faza živa/vodena otopina elektrolita ili uzorka, Hg elektroda se pokazala kao idealna površina na kojoj se adsorbiraju uglavnom hidrofobne površinski aktivne molekule organske tvari koje hidrofobnim interakcijama nastoje izbjeći kontakt s molekulama vode (Ćosović, 1994). Dobiveni rezultat adsorpcije, odnosno sniženja kapaciteta električnog dvosloja, predstavlja ukupni učinak svih prisutnih organskih tvari koje tijekom adsorpcije dođu na elektrodu.

Površinska aktivnost organske tvari obično se izražava se u ekvivalentima odabrane modelne neionske površinski aktivne tvari Triton X-100 (molekulske mase ~600 mg/L) koji se pokazao kao dobar predstavnik najreaktivnijeg dijela površinski aktivnih tvari u morskoj vodi (Ćosović i Vojvodić, 1982).

Dominantne komponente kompleksne smjese površinski aktivnih spojeva u moru grubo se mogu karakterizirati usporedbom krivulja ovisnosti kapacitetne struje o potencijalu elektrode za uzorak u odnosu na odabrane modelne tvari i smjese modelnih tvari (Vojvodić, 1991).

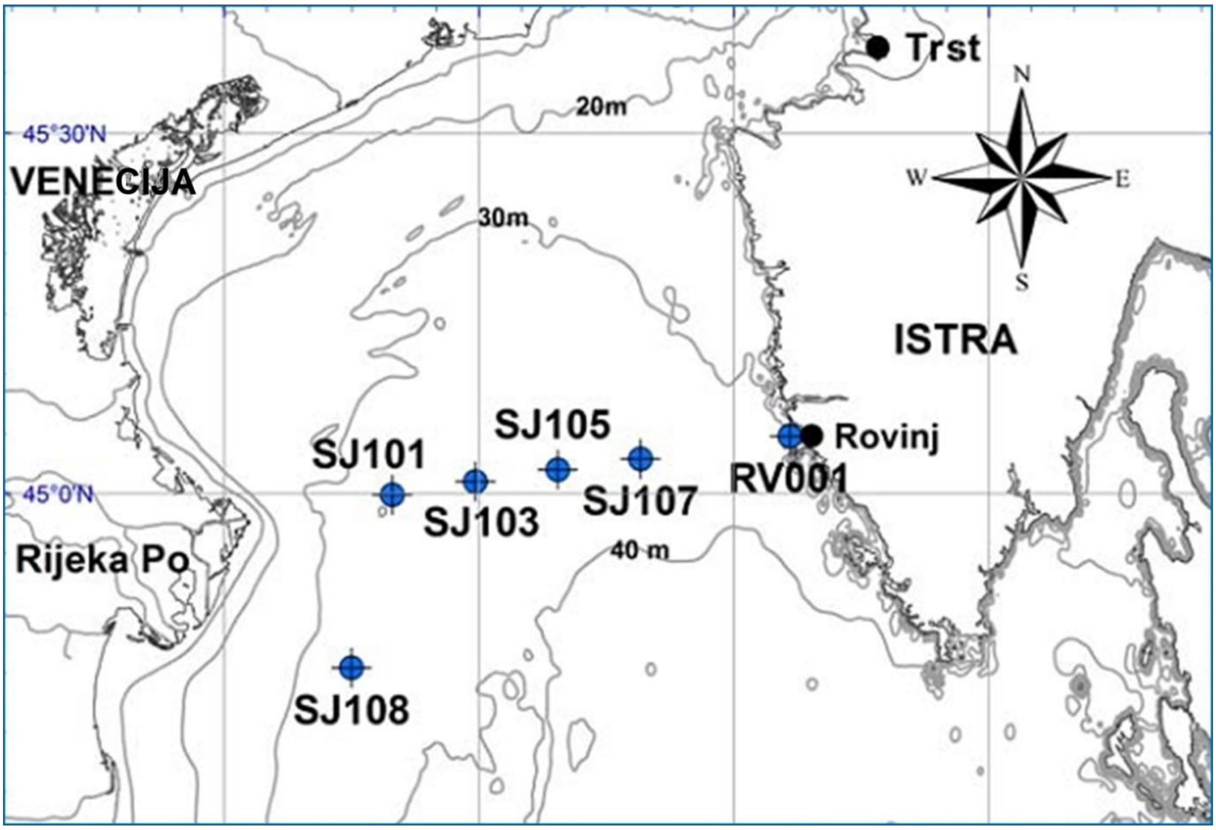
1.5. Područje istraživanja

U okviru ove disertacije istraživana su tri područja u Jadranu koja su pod različitim utjecajem unosa slatkih voda kao i različitih strujanja vodenih masa: sjeverni Jadran, Boka kotorska i albanski šelf (Slika 4).

Slika 4. Istraživana područja (označena crvenim): sjeverni Jadran, Boka kotorska i albanski šelf.

1.5.1. Sjeverni Jadran

Sjeverni Jadran plitko je poluzatvoreno područje pod jakim utjecajem donosa rijeke Po u zapadnom dijelu te pod utjecajem advekcije oligotrofnih voda srednjeg Jadrana u istočnom dijelu. Ovo područje karakterizira vrlo varijabilna i kompleksna cirkulacija (Orlić i sur., 1992; Supić i sur., 2000). U toplijem dijelu godine razvijaju se ciklonalni i anticiklonalni vrtlozi u području sjevernog Jadrana te istarska obalna protustruja što dovodi do zatvaranja anticiklonalne cirkulacije u području sjevernog Jadrana. Zimi prevladava opća ciklonalna cirkulacija, potpuno otvorena prema jugu (Supić i sur., 2000; Djakovac i sur., 2012). Najproduktivniji je dio Mediterana. Područje je epizodno eutrofno (Degobbis i sur., 1999), bogato hranjivim solima, primarno nitratima i fosfatima (Djakovac, 2003), što omogućuje intenzivno cvjetanje fitoplanktona, posljedica čega je nakupljanje organske tvari koja u povoljnim uvjetima može prerasti u velike nakupine, „mucilage aggregates“. U recentnim godinama vidljiva je oligotrofikacija ovoga područja (Djakovac i sur., 2012).



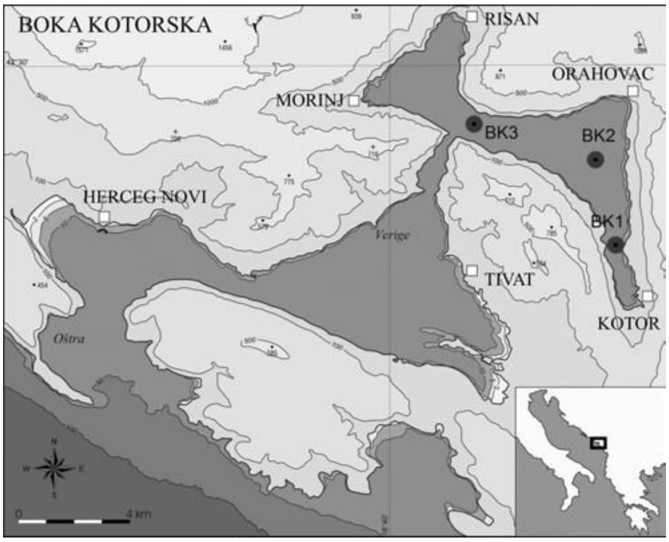
Slika 5. Postaje u sjevernom jadranu (profil Rovinj – ušće rijeke Po); SJ108 (44°45′24″N, 12°45′0″E); SJ101 (44°59′53″N, 12°49′48″E); SJ103 (45°1′0″N, 12°59′35″E); SJ105 (45°1′59″N, 13°9′18″E); SJ107 (45°2′52″N, 13°19′0″E); ZI032 (45°4′6″N, 13°30′54″E) i RV001 (45°4′48″N, 13°36′36″E).

Uz rijeku Po kao glavni izvor slatke vode (Janeković i sur., 2014; Supić i sur., 2004), u sjeverni Jadran se ulijevaju rijeke Soča i Adige, vode Venecijanske lagune, dotoci u području Trsta te manji potoci i podzemne vode duž Istarske obale.

Unos rijekama u sjeverni Jadran uglavnom je najveći u proljeće (svibanj-lipanj) i u jesen (listopad-studeni). Tijekom proljeća, otapanje leda čini većinu slatke vode koja dospijeva u sjeverni Jadran, dok u jesen količina te vode može biti jednako velika ali se radi uglavnom o oborinama, prvenstveno kiši. Unos slatke vode vrlo je varijabilan (Cozzi i Giani, 2011), pogotovo u posljednjih desetak godina.

1.5.2. Boka kotorska

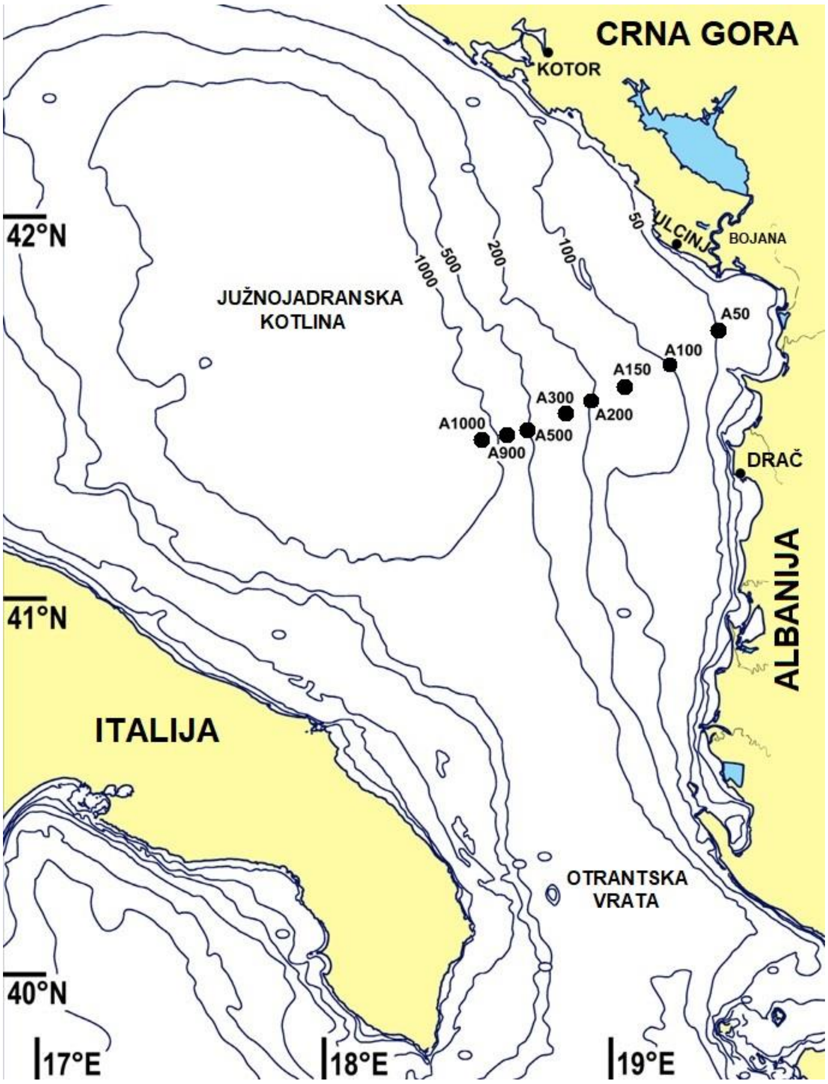
Boka kotorska (Slika 6) u južnom Jadranu pod izraženim je utjecajem slatke vode uslijed oborina, otapanja leda i podzemnih voda. Poviše zaljeva nalazi se geografska točka na kojoj su zabilježene najveće količine oborina u Europi (Crkvice, 4640 mm; Magaš, 2002; Ducić i sur., 2012). Slatka voda vrlo brzo prolazi kroz pukotine u krškom području te u obliku podzemnih voda ulazi u zatvoreni vodeni sustav zaljeva karakteriziran slabom izmjenom vode s otvorenim morem. Gradske otpadne vode također se ulijevaju u ovaj zaljev.



Slika 6. Postaje (označeno crnim točkama) u Boki kotorskoj.

1.5.3. Albanski šelf

2009. godine provedeno je istraživanje organske tvari na albanskom šelfu u području pod izrazitim utjecajem rijeka Bojane i Drima (Slika 7). Količina slatke vode koju donose albanske rijeke na jugu usporediva je s količinom koju u sjeverni Jadran donosi rijeka Po (Miho i sur., 2008; Cozzi i Giani, 2011). Cilj istraživanja bio je ispitati mogući antropogeni utjecaj iz poljoprivrede, industrije i gradskih otpadnih voda na kvalitetu vode albanskog šelfa.



Slika 7. Postaje (označeno crnim točkama) u albanskim vodama (profil A50-A1000).

Dinamika uzorkovanja triju istraživanih područja međusobno se razlikuju. Sjeverni Jadran istraživan je u vremenskom periodu od 28 godina (1989.-2017.) , pri čemu se dinamika mijenjala od sezonske do mjesečne u ranijim godinama, a od 1994. godine i u razdoblju 1998.-2011. dinamika uzorkovanja bila je konstantna, 10 do 12 puta godišnje (Tablica 1, Dautović i sur., 2017). Boka kotorska istraživana je kroz četiri sezone, od travnja 2008. do ožujka 2009. (Dautović i sur., 2012, koji je dio ove disertacije). Albanski šelf istraživan je jednokratno, u svibnju 2009. (Plavšić i sur., 2012, koji je dio ove disertacije).

2. Rasprava

Tri istraživana područja razlikuju se kako po sadržaju otopljenog organskog ugljika tako i po svojstvima/reaktivnosti organske tvari, što je vidljivo iz raspona i prosječnih vrijednosti izmjerenih koncentracija (Tablica 1). Rezultati dugoročnih istraživanja DOC, POC i PAT u sjevernom Jadranu, sezonska ispitivanja kroz jednu godinu u Boki kotorskoj, te jednokratno uzorkovanje na albanskom šelfu na jugu Jadrana omogućavaju komparativnu analizu raspodjele i svojstava organske tvari u području Jadranskog mora.

Najviše vrijednosti svih parametara izmjerene su u području sjevernog Jadrana, nakon čega slijedi područje Boke kotorske i na kraju područje albanskog šelfa (Tablica 1). Tablica 1 prikazuje uprosječene vrijednosti za čitav vodeni stupac, te vrijednosti za površinski i pridneni sloj. Za područje profila u sjevernom Jadranu posebno su istaknute vrijednosti parametara na zapadu (SJ108) te na istoku transekta (SJ107). Očekivano, najviše vrijednosti DOC/PAT/POC u sjevernom Jadranu mjerene su u površinskom sloju unutar kojega je opažena i najveća varijabilnost, s opadajućim trendom od zapada prema istoku. Što se tiče saliniteta uglavnom su najniže vrijednosti zabilježene u površinskom sloju, s trendom porasta od zapada prema istoku.

Tablica 1. Srednje vrijednosti i rasponi pojedinih parametara mjereni u tri istraživana područja

		S*1	**DOC mg/L**	**PAT F mg/L eq. T-X-100**	**PAT NF mg/L eq. T-X-100**	**POC mg/L**
sjeverni Jadran 1989-2017	srednja vrijednost	37,03	1,328	0,096	0,107	0,156
	raspon	8,17 - 38,88	0,769 - 7,160	0,015 - 0,650	0,010 - 1,220	0,013 - 3,026
sjeverni Jadran 1989–2017 0m	srednja vrijednost	35,45	1,499	0,116	0,137	0,269
	raspon	8,17 – 38,70	0,792 – 4,920	0,015 – 0,417	0,015 – 1,220	0,015 – 3,026
sjeverni Jadran 1989–2017 dno	srednja vrijednost	38,02	1,180	0,077	0,081	0,095
	raspon	36,00 – 38,88	0,769 – 4,010	0,015 – 0,034	0,015 – 0,415	0,013 – 0,428
SJ108 1989-2017	srednja vrijednost	36,29	1,365	0,105	0,120	0,206
	raspon	8,17 – 36,82	0,772 – 4,920	0,015 – 0,650	0,015 – 1,220	0,022 – 3,026
SJ107 1989-2017	srednja vrijednost	37,41	1,284	0,095	0,103	0,113
	raspon	28,25 – 38,70	0,784 – 4,200	0,015 – 0,272	0,015 – 0,382	0,013 – 0,707

Tablica 1, *nastavak*

		S*1	**DOC mg/L**	**PAT F mg/L eq. T-X-100**	**PAT NF mg/L eq. T-X-100**	**POC mg/L**
sjeverni Jadran 2002	srednja vrijednost	37,07	1,695	0,086	0,098	0,230
	raspon	13,01 - 38,49	1,020 - 3,250	0,017 - 0,215	0,025 - 0,330	0,033 - 1,945
sjeverni Jadran 2006	srednja vrijednost	37,71	1,068	0,081	0,086	-
	raspon	25,04 - 38,55	0,831 - 2,072	0,037 - 0,225	0,024 - 0,260	-
sjeverni Jadran 03/2008 - 05/2009	srednja vrijednost	37,09	1,089	0,084	0,090	0,158
	raspon	11,48 - 38,29	0,769 - 2,179	0,025 - 0,198	0,027 - 0,291	0,015 - 0,027
sjeverni Jadran 03/2008 - 05/2009 0m	srednja vrijednost	35,04	1,240	0,092	0,107	0,293
	raspon	11,48 – 38,07	0,890 – 2,180	0,043 – 0,191	0,045 – 0,291	0,015 – 1,797
sjeverni Jadran 03/2008 - 05/2009 dno	srednja vrijednost	38,02	0,990	0,076	0,080	0,102
	raspon	37,55 – 38,29	0,770 – 1,300	0,033 – 0,156	0,041 – 0,172	0,043 – 0,188
Kotor	srednja vrijednost	30,43	0,943	0,074	0,086	0,148
	raspon	5,20 - 37,00	0,641 - 1,425	0,031 - 0,198	0,035 - 0,256	0,041 - 0,591
Kotor 0m	srednja vrijednost	14,06	0,944	0,100	0,122	0,293
	raspon	5,20 – 27,30	0,641 – 1,425	0,036 – 0,199	0,054 – 0,256	0,091 – 0,591
Kotor dno	srednja vrijednost	36,16	0,921	0,058	0,066	0,083
	raspon	35,30 – 37,00	0,809 – 1,008	0,031 – 0,082	0,039 – 0,092	0,041 – 0,183
Albanija	srednja vrijednost	38,04	0,869	0,045	0,045	0,053
	raspon	33,82 - 38,80	0,721 - 1,051	0,027 - 0,076	0,026 - 0,078	0,007 - 0,194
Albanija 0m	srednja vrijednost	36,61	0,989	0,064	0,067	0,101
	raspon	33,82 – 38,17	0,898 – 1,051	0,051 – 0,076	0,054 – 0,078	0,063 – 0,194
Albanija dno	srednja vrijednost	38,60	0,795	0,036	0,034	0,028
	raspon	38,18 – 38,80	0,727 – 0,945	0,027 – 0,048	0,026 – 0,046	0,012 – 0,054

Rezultati ukazuju da je sjeverni Jadran najproduktivnije od sva tri uzorkovana područja, epizodno eutrofan, naročito na području pod direktnim utjecajem rijeke Po, a mezotrofan kada se taj utjecaj proširi i prema istočnim postajama, u skladu s literaturom (Degobbis i sur., 2005; Precali i sur., 2005; Djakovac i sur., 2012; Dautović i sur., 2017 koji je dio disertacije), Boka kotorska je klasificirana kao oligo-mezotrofno područje (Krivokapić i sur., 2011; Dautović i sur., 2012, koji je dio ove disertacije), dok je albanski shelf epizodno mezotrofan (Marini i sur., 2015).

2.1. Organska tvar u sjevernom Jadranu

Sjeverni Jadran istraživan je u vremenskom razdoblju od 28 godina, 1989.-2017. na postajama profila Rovinj – ušće rijeke Po (Slika 5). Uzorci su skupljani na 5-6 dubina s dinamikom naznačenom u tablici 1 (rad Dautović i sur., 2017, u privitku ovog doktorata).

Statističkom analizom odabranog podskupa podataka prikupljenih kroz period od 15 godina (1994., 1998.-2011.) utvrđeni su trendovi vremenske i prostorne raspodjele otopljenog organskog ugljika. U smislu sezonske distribucije, otopljeni organski ugljik akumulira se tijekom proljeća, dostiže maksimum u ljeto, te mu se smanjuje koncentracija tijekom jeseni i zime (kao godina s tipičnom sezonskom raspodjelom DOC ističe se 2009. godina, vidi niže). U smislu uobičajene prostorne distribucije, sadržaj otopljenog organskog ugljika opada od zapada prema istoku profila Rovinj – ušće rijeke Po, te opada s dubinom vodenog stupca (Tablica 1).

Dugoročna istraživanja otopljenog organskog ugljika pokazala su vrlo izražene međugodišnje oscilacije (rad Dautović i sur., 2017., dio ovog doktorata), s dvije osnovne značajke: područje sjevernog Jadrana je predominantno oligotrofnih karakteristika (1993.-1995., iza 2004. pa praktički sve do danas) s kratkotrajnim, ali izraženim mezotrofnim i eutrofnim epizodama (1991., 1997., 2000.-2004.), uz pojavu cvjetanja mora obilježenog stvaranjem gustih, prostorno često velikih sluzavih nakupina (mucilaginous aggregates) i desetak kilometara dugih želatinoznih slojeva širokih nekoliko stotina metara (Precali i sur., 2005).

Prosječna vrijednost otopljenog organskog ugljika i raspon izmjerenih koncentracija značajno se razlikuju za oligotrofni period 2005.-2016. (1,159 mg/L, 0,069-2,442 mg/L) u odnosu na eutrofne godine 2000.-2004. (1,469 mg/L, 0,920-3,980 mg/L). U čitavom istraživanom periodu (1989.-2017.) opažamo padajući trend DOC.

Ovi rezultati su u dobrom slaganju s drugim provedenim istraživanjima o oligotrofikaciji Jadrana: sniženje koncentracije klorofila *a* (Mozetič i sur., 2010), ortofosfata

(Solidoro i sur., 2009), povišenje saliniteta i sve rjeđa uspostava ciklonalne cirkulacije (Djakovac i sur., 2012) te promjena dominantnih fitoplanktonskih vrsta sa dominacijom vrsta sve manjih dimenzija stanica (Mozetič i sur., 2012; Gašparović i sur., 2012; Mikac, 2013; Godrijan, 2015). Konkretno, Djakovac i suradnici (2012) navode smanjenje koncentracije ortofosfata, uslijed smanjenog unosa nutrijenata rijekom Po te povećane izmjene vodenih masa između SJ i srednjeg Jadrana (jačanje istočnojadranske struje, eng. EAC nad istarskom obalnom protu-strujom, ICCC) kao glavne razloge za pojavu oligotrofikacije u SJ u periodu od 2000-2009.

Prema statističkim modelima definirana su tri karakteristična tipa godišnje distribucije otopljene organske tvari predstavljenih 2002., 2006. i 2009 godinom. 2002. godina karakterizirana je povišenim sadržajem otopljenog organskog ugljika kroz sve mjesece u godini bez izraženih sezonskih kolebanja ali s uobičajenim trendom opadanja koncentracija od površine prema dnu. 2006. godina karakterizirana je vrlo niskim sadržajem DOC uz definirana sezonska kolebanja, s porastom sadržaja DOC u proljeće i u jesen i to samo u površinskom sloju mora, dok su na ostalim dubinama koncentracije jednolično raspodijeljene (0,900-1,200 mg/L). U 2009. godini akumulacija sadržaja DOC počinje u proljeće, najveća je u ljeto, nakon čega koncentracije opadaju do zime, što predstavlja najčešću sezonsku raspodjelu DOC na ispitivanim postajama.

Nadalje, statistička analiza ukazala je na dvije statistički značajne postaje ispitivanog profila, SJ108 na zapadnoj i SJ107 na istočnoj strani profila ušće rijeke Po - Rovinj. Postaja SJ108 je pod najvećim, a postaja SJ107 pod najmanjim utjecajem rijeke Po (Slika 5). U tri gore spomenute godine (2002., 2006. i 2009.) na obje postaje opažene su iste sezonske raspodjele, samo što su na postaji SJ108 zbog značajnog utjecaja slatke vode pikovi pravih vrijednosti u cijelom vodenom stupcu povećani u odnosu na postaju SJ107 te se pojavljuju i u dubljim slojevima a ne samo u površinskom sloju kao na postaji SJ107.

Uz ispitivanje raspodjele DOC određivana su i svojstva, odnosno reaktivnost prisutne organske tvari u sjevernom Jadranu. U tu svrhu elektrokemijski su određene koncentracije ukupnih i otopljenih površinski aktivnih tvari (PAT NF i PAT F). Uočene su oscilacije PAT i u vremenskom i u prostornom smislu u cijelom razdoblju ispitivanja, no u okviru ovog doktorskog rada koristiti će se samo rezultati promjena svojstava otopljene organske tvari definirani odnosom PAT F/DOC, odnosno vrijednosti normalizirane površinske aktivnosti, NPA=PAT F/DOC. Usporedba NPA vrijednosti uzoraka s NPA vrijednostima odabranih modelnih površinski aktivnih tvari reprezentativnih za prirodno prisutan organski materijal u moru, omogućuje grubu karakterizaciju reaktivnosti prisutne organske tvari kao i usporedbu promjena tih svojstava tijekom utvrđenih vremenskih i prostornih kolebanja ukupne otopljene organske tvari u sjevernom Jadranu.

Slika 8. pokazuje odnos PAT F i DOC u SJ za odabrane godine 2002., 2006. i za razdoblje od 03/2008. do 05/2009. unutar kojega su istraživani Boka kotorska i albanski šelf. Vidljivo je da se vrijednosti grupiraju različito oko odabranih modela u pojedinim godinama, što ukazuje na različitost tipa dominantno prisutnog organskog materijala, odnosno različitost reaktivnosti prisutne organske tvari.

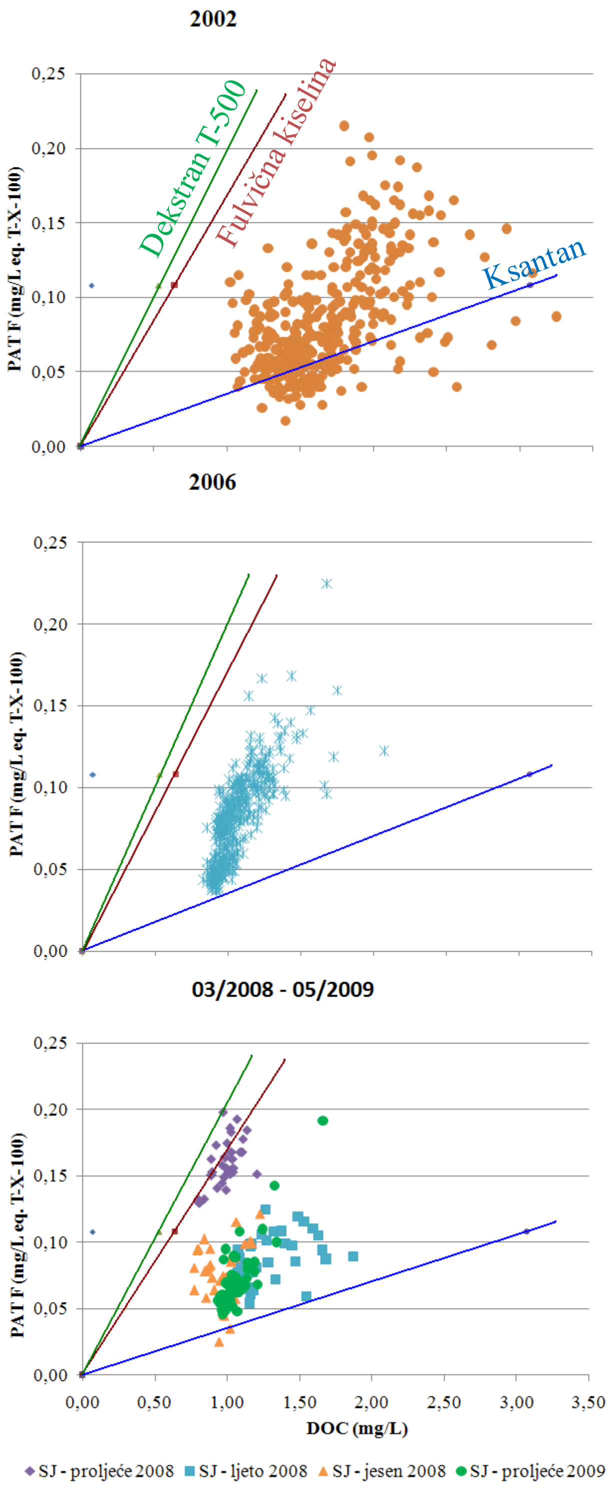
Točke se u 2002. godini u SJ grupiraju bliže modelnoj površinski aktivnoj tvari ksantanu već opisanih karakteristika, što ukazuje na hidrofilniji, manje adsorbabilan i slabije reaktivan materijal uz prosječnu vrijednost NPA od 0,051. U toj je godini zabilježena vrlo izražena akumulacija organskog materijala kao posljedica cvjetanja mora praćena stvaranjem velikih sluzavih nakupina organske tvari (mucilage-a). Kako je već opisano, u istom području sadržaj DOC bio je visok kroz cijelu godinu bez izraženijih sezonskih oscilacija.

Važno je napomenuti kako su uzorci obogaćeni mukoznim nakupinama u SJ tijekom 2000. i 2001. bili obogaćeni prisustvom dijatomeje *Cylindrotheca closterium* (Najdek i sur., 2005), čiji je uzgoj u laboratorijskim uvjetima pokazao produkciju površinski aktivnog organskog materijala s NPA vrijednostima od 0,04 na početku rasta do 0,08 kada je kultura bila na vrhuncu eksponencijalnog rasta (Ciglenečki i sur., 2019 *in press*).

Koncentracije PAT F u 2006. godini ne razlikuju se značajnije u odnosu na 2002. (Tablica 1) dok su koncentracije DOC bile značajno niže. Prisutna organska tvar je uz višu prosječnu vrijednost NPA u odnosu na 2002. (0,075) adsorbabilnija, reaktivnija, po svojstvima bliža modelnoj tvari fulvičnoj kiselini (Slika 8).

Prosječna vrijednost NPA za razdoblje od 03/2008. do 05/2009. najviša je od prosjeka svih do sad navedenih godina i iznosi 0,079, ukazujući na prisustvo reaktivnijeg organskog materijala. Od sezone do sezone opažene su očekivane promjene u svojstvima/reaktivnosti prisutne organske tvari, a posebno u proljetnom razdoblju 2008. i 2009. (prosječan NPA u proljeće 2008. iznosi 0,121, a u proljeće 2009. skoro je dvostruko niži i iznosi 0,065; Slika 8). U proljeće 2009. pojavljuje se u prosjeku hidrofilniji, manje reaktivan otopljeni površinski aktivni materijal u SJ u odnosu na proljeće 2008. godine. Takvi rezultati najvjerojatnije ukazuju na promjene u sastavu i vrstama fitoplanktonskih zajednica, kao na primjer promjena u sastavu fitoplanktonskih zajednica od primnezioficeja u proljeće 2008. godine do dijatomeja u 2009. godini (Žutić i sur., 1981; Kraus i Supić, 2011; Ivančić i sur., 2012; Mozetič i sur., 2012; Mikac, 2013; Godrijan, 2015), koje su osnovni izvori svježe OT u SJ. U novije vrijeme opažena je dominacija flagelata, za razliku od ranije kad su dominirale dijatomeje (Ciglenečki i sur., 2019 *in press*).

Normalizirana površinska aktivnost na SJ108 na zapadnoj strani transekta kreće se u rasponu 0,006 – 0,363, te je u pravilu viša u odnosu na postaju SJ107 (0,009 – 0,183). Reaktivniji, adsorbabilniji materijal opažamo na postaji SJ108 koja je najviše izložena utjecaju slatke vode koju donosi rijeka Po.



Slika 8. Odnos PAT F - DOC u sjevernom Jadranu za odabrane godine (sve postaje i sve dubine profila Rovinj - Po).

Uz DOC i PAT, partikularni organski ugljik (POC) u sjevernom Jadranu određivan je sustavno kao dodatan, važan parametar u razdoblju 2008.-2017. godine (neobjavljeni podaci). Kao i kod otopljene frakcije, dinamika promjena sadržaja najizraženija je u površinskom sloju

(0,015-3,026 mg/L). Maksimalne prosječne vrijednosti POC redovito se pojavljuju u proljeće i u jesen, što je vezano uz donos slatke vode rijekom Po te povećanom produkcijom zbog unosa hranjivih soli. Najveća prosječna vrijednost zabilježena je u proljeće 2014. (0,75 mg/L), a najniža u zimi 2012. (0,08 mg/L). Iako svi rezultati DOC ukazuju na iscrpljivanje organske tvari, odnosno oligotrofikaciju u razdoblju 2008.-2011., povremeno odstupanje, odnosno povišenje prosječnih vrijednosti DOC, kao i POC zabilježene su u ljetnim mjesecima i u jesen 2008. te u proljeće 2017. (POC do 0,500 mg/L). Dobiveni rezultati u dobrom su slaganju s ranijim istraživanjima POC u sjevernom Jadranu (Gilmartin i Revelante, 1991; Giani i sur., 2005).

Udio POC u ukupnoj organskoj tvari u sjevernom Jadranu kretao se u vrlo širokom rasponu od 1% do 61%, s prosječnim udjelom partikularnog organskog ugljika od 10%. Udio ispod 5% i iznad 20% opažen je u 12% slučajeva, što znači da se udio partikularnog organskog ugljika u sjevernom Jadranu najčešće kreće u granicama 5-20%, značajno iznad prosjeka za svjetska mora i oceane od 3% (Hansell i Carlson, 2002). Time je još jednom potvrđeno da je sjeverni Jadran produktivno područje Mediterana.

Uz sve ranije spomenute čimbenike koji utječu na raspodjelu organske tvari u Jadranskom moru, razmotreni su i utjecaji hidrografskih uvjeta te cirkulacije voda koji su pod snažnim utjecajem klimatskih varijabilnosti i ljudskih djelatnosti.

Dugoročna istraživanja otopljene organske tvari (DOC) u Jadranu omogućila su usporedbu trendova kroz skoro tri desetljeća. Pokazano je u grubo kako saliniteti u Jonskom moru na dubini od 800m i sjevernom Jadranu pokazuju iste trendove na dugogodišnjoj skali.

U razdoblju od 1997. do 2006. u sjevernom Jonskom moru bila je prisutna ciklonalna cirkulacija (Gačić i sur., 2010), za vrijeme koje vrijednosti saliniteta u Jonskom i Jadranskom moru pokazuju isti uzlazni trend (slika 4 u radu Dautović i sur., 2017, koji je dio ove disertacije).

Indikativno je da se trendovi otopljenog organskog ugljika poklapaju s promjenama cirkulacije: u vrijeme ciklonalne cirkulacije i unosa vode visokog saliniteta iz Jonskog mora u Jadran istovremeno je detektiran porast saliniteta i u sjevernom Jadranu koji prati sniženje otopljenog organskog ugljika.

Nakon 2006. godine anticiklonalna cirkulacija unosi u Jadran atlantsku vodu nižeg saliniteta bogatiju nutrijentima, što je popraćeno padajućim trendom saliniteta u sjevernom Jadranu i povećanjem sadržaja otopljenog organskog ugljika (Dautović i sur., 2017 koji je dio ove doktorske disertacije). U razdoblju 2011. do 2017. u sjevernom Jonskom moru dominira ciklonalna cirkulacija. Zadnja promjena cirkulacije dogodila se u 2017. godini, ciklonalna u anticiklonalnu (osobno priopćenje Milena Menna, THEMES 2018).

Dobro podudaranje različitih cirkulacija i trendova promjena sadržaja i svojstava prisutne otopljene organske tvari u različitim periodima jasno ukazuje da na događaje/procese u sjevernom Jadranu utječu dva faktora: 1.) unos slatke vode koja dolazi rijekom Po, što može rezultirati uspostavljanjem istarske obalne protustruje koja slatku vodu može donijeti sve do istarske obale (Djakovac i sur., 2012) i 2.) utjecaj različitih vodenih masa koje kao posljedica BiOS mehanizma ulaze u Jadran (Gačić i sur., 2010; Vilibić i sur., 2013). S obzirom da je u periodu od 2000. do 2009. smanjeni unos slatke vode u sjeverni Jadran rijekom Po (Cozzi i Giani, 2011), dugoročna istraživanja DOC pokazala su da u tom periodu unos vode iz Jonskog mora ima važan, ako ne i prevladavajući utjecaj na događaje/procese u sjevernom Jadranu.

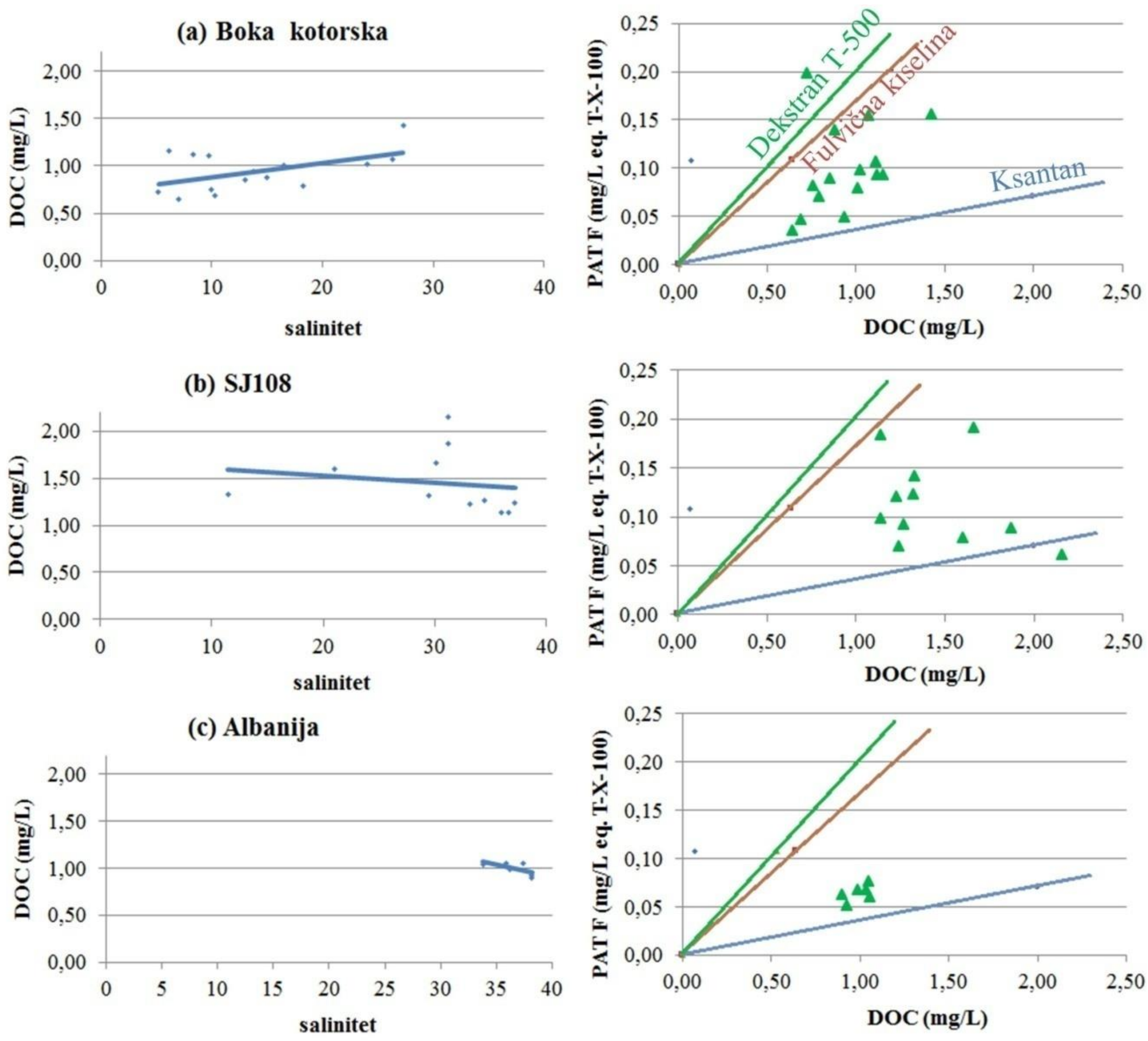
Utjecaj BiOS-a na Jadran vidljiv je također i po prisutnosti organizama koji su alohtoni u različitim mediteranskim vodenim masama, a čija se prisutnost u Jadranu upravo podudara s razdobljima ciklonalne i anticiklonalne cirkulacije u Jonskom moru (Civitarese i sur., 2010; Batistić i sur., 2014).

2.2. Organska tvar u izdvojenom, krškom južnojadranskom zaljevu (Boka kotorska)

Dinamika promjena sadržaja i svojstava organske tvari u Boki kotorskoj istraživana je u vremenskom razdoblju od jedne godine, sa sezonskom dinamikom od proljeća 2008. do proljeća 2009., na tri postaje unutar zaljeva (Slika 6). Uzorci su skupljani na 5-6 dubina.

Trendovi opaženi tijekom dugoročnih istraživanja sjevernog Jadrana primjećeni su također i u području Boke kotorske, istraživane u navedenom jednogodišnjem razdoblju. Otopljeni organski ugljik slijedi uobičajenu sezonsku distribuciju: nakupljanje u proljeće (0,641-1,219 mg/L, prosjek 0,894 mg/L), maksimum u ljetnim mjesecima (0,902-1,425 mg/L, 1,018 mg/L), te sniženje s dolaskom jeseni (0,933-1,153 mg/L, 1,017 mg/L). Specifična je pojava koja karakterizira ovo područje u stupcu morske vode detektirana u proljetnim mjesecima (4/2008. i 3/2009.). Naime, tada je koncentracija DOC u površinskom sloju niža nego u dubljim slojevima vodenog stupca (slika 4a i slika 6 u radu Dautović i sur., 2012, koji je dio ovog doktorata). Partikularni organski ugljik kretao se u rasponu 0,041-0,591 mg/L, a udio partikularnog u ukupnom organskom ugljiku iznosio je 4% do 43% s prosječnom vrijednosti od 13%.

Utjecaj slatke vode u Boki kotorskoj vrlo je kompleksan – vrulje prevladavaju u ljeto, oborine u jesen, a otapanje leda u proljetnim mjesecima. Različiti utjecaji slatke vode na pojedina ispitivana područja vidljivi su iz odnosa salinitet-DOC u površinskom sloju (Slika 9a i 9b).



Slika 9. Odnos sal-DOC i DOC-PAT F u (a) Boki kotorskoj, (b) sjevernom Jadranu (postaja SJ108) i (c) Albaniji; površinski sloj.

U Boki kotorskoj taj je odnos pozitivan, odnosno s porastom saliniteta raste i koncentracija DOC. U sjevernom Jadranu odabrana je postaja SJ108 koja je pod najvećim utjecajem dotoka slatke vode rijekom Po (Slika 5). Na toj postaji vidimo obrnuto proporcionalan odnos salinitet-DOC, što znači da s porastom saliniteta opada DOC. Nadalje, vidljiva je razlika u tipu materijala prisutnog u površinskom sloju ovih dvaju područja (Slika 9). U Boki kotorskoj vrijednosti se grupiraju bliže modelnim tvarima fulvičnoj kiselini i dekstranu, što ukazuje na hidrofobniji, adsorbabilniji, po svojstvima reaktivniji materijal. U sjevernom Jadranu u istom tom periodu prisutan je manje reaktivan organski materijal, po svojstvima bliži modelnoj tvari polisaharidu ksantanu.

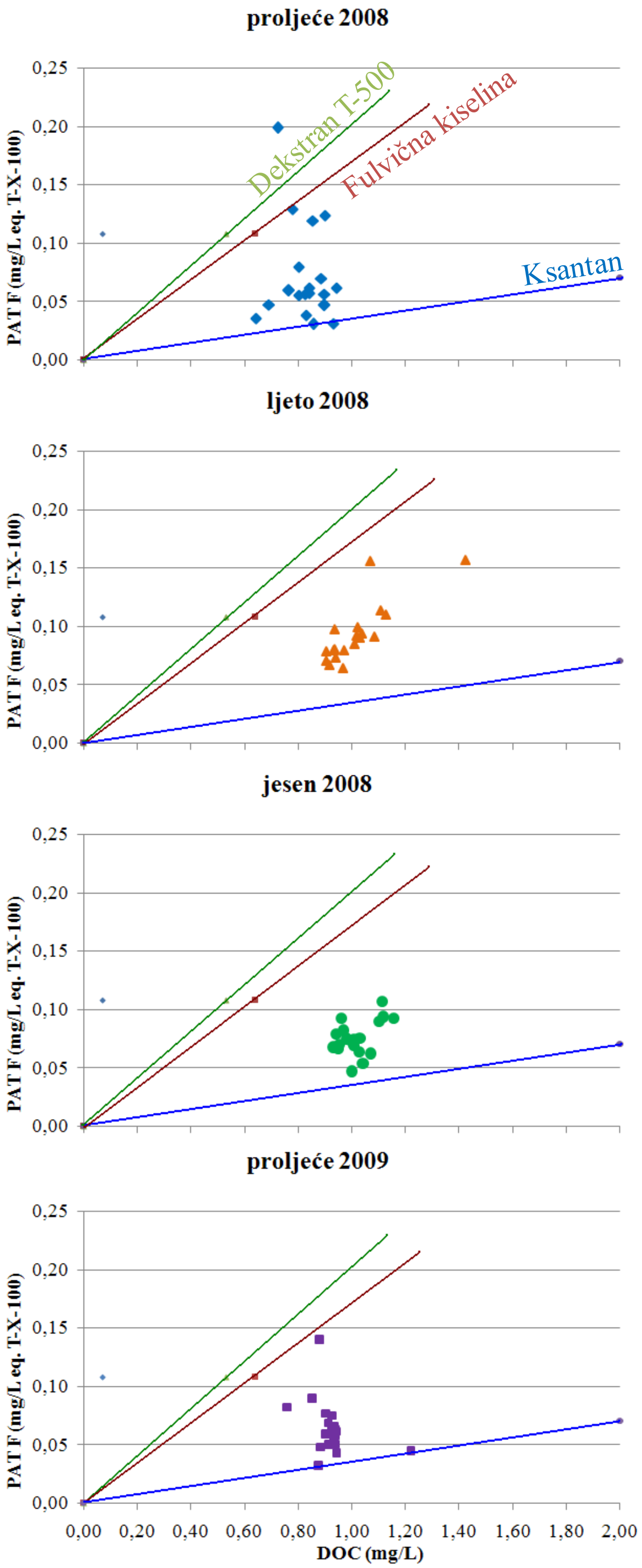
Slatka voda dospjela putem vrulja siromašna je organskom tvari i pri transportu od dna prema površini razrijeđuje/pročišćava ovaj zatvoreni sustav sa slabom izmjenom vode u zaljevu s okolnim morem. Visoke vrijednosti PAT NF (0,035-0,256 mg/L eq.T-X-100) te činjenica da je 67% vrijednosti NPA veće od 0,12, ukazuju na visoku reaktivnost organskog materijala u Boki kotorskoj. Za usporedbu, u sjevernom Jadranu preko 90% vrijednosti NPA nalaze se unutar raspona 0,04-0,12.

Budući da je reaktivnost prisutne organske tvari velika, vjerojatno se organska tvar uklanja iz vodenog stupca dovoljno brzo da ne dolazi do značajnije akumulacije koja bi mogla dovesti do eutrofikacije.

Rezultati istraživanja organske tvari u Boki kotorskoj uspoređeni su s rezultatima dobivenima u sjevernom Jadranu za isti period. Koncentracije svih mjerenih parametara u zaljevu niže su i po rasponu i po srednjim vrijednostima u odnosu na sjeverni Jadran u istom vremenskom periodu (Tablica 1).

Otopljeni organski ugljik kretao se u rasponu 0,641-1,425 mg/L, s prosječnom vrijednosti 0,943 mg/L. Raspon koncentracija DOC u sjevernom Jadranu u istom periodu značajno je širi (0,769 – 2,179 mg/L), dok se PAT F izmjeren u ovom području ne razlikuje puno od raspona istog parametra u sjevernom Jadranu (Tablica 1).

Usporedba koncentracija DOC i PAT F prikazanih na slici 10 ukazuje na izraženije promjene reaktivnosti i tijekom različitih sezona u SJ u odnosu na svojstva/reaktivnost opaženu u Boki kotorskoj (slike 8 i 10).



Slika 10. Odnos PAT F - DOC u Boki kotorskoj (sve postaje, sve dubine).

2.3.Organska tvar u jugoistočnom Jadranu (albanski šelf)

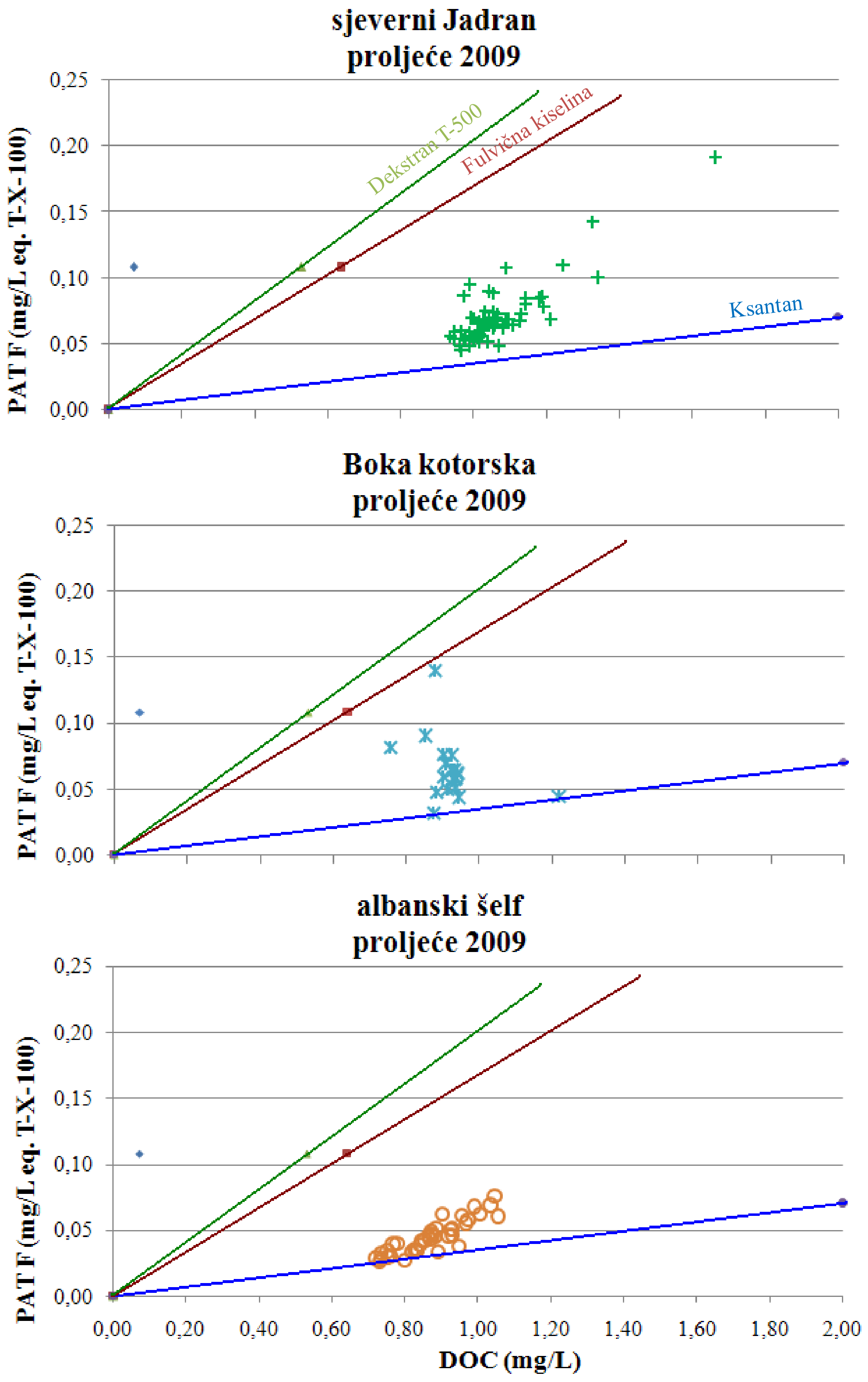
Organska tvar u albanskom šelfu istraživana je u svibnju 2009. na 8 postaja profila A50-A1000 (Slika 7). Uzorci su skupljani na 4-8 dubina (detalji u radu Plavšić i sur., 2012, koji je dio ovog doktorata).

Utjecaj slatke vode u ovom području vidljiv je iz obrnuto proporcionalnog odnosa između DOC i saliniteta u svibnju 2009. (Slika 9c) te iz ranije utvrđene negativne korelacije chl a i saliniteta (Marini i sur., 2015). U dobrom su slaganju s navedenim i drugi rezultati ispitivanja prikazani u radu Plavšić i sur. (2012) koji je dio ove disertacije: povišene koncentracije nutrijenata anorganskog dušika i fosfora, dok su visoke koncentracije ortosilikata koji dospijevaju rijekom Bojanom specifičnost ovog sustava. S druge strane, koncentracija organske tvari dospjela riječnim unosom procijenjena je kao relativno niska (Plavšić i sur., 2013, koji je dio ovog doktorata).

Raspon koncentracija DOC najmanji je u albanskom obalnom području (0,721 – 1,051 mg/L) u odnosu na preostala dva istraživana sustava.

Prosječna NPA vrijednost za albanski šelf (0,051) manja je u odnosu na ranije navedenu prosječnu vrijednost za sjeverni Jadran i Boku kotorsku (0,079). Grafički prikaz koncentracija DOC i PAT F za sva tri istraživana područja provedena u proljeće 2009. (Slika 11, Slika 9c) pokazuje da se u Albaniji i sjevernom Jadranu koji su pod utjecajem velikih rijeka nalazi sličniji tip otopljenog organskog materijala u odnosu na Boku kotorsku, koja je izložena slatkim vodama u obliku vrulja i padalina u kojima je organska tvar po svojstvima reaktivnija (Slika 11).

Iako su Marini i suradnici zatekli oligotrofne do mezotrofne uvjete u kasno proljeće (lipanj 2008.), istraživanje provedeno u okviru ove doktorske disertacije potvrdilo je oligotrofne uvjete u području pod utjecajem rijeke Bojane u svibnju 2009. U ovom istraživanom području zatekli smo relativno nizak sadržaj svježe proizvedene organske tvari, što je vidljivo po niskim koncentracijama PAT NF (0,026 – 0,078 mg/L) koja je bila uglavnom u otopljenoj formi i gotovo istih koncentracijskih raspona kao i PAT F (0,027-0,076 mgL).



Slika 11. Odnos PAT F - DOC u proljeće 2009 – usporedba triju istraživanih područja.

Partikularni organski ugljik kretao se u rasponu 0,007-0,194 mg/L, što je najniži raspon koncentracija od svih istraživanih područja. Udio partikularnog u ukupnome organskome ugljiku kretao se u rasponu od 1-16% s prosječnim udjelom od 5%, što je najniži udio u odnosu na rezultate iz sjevernog Jadrana (10%) i Boke kotorske (13%).

Istraživanja su također obuhvatila slatkovodne sustave rijeka Bojana i Drim, Skadarsko jezero te dvije lagune. Ispitivana je, uz ostale parametre (Tablica 1 u radu Plavšić i sur., 2013, koji je dio ove disertacije) i raspodjela te svojstva prisutne organske tvari (DOC, POC, PAT), s posebnim naglaskom na rijeku Bojanu koja predstavlja najveći dotok slatke vode u južni Jadran, usporediv s unosom rijeke Po u sjevernom Jadranu. Ta su istraživanja pokazala da je sadržaj organske tvari (DOC) u rijeci Bojani niži u usporedbi s rijekom Po (Pettine i sur., 1998; Cozzi i Giani, 2011; Plavšić i sur., 2013, koji je dio ove disertacije), dok su u albanskim rijekama izmjerene velike količine ukupne suspendirane tvari (TSS) što ukazuje na visoku brzinu erozije uglavnom silikatnog materijala okolnog područja.

Postaje iznad Skadarskog jezera karakterizira vrlo niski sadržaj organskog ugljika, kako otopljenog tako i partikularnog.

U dvije lagune pod utjecajem morske vode te rijeci Drim izmjerene su najviše koncentracije ispitivanih parametara.

Osim najnižih vrijednosti DOC u Bojani i obalno područje Albanije pod utjecajem te slatke vode puno je siromašnije organskom tvari u usporedbi s područjem sjevernog Jadrana. Tome također doprinosi i dubina mora, otvorena cirkulacija, odnosno unos vodenih masa iz Jonskog mora.

Utjecaj slatke vode na tri odabrana istraživana područja

Jedan od ciljeva ovoga rada jest usporediti istraživana tri područja s obzirom na različite izvore slatke vode koji na njih utječu. Različiti tipovi slatkih voda imaju različit utjecaj na istraživane sustave u Jadranskom moru.

Rijeke Po i Bojana usporedive su po količini slatke vode koju unose u more, no razlikuju se po količini unesenog organskog materijala i nutrijenata (Cozzi i Giani, 2011; Miho i sur., 2008). Cozzi i suradnici navode da je median za koncentracije DOC u rijeci Po u periodu 1995.-2007. 2,14 mg/L (Cozzi i Giani, 2011), dok je maksimalna vrijednost izmjerena u okviru izrade ove disertacije 1,36 mg/L (na postaji iznad Skadarskog jezera), iz čega proizlazi da Po donosi puno više organskog materijala u Jadran u odnosu na albanske rijeke. Povrh riječnog unosa slatke vode, i režim cirkulacije je bitno različit na odabranim područjima juga i sjevera. Albansko priobalje definira 'otvorena' cirkulacija kroz Otrant, dok je sjeverni Jadran uvučeno, poluzatvoreno, puno pliće područje koje karakterizira kompleksna cirkulacija (ciklonalna/anticiklonalna). Krški reljef koji okružuje zatvorenu Boku kotorsku u more donosi slatku vodu siromašnu organskom tvari i nutrijentima koji potječu s kopna (Krivokapić, 2005). Boka kotorska ima vrlo slabu izmjenu vode s okolnim morem.

Istraživanja rađena u okviru ove disertacije pokazala su povezanost dinamike promjena organske tvari s promjenama u Jonskom moru te je pokazano da na obalno more uz lokalni utjecaj slatke vode mogu utjecati i vodene mase donesene s velike udaljenosti iz Mediterana. Potrebno je nastaviti istraživanja u smislu detaljnijeg povezivanja dinamike promjena organske tvari u Jadranskom moru s raznim globalnim utjecajima, kako hidrografije tako i biologije te drugih grana vezanih uz ekosustav Jadranskog mora.

3. Zaključak

1. Dugoročna istraživanja organske tvari (otopljeni organski ugljik, partikularni organski ugljik, i površinski aktivne tvari) u poluzatvorenom, biološki produktivnom plitkom bazenu sjevernog Jadrana (SJ) pokazuju vrlo izražene promjene u količini i svojstvima. Tijekom istraživanih godina izmjenjuju se razdoblja visokog i niskog sadržaja organskog ugljika te promjena reaktivnosti, ukazujući na eutrofnost i učestaliju oligotrofnost područja SJ.
2. Promjene u koncentraciji i svojstvima organske tvari u SJ na dugoročnoj skali posljedica su: a) godišnjih kolebanja donosa slatke vode, uglavnom rijekom Po i b) cirkulacije vodenih masa u Jadranu uvjetovane takozvanim BiOS sustavom (interakcija izmedju Jonskog i Jadranskog mora koja dovodi do unosa različitih vodenih masa u Jadran).
3. Promjene sadržaja i svojstava organske tvari u sjevernom Jadranu podudaraju se s drugim dugogodišnjim istraživanjima koja ističu značajne promjene u ekosustavu SJ (količina nutrijenata, vrsta, veličina i brojnost planktonskih organizama te uspostava istarske obalne protustruje, sastav i vrsta fitoplanktonskih zajednica).
4. U cijelom razdoblju istraživanja 1989.-2017. u SJ uočen je generalni trend smanjenja sadržaja otopljene organske tvari.
5. Godine 2002., 2006. i 2009. predstavljaju tri karakteristična tipa sezonskih raspodjela sadržaja DOC: u prvom slučaju (2002.) sadržaj otopljenog organskog ugljika izrazito je visok kroz cijelu godinu, bez izraženih sezonskih kolebanja i s eutrofnim karakteristikama, u drugom slučaju (2006.) koncentracije DOC izrazito su niske, uz uznapredovali proces oligotrofikacije, a u okviru tih vrijednosti povišen DOC opažen je u proljeće uz maksimum u kasno ljeto/jesen, dok u trećem slučaju (2009.), inače najčešće zastupljenoj sezonskoj raspodjeli u SJ, porast DOC počinje u proljeće, dodatna akumulacija i dostizanje maksimuma u ljeto i opadanje koncentracija od jeseni do zime.
6. Sadržaj otopljenog organskog ugljika smanjuje se od zapadne prema istočnoj strani profila Rovinj – ušće rijeke Po, te se smanjuje s dubinom vodenog stupca.
7. Organska tvar u obalnom sustavu južnog Jadrana (Boka kotorska, obalni pojas albanskog dijela Jadrana) pod utjecajem je donosa različitih tipova slatkih voda, kao što su lokalni unosi rijekama (Bojana, Drim), podzemnih voda (Boka kotorska) te dotoka različitih tipova vodenih masa (LIW, MAW) iz Mediterana.
8. Boku kotorsku karakteriziraju niže vrijednosti DOC nego u SJ. Također, u proljetnim razdobljima sadržaj otopljenog organskog ugljika u površinskom sloju niži je nego u

dubljim slojevima, što predstavlja fenomen koji nije opažen niti u jednom drugom području obuhvaćenom ovom disertacijom. Ta se pojava pripisuje prisutnosti obilnih podzemnih voda, to jest vruljama koje od dna prema površini razrijeđuju stupac vode u Boki kotorskoj i utječu na sniženje koncentracije DOC u površinskom sloju.

9. Albanske rijeke znatno su siromašnije organskom tvari u usporedbi s rijekom Po na sjeveru, što direktno utječe i na manji sadržaj DOC u obalnom moru pod utjecajem tih rijeka u odnosu na vrijednosti u SJ. Usprkos povišenim koncentracijama nutrijenata, u svibnju 2009. zabilježeni su oligotrofni uvjeti u albanskom priobalnom području.
10. S obzirom na rezultate dugoročnog praćenja sadržaja DOC u SJ, može se zaključiti kako je to jedan od važnih indikatora za praćenje globalnih promjena.
11. Normalizirana površinska aktivnost koja odražava odnose između reaktivne komponente otopljene organske tvari PAT i DOC pokazala se kao dobar alat za praćenje promjena u svojstvima otopljene organske tvari, poglavito oscilacija reaktivnosti prisutnog organskog materijala u jadranskom morskom okolišu.
12. Normalizirana površinska aktivnost, odnosno reaktivnost prisutne organske tvari, razlikuju se na mjesečnoj i godišnjoj skali u sjevernom Jadranu kao i u različitim područjima Jadrana. Iz toga proizlazi da se dominantni tip organskog materijala mijenja kako na vremenskoj tako i na prostornoj skali. Pretpostavka je da se promjena u prevladavajućem tipu organskog materijala događa kao posljedica drugih promjena u ekosustavu, poglavito promjene u prevladavajućim fitoplanktonskim vrstama (dominacija različitih vrsta dijatomeje-flagelate posebno onih manje veličine stanica).

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5. Životopis i popis znanstvenih aktivnosti

Jelena Dautović rođena je 6. veljače 1978. godine u Zagrebu, gdje je završila osnovnu školu Jordanovac i XV gimnaziju. Dodiplomski studij završila je na kemijskom odsjeku Prirodoslovno-matematičkog fakulteta. Eksperimentalni dio diplomskog rada izradila je na Institutu Ruđer Bošković koji je obranila 2006. godine na prirodosovno-matematičkom fakultetu i time stekla svanje diplomirani inženjer kemije. Studentica je doktorskog studija oceanologije.

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Dobitnica je nagrade Instituta Ruđer Bošković za najbolji znanstveni rad u 2017. godini. Koautorica je na 10 znanstvenih radova, od kojih je prvi autor na 3 znanstvena rada u časopisima koje citira Current Contents (CC) baza podataka. Koautorica je na 28 priopćenja u obliku postera ili predavanja.

Objavljeni znanstveni radovi

1. **Dautović J.**, Vojvodić V., Tepić N., Ćosović B., Ciglenečki I., Dissolved organic carbon as potential indicator of global change : A long-term investigation in the northern Adriatic, Science of the total environment 587/588 (2017) 185-195

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6. Znanstveni radovi na kojima se temelji disertacija

Rad 1:

Dautović J., Vojvodić V., Tepić N., Ćosović B., Ciglenečki I.

Dissloved organic carbon as potential indicator of global change: A long-term investigation in the northern Adriatic.

Science of the Total Environment, 587-588 (2017) 185-195

Rad 2:

Dautović J., Strmečki S., Pestorić B., Vojvodić V., Plavšić M., Krivokapić S., Ćosović B.

Organic matter in the karstic enclosed bay (Boka Kotorska Bay, south Adriatic Sea). Influence of freshwater input.

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Characterization and distribution of organic matter using specific physico-chemical methods: A case study of the southeast Adriatic continental and shelf slope (Albania)

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Science of the Total Environment 587–588 (2017) 185–195

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Dissolved organic carbon as potential indicator of global change: A long-term investigation in the northern Adriatic

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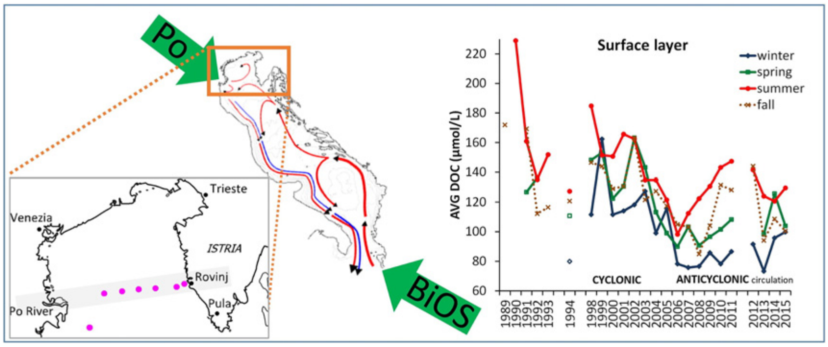
HIGHLIGHTS

- Long-term study of temporal and spatial distribution of DOC in the Adriatic Sea
- The northern Adriatic-periodically eutrophic and oligotrophic system
- DOC content in the northern Adriatic is highly affected by salinity changes.
- DOC variations as a good proxy for the BiOS
- DOC as a potential indicator of climate change

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 November 2016
Received in revised form 12 February 2017
Accepted 13 February 2017
Available online 24 February 2017

Editor: D. Barcelo

Keywords:
Dissolved organic carbon
Long-term monitoring
Northern Adriatic
Random coefficient model
BiOS and climate impacts
Eutrophication-oligotrophication

ABSTRACT

Dissolved organic carbon (DOC) is an essential component of the biogeochemical marine system, effecting biological and chemical reactions that take place in the sea. DOC represents a dynamic component of the global carbon cycle.

This paper reports 25 years of measurements of DOC content and distribution at seven stations along the transect Po River delta – Rovinj in the northern Adriatic (NA). The results show strong temporal and spatial variability: (1) The highest average DOC concentrations were observed in 1998 and 2002 (143 µmol/L and 137 µmol/L, respectively); (2) The minimum average DOC was recorded in 2006 (88 µmol/L) and (3) The short-term DOC accumulation (up to 203, average 102 µmol/L) for the years 2009 to 2012, was observed during the summer and autumn months followed by unusually low DOC concentrations during the winter and spring. The DOC results from the more recent monitoring at the same stations indicate primarily oligotrophic characteristics of the NA seawater (88 µmol/L).

The results of DOC variability and distribution in the NA appears to be strongly influenced by complex circulation patterns. This paper provides a "link" between the Ionian circulation and the NA ecosystem as a part of the recently identified Adriatic-Ionian Bimodal Oscillating System (BiOS). A good agreement between the BiOS oscillation and other variables related to the DOC concentration, like the NA A and B winter types, the Po River discharge, salinity, chlorophyll *a*, occurrence of hypoxic-anoxic conditions, eutrophication and oligotrophication, suggests that DOC might be a good tool and indicator of global change.

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http://dx.doi.org/10.1016/j.scitotenv.2017.02.111

1. Introduction

Primary photosynthetic production by phytoplankton in surface seawaters is the largest source of organic carbon in marine systems. Dissolved organic carbon (DOC) in the global seas is the Earth's largest reservoir of organic matter (~640 Pg C), comparable to the amount of carbon found in a pool of atmospheric CO_2. It is a significant component of the biogeochemical marine system, now recognized as a possible barometer of the global change (Church et al., 2002; Ducklow, 2002). DOC represents a dynamic component of the global carbon cycle modifying many of the biological and chemical reactions that take place in the sea. It provides nutritional and energy base for micro- and macro-organisms. DOC has major impact on the speciation of many metals by complexation and adsorption processes, and it serves as a precursor for fossil fuels such as petroleum and oil shale.

Improvements in measurement precision, in particular the high-temperature catalytic oxidation method (HTCO), enabled detection of the fine temporal and spatial DOC concentration gradients and their variability. This is important for better understanding of the role of DOC in global changes in the oceans, marginal seas, and coastal areas (Williams et al., 1993; Cauwet, 1994, 1999; Hansell and Carlson, 2001).

The northern Adriatic (NA) is a semi-closed shallow basin with open and coastal waters characteristics, located north-east in the Mediterranean. The mean depth is 33.5 m, total area 118,000 km^2, and volume of 635 m^3. The NA is a dynamic system strongly influenced by anthropogenic pressure and climate changes, now confirmed to be present in the Mediterranean areas (Schiano et al., 2005; Grbec et al., 2009; Giani et al., 2012; Djakovac et al., 2015). Changes in riverine inputs, particularly the Po River discharge with the mean flow rate of 1469 $m^3\ s^{-1}$ (Cozzi and Giani, 2011), advection of the central Adriatic water along the eastern coast, a southerly flow in the coastal zone off Istria, the Istrian Coastal Counter Current (ICCC; Supić et al., 2000), a variable and complex circulation driven by the Adriatic-Ionian Bimodal Oscillating System, BiOS (Gačić et al., 2010, 2014), and intense air-sea interactions were suggested to play a fundamental role in physical and biogeochemical processes in the NA (Zavatarelli et al., 1998; Kraus and Supić, 2011; Djakovac et al., 2012, 2015; Kraus et al., 2016).

The NA is one of the most productive areas of the generally oligotrophic Mediterranean (Fonda Umani et al., 2005, 2007). The annual primary production rates in the NA show strong inter- and intra-annual variability, from 55 to 414 g C $m^{-2}\ yr^{-1}$, measured at the Po delta (Revelante and Gilmartin, 1983; Zoppini et al., 1995; Harding et al., 1999; Sellner and Fonda-Umani, 1999; Fonda Umani et al., 2007). This is often accompanied by the appearance of strong phytoplankton blooms and formation of large gelatinous-mucous aggregates recorded for the NA as far as year 1729 (Vollenweider and Rinaldi, 1995). More recently, this blooming phenomenon occurred rather frequently (1988, 1989, 1991, 1997, 2000–2004) (Iveša et al., 2016), and was often followed by an accumulation of organic matter primarily at the stratification zones characterized by pycnocline (Ciglenečki et al., 2000, 2003; Ćosović and Vojvodić, 2000; Giani et al., 2005).

Significant changes in the NA physical and biological conditions for the past 30 years were reported indicating a process of oligotrophication during the last decade (Mozetič et al., 2010; Djakovac et al., 2012, 2015; Gašparović, 2012; Giani et al., 2012; Colella et al., 2016; Iveša et al., 2016). These observations are consistent with the results of the Intergovernmental Panel on Climate Change, IPCC report (IPCC, 2013), showing that the climate in the Mediterranean region is changing. Significant changes in DOC have been recognized as a possible indicator of long-term biogeochemical- and climate-induced variabilities (Hansell and Carlson, 2015).

Rising atmospheric CO_2 levels and climate change associated with concurrent shifts in temperature, circulation, stratification, nutrient input, oxygen content and ocean acidification could have potentially wide-ranging biological effects (Grbec et al., 2009 and references therein). Changes in temperature and pH could have synergistic negative effects on species composition and growth, survival and development (Noone et al., 2013). Both organisms and ecosystems are changing in response to ocean warming, acidification, and de-oxygenation. That reflects on primary production, and further on organic matter content and composition in the oceans, by changing the ratio between the DOC fraction and the particulate organic carbon (POC) fraction (Wakeham and Lee, 1993).

A comprehensive study of DOC in specific areas of the NA basin and different periods has been conducted since 1989 (Vojvodić and Ćosović, 1996; Pettine et al., 1999, 2001; Giani et al., 2005, 2012). While riverine/estuarine environments were extensively studied with focus on investigation of long-term organic matter (1997–2010) (Wu et al., 2015), similar DOC data are scarce for the marine environment including the NA (Pettine et al., 1999; Berto et al., 2010; Giani et al., 2005; De Vittor et al., 2008). Studies by Giani et al. (2005) and De Vittor et al. (2008, Gulf of Trieste) are the only studies that describe long-term distribution of DOC in the NA, but over a shorter time period. In the Mediterranean Sea, one Dyfamed station in the Ligurian Sea has been studied 3-years (Avril, 2002). Globally, a long-term investigation of organic carbon was carried out at a single ALOHA station (Ducklow et al., 2009), thus not providing information on its spatial pattern that was the aim of this work.

This paper describes the results of 25-years (1989–2015) observations of temporal and spatial distribution of DOC at seven stations along the transect Po River delta – Rovinj in the NA (Fig. 1). The paper examines the complex spatial (horizontal and vertical), as well as temporal (seasonal and annual) DOC distribution with several linear and quadratic random coefficient models to confirm main trends. In a longitudinal analysis, observations (statistical) are made at units, in this case, station-specific sequences of time points, so units are occurring naturally in clusters. The main idea is that observations within a cluster tend to be more similar than observations in general. The observed DOC data were primarily discussed in relation to the recently reported the NA local hydrographic and water circulation conditions (Civitarese et al., 2010; Gačić et al., 2010, 2014; Djakovac et al., 2012, 2015; Kraus and Supić, 2011; Supić et al., 2012; Mihanović et al., 2013, 2015; Janeković et al., 2014; Kraus et al., 2016).

2. Materials and methods

2.1. Sampling

Seawater samples were collected by Niskin samplers in dark 1.3 L bottles. Filtration was performed on-board the cruise vessel mostly within the 4 h after the sample collection. In-line filtration of the samples was performed on glass fibre GF/F filters (Whatman, pore size 0.7 μm) in all-glass filter holders under the pressure < 5 psi. Sub-samples of the filtrate were collected in 20 mL glass vials, preserved with 100 μL of mercury (II)-chloride solution (10 mg/L), closed with Teflon-lined screw caps and stored in the dark until analysis.

Glassware used for the sampling and sample filtration were washed with chromic-sulphuric acid and rinsed well with organic-free Milli-Q water (Millipore) and seawater samples. Glass vials and Whatman GF/F filters were combusted at 450 °C for 4 h.

Continuous monitoring of DOC in the NA started in 1989. Monitoring frequencies and cruise plans varied from year to year (Table 1, Fig. 1): during the first 6 years (1989, 1990, 1991, 1993, 1995, 1997) sampling was done sporadically, mostly in summer (Period I); in year 1994 and during the period 1998–2011 the samples were collected approximately once a month, and more frequently in months characterized with an unusually high organic content and specific biological conditions (Period II). During the last three years (from the summer of 2012 until the end of 2015) the monthly sampling regime was followed, but only at 3 stations (SJ107, SJ101 and SJ108) (Period III), Fig. 1.

Period of 15 years (1994; 1998–2011 - Period II) was chosen for detailed statistical analysis. Seven stations placed on transect Po River

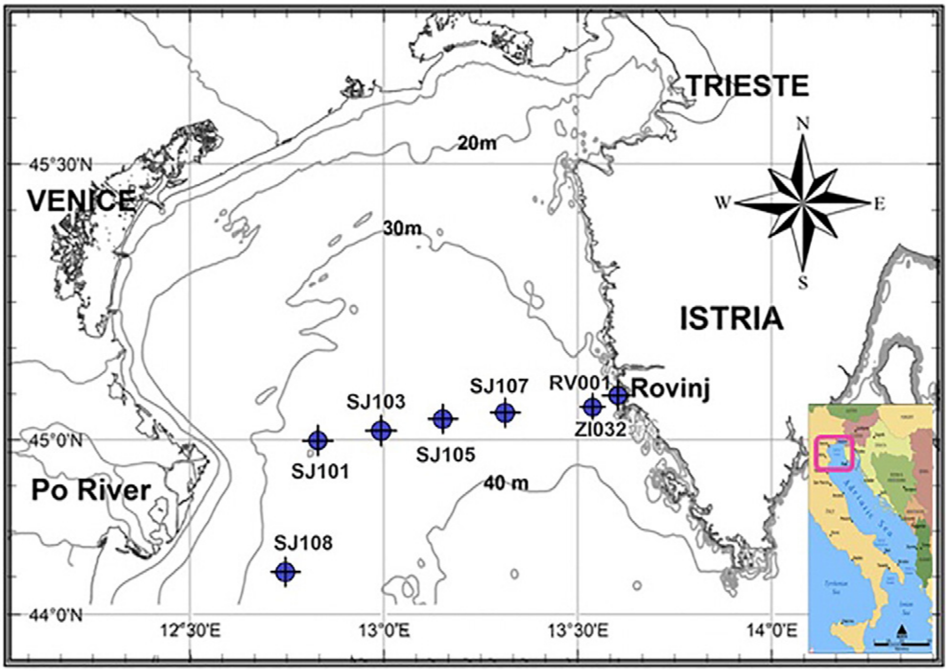

Fig. 1. Sampling stations along the transect Po River delta - Rovinj: SJ108 (44°45′24″N, 12°45′0″E); SJ101 (44°59′53″N, 12°49′48″E); SJ103 (45°1′0″N, 12°59′35″E); SJ105 (45°19′59″N, 13°9′18″E); SJ107 (45°2′52″N, 13°19′0″E); ZI032 (45°4′6″N, 13°30′54″E) and RV001 (45°4′48″N, 13°36′36″E).

delta – Rovinj (SJ108, SJ101, SJ103, SJ105, SJ107, ZI032, RV001; Fig. 1), each with five depths (0 m, 5 m, 10 m, 20 m, bottom), were sampled for the examination of spatial patterns. The seasonal pattern was examined in accordance to the other NA studies (Giani et al., 2005; Tepić et al., 2009; Gašparović, 2012): spring = March, April and May; summer = June, July and August; autumn = September, October and November; winter = December, January and February.

2.2. Analytical methods

2.2.1. DOC determination

DOC concentrations were determined using the sensitive High-Temperature Catalytic Oxidation (HTCO) method at 680 °C (Cauwet, 1994, 1999; Sharp et al., 1995; Dafner and Wangersky, 2002). Shimadzu carbon analysers, TOC 500 (years 1989–2000) and TOC-V_{CPH} - 5000 (from year 2000) with Pt/Silica catalyst (from year 2007, Elemental microanalysis; before the high sensitivity Pt-Quartz wool catalyst, Shimadzu) and Non-Dispersive Infrared (NDIR) detector for CO_2 were used for DOC measurements. In both periods, TOC instrumentations and measurements were checked by standard analytical procedures including validation, international and inter-laboratory comparison and inter-calibration, to ensure that DOC data for all 25 years presented here are valid, reliable and comparable. A fraction of these data was published before as a part of the MAT project (Giani et al., 2005).

Milli-Q water was used to assess the instrument blank and for the preparation of calibration solutions. Values adjusted for the blank were based on the 50 μL sample volume and had a significant precision (1–2 μmol/L org C). Three to four data points were used for the calibration curve with potassium hydrogen phthalate in the concentration range 0–5 mg/L. Samples were acidified to pH = 2 with 2 mmol/L HCl and purged with pure air for 10 min prior to analysis in order to eliminate the inorganic carbon. The concentration was calculated as an average (AVG) of three to five replicates with coefficient of variation <2% and standard deviation <0.1. The AVG instrument blank and Milli-Q blank corresponded to 2.5 μmol/L (n = 32); the reproducibility of measurements were high (1.6%).

Temperature and salinity were determined by CTD probe (SBE 25 Sealogger CTD, Sea-Bird Electronics, Inc., Bellevue, Washington, USA) and were provided for all analysed samples by the Center for Marine Research, IRB, Rovinj, Croatia.

2.2.2. Statistical analysis

Data were analysed by SAS/STAT® 13.2 and SAS/QC® 13.2 software (Version 9.4, SAS System for Windows., Copyright© 2002–2012 SAS Institute Inc.). Boxplots were generated using PROC SHEWHART with boxchart statement.

To investigate curve parameters for the DOC data along temporal and spatial component, a random coefficient model was used (Littell et al., 1996) because of the relatively high intra-class correlation coefficient (ICC = 0.686) that indicates substantial inter-observer agreement (Landis and Koch, 1977) and justifies the use of this particular modelling approach. The random coefficient model was utilized using the PROC MIXED procedure with REML estimation method and unstructured covariance (option type = UN in random statement). With the same procedure intra-class correlation coefficient is calculated to show the fraction of the total variation of the data that is accounted for by the between-group variation. All DOC data were logarithmic transformed to achieve the assumption of normality. Additionally, continuous predictor variables were grand-mean centred (Enders and Tofighi, 2007; Hofmann and Gavin, 1998) in order to ensure numerical stability in estimating hierarchical linear models. All testing was performed at the 0.05 level of significance.

3. Results

3.1. Descriptive statistics

The whole dataset (years 1989–2015) consists of 6539 DOC values, while Period II subset, that was subjected to detailed statistical analysis, incorporates 5608 DOC observations. The majority of DOC values are quite low - the minimal (Q0) DOC value was 62 μmol/L (ZI032 bottom, summer 2008) and 87 μmol/L for the first quartile (Q1; the lowest 25% of the data, Table S1, Supplemental material). Even the DOC data for the third quartile (Q3; 75% of all data) were <125 μmol/L. The higher AVG values then medians (Q2; the lowest 50% of data), as well as boxplots (Figs. 2 and 3), indicate positive asymmetry that is in

Table 1
Sampling frequencies of the northern Adriatic Sea water along the transect Po River delta–Rovinj for years 1989–2015 (o = Period I, sporadically; + = Period II, all stations and statistically analysed; x = Period III, Stations SJ107, SJ101 and SJ108; oo, ++ = two times per month).

Months	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
January						+						+		+	+	+		+	+	+	+	+	+	x	x	x	
February						+	o			+	+	+	+		+	+	+	+	+	+	+	+	+				x
March			o	o		+	o			+		+	+	+	+	+	+	+	+	+	+	+	+		x	x	x
April						+	o				+	+		+			+	+		+	+	+	+		x	x	x
May						+				+	+		+	+	+	+	+	+	+			+	+		x	x	x
June			o			+				+ +	+ +	+ +	+	+ +	++	++	+	+	+	++	+	+	+			x	x
July						+			o	+	+	+	+	+ +	+	+	+	+	++	+	+	+	+	x	x	x	x
August		o	o	o	o	+			o	+	+ +	+ +	+	+	+	+	+		+	+	+	+	+	x	x	x	x
September			o		o	+			o o	+	+	+	+	+	+	+	+	++	+	+	+	+	+	x	x	x	
October					o					+	+	+	+	+		+	+	+	+	+	+	+	+	x	x	x	x
November	o			o	o	+				+			+		+	+		+	+		+		+	x	x		
December										+	+	+	+		+	+	+	+	+	+				x			

concordance with the maximal (Q4) DOC values. The value for Q4 (596 μmol/L, SJ103 5 m, summer 1998) is 9.5-times higher than for Q1 (62 μmol/L) and 5.7-times higher than for Q2 (104 μmol/L). The range for the highest 25% of the data (Q4–Q3) is 7.7-fold of the range for the lowest 75% of the data (Q3–Q0). The highest 25% of the data (Q4–Q3) is the most variable part of the investigated DOC data.

Comparing descriptive statistics of the complete dataset with statistics by the transect (Fig. 2a and Table S1, Supplemental material) any remarkable deviation from the previously described pattern is not recognized. All statistics, except for Q4 and Q3, are quite uniform with the small reduction in DOC values from station SJ103 towards the eastern part of the basin (stations ZI032 and RV001) (Fig. 2a).

A little discrepancy was noticeable with respect to the vertical DOC distribution. Highest DOC values were observed in the uppermost 10 m of the seawater with decreasing trend towards the sea bottom (Fig. 2b). The first quartile, median and AVG DOC are somewhat higher for the upper water layers than for the water samples collected at other depths at each station (Table S1, Supplemental material). The Q2 at 0.5 m and 10 m is 119 μmol/L and 112 μmol/L, respectively. However, >75% of the DOC values at 20 m or near the bottom are below these values. Furthermore, 29% of the surface layer DOC data and 62% of the bottom layer DOC data were below 100 μmol/L. Almost identical DOC values for the surface water layer were measured during the summer. This period is characterized with the highest overall DOC values for the location. In contrast, winter was the season with the lowest DOC values. The percent of non-missing observations less than 100 μmol/L (interval with the most frequent DOC values) for winter is 65%, for summer only 28%, and for the whole dataset is ~ 31%. Unlike the other quintiles (Q1, Q2, Q3), Q4 value for winter (334 μmol/L) was higher than that for the spring (289 μmol/L, Table S1, Supplemental material).

Descriptive statistics and boxplots by stations, depths, seasons and years (Figs. 2 and 3), indicate that the NA basin is quite dynamic.

Annual distribution of DOC alternated between two groupings: the first group, years 1998–2003, is characterized by the higher DOC values (75% of all values are higher than 100 μmol/L); the second group, years 1994 and 2004–2011, had lower values (~50% of all values were lower than 100 μmol/L). The most illustrative years are 1999 and 2002 for first group and 2006 and 2008 for the second group. The widest annual quartile ranges are between the third and the fourth quartile with the largest DOC values for years 1999 (265 μmol/L) and 1998 (438 μmol/L). The variability inside the particular year is rather specific. For example, the range (Min to Max) for the year 2009 is only 78 μmol/L or 6.5-times less than the range for the year 1998 (510 μmol/L). In addition, there are differences among the Q0 values for the particular years: the minimal Q0, 87 μmol/L, in year 2000 is 40% higher than the maximal Q0, 62 μmol/L, in year 2008. All these suggest a different behaviour of DOC complete subgroups and not only of some isolated subgroup parts. Therefore, the need for further analysis was accordingly justified.

Distribution of DOC within the water column of all studied stations along the transect for the three characteristic years (2002, 2006, 2009) are presented in Fig. S1 (Supplemental material). These years are by the statistics underlined as different: year 2002 with the high DOC of significant variability within the water column and expressed water column stratification; year 2006 with the low DOC and low variability within the water column; and year 2009 with accumulation of DOC during the summer and autumn.

3.2. Random coefficient models

Statistical models were used to investigate and confirm previously observed main DOC trends during the Period II (years 1994 and 1998–2011) (Vojvodić and Ćosović, 1996; Pettine et al., 1999; Giani et al., 2005, 2012), as well as the DOC patterns from Section 3.1 above. Many standard statistical methods (e.g. analysis of variance (ANOVA) and regression) have the key assumption of an observational independence. As a result, these models are not suitable for longitudinal data

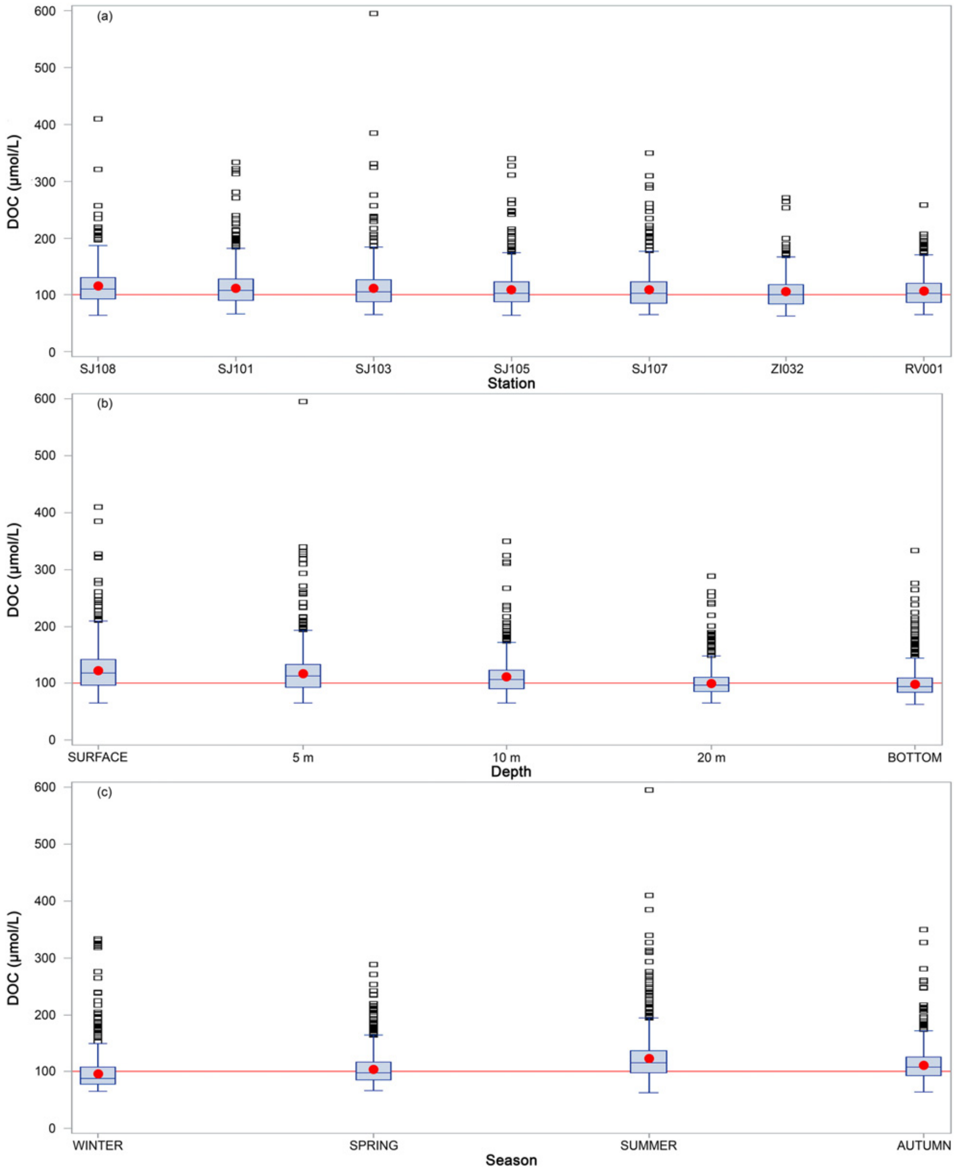

Fig. 2. DOC distribution in the northern Adriatic Sea water plotted versus (a) Sampling stations, (b) Water depth and (c) Sampling seasons. For each group the median is shown as a line inside the rectangle and the average as a dot. The bottom of each rectangle represents the first quartile, the top represents the third quartile and the rectangle itself is an Inter-Quartile Range (IQR, mid-spread or middle fifty). The whiskers are the most extreme points in the group that lies within the 1.5 IQR. If all values fall within that range the whiskers show the maximum and the minimum value. DOC values that are lower or higher than 1.5 IQR are shown outside the whiskers as open squares. The red line marks the most frequent DOC values in the northern Adriatic, i.e., 31% of all analysed samples are within this DOC concentration.

analysis. However, the mixed model and its special case - the hierarchical linear model (or multilevel model) are built to allow within- and between-cluster variation, so these models are a natural choice for investigation in longitudinal and spatial studies, as was done here.

In the random coefficient model, each station is represented with its own trajectory. Often, each trajectory is almost identical to trajectories of all other stations. Consequently, global trajectory, which includes all stations, would represent well all trajectories for every individual station (there is no statistically significant differences in intercepts and/or slopes) and it could be concluded that the spatial component well describes data for all stations. However, it is possible for each station's trajectory to have its own parameters, which are different (positive or negative) from the global. In cases like this, it is justified to assume the existence of some additional influence which is necessary to incorporate in the model in order to better describe the data.

Initially, the complete dataset was analysed to detect a possible additional influence on horizontal spatial component (the transect Po River delta – Rovinj, without the station SJ108) due to prior knowledge (Vojvodić and Ćosović, 1996; Pettine et al., 1999; Giani et al., 2005, 2012). DOC concentrations were modelled by the change of the distance from the Po River mouth (Model I). Slopes of the curves for the each sampling are generally negative (not shown here), indicating that the DOC concentrations were decreasing from the western towards the eastern part of the transect. All fit statistics, (−2 Res Log Likelihood, Akaike's information criterion (AIC), corrected Akaike's information criterion (AICC) and Bayesian information criterion (BIC) are in the range from 32437 to 32450 depending on the statistics. In addition, the aggregated findings of that model are shown in Table S2 (Supplemental material). Evidently, there are numerous DOC samplings characterized with aberrations from global parameters. Besides different aberration frequencies by years, the intercept aberrations (n = 132) are more common than the slope aberrations (n = 28), and the number of positive (n = 67) and negative (n = 65) intercept aberrations are almost identical (n = 37), as well as the slope aberrations (n = 14 for both).

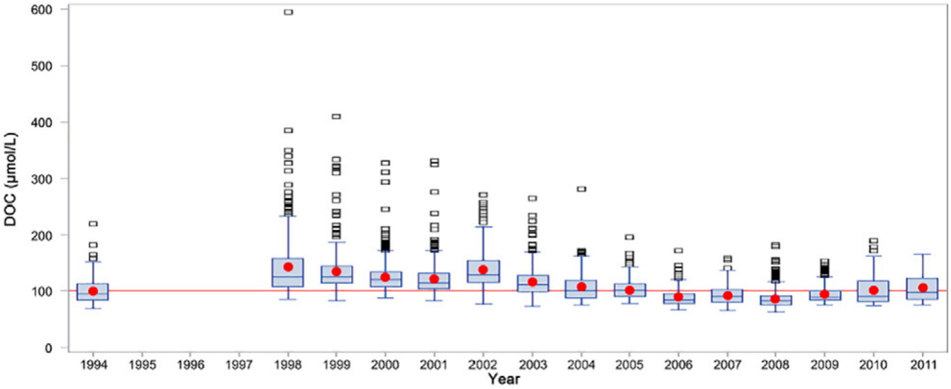

Fig. 3. DOC distribution in the northern Adriatic Sea water plotted versus the years of sampling. For each group the median is shown as a line inside the rectangle and the average as a dot. The bottom of each rectangle represents the first quartile, the top represents the third quartile and the rectangle itself is an Inter-Quartile Range (IQR, mid-spread or middle fifty). The whiskers are the most extreme points in the group that lies within the 1.5 IQR. If all values fall within that range the whiskers show the maximum and the minimum value. DOC values that are lower or higher than 1.5 IQR are shown outside the whiskers as open squares. The red line marks the most frequent DOC values in the northern Adriatic, i.e., 31% of all analysed samples are within this DOC concentration.

The more frequent intercept aberrations indicate uniform changes in DOC concentrations along the whole transect, while the slope aberrations indicate changes in local, isolated part of the transect. Years characterized with a lot of aberrations are the most interesting. More detailed exploration of Table S2 (Supplemental material) confirmed our expectations, the previous knowledge and the pattern noticed in Fig. 3. The period from 1998 to 2002 (except year 2001) is characterized by the majority of samplings with positive intercept aberrance (71–100%, Table S2, Supplemental material) - meaning that the DOC values along transect within individual sampling campaign were significantly higher than the values from the global trajectory. In contrast, the period from 2006 to 2008 is typified by the negative intercept aberrance for the most of sampling campaigns (67–100%, Table S2, Supplemental material). The other years are representative examples of more complex behaviour in which alternate both negative and positive intercept aberrances from the global trajectory. Slope aberrances are quite rare; 2006, 2009, 2010 and 2011 are years without any slope aberration. The year with the maximal amount of slope aberrances (50%) is 2003. The proportions for negative aberrances are 0% - 33% and up to 18% for the positive aberrances (Table S2, Supplemental material). Our model confirmed an overall DOC change and not increasing of the few extreme DOC values.

To check for the consistency of the previously described pattern within separated water layers, the five sub-models were used, one for each water depth (Models II). Their fit statistics are in the range of 6485to 6933. Skimming of Table S3 (Supplemental material) substantiates previously described findings (no significant positive intercepts for the 2006–2008 period; no significant negative intercepts for 1999 and 2002), but a closer look revealed few differences. The individual sampling intercepts from 1999 and from 2002 year are largely (73–100%) significantly higher than the global one, without any exception with significant, negative intercepts. Few negative intercepts in the surface layer with predominant significant positive intercepts are characteristics of 1998, 2000 and 2001 year. Remaining years are marked with at least 25% of intercept aberrances and mixture of positive and negative intercept aberrances. The 2002 year is the year with the lowest amount of non-significant intercepts - even 20 m layer has only 18% while 10 m and bottom layer have 0%.

Obviously, DOC distribution in separate water layers is rather complex and under the influence of some additional parameters, so the existing model was expanded to include seasonality (Models III). This has resulted in a small, additional reduction of fit statistics (6476–6880). Notwithstanding, yet there is a notable body of significant intercept aberrations; from 5.8% to 6.7% for the negative intercept aberrations within the individual depth model, and from 4.9% to 6.0% for the positive. The negative slope aberrance proportions are about 10-times lower (0.2%–0.8%) than for the intercept, and the positive slope aberrance occurred only for 20 m water layer.

Concurrently to spatial dependency models, after expansion of extra sub-models by every category within the season (Models IV), better models were developed, what is noticeable from the all fit statistics reduction to only 1345–2364. Although fit statistics reduction suggested optimal model for the DOC data, the individual trajectories contradict this. As in the previous models, significant intercept aberrations, either positive or negative, are the most frequent (up to 2% at the bottom water layer in summer). The minimal number of deviations are in the 0.5 m water layer during the autumn (1%). As opposed to intercept aberrations in the previous models, the slope aberrations are quite often; only 3 models do not have any negative slope aberrations and all 3 are from the spring. In case of positive slope aberrations, there are 10 models without any aberration at all, an increase compared to the prior models.

The minimization of the all fit statistics by several times (from roughly 32500 to only 1340) supports superiority of the final model over the starting one, but the increasing of the aberration amount suggested a need for additional options. After focusing on spatial dependencies, supplementary approach for the identification of temporal influenced was implemented. The order in the hierarchy was switched, and the emphasis was on temporal component. Data within the individual water layer were modelled as the year days (continuous approach), an alternative to the four seasons categorical approach. The station SJ108 is included in this particular model but the easternmost stations ZI032 and RV001 are not. The linear models (Models V) were adequate to describe the data from all water layers except the surface layer. The often approach to repeated measures with random coefficient is based on polynomial trend models as polynomial functions of time, what is relevant for the DOC surface layer data in this case. Obviously, DOC variation in the surface water column during the year is so pronounced that the model with quadratic members better describes the data. The all fit statistics are larger (5611–5619) than those of the models with the categorical seasonal approach (~1340), but the quantity of the data is 4-times higher (822 versus ~200).

3.3. Comparison with recent years

In the last few years (2012–2015, Period III) of the DOC monitoring the number of the sampling stations decreased. The DOC measurements continued at 2 westernmost stations (SJ108, SJ101) that are under the direct influence of the Po River, and 1 easternmost station (SJ107), that is more influenced by the open waters with the higher salinities (Djakovac et al., 2012). Period III was not included in the detailed statistical part of the study (done by random coefficient models), because of the different sampling regime, but it was used to show the most recent trends in the NA system.

The average seasonal DOC in the surface water layer at all stations along the studied transect, for the entire period of investigation 1989–2015, is shown in the Graphical abstract. Standard deviations for the seasonal values are given in Table S4 (Supplemental material).

The average surface DOC analysis shows that during the entire period of the investigation the NA was a highly dynamic system with periods of high and low DOC content that is consistent with the results of the statistical analysis of a Period II. The highest AVG DOC was measured in the summer of 1990, followed by a period of significant DOC accumulation accompanied with the appearance of mucilaginous aggregates (2000–2004). However, it is important to keep in mind different sampling regimes with significantly smaller number of data in the period before 1993 (see Section 2.1 Sampling, Table 1). Minimum AVG DOC was measured in 2006. A slight increasing trend is observed from 2006 until 2011. Recent years (2012–2015) are characterized by relatively low DOC content that are in line with the oligotrophic characteristics of the NA water column (AVG DOC 88 μmol/L) reported for the earlier period (2000–2009, Mozetič et al., 2010; Djakovac et al., 2012; Gašparović, 2012; Catalano et al., 2014; Colella et al., 2016), and for the more recent period up to year 2013 (Iveša et al., 2016).

4. Discussion

The random coefficient models used in this study have confirmed existence of the patterns obtained using simpler methods in the previous studies (Vojvodić and Ćosović, 1996; Pettine et al., 1999; Giani et al., 2005, 2012). Results of statistical analysis revealed a strong vertical and horizontal spatial variability, as well as the seasonal and inter-annual variability. The main patterns are: 1) Decrease in DOC with seawater column depth; 2) Decrease in DOC from the western towards the eastern part of the basin; 3) Accumulation of DOC during the summer followed by a gradual DOC depletion in winter; 4) Seasonal influence appear to be the most prominent in the surface water; and 5) The strong inter-annual variability is very prominent.

The seasonal signal is dominant in the uppermost seawater layer and its pattern is under the influence of the quadratic member. In contrast, seasonality in the bottom seawater layer is accurately described without a quadratic member. DOC values varied from year-to-year, but the hypothetical regular annual cycle of DOC distribution could have been investigated only by analysing a longer observational dataset.

The DOC seasonality here was defined as is usually for the Adriatic (Vojvodić and Ćosović, 1996; Giani et al., 2005; Tepić et al., 2009; Ciglenečki et al., 2015), considering that the seasons were similar for the terestial ecosystems. Even though there is evidence that the seasons in the sea could be as much as one month delayed with the respect to the seasons on the land, the DOC seasonality defined that way (Artegiani et al., 1997) did not show a different picture (data not shown). That suggest that both seasonal definitions, at least in the case of the DOC distribution in the NA, could be operative.

The results of this long-term study of DOC in the NA show strong spatial, seasonal and inter-annual variability in DOC content during the entire period of investigation. Alternating periods of relatively high DOC concentrations (600 μmol/L, average 121 μmol/L for 1989–1993 and 1998–2004) and relatively low DOC concentrations (~200 μmol/L, average 88 μmol/L in 2006) with clearly visible decreasing trends from 1990 to 2015 (Fig. 3, as well data in the Graphical abstract and Table S1, Supplemental material) support the thesis of oligotrophication in the NA already reported by other authors (Mozetič et al., 2010; Djakovac et al., 2012, 2015; Gašparović, 2012; Catalano et al., 2014; Iveša et al., 2016; Colella et al., 2016). Statistical models have shown that changes in DOC concentrations in the NA system are mostly season dependent, thus supporting previous observational and modelling results (Pettine et al., 2001; Polimene et al., 2007; Giani et al., 2005, 2012 and references therein). The highest DOC content was recorded during the summer months followed by autumn, spring and winter.

Alternating periods of high and low DOC content, especially during the Period II (1994, 1998–2011) appear to be closely related to the local Adriatic hydrographic conditions (Oddo and Guarnieri, 2011). Changes in the Po River regime and the ICCC (Supić et al., 2000) including a wide Adriatic water circulation driven by the recently discussed BiOS (Gačić et al., 2010; Civitarese et al., 2010) are the main characteristics of the NA hydrodynamics. The long-term variation in nutrients (Djakovac et al., 2015), phytoplankton (Marić et al., 2012, 2013; Kraus and Supić, 2011; Kraus et al., 2016), seasonal accumulation of organic matter and occurrence of hypoxic events in the open NA water areas (Djakovac et al., 2015) are shown to coincide with the formation of cyclonic or anti-cyclonic gyres, whose stability was estimated by the appearance of the ICCC (Djakovac et al., 2015).

However, averaging of data collected at stations that are under different environmental regimes e.g. within and out of different the NA gyres, can lead to under/over estimation of important processes which take place in the region. In addition, variability in the NA environment is induced by the changes in the Ionian Sea circulation (Civitarese et al., 2010; Batistić et al., 2014).

The interaction between the Ionian Sea and the Adriatic Sea is intimately linked by means of the BiOS mechanism that changes on a decadal time scale the upper-layer circulation in the Ionian Sea, from cyclonic to anti-cyclonic and vice versa (Gačić et al., 2010; Civitarese et al., 2010). Anti-cyclonic circulation brings a low-salinity Modified Atlantic Water (MAW) into the Adriatic, while the Levantine Intermediate Water (LIW) is advected during the cyclonic circulation. The anti-cyclonic gyre was evident in year 1994 in the northern Ionian Sea (Gačić et al., 2010). It started to weaken in year 1995, and in 1998 a fully developed cyclonic circulation was evident throughout the basin. At the same time the salinity of the seawater overall increased in the Adriatic, including the NA (Fig. 4a and c). According to data presented here, DOC content in seawater appears to be closely related to the salinity, mainly controlled by the Po River inflow and different types of waters advected into the Adriatic. That pattern was dependent on the circulation regime in the Ionian Sea controlled by the BiOS. As shown in Fig. 4b DOC amounts are dependent on the salinity and the potential density trends of the seawater layer (200–800 m) in the southern Adriatic (Fig. 4c), as well the NA average bulk salinities (Fig. 4a). It appears that DOC values were inversely proportional to the salinity. In general, when salinity was increasing the DOC values were decreasing (Fig. 4, a–c) during the cyclonic BiOS circulation (years 1998–2006) that persisted until the year 2006. In addition, the concentration of phosphate and chlorophyll *a* was lower in the period of higher seawater salinities recorded in years 2000–2009 (Djakovac et al., 2012; Giani et al., 2012). During the same period the ICCC, shown to be correlated with the phytoplankton activity (Kraus and Supić, 2011; Supić et al., 2012) and accumulation of the organic matter, was less frequent (Djakovac et al., 2012, 2015).

Higher water salinities in the NA in years 2000–2009, as stated by Djakovac et al. (2012, 2015) were due to the strong reduction of the Po River flow rate and different circulation regime with frequent inflow of highly saline and oligotrophic water from the central Adriatic. The change in circulation is evidenced by the lower frequency of the ICCC with respect to the Eastern Adriatic Current (EAC) after the year 2000, particularly in spring. Increase in EAC after the year 2000 appears to be related to the cyclonic BiOS and LIW inflow into the Adriatic. Moreover, the analysis of the NA salinity trends over the last 30 years shows an increase in the seawater salinity and a clear reduction in concentrations of phosphate and ammonia in the coastal and open water areas (Solidoro et al., 2009; Djakovac et al., 2012). Years 2002 and 2006 belong to the same high salinity period 2000–2009, but are examples of two different patterns (underlined by statistics, Table S1 and S2, Supplemental material) of seasonal salinity changes, as shown for the station SJ105 in the middle of the studied transect, Fig. 4d. High variation of salinity within the seawater column enabled a stronger

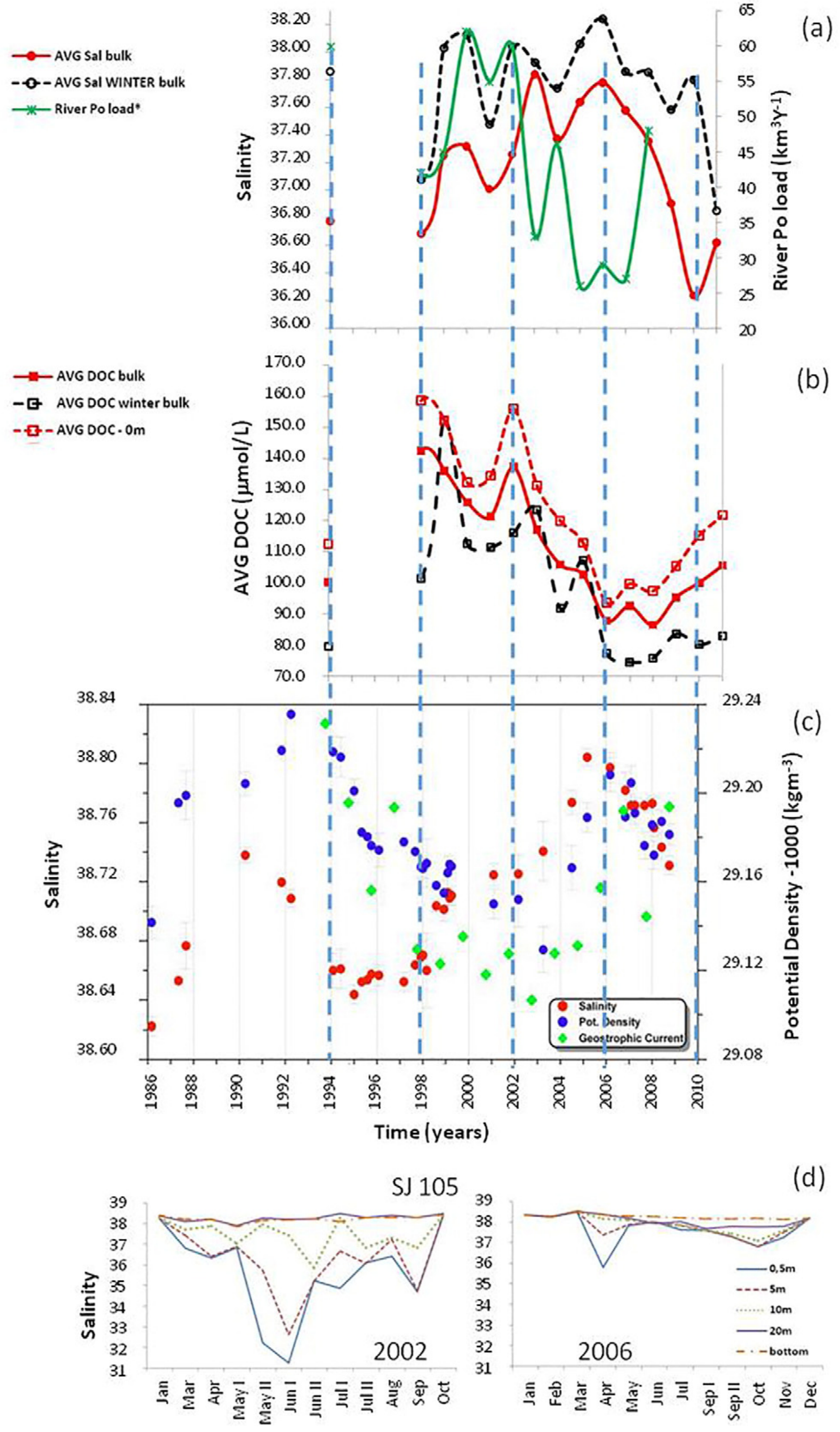

Fig. 4. (a) Relationship between the AVG bulk salinity of the northern Adriatic Sea water for winter months (black circles) and AVG bulk salinity for all 4 seasons (red circles) for the period 1994–2011, and the Po River load (green crosses, from Cozzi and Giani, 2011) for the period 1994–2009; (b) Relationship between the AVG bulk DOC concentrations in the NA seawater for the winter months (black open squares) and for all 4 seasons (red squares), and the DOC data for the surface waters (red open squares) for the period 1994–2011; (c) AVG salinity, potential density and geostrophic current in the southern Adriatic Sea (adopted from Gačić et al., 2010); (d) Salinity in the water column at the station SJ105 in the northern Adriatic Sea during the two years characterized by different BiOS circulation.

stratification that was followed by a significant accumulation of DOC in year 2002. In contrast, the more uniform salinity within the water column was measured at the same station in year 2006. Years 2002 and 2009 were underlined as years with the high flow rate peaks of the Po River while year 2006 had extremely low flow rates (Djakovac et al., 2012, 2015). The selected years also differ in the intensity of the ICCC and its decreasing trend was noticed for the same period before (Djakovac et al., 2015).

This long-term study of DOC in the NA also indicates changes in DOC concentration during the winter season throughout the studied period (data in the Graphical abstract and Fig. 4b). It is apparent that years 1998–2005 were characterized by the relatively high DOC content and high variability through the water column. During these winters the higher discharge rates of the Po River and the BiOS-driven cyclonic circulation took effect that consequently resulted in the higher water salinities. Several episodes of higher discharge of the Po River (Cozzi and Giani, 2011) that decreased the salinity levels were also recorded (Fig. 4a). Winters after year 2006 had, in general, reduced discharge of the Po River and the BiOS anti-cyclonic circulation that advected low saline waters into the Adriatic. Seawater samples from these winters are characterized by the relatively low DOC content and the lack of DOC accumulation and variability through the water column.

DOC results for the period 1994–2006 (Fig. 4b) was well correlated with the analysis of the meteorological conditions and the geostrophic circulation for the preceding autumns, particularly B type winters reported by Supić et al. (2012). Winter types A and B were identified on the basis of the bottom density differences between the eastern and the western part of the NA. During the winters type A (1993, 2001, 2004 and 2007) the seawater salinity was lower and the phytoplankton production was higher than during the most frequent type B winters (1987, 1990, 1991, 1994, 1999, 2000, 2003, 2005, 2006), indicating that the impact of the Po River waters on the NA was more pronounced during the type A winters. The abundance of the phytoplankton in the type A winters was much higher than in the type B winters, especially in the eastern part of the NA (Supić et al., 2012). However, in the type B winters the Po River waters were reported to be retracted from the NA, while the waters from the southern part of the Adriatic entered the region (Supić et al., 2012).

The long-term study of DOC presented here generally shows type B winters to be characterized by the relatively higher DOC content as well as evident DOC accumulation than the winters of type A (Fig. 4b), indicating prevailing influence of the BiOS on the DOC distribution in the NA. Thus, the presence of the specific A or B winter circulation patterns seems to be closely related to the specific type of the Ionian circulation, i.e., BiOS (Gačić et al., 2010) as already hypothesized by Supić et al., 2012.

The winter DOC content in the NA was very low (76–78 μmol/L) for years 2006–2008 with only minor DOC accumulation. These DOC values were even lower than the DOC concentration detected in winter 1994 which was the year with the lowest DOC measured ever in the NA (data in the Graphical abstract and Fig. 4b) (Pettine et al., 2001, this study). This could be the result of the changes that happened in the NA ecosystem and were discussed before in this paper. These changes (nutrient availability, low chlorophyll *a*, shift towards larger winter bioproduction and smaller phytoplankton species) already discussed as the consequence of different water circulations, directly reflect the evidenced reduction in DOC in the NA. So far, a decreasing trend of the freshwater discharge since the 1980s (Cozzi and Giani, 2011), and the 50% reduction of the phosphorus load in the Po River (Degobbis et al., 2000) were claimed as principal causes of oligotrophication in the NA (Djakovac et al., 2012).

The advection of different water masses into the Adriatic is potentially one of the main factors affecting the Adriatic ecosystem in general (Civitarese et al., 2010; Vilibić et al., 2012, 2013; Batistić et al., 2014). Changes in phytoplankton communities, which are the first to react to changes in the ecosystem, because of their short life cycle and their position in the food chain, could further influence microbial diversity and activities, with direct influence on the DOC distribution and content (Wakeham and Lee, 1993). So far, phytoplankton abundance and seasonality in the NA was directly related to the annual regime of the Po River discharge (Viličić et al., 2009; Kraus et al., 2016), while salinity and persistence of different circulation cells (cyclonic and anti-cyclonic) were reported to be the main factor driving the microbial activity in the NA (Orlić et al., 2013; Catalano et al., 2014, and references therein).

Time series in salinity changes, affected by the Po river inflow, the NA circulation (Cozzi and Giani, 2011; Djakovac et al., 2012) and the Adriatic wide-circulation regime controlled by the BiOS (Gačić et al., 2010), indicate that these driving factors are synergistically reinforcing each other. This is evident for the year 2006 (Fig. 4d) and later, when salinity was higher due to both circulation regimes (Oddo and Guarnieri, 2011; Djakovac et al., 2015) and evaporation during the episode of the NA dense water formation (Janeković et al., 2014) that was followed by very low DOC content and accumulation. In the nineties, the situation was completely different, the salinity and DOC appear to be more under the influence of the Po River discharge that brought the freshwater enriched with nutrients (prior to the ban of phosphates-based detergents) and considerable concentration of organic matter to the NA (165–218 μmol/L, 1995–2007, Cozzi and Giani, 2011). However, due to the pronounced seasonal component in the circulation regime (both the local NA and the BiOS) and the Po River discharge rates, the relative importance of these factors that direct impact on biomass and DOC production, changes on monthly, seasonal and inter-annual scales (Gačić et al., 2010, 2014).

Recently, the BiOS was identified as a dominant driver of the Adriatic-wide decadal variability (Mihanović et al., 2015). In support to this hypothesis, our long-term data indicate that DOC in the NA is predominantly under the influence of BiOS. It apparently changes cyclically on timescales between 4 and 11 years (Gačić et al., 2014; Janeković et al., 2014; Mihanović et al., 2015). The extreme and unexpected reversals that were recorded lately are closely related to the formation of the cold and denser Adriatic bottom waters in the NA (extremely dense in years 2006 and 2012). Their formation was, so far, underestimated and appears to be influenced by the ongoing climatic change (Janeković et al., 2014).

Climatic pressures in the Mediterranean, evident by the increase in air (an increase in air temperature of 0.9 °C was detected in Europe from 1901 to 2005, with a significant trend since 1980s, +0.4 °C/decade; Alcamo et al., 2007) and seawater temperatures (linear trend of increasing surface temperature in 0–5 m depth layer in the seawater lake, Rogoznica Lake in central Dalmatia (Croatia) by 1.7 °C/decade is along the record of other studies in the Adriatic showing a similar trend in the last 50–60 years; Ciglenečki et al., 2015 and references therein), water column stratification (changes in density from 5.0–5.5 kg m^3 for years 1972–1999 vs. 4.2–4.5 kg m^{-3} for years 2000–2009 in the NA; Djakovac et al., 2012), water circulation (a decrease in thermohaline circulation in the central Adriatic Sea in years 1952–2010; Vilibić et al., 2013; changes in the BiOS regimes, Gačić et al., 2010, 2014; Mihanović et al., 2015), seawater acidification (0.05–0.14 pH units in the Western Mediterranean Sea; The MerMex Group et al., 2011, and in the NA dense waters, 0.06 pH units from year 1983 to 2008; Luchetta et al., 2010), the NA dense water formation (extremely dense in 2012, with 30, 6 kg/m^3; Mihanović et al., 2013, Janeković et al., 2014) are expected to highly influence biogeochemical processes and marine ecosystem shifts (see http://www.beringclimate.noaa.gov). Observed and expected changes appear to be visible through the DOC variability.

5. Conclusions

The result of this long-term study (25 years, 1989–2015) is a quantitative estimate of the significant inter-annual variability of seawater

DOC content at the sampling stations along the transect Po River delta – Rovinj in the NA (Fig. 1). Main findings are:

1) The existence of the high spatial and temporal trends. In vertical, DOC values decrease with the seawater depth. In horizontal, DOC values decrease from the west of the basin to the east coast. A dominant temporal variability is on the seasonal and inter-annual scales, with DOC decreasing trend in all water layers and all seasons. The seasonal cycle is the most prominent in the surface layer, with DOC accumulation during the summer and DOC depletion during the winter months. The spring and autumn are transitional periods. Above the confirmation of these previously known patterns, the evident significant inter-annual variability, that periodically could turn the oligotrophic system into eutrophic, emphasize the importance for the continuous DOC monitoring in the future.
2) Several factors are affecting the DOC distribution in the NA. Dominant are the hydrographic conditions and water circulation that are under the strong impact of the already reported anthropogenic and climatic variabilities. The variability of DOC seems to be influenced by the local and global conditions that include variable freshwater discharge, mainly by the Po River, and changes in the circulation patterns directed by the orography and sea-land interactions as a part of the global change.
3) Variability of the seawater DOC content is strongly related to salinity changes. The DOC results for the period 1994–2006 are well correlated with the analysis of the meteorological conditions and the geostrophic circulation, particularly for the type B winters (Supić et al., 2012). These winters were characterized with the lower Po River impact and the higher influence of the waters from the southern Adriatic.
4) DOC variability in the NA is a good proxy for the BiOS. For the first time, on the yearly basis, it is shown that DOC oscillations in the NA seem to be strongly related to the large-scale variability in the upper water layer circulation regimes of the Ionian Sea, driven by the feedback mechanism, the BiOS. From the altimetric data, the occurrence of two anti-cyclonic phases (1987–1997 and 2006–2010) and two cyclonic phases (1998–2005 and 2011–2012) was identified in the Ionian Sea (Gačić et al., 2014, Vilibić personal communication) that coincide precisely with the DOC data presented in Fig. 4b and Graphical abstract. From year 1991 to year 1998 the anti-cyclonic BiOS, with a flow of the water carrying rich nutrients from the western Mediterranean, was anomalously strong resulting in the higher DOC values. In years that followed (1998–2006) the BiOS was cyclonic bringing the seawater with lower concentrations of nutrients thus potentially reducing the DOC content. From 2006 to 2010/2011 the anti-cyclonic circulation again coincided with the increased DOC values. Since year 2011, the cyclonic BiOS was not as strong as in years 1998–2006, resulting in the neutral DOC trend (data in the Graphical abstract). Preliminary statistical models have shown significant difference in the DOC content in the years with different regimes of the BiOS circulation and the Po River influence. However, a further work is planned to generate a more detailed association.
5) A good agreement was obtained with the results from other studies that used different variables to monitor the environmental changes that occurred as a consequence of the climatic forcing. Results from this study indicate that DOC could be an invaluable tool serving as a potential indicator of global climate change. This emphasizes further the importance of the long-term monitoring as conducted in this study.

Acknowledgements

The study presented in this paper was funded by the following Projects: 1) Project "Adriatic" (1998–2011) and “Nature of organic matter and interaction with traces and surfaces in the environment” funded by the Ministry of Science, Education and Sports of the Republic of Croatia, 098-0982934-2717 (2007–2013); 2) MAT project “Mucilages and the Adriatic and Tyrrhenian seas” funded by the Italian Ministry of Environment (1998–2002); 3) “Sulphur and Carbon dynamics in the marine and fresh water environment” (SPHERE) funded by the Croatian Science Foundation, IP-11-2013-1205 (2014–2018). The authors acknowledge contribution of Z. Kodba and Z. Zovko during the sampling and measurements as well as the Center for Marine Research Rovinj, Rudjer Boskovic Institute, Rovinj, Republic of Croatia for providing the salinity and temperature data; the crew of the research vessel Vila Velebita, Center for Marine Research Rovinj, Rudjer Boskovic Institute, Rovinj, Republic of Croatia for the technical assistance during the sampling. The authors also thank I. Janeković and I. Vilibić for valuable discussions of BiOS circulation, and anonymous reviewers for valuable comments that improved the paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.02.111.

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ORGANIC MATTER IN THE KARSTIC ENCLOSED BAY (BOKA KOTORSKA BAY, SOUTH ADRIATIC SEA). INFLUENCE OF FRESHWATER INPUT

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ABSTRACT

Coastal systems are sensitive to eutrophication and organic matter (OM) produced in such systems influences the fate and distribution of other microconstituents and pollutants. The Boka Kotorska Bay is a jeopardized karstic area due to anthropogenic pressures. The concentrations of dissolved organic carbon (DOC) increase from spring to autumn months, with the values ranging from 0.64 to 1.43 mg C L^{-1}. Particulate organic carbon (POC) represents a significant portion of OM, up to 43% of total organic carbon (TOC). The concentrations of surface active substances are typical of coastal seawater, ranging from 0.026 to 0.311 mgL^{-1} equiv. Triton-X-100, with an increase in the spring/summer months. The normalized surfactant activity values were significantly higher than in other parts of the Adriatic. The presence of organic ligands and particles contribute to the copper complexing capacity values which are in general higher (up to 714 $nmolL^{-1}$) compared to those found in other coastal areas. Even though preconditions were documented for the inner part of Kotor Bay i.e. elevated nutrient concentrations that lead to high biological production within the system and hence the accumulation of reactive organic matter in spring/summer months, our integrated chemical-biological approach showed that no eutrophic episodes were detected in the period 2008/2009.

KEYWORDS: DOC, POC, surface active substances, copper complexation, seasonal distribution, southern Adriatic Sea, karstic Boka Kotorska Bay

1. INTRODUCTION

Organic matter plays an important role in biogeochemical cycles by influencing the fate and distribution of other microconstituents and pollutants, both inorganic and organic ones, in the bulk water as well as at natural phase boundaries. There are different sources of organic carbon, either autochthonous such as the fixation by primary producers within the system, plant and animal excretions, bacterial degradation, autolysis of dead organisms, or allochthonous, which implies an input of organic matter from outside the system, e.g. from rivers, waste waters or the atmosphere. DOC and POC concentrations and their evaluation are considered key parameters in the description of natural water systems.

A large part of aquatic organic matter exhibit the property of surfactant activity and are named surface-active substances (SAS). SAS accumulate at different phase boundaries (air/water; water/sediment; water/living or non living suspended particles) influencing the structure and physico-chemical properties of these interfaces and mediating the processes of mass and energy transfer [1]. Surfactant activity of different classes of organic substances representative for organic matter present in natural waters have been widely investigated by using electrochemical methods [2-6]. Clear evidence of surfactant production by marine phytoplankton based on laboratory and field experiments is also available [7-9]. Due to the specific reactivity of SAS at natural phase boundaries, their distribution and fate in the sea could be different, compared to those of organic matter pool values, *i.e.* dissolved organic carbon (DOC) [10]. A combination of collective parameters (DOC and POC) and SAS provides information about both, the content and the reactivity of organic matter in a particular aquatic system.

Speciation studies have shown that metal affinity for different ligands constitutes an important factor influencing metal distribution in the environment [11]. Metal complexation by inorganic ligands in water (oceans, estuaries, freshwater) is well studied whereas less is known about organic ligands. With the development of a number of sensitive and selective metal speciation techniques metal-organic interactions have been studied as well [12-15]. Copper is the most studied metal [16, 17]. Its complexa-

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tion to organic ligands in all aquatic systems, with exception of deep ocean water, is >99% [16]. Complexation of metal ions with organic ligands reduces metal ion toxicity [17].

During the last few decades many biological, but few chemical studies have been conducted in Boka Kotorska Bay, focusing mainly on the basic chemical parameters. Due to significant antropogenic exposure of Boka Kotorska Bay which is increasingly felt in the inner part of the Bay in the last decade, we have conducted an extensive analysis of basic and more specific organic chemical parameters that are important for eutrophic areas.

The scope of our research was to investigate the content, seasonal and spatial distributions and physico-chemical properties of organic matter in relation to nutrients, chlorophyll *a* and hydrography in the area of the Kotor Bay (southern Adriatic Sea, Montenegro). The Kotor Bay is a representative of closed karstic bay of a temperate sea, influenced at the same time by sea bottom input of freshwater called «vruljas» and by strong anthropogenic pressures. The Boka Kotorska Bay (Fig. 1) is characterized by complex hydrogeological relations that enable formation of a specific transitional zone between fresh and saline waters [18]. Crucial characteristics of the studied area are considerable precipitation events as well as numerous vruljas in the sea bottom [18-20] that create constant inflow of freshwater. Slow circulation of seawater is another very important characteristic of this area [20]. Surrounding mountains shelter this very closed bay from the wind influence. The plankton species (*Chaetoceros affinis*, *Guinardia flaccida, Pseudonitzschia spp., Thalassionema nitzschioides*), known as eutrophication indicators, were found dominant in the course of summer months [21,22]. Recent research conducted in the inner part of the Bay (Kotor Bay) has shown that the phytoplankton biomass ranged between < 1 to > 4 μgL^{-1} expressed as chlorophyll *a* (Chl *a*), reaching maximum values in the late winter and spring period. On the basis of Chl *a* and nutrient concentrations, the study area can be defined as oligo-mesotrophic [23].

Our research was performed during the period of one year (2008-2009) in spring, summer, autumn and winter, which provided an insight into the yearly cycle of organic matter. Comparison is made with other sites in the Adriatic Sea.

2. MATERIALS AND METHODS

2.1. The area of investigation

The Boka Kotorska Bay (Fig. 1) is situated in Montenegro and is a winding bay of the Adriatic Sea. The Bay, sometimes called Europe's southernmost fjord, is in fact a submerged river canyon of the Bokelj River, which used to run from the plateaus of Mt. Orjen (1894 m) [19]. The Verige strait is the narrowest section of the Bay, separating the inner Bay which belongs to the natural and culturo historical region of Kotor, a World Heritage Site, from the rest of the Bay. Its hydrology is a karst type system with submerged sources of freshwater. Water area in the Bay is 87 km^2, with the maximum depth of 60 m and average depth of 27.3 m. At its widest point the Bay is 7 km wide and at the narrowest point 0.3 km wide. The climate is of the Mediterranean type with a peculiarity of littoral Dinarids precipitation regime. Mt. Orjen receives the Europe's highest amount of precipitation [19].

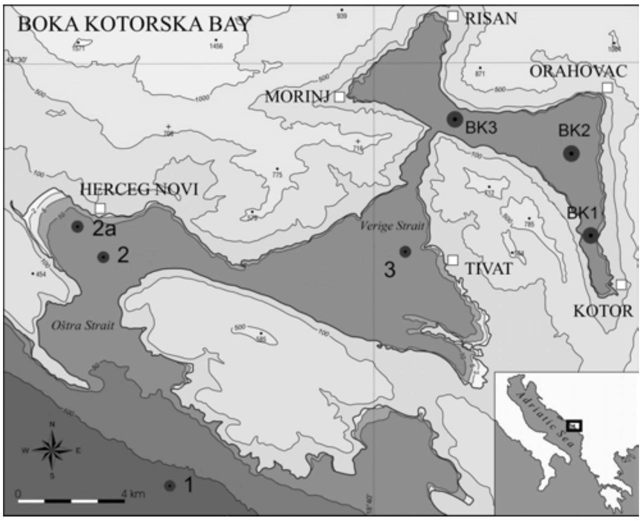

FIGURE 1 - Study area and the sampling stations

2.2. Sampling

Sampling was carried out seasonally in April (04), July (07) and November (11) 2008, and in March (03) 2009, at three stations in the inner part of the Boka Kotorska Bay (stations BK1, BK2, BK3), (Fig. 1). Samples were collected from a small ship at five depths at station BK1 (surface, 2 m, 5 m, 10 m, and 15 m depths) and at seven depths at BK2 and BK3 stations (surface, 2 m, 5 m, 10 m, 15 m, 20 m, and 25m depths). In May 2008 sea water samples were taken at four additional stations (1, 2, 2a, and 3), (Fig. 1) for comparison with the stations BK1, BK2 and BK3.

Samples for the determination of DOC, POC and SAS were collected directly with Niskin samplers in precleaned dark glass bottles (1.3 L). Filtration of samples was performed immediately after sampling with precombusted glass fiber filters (Whatman, GF/F, 0.7 µm) in all-glass filter holder. Samples for the copper complexing capacity (CuCC) determination were collected in precleaned FEP bottles (0.5 L) and measured without filtration.

Salinity and temperature were determined by using a Sea-Bird SBE19plusV2 CTD probe. Chl *a* was determined as absorbance with a Perkin-Elmer UV/VIS spectrophotometer and calculated according to Jeffrey *et al.* [24]. Nutrients were analyzed by standard method [25].

2.3. DOC and POC determination

Filtered samples for DOC analysis were collected in triplicates in the precleaned glass vials. The samples for

DOC were preserved with mercury chloride (10 mgL^{-1}) and stored at +4 ^{o}C in the dark until analysis. GF/F filters were rinsed with several mL of Milli-Q water to remove salts and stored on board at -80 ^{o}C for POC analysis.

DOC concentrations were analyzed in duplicates using the sensitive high-temperature catalytic oxidation (HTCO) technique [26]. A TOC-V$_{CPH}$ (Shimadzu) with platinum silica catalyst and nondispersive infrared (NDIR) detector for CO_2 measurements was used. The concentration of each sample was calculated as an average of three to five replicates. The average instrument blank and Milli-Q blank correspond to 0.03 mg C L^{-1} (n=32) and the reproducibility was high (1.6%).

POC was analyzed with a solid sample module SSM-5000A associated with a Shimadzu TOC-V$_{CPH}$ carbon analyzer. POC concentrations were corrected on the basis of blank filter measurements. The average filter blank including instrument blank corresponds to 0.005 mg C L^{-1}. The reproducibility obtained for the glucose standard was high (3%).

2.4. SAS determination

Surface active substances were analyzed electrochemically by a.c. voltammetry [3] using a PalmSens portable instrument (Palm Instruments BV, Netherlands). Three-electrode system was used: hanging mercury drop electrode (HMDE, drop surface area 0.6 mm^2) as a working electrode, Ag/AgCl (3M KCl) as the reference electrode, and platinum electrode as the counter electrode. The deposition potential of -0.6V vs. Ag/AgCl reference electrode and the deposition time of 30 s, were applied. Surfactant activity was expressed in terms of surfactant equivalents of the non-ionic surface active substance Triton-X-100 (MW=600 mgL^{-1}) with the detection limit of 0.02 mgL^{-1} and reproducibility of 5%.

Surface active substances were determined in non-filtered samples (SAS$_T$, total *i.e.* dissolved and particulate) and in filtered samples (SAS$_{diss}$, dissolved) immediately after sampling. Normalized surfactant activity (NSA) values were calculated by dividing the concentration of SAS in mgL^{-1} as the equivalent of Triton-X-100 with the content of organic carbon in mgL^{-1}.

2.5. Copper complexing capacity (CuCC) measurements

The experiments were performed with electrochemical system consisting of a 663 VA-Stand (Metrohm, Herisau, Switzerland), IME663 module and a computer controlled voltammeter (EcoChemie, Utrecht, The Netherlands). The working electrode was a static mercury drop electrode (SMDE, drop surface area 0.54 mm^2). The reference electrode was a double-junction Ag/AgCl (3 M KCl) electrode, and the counter electrode was a glassy carbon rod. The solutions were stirred with a rotating teflon rod (stirring rate = 3000 rpm). The potential of deposition was -0.6 V vs. Ag/AgCl reference electrode with the deposition time of 60 s. The reproducibility of the method is ±2x10^{-9} M Cu^{2+}, from which the detection limit equal to 6x10^{-9} M Cu^{2+} can be calculated. Determination was performed by the direct titration method of the sample with increasing the amount of copper ions, and their response was measured by the method of differential pulse anodic stripping voltammetry (DPASV) [27]. To obtain complexing capacity values and the conditional stability constant, titration data were linearly transformed assuming 1:1 metal to ligand complexes. The equation used for calculation is: [Cu]/[CuL] = [Cu]/CuCC + 1/KCuCC, where Cu is the copper ion detected by anodic stripping voltammetry, CuL is the copper ion bound in a complex with ligand L, CuCC is the total concentration of binding ligands (*i.e.* complexing capacity) and K is the apparent stability constant. [Cu] and [CuL] are calculated from the titration data, where $[Cu] = I_p/S$ and $[CuL] = [Cu_T] - [Cu]$. In these equations, I_p is the height of DPASV detected copper peak, S is the sensitivity of the DPASV method to labile copper, which corresponds to the slope of the linear portion of the titration graph after all complexing sites have been saturated with copper ions, $[Cu_T]$ is the concentration of copper ions added + copper ions originally present in the sample. The plot of [Cu]/[CuL] vs. [Cu] yields a straight line with a slope of 1/CuCC and the intercept 1/KCuCC [12, 27, 28].

3. RESULTS AND DISCUSSION

3.1. Salinity, temperature and chlorophyll *a*

At BK1 station annual distributions of salinity (Fig. 2a), temperature (Fig. 2c) and chlorophyll *a* (Fig. 2d) were followed from 02/2008 to 03/2009.

Measurements for the station BK1 showed significant variability of salinity which ranged from 2.3 to 36.5 (Fig. 2a). Salinity fluctuations were mostly pronounced in the upper water layer (0 m and 2 m depth), with the lowest values found in the spring of 2008 (2.3 - 14) and the highest values in the autumn of 2008 (6.8 – 34.6). In deeper layers salinity values were more uniform (at the bottom they ranged from 28.4 to 36.5).

Daily precipitation regime in the inner part of the Kotor Bay is shown in Fig. 2b. Seasonal oscillations are evident, with high amount of precipitation in spring and yet higher amount in autumn and winter periods. During October and at the very beginning of November low salinity values were observed at BK1 station but no correlation was found with daily precipitation regime (Fig. 2b). It is evident that low salinity is not only the consequence of high local precipitation but also the consequence of many vruljas due to a typical karstic regime of groundwater outflow with extremely high capacity oscillations [18,20].

Annual variations in seawater temperature for station BK1 are illustrated in Fig. 2c. They were in the range between 8.6 and 28.2 °C, with the maximum temperature measured in the middle of July 2008 and the minimum temperature in January 2009 (Fig. 2c).

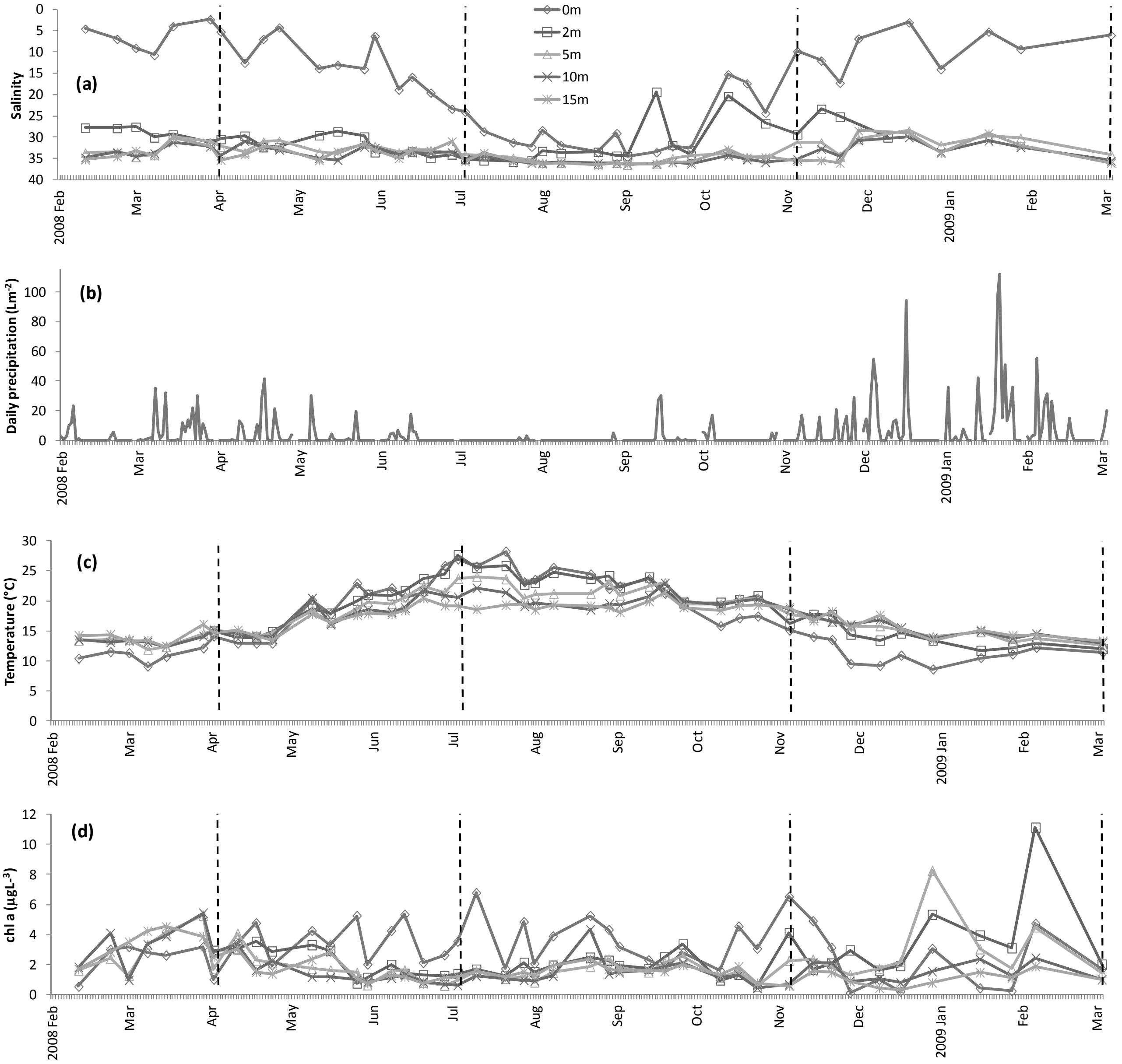

FIGURE 2 - Temporal variations of (a) salinity, (b) daily precipitation regime, (c) temperature and (d) chl *a* at BK1 during the period 02/2008 – 03/2009 (dash lines represent seasonal samplings when all parameters were analyzed at BK2 and BK3 as well)

Annual distribution of chlorophyll *a* was in the range from 0.12 to 11.13 µgL^{-1}. Several maxima are visible in the surface layer of station BK1, with the highest value observed in February 2009 at 2m depth. In general, chl *a* values were increased in the surface layer from the beginning of April until middle November in comparison with the rest of the water column, while during the winter of 2008 maximum chl *a* values were observed in the bottom layer (Fig. 2d).

3.2. Nutrients

Dissolved inorganic and organic nitrogen (DIN and DON) as well as phosphorus (DIP and DOP) were measured seasonally for all three stations in the surface layer (0-2m) and in the deeper layer (10-20m). Average values for the three stations for DIP and DOP and DIN and DON in the upper (0m) and in the deeper layer (15m) are presented in Fig. 3. Both nitrogen and phosphorus concentrations, were higher at the surface when compared to the concentrations in the deeper layer.

The highest DOP/DIP ratios calculated as average of three stations were 3.7 in 07/2008 at the surface and 2.9 in 11/2008 in the deeper layer. DON/DIN ratio calculated as average for three stations was the highest in 07/2008 at the surface (4.5) and in 11/2008 in the deeper layer (4.2). In the deeper layer the variability of DIN and DON was not so pronounced as it was at the surface (Fig. 3a and 3b).

The inner part of the Boka Kotorska Bay can be classified as a polyhaline shallow coastal area, with decreased salinity values observed throughout the year (down to 5.2) showing that this area is under constant freshwater inflow which maintained the supply of nutrients. Differences were observed between freshwater influence according to the freshwater sources in various seasons. In 04/2008 and 03/2009 snow melting is assumed to be a very important source of freshwater, while in 11/2008 precipitation is the dominant source. In 07/2008 vruljas are contributing the most to the freshwater input. At the surface, DON/DIN and DOP/DIP ratios were the highest in 07/2008 (4.5 and 3.7, respectively) when freshwater input of inorganic nitrogen and phosphorus were low, indicating their fast transformation to organic nitrogen and phosphorus occurring in the water column due to high biological activity. The Mediterranean primary production is phosphorus limited [29, 30] and limited availability of this nutrient leads to its full incorporation in the freshly produced OM.

Krivokapić [31] reports the concentrations of dissolved inorganic nitrogen (NO_3^-) in the inner part of the Boka Kotorska Bay to be in the range from 2.42 to 102.74 µmolL^{-1}, which is higher compared to the data obtained in this study (0.07 – 13.10 µmolL^{-1}). Dissolved inorganic phosphorus in the inner part of the Boka Kotorska Bay was reported to be in the range from 0.43 to 16.52 µmolL^{-1} [31].

Here we may compare nutrient levels in the inner part of the Boka Kotorska Bay with two other systems in the Adriatic Sea which are influenced by freshwater input, namely the Krka River estuary in the middle Adriatic Sea and the surface layer of the selected station SJ108 in the northern Adriatic Sea region, which is under the influence of the Po River discharges.

In Krka River estuary NO_3^- values were up to 59.2 µmolL^{-1}, with an average of 17.8 µmolL^{-1} [29], similar to the northern Adriatic Sea (0.92-16.35 µmolL^{-1}) (Djakovac - unpublished data, long-term from 1972 to 2010 average for northern Adriatic Sea station SJ108).

In Krka River estuary PO_4^{3-} concentrations up to 1.73 µmolL^{-1} with an average of 0.22 µmolL^{-1} were reported [29], while in the northern Adriatic Sea PO_4^{3-} was in the range from 0.09 to 0.29 µmolL^{-1} (Djakovac – unpublished data, long-term from 1972 to 2010 average for northern Adriatic Sea station SJ108).

According to the TRIX index [30] nutrients data obtained in our study are in the range for mesotrophic levels, some values even pointing to eutrophic levels regarding both DIN and DIP.

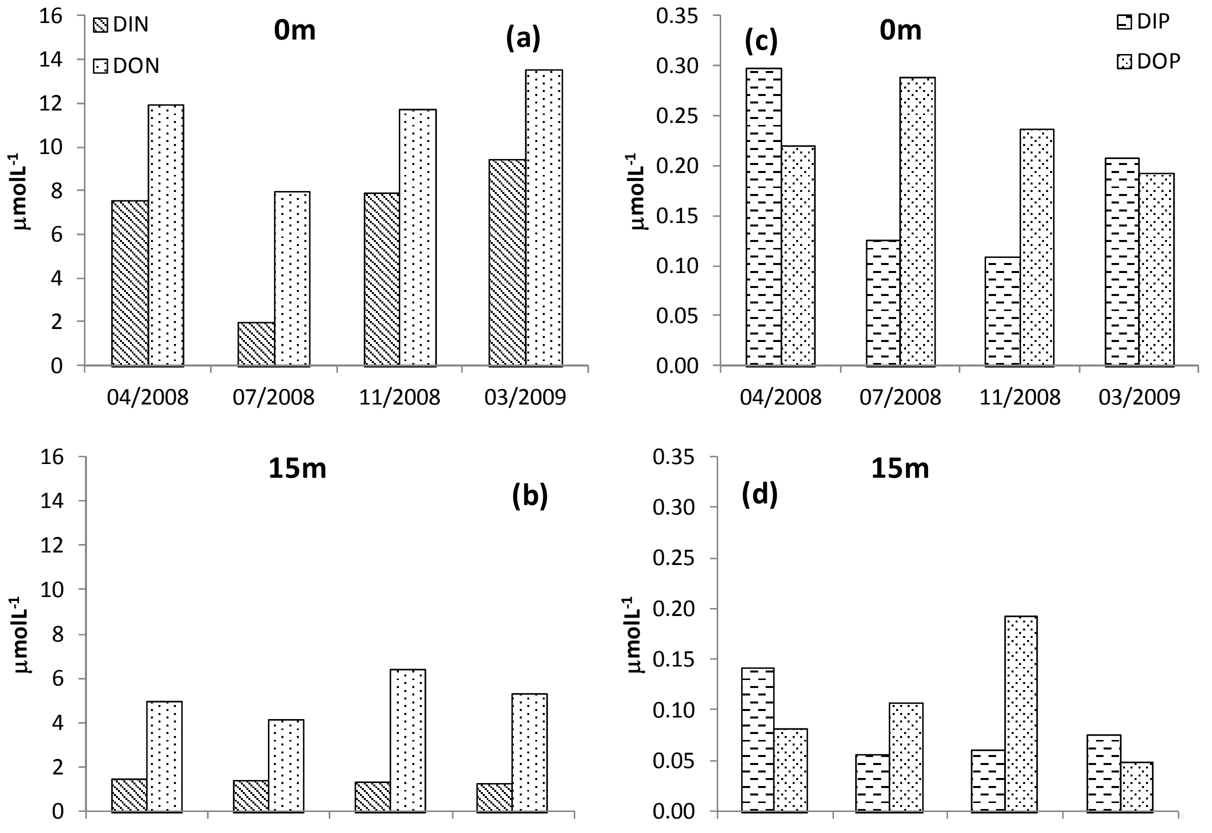

FIGURE 3 - Organic and inorganic nitrogen (a,b) and phosphorus (c,d) in the surface layer, (0m)(a,c) and in the deeper layer, (15m)(b,d)

3.3. Primary production characteristics

Elevated nutrient concentrations in the surface layer of the inner part of the Boka Kotorska Bay favor phytoplankton growth in all seasons, especially in 04/2008 when phytoplankton abundance was up to $3.1x10^6$ cell L^{-1} [32]. An exception was found in autumn 2008, when very low phytoplankton abundances were observed (down to $1.1x10^4$ cell L^{-1}), possibly due to zooplankton grazing [33], which was supported by significantly higher pheophytin concentrations found in the water column in 11/2008.

Phytoplankton was observed to be dominated by microphytoplankton (64 – 88%), namely diatoms (up to $2.9x10^6$ cell L^{-1}) in 04/2008 and 03/2009 at all investigated stations, whereas in 07/2008 picophytoplankton, *i.e.* cyanobacteria (up to $2.97x10^6$ cell L^{-1}) were found to be dominant (63 to 84%) [32]. According to the available literature sources, oxygen saturation was in the range from 62 to 149% [31], indicating that this area is seldom exposed to hypoxia; however the determined values are often increased in the upper layer, exceeding 100% saturation, which indicates this area as a potential candidate for eutrophic episodes.

3.4. Dissolved organic carbon (DOC) and particulate organic carbon (POC)

DOC values in the inner part of the Boka Kotorska Bay ranged from 0.64 to 1.43 mg C L^{-1}. The lowest values were detected in April 2008 at all stations (0.64 – 0.94 mg C L^{-1}), while summer (07/2008) was characterized by the highest DOC values at all stations (0.90 – 1.43 mg C L^{-1}) Average values for three stations and for three different depths (upper 0m and 5m and the bottom layer) are given in Fig. 4a. Along the vertical profile specific distribution of DOC values was observed. In 04/2008 and 03/2009 lower DOC values were obtained at the surface compared to those in the deeper water layer. In 11/2008 the opposite was found, *i.e.* higher DOC concentrations were measured at the surface and lower values in deeper layer. Accumulation of DOC, expressed as average DOC values, was observed throughout the water column at all stations from April until July 2008 (Fig. 4a.), with the most pronounced increase in the upper 5 m of the water column. When correlating DOC to the salinity values, two different situations were observed. In upper water layer DOC is positively correlated to the salinity ($P<0.0001$, $R=0.548$, $n= 12$) (Fig. 5a), while on the contrary for deeper layers the correlation does not exist (Fig. 5b).

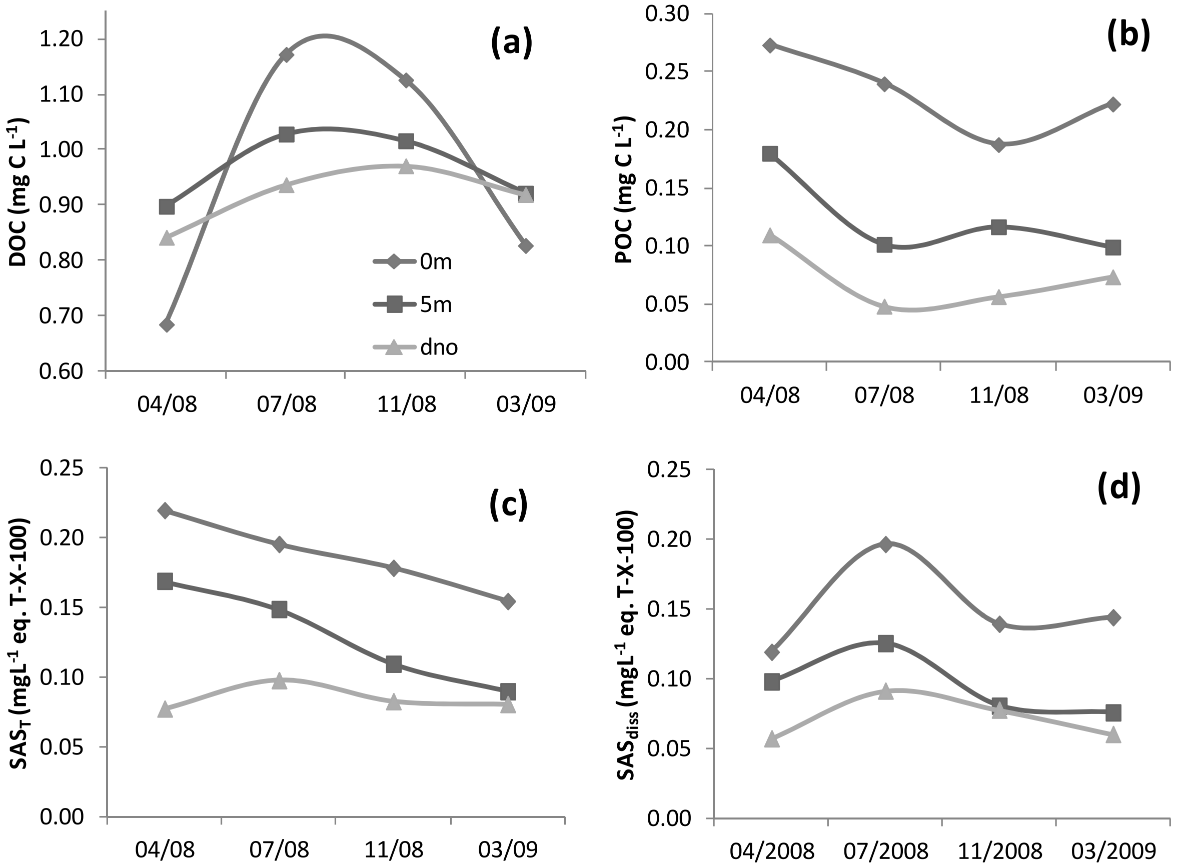

FIGURE 4 - Average water column parameters (a) DOC, (b) POC, (c) SAS_T and (d) SAS_{diss} in the upper layer (0m and 5m) and in the bottom layer

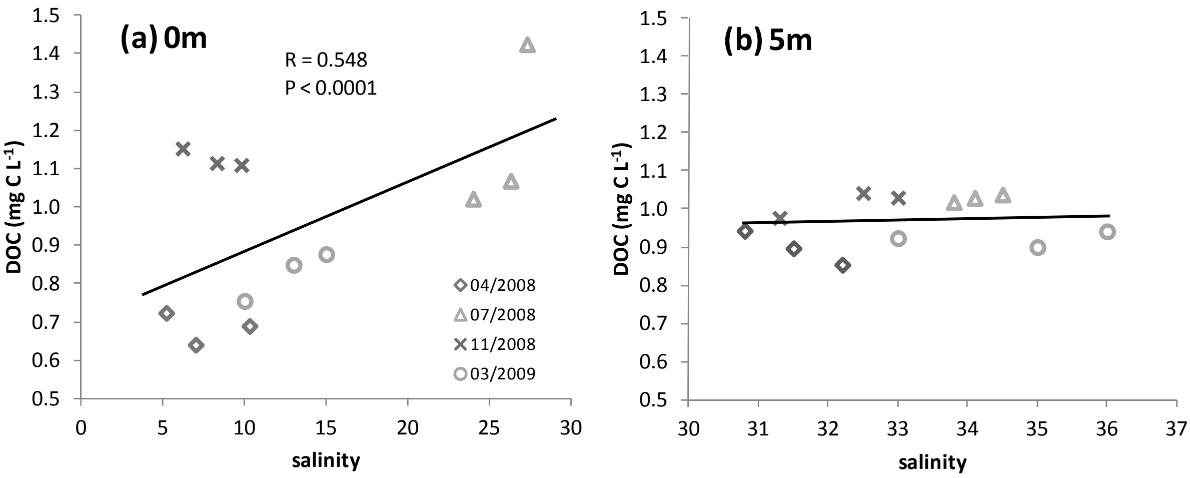

FIGURE 5 - Relationship between DOC and salinity at 0m and 5m for all three stations

TABLE 1 - Average DOC, POC and SAS parameters per station (all stations, all depths)

	BK1	BK2	BK3
Average DOC (mg C L^{-1})	0.93	0.97	0.93
Average POC (mg C L^{-1})	0.167	0.131	0.096
Average SAS_T (mgL^{-1} eq. T-X-100)	0.135	0.115	0.111
Average SAS_{diss} (mgL^{-1} eq. T-X-100)	0.112	0.090	0.093

Particulate organic carbon values were in the range from 0.041 to 0.475 mg C L^{-1}. The minimum POC value was obtained at BK2 station in bottom layer in 07/2008, and the maximum value at BK2 station in surface layer in 04/2008. In all seasons higher POC values were observed for the surface compared to the bottom layer (Fig. 4b).

POC values were compared on the basis of an average calculated per sampling – a decreasing trend was observed from April to July 2008 (39.1%), which was followed by almost constant average POC values obtained in the two remaining sampling periods (11/2008 and 03/2009), (Fig. 4b).

Spatial distribution was followed as the average of all values obtained per parameter (Table 1).

Freshwater entering the inner part of the Boka Kotorska Bay is rich in nutrients but not in organic matter. This is clearly visible from Fig. 5a, which shows positive correlation of DOC and salinity – in the upper, brackish layer, the lower the salinity, the lower is the DOC content. This is also observed from the DOC values in 04/2008 when DOC was found to be down to 19.7% lower at the surface when compared to the bottom, and the salinity values at surface were extremely low (down to 5.2).

Accumulation of organic matter starts in spring and lasts until autumn (about 20% in average) throughout the water column at all stations, with accumulation first visible in the surface layer (in 07/2008). DOC remains increased until 11/2008, with the concentrations becoming uniform throughout the water column. This implies that the accumulation of organic matter, visible through the increase in DOC in this area from spring until the summer 2008 (Fig. 4a) is most likely the consequence of biological processes, *i.e.* phytoplankton blooms induced by input of nutrients. If we compare inner part of the Bay to the rest of the Boka Kotorska Bay it is clearly visible from Fig. 6 that DOC content is the highest in the inner part of the Boka Kotorska Bay and that the vertical distribution is a much more uniform when compared to the rest of the Boka Kotorska Bay. POC was also significantly higher in the inner part of the Boka Kotorska Bay, with lower values found for deeper parts of the water column (Fig. 6b). This indicates that inner part of the Bay is characterized by higher organic matter accumulation throughout the water column in comparison with the rest of the bay. Long-term investigations (1984 – 1993) in the northern Adriatic Sea showed that DOC concentrations are in the range from 1.13 to 3.06 mg C L^{-1} [35]. The seasonal variations in DOC concentrations in the northern Adriatic are significant, doubling the value in summer with respect to the winter period [35]. In comparison with the Boka Kotorska Bay, DOC content is higher in the northern Adriatic Sea which is in accordance with the reported eutrophication problems in the northern Adriatic Sea [36].

The portion of the particulate in the total organic carbon in the inner part of the Boka Kotorska Bay was found to be in the range from 4 to 43%, with the highest percent of POC found in 04/2008 at all stations.

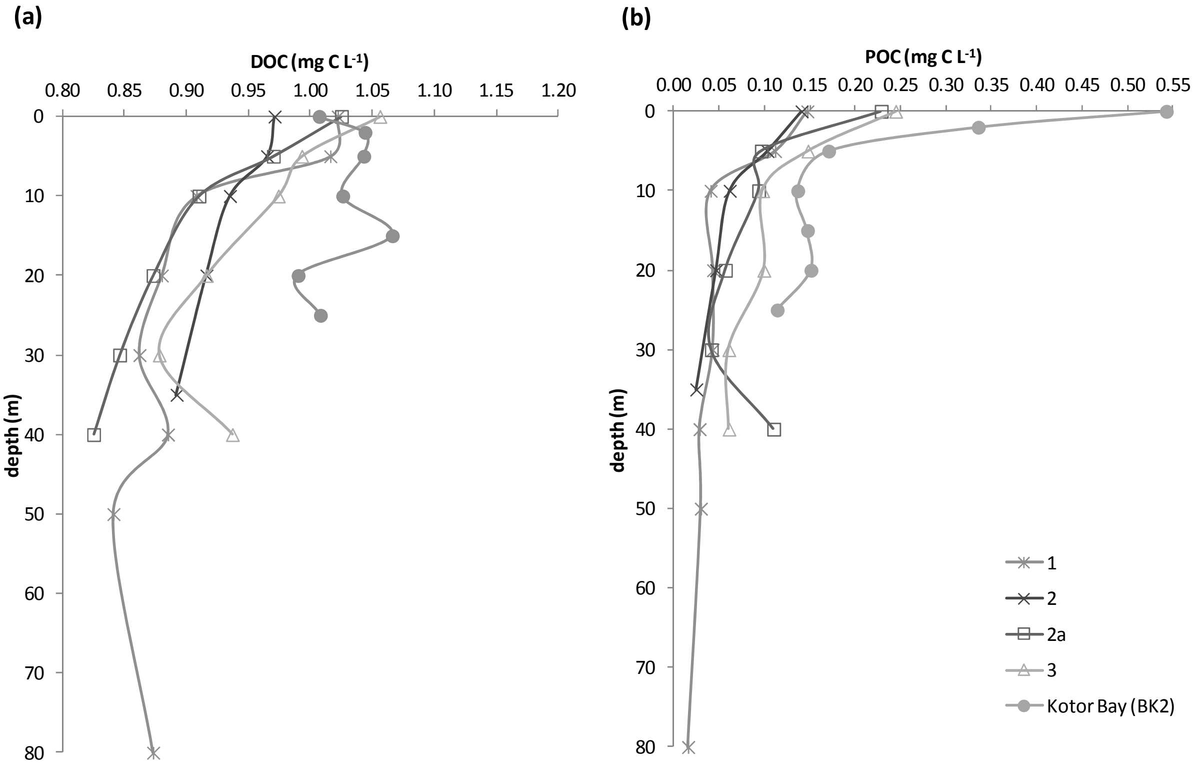

FIGURE 6 - DOC (a) and POC (b) in Boka Kotorska area (May 2008) at stations presented in Fig. 1a

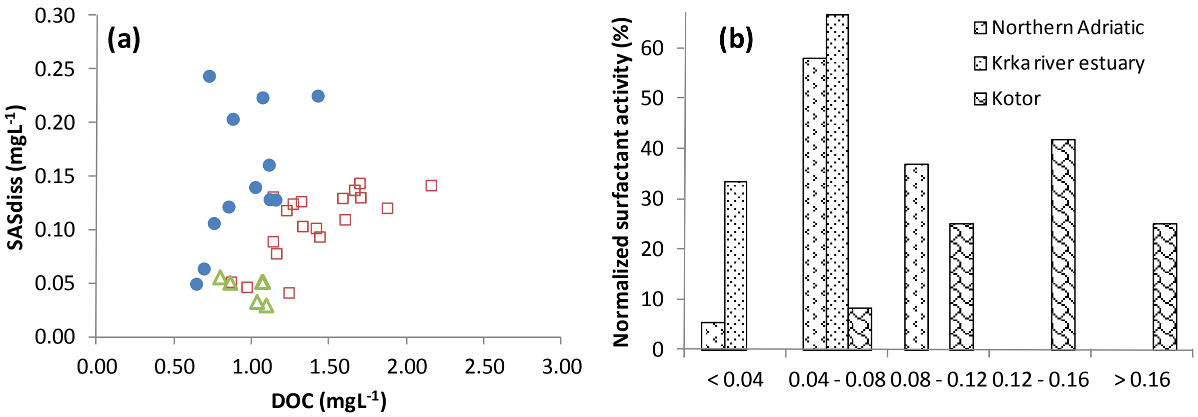

FIGURE 7 - (a) DOC-SAS$_{diss}$ relationship and (b) frequency distribution of normalized surfactant activity for Krka river estuary △ Northern Adriatic and the □ inner part of the Boka Kotorska Bay ● (Krka river estuary: N43°44'11.71'', E15°53'4.53''; SJ108: N44°45.4', E12°45.0') (NSA for model substances: xanthan 0.04; dextran T-500 0.20; fulvic acid 0.17)

POC concentrations measured during this study are typical for coastal waters of the Adriatic Sea [35]. They are lower than the values obtained for the Krka River estuary by Svensen *et al.* [37] but higher than the values reported by Sempéré and Cauwet [38].

3.5. Surface active substances (SAS)

During the whole period of investigation total SAS (SAS$_T$) showed significant fluctuations ranging from 0.026 to 0.311 mgL^{-1}, while dissolved SAS (SAS$_{diss}$) ranged from 0.023 to 0.244 mgL^{-1} equiv. Triton-X-100.

A decreasing trend of the surfactant activity along the water column from the surface towards the bottom was observed for all stations. Seasonal variations of SAS were followed as the average of values obtained per sampling in the upper (0 and 5m depth) and bottom layers at BK1, BK2 and BK3 stations, as presented in Fig. 4c and 4d.

Average of all SAS values obtained for three stations showed higher values for BK1 station while no significant differences were observed between the stations BK2 and BK3 (Table 1).

Production of fresh, very reactive organic material exhibiting surface active properties is evident to occur in 04/2008 (Fig. 4c). In 04/2008, DOC was still rather low (Fig. 4a). Biological activity remained high throughout the summer, accompanied with a DOC accumulation. A decrease in SAS_T is not visible before 11/2008, with DOC remaining increased. Depletion of both SAS_T and DOC is visible in 03/2009, a period just before the beginning of another cycle of organic matter accumulation. Surface active substances represent a reactive part of organic matter which is in close relation with biological activity in the area. These substances are subjected to adsorption/desorption processes at natural phase boundaries which affect their fate and distribution in the aquatic environment. Production of fresh reactive surface active material during spring phytoplankton activity is evident while the organic matter pool is poor at the beginning of biological production period.

Surfactant activity values obtained in the inner part of the Boka Kotorska Bay differ from those obtained in the northern Adriatic Sea and in the Krka River estuary [34, 38], all of which are the systems under the influence of freshwater (Fig. 7a). DOC values as well as SAS_{diss} values are the lowest for the Krka River estuary (33% DOC < 1 mgL^{-1} and 100% SAS_{diss} < 0.1 mgL^{-1}). In the northern Adriatic Sea, both, DOC and $SAS_{diss,}$ were higher (only 11% DOC < 1 mgL^{-1}, and 32 % SAS_{diss} < 0.1 mgL^{-1}). In the inner part of the Boka Kotorska Bay the SAS_{diss} values were higher than in the Krka River estuary and in the northern Adriatic Sea, while DOC values were lower (50 % DOC < 1 mgL^{-1} and 33% SAS $_{diss}$> 0.2 mgL^{-1}). Increased SAS values obtained in the inner part of the Boka Kotorska Bay are believed to be the consequence of the presence of the eurihaline organisms which might be producing reactive organic matter, *i.e.* SAS in brackish water. However, in the other parts of the Adriatic, this is not so pronounced.

Surface active properties of organic matter in different marine and estuarine systems were characterized by the normalized surfactant activity, NSA (NSA= [SAS (equiv. Triton-X-100) / DOC]). Comparison can be made with model SAS, such as fulvic acid (NSA = 0.17) and polysaccharides dextrane T-500 (NSA = 0.20) and xanthan (NSA = 0.04) as representatives of naturally occurring organic substances [4]. As presented in Fig. 7b., 66.7% NSA values obtained for the inner part of the Boka Kotorska Bay are higher than 0.12 in comparison with the Krka River estuary and northern Adriatic Sea, where NSA values were predominantly in the range from 0.04 to 0.12, indicating that surfactant activity is higher in the inner part of the Boka Kotorska Bay and that organic matter present in the Bay is more adsorbable and therefore more reactive.

3.5. Copper complexing capacity (CuCC)

CuCC values were higher for the surface samples and lower for deeper layer samples (Table 2). Copper complexing capacity (CuCC) ranged from 53 – 714 $nmolL^{-1}$, with an average of 183 $nmolL^{-1}$ in the surface layer (0 m and 2 m depth), while in the bottom layer it was in the range between 39 and 172 $nmolL^{-1}$ with an average of 110 $nmolL^{-1}$. The highest value was measured at BK3 station surface layer in November 2008 (714 $nmolL^{-1}$) and the lowest at BK2 station bottom layer in March 2009 (75 $nmolL^{-1}$). The Ružić-van den Berg method [12, 28] is suitable as it calculates CuCC from the whole titration curve, even when full saturation of the binding sites is not achieved. When the inert complex is present in the solution, it does not dissociate during the measurement (which in DPASV depends on the chosen stirring rate), so only free copper ions (and copper inorganic or organic complexes being labile for the applied experimental condition) diffuse to the electrode surface to form an amalgam. It is possible that apparent complexing capacity can be reduced by adsorption of the organic ligand on the electrode surface [39]. This would result from a different sensitivity for the metal ion. In our case the adsorption of SAS did not influence the sensitivity very much and after 60s of accumulation we were able to evaluate the copper peak height. Regarding different salinity values, due to the changed amount of Cl^- ions in some cases, in electrochemical anodic oxidation processes, we observed both stages of copper oxidation processes from amalgam. By the titration of the sample with increasing amount of copper ions either first or second oxidation peak become stabilized and increased

TABLE 2 - Copper complexing capacity values and apparent stability constant measured in the inner part of the Boka Kotorska Bay in 2008/2009

		04/2008		07/2008		11/2008		03/2009	
station	Depth (m)	CuCC/ nmol L^{-1}	log K_{app}	CuCC/ nmol L^{-1}	log K_{app}	CuCC/ nmol L^{-1}	log K_{app}	CuCC/ nmol L^{-1}	log K_{app}
BK1	0	-	-	147	-	116	8.0	167	7.9
BK1	2	169	7.1	167	7.0	110	7.3	181	7.1
BK1	15	143	6.9	118	7.1	120	7.1	120	7.7
BK2	0	357	6.7	109	-	182	8.5	166	8.7
BK2	2	270	7.2	73	6.7	250	8.4	256	7.9
BK2	25	91	7.4	96	7.5	93	7.00	75	8.6
BK3	0	232	7.2	149	-	714	7.6		-
BK3	2	173	7.2	112	8	94	7.4	192	-
BK3	25	149	7.0	54	-	-	-	111	9.3

with the further copper ion additions. Our chosen potentials for the accumulation of copper (-0.6 V) could have lead to the underestimation of the complexing capacity, as possibly some complexes could have been reduced, increasing the concentration of the labile metal ions. It must be stressed that any measurements of complexing capacities are operationally defined and only valid for the chosen experimental conditions.

Determination of the apparent stability constants could be rendered in some cases regarding the use of linearization method by Ružić-van den Berg, because if as the first addition too high concentration of copper ion is added the curvature on the titration graph can not be evaluated precisely enough. The upper- part of the titration curve is obtained from which only the CuCC could be evaluated (in Table 2, samples for which there is no log K_{app}). Titration curves, *i.e.* their linearization plots indicated 1:1 complexes, i.e. there was not data by which were possible to prove the presence of multiple ligand complexes. Apparent stability constants (log K_{app}) were in the range from 6.7 to 9.3, which are the values similar to those from other parts of the Adriatic Sea [40, 41, 42] as well as to the ones obtained for humic material and melanoidins [43]. In Fig. 8 the copper DPAS voltammograms for UV-irradiated (pH=2) sample and sample at pH=8 (station BK3, 2m, July 2008) together with the titration curve and Ružić-van den Berg plot are presented.

The results for CuCC in April 2008 were higher than those recorded in other seasons, probably as the consequence of spring biological production (induced by freshwater input of nutrients).

Statistically significant negative correlation was obtained between CuCC and salinity (n=33, R=0.563, P<0.0001) (Fig. 9a). This was found also for the Krka

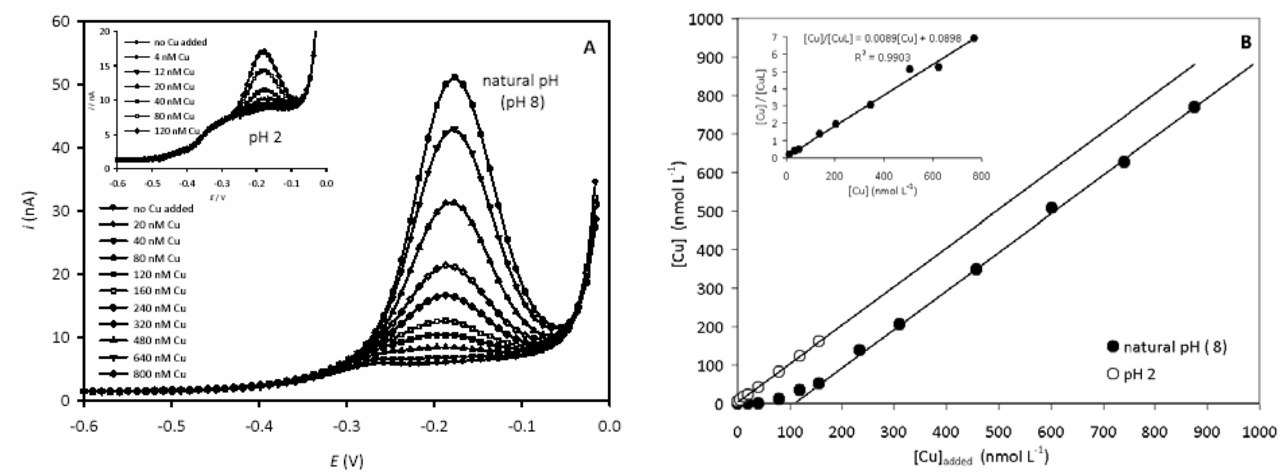

FIGURE 8 - DPASV measurement of CuCC for sample BK3, 2m depth (July 2008): A) voltammograms of increased copper ion additions in sample at natural pH (pH 8) and (inset) in acidified sample (pH 2); B) copper ion concentration added vs. copper ion concentration found, inset: linearization of these titration curves according to the Ružić-van den Berg method.

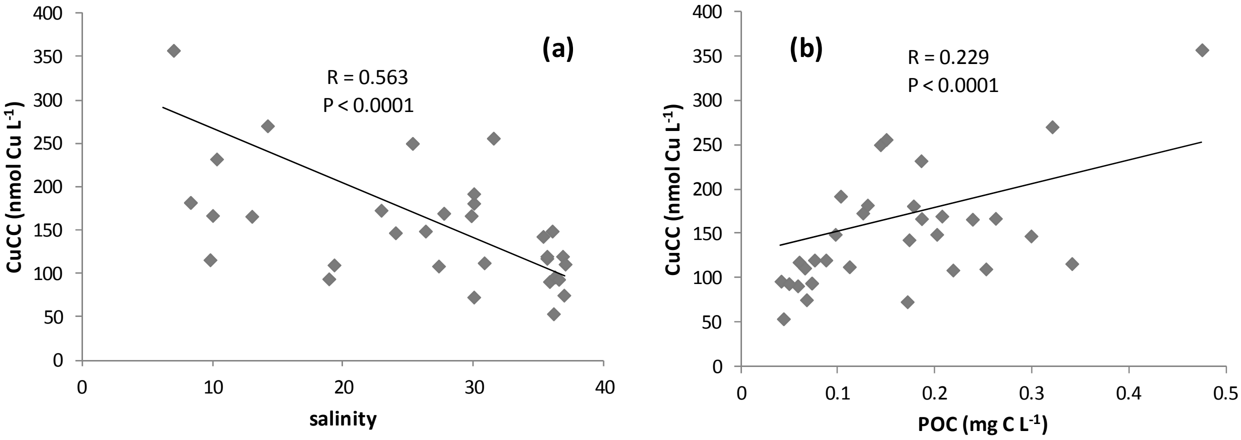

FIGURE 9 - Correlation of CuCC with (a) salinity, (b) POC

River estuary [40, 41]. Statistically significant positive correlation ($P<0.0001$) with very low correlation coefficient was found between CuCC and POC ($n=33$, $R=0.229$, $P<0.0001$) (Fig. 9b). No statistically significant correlation was found between CuCC and DOC, pointing to the importance of POC as significant ligand for copper complexation.

CuCC values are typical for coastal systems in the Adriatic Sea [41, 42] and the main contributor to the complexing ligands in the Boka Kotorska Bay is autochthonous biological production. It is known that the particles in the case of Langmurian type of Cu ions adsorption are treated as additional ligands for copper ion by this method of calculation [12, 14, 28]. There is a high input of metal ions to the Boka Kotorska Bay [44] and higher amount of available ligands could exert a beneficial role in the system as they buffer the toxicity of metal ions, which is decreased in the case of their complexation by the ligands [17].

4. CONCLUSIONS

The importance of characterizing and protecting the karstic regions in the world cannot be emphasized strong enough, given the increasing population density of humans residing in these settings, and the ecosystems that rely on karstic environments and karstic water to sustain life [45].

Even though preconditions were documented for the inner part of Kotor Bay *i.e.* elevated nutrient concentrations that lead to high biological production within the system and hence the accumulation of reactive organic matter in spring/summer months our integrated chemical-biological approach showed that no eutrophic episodes were detected in the period 2008/2009. It seems that freshwater in the forms of vruljas, poor in dissolved organic carbon, has the ability to purify the system. This is proved by the statistically relevant positive correlation between DOC and salinity in the upper layer. Due to high reactivity of organic matter present in this area (high SAS_T values), one could assume that organic matter could be removed from the water column fast enough (sticking to particles/agglomerating, sinking to the sediment) to prevent major organic matter accumulation that might lead to eutrophic episodes in this very delicate area.

ACKNOWLEDGEMENT

The authors are indebted to the joint educational and research project entitled Marine Science and Coastal Management in the Adriatic, Western Balkans, An Education and Research Network, funded by the Norwegian Research Council (period 2006 - 2010), with the project leaders Paul Wassmann, University of Tromsø, Norway and Božena Ćosović, Ruđer Bošković Institute, Zagreb, Croatia. The authors also thank the Ministry of Science, Education and Sports of the Republic of Croatia for funding the project “Nature of the organic matter, interaction with traces and surfaces in environment” (No. 098-0982934-2717). Grozdan Kušpilić is thanked for providing nutrient data.

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Received: September 05, 2011
Revised: November 18, 2011
Accepted: December 07, 2011

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FEB/ Vol 21/ No 4a/ 2012 – pages 995 - 1006

Continental Shelf Research 39–40 (2012) 41–48

Contents lists available at SciVerse ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Research papers

Characterization and distribution of organic matter using specific physico-chemical methods: A case study of the southeast Adriatic continental and shelf slope (Albania)

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ARTICLE INFO

Article history:
Received 19 October 2011
Received in revised form
23 March 2012
Accepted 31 March 2012
Available online 9 April 2012

Keywords:
South Adriatic Sea
Albanian continental shelf
Organic matter characterization
DOC
POC
Copper complexing capacity

ABSTRACT

In May 2009, we characterized the organic matter in the area where Albanian shelf riverine plume waters enter the Southern Adriatic Pit region. Due to stable weather and hydrological conditions at the time of sampling a longitudinal thermal front was present around the Albanian shelf break. Our measurements point to the input of inorganic nutrients, including phosphorus (average P-PO_4 concentration was 0.71 μg/L) and nitrogen (average as total inorganic nitrogen (TIN) concentration was 25.33 μg/L) due to the intrusion of Levantine Intermediate Water (LIW) through the Otranto Strait. The input of LIW brings high salinity (~38.7) water that is poor in organic matter content. Low concentrations of dissolved organic carbon (DOC) (0.7 mg C/L) and particulate organic carbon (POC) (0.06 mg C/L), surface active substances (SAS) (in the range from 0.025 to 0.078 mg/L equiv. Triton-X-100) and copper complexing capacity (CuCC) (24 nmol Cu^{2+}/L) were measured in the area. All the values for DOC, POC, SAS and CuCC were significantly lower in the Albanian coastal waters than in the North Adriatic. The measurable influence of the inflowing Albanian rivers was observed from the inverse dependance of the DOC concentrations and salinity data. The Albanian rivers contribute to the elevated nutrient concentrations especially those of silicate, which displayed concentrations up to 380 μg/L in the shallowest coastal station.

1. Introduction

Seawater organic carbon represents a dynamic component of the global carbon cycle and is now recognized as a possible barometer of global climate changes (Liss and Duce, 1997).

The concentrations of the dissolved organic carbon (DOC) and particulate organic carbon (POC) in natural waters are measured as general parameters. Many components of aquatic organic matter exhibit the property of surfactant activity and are referred to as surface-active substances (SAS) (Hunter and Liss, 1981). SAS accumulate on different phase boundaries (air/water; water/sediment; water/living or non-living suspended particles) influencing the structure and physico-chemical properties of these interfaces and mediating the processes of mass and energy transfer (Hunter and Liss, 1981). Surfactant activity of different classes of organic matter as representative for organic matter present in aquatic systems has been widely investigated by using electrochemical methods (Ćosović and Vojvodić, 1982, 1998). Clear evidence of surfactant production by marine phytoplankton based on laboratory and field experiments is also available (Zhou et al., 1989; Plavšić et al., 1990). Due to the specific reactivity of SAS at natural phase boundaries, their distribution and fate in the sea could be different, than other organic matter pools, such as dissolved organic carbon (DOC) (Ćosović et al., 2000; Dautović et al., 2012). A combination of general parameters (DOC and POC) and SAS gives the information about both content as well as the reactivity of organic matter in a particular aquatic system (Ćosović and Vojvodić, 1998; Ćosović et al., 2000; Dautović et al., 2012).

Metal complexation by inorganic ligands in water (ocean, estuaries, freshwater) is well studied whereas less is known about speciation of metal ions in the presence of organic ligands (Buffle, 1988). With the development of a number of sensitive and selective metal speciation techniques like electrochemical techniques, also metal–organic interaction has been studied (Van den Berg, 1982; Scoullos et al., 2004). Copper is the metal ion studied the most (Phinney and Bruland, 1994; Andrade et al., 2006) as it forms very stable organic complexes and is an essential metal ion

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http://dx.doi.org/10.1016/j.csr.2012.03.014

(Buffle, 1988; Buck and Bruland, 2005). Its complexation to organic ligands in all aquatic system, with the exception of deep ocean water, is $>99\%$ (Buck and Bruland, 2005). Catalytic and surface activity of nitrogen containing polymeric organic material (N-polymeric) could be also analysed by electrochemical techniques such as constant current chronopotentiometric stripping analysis (CPSA). Recently, CPSA proved to be a suitable method for determination of low concentrations of N-polymeric compounds in seawater by measuring "presodium" catalytic peak "H" (Strmečki et al., 2010).

The Albanian coastal zone circulation is greatly influenced by inflowing Ionian waters, strong riverine discharge, and wind action (Gačić et al., 2001, 2010). The northward turning of the rivers' plume in the area is consistent with the Coriolis effect (Kourafalou, 1999) and it is also in the direction of the prevailing currents in the southeastern Adriatic (Artegiani et al., 1997). In winter, when southeast winds prevail and Adriatic waters are denser than Ionian, the Ionian Surface Waters (ISW) extend well into the central part of the Adriatic basin, keeping the Adriatic Surface Waters (ASW) close to the western shores. The situation reverses in summer, when oceanographic and meteorological conditions favour lateral expansion of the ASW, pushing the ISW closer to the eastern shores (Orlić et al., 2006). The spring, represent a transitional period, which is characterized by gradual warming of the surface waters and a change from the winter situation in which waters closer to the shore are colder than those off-shore imposed by changes in riverine input and Ionian inflows. The Levantine Intermediate Water (LIW) with the current vein flowing in the layer below 40 m depth, with salinity greater than 38.7 (Zore-Armanda, 1969; Socal et al., 1999; Vilibić and Orlić, 2002) influence the area. The physical disturbances determine water column stability and the magnitude of vertical mixing, consequently affecting the flux of nutrients and biological processes (Viličić et al., 2010; Šilović et al., 2011).

Our research was performed in May 2009, after stabilization of weather and hydrological conditions and the formation of longitudinal termal front around the Albanian shelf break (Viličić et al., 2010). The scope of our research on the Albanian shelf was to determine the influence of Buna River (as the river with highest discharge rate in the area) to the southeast Adriatic shelf water concentration and distribution of DOC, POC, nutrients, SAS and CuCC in relation to the established hydrological situation in late spring. This is the first research in the area of Albanian shelf in South Adriatic Pit regarding the organic matter characterization and distribution.

2. Sampling and analytical methods

2.1. Study area

The morphology of the Southern Adriatic Sea is characterized by the South Adriatic Pit, reaching a depth of 1250 m (Fig. 1) (Civitarese et al., 2010). The bottom of the South Adriatic Pit rises to a 780 m deep sill in the 75 km wide Strait of Otranto, where the Adriatic is connected to the Ionian Sea and the rest of the Mediterranean. The Albanian coastal zone is a narrow shelf smoothly sloping into the South Adriatic Pit. There are several rivers in the Albanian coastal zone with an average discharge of 1308 m^3 s^{-1} or 4.1×10^4 km^3 year^{-1} (Çullaj et al., 2005). The average Buna river discharge is about 700 m^3 s^{-1} (Fig. 1). The Buna river is the southeastern Adriatic counterpart to the Po River in the northwestern Adriatic (Marini et al., 2010).

2.2. Sampling

The research cruise was carried out using MV Rozafa3 along the 91-km long cross-section through the continental slope of the Southern Adriatic Pit and Albanian shelf, extending to the southwest of the Buna River mouth in May 2009 (Fig. 1). Before the beginning of the field work, infrared satellite imagery revealed longitudinal thermal front around the Albanian shelf break, between isobaths of 300 and 900 m (M. Kuzmić, personal comm.; Viličić et al., 2010). Temperature and salinity were recorded at six stations A50–A1000 (Fig. 1) using a CTD profiler Sea Bird Electronic SBE 9 plus. Hydrographic profiles were measured between the surface and the depth of 380 m. Sampling has been done to the depth of maximum of 380 m depending on the available equipment for sampling taking into account that the upper water layer under the influence of river input was included. Seawater samples were collected by Niskin samplers at six stations (A50, A150, A200, A300, A900 and A1000) (Table 1) at four to eight depths (0.5, 5, 20, 50, 75, 100, 200, 300 and 400 m), depending on the station depth (Fig. 1).

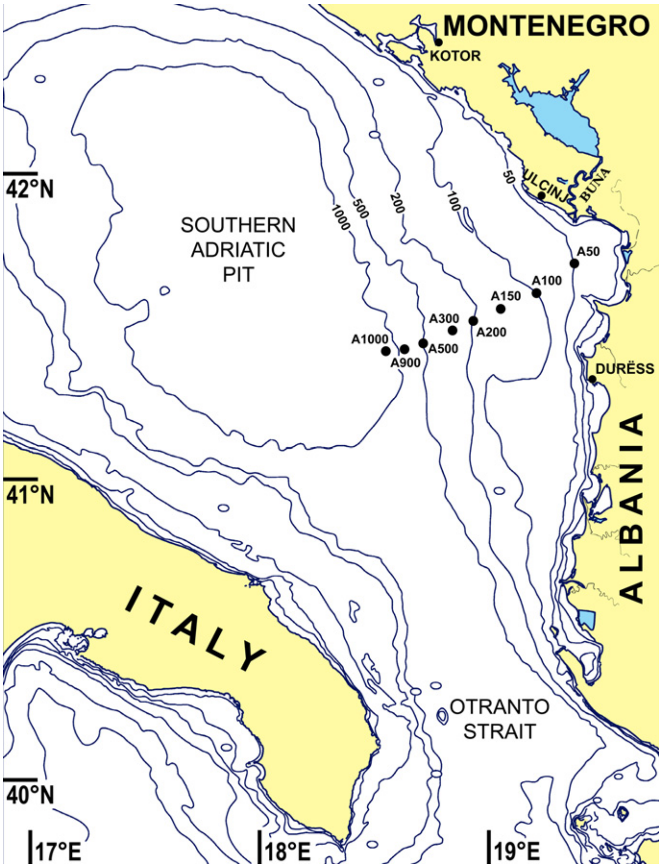

Fig. 1. The transect and sampling stations (A50, A100, A150, A200, A300, A500, A900 and A1000) in southern Adriatic Sea (Albania).

2.3. Analytical methods

2.3.1. DOC and POC determination

For the DOC and POC determination, seawater samples were collected directly from the Niskin samplers in the dark, glass (1.3 L) bottles, previously washed with chromic-sulphuric acid and rinsed with organic free water (Milli-Q water) and seawater sample. The filtration of collected samples was performed immediately after sampling on Whatman GF/F glass fibre filters, pore size 0.7 μm, previously combusted for 4 h at 450 °C. Precleaned, all glass filtration system (Millipore, USA) connected to a vacuum pump (Millipore, USA) was used. Filtered samples for DOC analysis were collected in duplicates in the 22 mL glass vials washed with chromic-sulphuric acid and several times with

Table 1
Salinity, temperature, nutrients, SAS_T and SAS_{diss}, CuCC and logarithmic value of apparent stability constant for copper complexation for all stations and depths measured.

Station	Depth (m)	S	T (°C)	SiO_4 (µg/L)	PO_4 (µg/L)	OP[a] (µg/L)	TIN[b] (µg/L)	ON[c] (µg/L)	SAS_T (mg/L equiv. T-X-100)	SAS_{diss} (mg/L equiv. T-X-100)	CuCC (nmol Cu^{2+}/L)	Log K_{app} (L/nmol)
A50	0	33.82	20.28	379.6	0.61	2.63	26.6	43.3	0.078	0.069	54	7.8
	5	36.75	18.88	116.7	0.07	2.12	11.2	35.6	0.069	0.059	59	7.6
	20	38.08	16.08	66.9	0.10	1.91	8.0	63.0	0.051	0.049	–	–
	40	38.18	13.90	68.0	0.07	1.82	8.1	35.9	0.046	0.048	–	–
A150	0	35.93	20.14	29.1	0.12	2.15	20.1	131.2	0.074	0.076	–	–
	5	36.90	17.57	17.4	0.06	2.30	10.1	36.0	0.059	0.063	55	7.6
	20	38.21	15.98	15.0	0.13	1.76	8.6	51.5	0.054	0.045	52	7.9
	50	38.46	14.51	9.6	0.27	1.88	8.9	45.7	0.045	0.042	–	–
	75	38.51	14.16	6.4	0.04	1.61	17.3	34.6	0.042	0.036	–	–
	100	38.47	13.83	21.8	0.06	2.05	29.5	37.9	0.038	0.038	81	7.6
A200	0	36.22	20.88	58.3	0.04	1.66	13.3	46.1	0.061	0.068	–	–
	5	37.56	17.18	38.4	0.16	1.76	11.1	19.8	0.069	0.062	480	9.0
	20	38.23	15.83	20.1	0.12	1.78	12.9	45.2	0.047	0.047	71	7.2
	50	38.46	14.35	5.2	0.29	1.33	10.5	26.6	0.040	0.040	–	–
	75	38.43	13.87	13.3	0.03	2.02	18.7	29.8	0.031	0.035	–	–
	100	38.49	13.97	9.0	0.12	1.37	23.5	28.4	0.035	0.034	–	–
	180	38.80	14.18	37.7	2.88	0.15	51.6	2.4	0.033	0.027	72	7.4
A300	0	37.37	20.84	38.0	0.04	2.11	10.2	43.3	0.072	0.060	–	–
	5	37.41	19.61	42.5	0.06	2.11	9.3	31.2	0.046	0.055	76	7.0
	20	38.12	14.76	23.3	0.07	2.03	8.0	36.0	0.050	0.047	91	7.4
	50	38.31	13.86	21.2	0.07	2.12	12.8	33.9	0.045	0.045	–	–
	75	38.49	14.02	3.4	0.07	1.69	22.0	30.1	0.038	0.034	–	–
	100	38.50	13.93	15.7	0.09	2.02	29.1	28.5	0.041	0.043	–	–
	200	38.74	14.13	37.6	1.97	1.25	54.4	22.6	0.027	0.028	–	–
	280	38.80	14.13	71.7	4.06	0.66	71.7	13.5	0.033	0.039	–	–
A900	0	38.15	20.65	17.1	0.12	1.96	16.5	37.0	0.063	0.063	–	–
	5	38.27	18.60	8.0	0.06	1.60	12.2	18.3	0.041	0.044	287	8.1
	20	38.23	15.94	24.2	0.06	2.06	10.9	36.2	0.051	0.052	434	8.1
	50	38.36	13.58	10.7	0.09	2.32	24.1	21.3	0.032	0.037	–	–
	75	38.54	13.93	40.5	0.36	2.29	53.1	28.7	0.032	0.041	–	–
	100	38.77	14.36	45.5	2.89	0.96	61.0	11.7	0.026	0.028	–	–
	200	38.60	13.35	41.1	2.08	1.09	52.6	18.3	0.029	0.029	–	–
	300	38.67	13.49	53.5	2.40	1.54	57.4	52.8	0.027	0.029	24	8.7
A1000	0	38.17	19.71	24.8	0.12	1.78	10.4	35.2	0.054	0.051	–	–
	5	38.19	17.47	25.3	0.04	2.08	10.0	50.3	0.060	0.046	77	7.7
	20	38.24	14.17	23.2	0.09	1.93	8.0	40.5	0.042	0.051	105	7.6
	75	38.69	13.94	45.5	1.98	1.21	57.5	24.9	0.029	0.031	–	–
	200	38.62	13.34	44.3	2.32	0.82	49.4	13.1	0.031	0.034	–	–
	300	38.69	13.56	58.5	3.19	0.45	57.2	10.9	0.026	0.033	137	8.4

[a] Organic phosphorus.
[b] Total inorganic nitrogen.
[c] Organic nitrogen.

Milli-Q water (Millipore, USA). Vials were supplied with solid top screw caps with PTFE liner (Supelco, USA). The samples were preserved with mercury chloride (10 mg/L) and stored at +4 °C in the dark until analysis. After collection of the DOC subsamples GF/F filters were rinsed with a few ml of Milli-Q water to remove salts from the filter and stored in liquid nitrogen (at −80 °C) until POC analysis.

The DOC concentrations were analysed in duplicate using the sensitive high temperature catalytic oxidation (HTCO) method (Dafner and Wangersky, 2002). A Model TOC-V_{CPH} (Shimadzu) with silica catalyst (Elemental microanalysis, UK) and nondispersive infrared (NDIR) detector for CO_2 was used. Potassium hydrogen phthalate was used as a standard. Samples were acidified (pH 2) with 2 μmol/L HCl and purged with pure air for 10 min immediately prior to analysis. The concentration was calculated as an average of three to five replicates. The average instrument and Milli-Q blank correspond to 0.03 mg C/L ($n=32$) and the reproducibility was high (≤1.6%).

POC was analysed with a solid sample module SSM-5000A associated with a TOC-V_{CPH} carbon analyser, calibrated with glucose. After acidification with HCl (8 N) to remove inorganic carbonate fraction, the filters were folded in aluminium foil in a ceramic sample boat and dried at 50 °C for 12 h. Then the samples were burned in a flow of oxygen at 900 °C. The average filter blank including instrument blank corresponds to 0.005 mg C/L. The reproducibility obtained for the glucose was high (≤3%).

2.3.2. SAS determination

Surface active substances were analysed electrochemically by a.c. voltammetry (Ćosović and Vojvodić, 1998) using Metrohm 797VA Computrace instrument. Three-electrode cell system was used: hanging mercury drop electrode (HMDE), as a working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and platinum electrode as the counter electrode. The deposition potential of −0.6 V vs. Ag/AgCl ref. electrode and deposition time of 30 s controlled by stirring were applied. Surfactant activity was expressed in terms of surfactant equivalents of the non-ionic surface active compound Triton-X-100 (MW=600 mg/L) with detection limit of 0.01 mg/L and reproducibility of 3%. Surface active substances were determined in both non-filtered (SAS_T, total, i.e. dissolved+particulate) and filtered (SAS_{diss}, dissolved) samples immediately after sampling. Normalized surfactant activity (NSA) values were calculated by dividing the concentration of SAS in mg/L equiv. of Triton-X-100 with the DOC in mg C/L (Ćosović and Vojvodić, 1998).

2.3.3. Copper complexing capacity (CuCC) measurements

The experiments were performed on the electrochemical system consisting of a 663VA-Stand (Metrohm, Herisau, Switzerland) connected via an IME663 module to a computer controlled μ-Autolab instrument (EcoChemie, Utrecht, The Netherlands). The working electrode was a static mercury drop electrode (SMDE, drop surface area 0.52 mm^2). The reference electrode was a double-junction Ag/AgCl (3 M KCl) electrode and the counter electrode was a glassy carbon rod. The solutions were stirred during the deposition step of measurements. Potential of deposition was −0.6 V vs. Ag/AgCl ref. electrode with the deposition time of 60 s. The complexing capacity was determined in unfiltered seawater samples. The reproducibility of the method is $\pm 2\times10^{-9}$ M Cu^{2+} from which the detection limit equal to 6×10^{-9} M Cu^{2+} can be calculated. Determination was performed by the direct titration method of the sample with increasing amounts of copper ions and their electrochemical response was measured by the method of differential pulse anodic stripping voltammetry (DPASV) (Plavšić et al., 1982; Plavšić, 2003). To obtain complexing capacity values and conditional stability constant, titration data are linearly transformed assuming 1:1 metal to ligand complexes (Van den Berg, 1982; Ružić, 1982). The equation used for calculation is: $[Cu]/[CuL]=[Cu]/CuCC+1/KCuCC$, where Cu is the copper ion detected by anodic stripping voltammetry, CuL is the copper ion bound in a complex with ligand L, CuCC is the total concentration of binding ligands (i.e. complexing capacity) and K is the apparent stability constant. The plot of [Cu]/[CuCC] vs. [Cu] yields a straight line with a slope of 1/CuCC and intercept $1/K$CuCC.

2.3.4. N-containing polymeric material (N-polymeric)

Measurement conditions for electrochemical constant current potentiometric stripping analysis (CPSA) method were: accumulation potential $E_a=-0.6$ V and time of accumulation $t_a=60$ s, with stirring, constant reduction current $I=-1$ μA and maximum time of measurement 5 s. CPSA measurement were performed on unfiltered samples, in the presence of oxygen, instrument and cell were as in CuCC determination. The results were expressed as the equivalents of the model polymer substance i.e. protein human serum albumin (HSA, Sigma, USA, MW=67 kDa) and/or as equivalents of N atoms present in HSA taking into account the 15.7% of N content in HSA (Strmečki et al., 2010).

2.3.5. Nutrients

Seawater samples for nutrients were deep frozen on board and were kept frozen (at −20 °C) in 500 mL polyethylene bottles until analysis. Nutrient concentrations were determined by colorimetric method using a Shimadzu UV-1800 spectrophotometer (wavelength range 190–1100 nm). Proportionality factors were determined by measuring the extinction of the standard solutions. The reproducibility was ≤3%. Method of determining phosphate is based on the reaction of phosphate with ammonium molybdate (Murphy and Riley, 1962). Extinction was measured at a wavelength of 885 nm. The accuracy of the method was ±0.0025 μg/L. Silicate was measured at a wavelength of 830 nm. Reactions of the "reactive" silicate with molybdate result in the formation of silicomolybdate complex (Mullin and Riley, 1955). The accuracy of the method was ±0.0028 μg/L. Nitrate was determined by the modified method in which nitrate was reduced to nitrite by passing the sample through a cadmium reduction column (Wood et al., 1967). The accuracy of the method was ±0.0007 μg/L. Nitrite was determined by the same method as nitrate, but without passing the sample through the reduction column. The accuracy of the method was ±0.0007 μg/L. The concentration of ammonia was determined by the method of Ivančić and Degobbis (1984). Extinction was measured at a wavelength of 640 nm. The accuracy of the method was ±0.0004 μg/L.

Organic P was calculated as the difference between total phosphorus (P_{tot}) and phosphate. Total P was determined by decomposition of present organic compounds and polyphosphates. Unfiltered seawater sample was subjected to UV-radiation at a wavelength of 250 nm (Parsons et al., 1985). Organic N was calculated as the difference between total nitrogen concentration (N_{tot}) and TIN ($TIN=NH_4+NO_2+NO_3$). N_{tot} was determined by oxidation of organic compounds in the unfiltered sample and measuring the free nitrate (Parsons et al., 1985).

3. Results

Temperature, salinity, nutrients, SAS and CuCC concentrations (together with corresponding apparent stability constants ($\log K_{app}$)) for all the samples measured are given in Table 1. Silicate concentrations were high for station close to the coast, while all the other nutrient concentrations were relatively low especially regarding phosphate. High concentration of silicate (up to 380 μg/L) in the coastal station was the consequence of the Buna River load. Organic nitrogen and organic phosphorus concentrations increased in certain stations and at specific depths (e.g. concentrations of ON for A50: 20 m; A150: 0 m; and A900: 300 m and concentrations of OP for A50:0 m; A150: 5 m; and for A1000 5 m) (Table 1). The distribution of salinity and temperature, DOC, POC, and SAS for the surface samples are illustrated in Fig. 2. Surface salinity values increased from A50 station to A1000 station (Fig. 2A) due to the decreasing influence of the freshwater input from the Albanian rivers. The salinity values ranged from 34 to 38.5, while the temperature values fluctuated from 19.8 to 20.9 °C, being highest at sampling stations A200, A300 and A900.

The highest DOC value for surface samples was detected at the station A300 (1.05 mg C/L) (Fig. 2B). At the A300 station there was also the greatest difference between DOC and POC concentrations (Fig. 2B). The majority of the organic matter was present in the dissolved phase. Only about 6% of TOC was present as POC. On A300 station there was a greatest difference in the concentration of SAS_T and SAS_{diss}. No significant difference between total and dissolved SAS was observed for other sampling stations (Fig. 2C). There was a significant correlation ($R=0.89$; $p<0.0001$) of DOC and SAS_{diss} concentrations (Fig. 3) with both parameters decreasing with depth. The lowest DOC values (<0.75 mg C/L) were measured at stations A200, A900 and A1000 which is however low value for the Adriatic Sea samples. SAS_T concentrations were also low and for the few samples it was almost at the limit of detection i.e. 0.02 mg/L in equiv. of Triton-X-100. Calculated normalized surfactant activity data (NSA) i.e. SAS_{diss}/DOC values have shown that in the upper 10 m layer of all stations different types of OM predominate in comparison to the OM in the deeper layers of the water column. The NSA value for the upper 10 m was 0.061 ± 0.007, while for the deeper layers NSA value was 0.042 ± 0.006 which means that in the upper water column slightly more hydrophobic material was present (Ćosović and Vojvodić, 1998). Salinity and temperature values for the deeper samples were $S > 38.5$ and $T > 13.8$ °C pointing to the core of LIW current at these depths (Viličić et al., 2010). DOC values for these samples were very low varying in the range from 0.721 to 0.796 mg C/L. LIW brought inorganic nutrients (Gačić et al., 2002) as illustrated by the TIN and inorganic P as PO_4 concentrations in the layer of app. 200 m depth (Table 1).

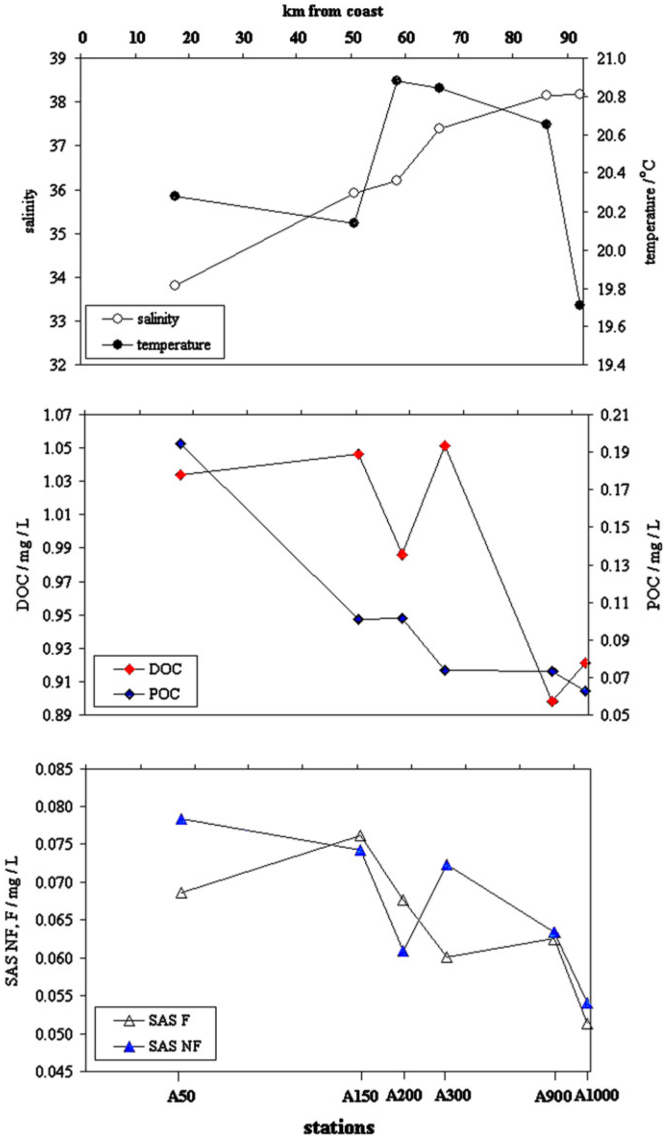

Fig. 2. (a) Distribution of the salinity and temperature, (b) DOC and POC concentrations, and (c) SAS for non-filtered and filtered samples, for the surface samples for stations A50–A1000. The distances of the stations from the coast are expressed in km.

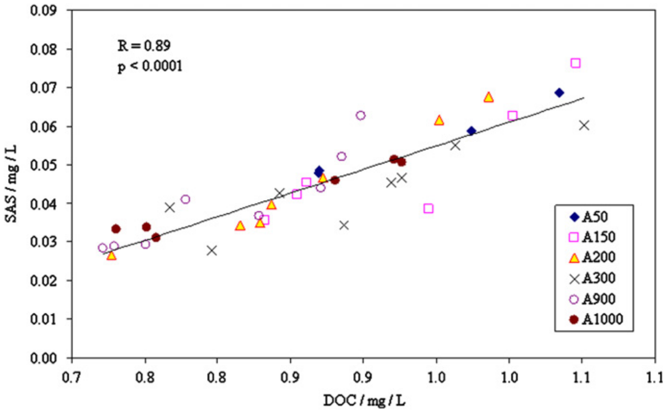

Fig. 3. DOC vs. SAS concentrations for the stations A50–A1000 for all the depths.

The relationship between DOC concentrations and salinity for all samples is illustrated in Fig. 4. The increasing salinities from the station A50 to the station A1000 were measured. DOC concentrations decreased from the station A50 to the station A1000 for all depths (with the exception of A150, 100 m). DOC concentrations were significantly negatively correlated with salinities ($R=-0.758$; $p<0.05$). DOC concentrations were significantly positively correlated with ON and OP, with correlation coefficients of 0.557 and 0.735 respectively ($p<0.05$). Also, POC concentrations were significantly positively correlated with ON and OP but with lower correlation coefficients of 0.409 and 0.602 respectively ($p<0.05$). The CuCC were for all stations low, with only few exceptions, which meant that the amount of organic ligands complexed to copper ions was low in comparison to the other Adriatic seawater samples (Fig. 5). The highest values for CuCC were obtained for surface samples at the stations A200 and A900 (Fig. 5). The log K_{app} values, which represent the values for the apparent stability constants of the formed copper complexes, were in the range from 7.0 to 9.0, as found for the complexation of copper ions with humic and fulvic acids as well as for melanoidins (Plavšić et al., 2006). Beside the CuCC determination, we measured the concentration of “N-polymeric organic material” (N-polymeric) by the recently proved constant current potentiometric stripping analysis (Strmečki et al., 2010). The partition of N-polymeric in total organic nitrogen fraction (ON) varied from 0% to 97% at the station A200 (180 m depth) (Table 2). Basic

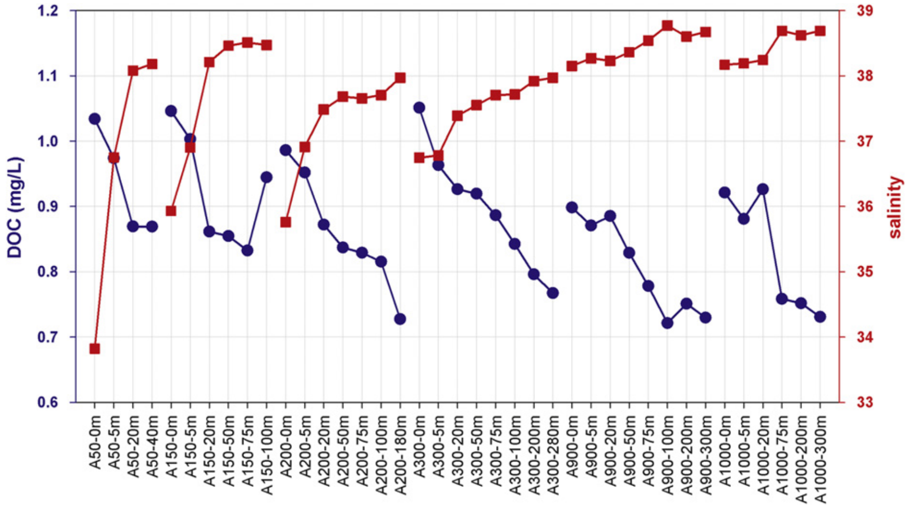

Fig. 4. DOC concentrations vs. salinity for the stations A50–A1000 for all the depths.

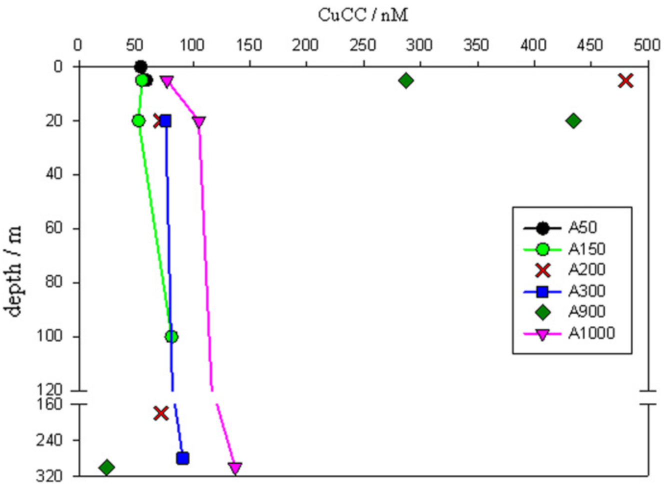

Fig. 5. CuCC vs. depths for the stations A50–A1000.

statistics for the measured parameters, with minimum, maximum, average and standard deviations are presented in Table 3. In Table 4 we also present the correlation coefficients and statistical significance between selected parameters.

4. Discussion

The characteristics of the top 300 m of the water column investigated in this study, which include the isohalines between 38.5 and 38.6, as well as isotherms between 13.6 and 13.8 °C, indicate the boundary layer between the coastal sea and the northwesterly inflowing LIW in the 100- to 350-m layer, ca. 80 km to the southwest of the Albanian mainland (Viličić et al., 2010; Šilović et al., 2011). Low phosphorus concentrations in the coastal area are probably due to mineralogical composition of sediments in the area characterized by silicates (I. Sondi, personal comm.). For silicate concentrations, weathering of soil and rocks and runoff become dominant controlling factor, even if minor contributions from anthropogenic point sources have been reported (Ludwig et al., 2009). The most critical physico-chemical parameter for Albanian rivers is total particulate content (TSS) caused by very high erosion rate (Çullaj et al., 2005). The concentration of silicate in the Buna River estuary is reported to be in the range from 60 to 630 μg/L depending on salinity (Marini et al., 2010). The concentration of dissolved inorganic nitrogen is reported to be in the range 14–252 μg/L, also depending on the salinity, being higher in low salinity water (Marini et al., 2010). The majority of the concentrations of phosphorus as P-PO_4 in all Albanian rivers are below 60 μg/L (Çullaj et al., 2005).

While POC concentrations increased coastward, the highest DOC and SAS values are detected at A300 station in the upper water layer. Normalized surfactant activity values (NSA) show that the organic material in the upper 10 m differs from the OM in the samples from the deeper layers, indicating that they differ in hydrophilic/hydrophobic properties (Ćosović and Vojvodić, 1998). Among different phytoplankton species, dinoflagellates are known to produce organic material with pronounced hydrophobic character which is reflected by strong adsorption and elevated SAS (Žutić et al., 1981). As reported by Viličić et al. (2010), the maximum dinoflagellate abundance in Albanian coastal waters in May 2009 is detected at station A300. At the same time diatom abundances increase coastward (Viličić et al., 2010). However, the samples we collected were characterized by low abundances of nanoplankton and bacteria, indicating an oligotrophic marine environment (Viličić et al., 2010). Our results show that in the water samples of higher salinity and temperature, which indicate the origin of the water is the LIW, lower DOC values are measured (below 0.75 mg C/L). In the Buna River and its estuary we determined DOC values in the range from 0.95 to 3.5 mg C/L, so, in a much higher concentration range than in the seawater samples at A50–A1000 stations.

All DOC values measured are negatively correlated with the salinity values (Fig. 4 and Table 4). This type of behaviour was previously observed in North Adriatic which is influenced by the Po River discharge (Giani et al., 2005). Seritti et al. (2003) identified the main water masses circulating in the Ionian Sea through potential temperature vs. salinity and determined the DOC in LIW to be 0.468–0.504 mg C/L. In Ionian Sea water masses the DOC concentrations range from 0.6 to 0.876 mg C/L, while POC values range from 0.0084 to 0.0324 mg C/L (Seritti et al., 2003). There are several studies performed in the area of South Adriatic Pit (Miserocchi et al., 1999; Turchetto et al., 2007, 2011). These studies indicated the importance of advection processes in the area of South Adriatic and also the predominance of mainly siliceous phytoplankton in the early spring months. Due to advection processes high silicate concentrations from Albanian coastal waters influence the area of South Adriatic Pit. Turchetto et al. (2007, 2011) and Boldrin et al. (2002) point to the importance of complex interactions among climatological events,

Table 2
Concentrations of N-polymeric compounds, organic nitrogen (ON) and total nitrogen (TIN+ON), and partition of N-polymeric in ON and ON in total nitrogen.

Station	Depth (m)	N-polymeric (equiv. μg/L HSA)[a]	N-polymeric (equiv. μg/L N in HSA) (15.7% N in HSA)	ON (μg/L)	TIN+ON (μg/L)	N-polymeric/ON	ON/TIN+ON
A50	0	4.79	0.75	43.30	69.89	0.02	0.62
	5	0.60	0.09	35.60	46.80	0.00	0.76
	45	2.52	0.39	35.87	43.95	0.01	0.82
A150	5	3.99	0.63	36.02	46.13	0.02	0.78
	20	0.00	0.00	51.46	60.12	0.00	0.86
	100	0.95	0.15	37.88	67.39	0.00	0.56
A200	5	1.44	0.23	19.78	30.88	0.01	0.64
	20	0.00	0.00	45.23	58.10	0.00	0.78
	180	14.96	2.35	2.42	53.99	0.97	0.05
A300	5	9.71	1.53	31.18	40.49	0.05	0.77
	20	0.00	0.00	35.99	44.02	0.00	0.82
	280	0.00	0.00	13.52	85.20	0.00	0.16
A900	5	0.00	0.00	18.31	30.55	0.00	0.59
	20	1.80	0.28	36.22	47.14	0.01	0.77
	300	0.00	0.00	52.77	110.21	0.00	0.48
A1000	5	5.53	0.87	50.27	60.31	0.02	0.83
	20	18.27	2.87	40.46	48.41	0.07	0.84
	300	0.00	0.00	10.93	68.11	0.00	0.16

[a] HSA=human serum albumin.

Table 3
Basic statistics for the measured parameters. Minimum, maximum, average and standard deviations are presented.

Parameters	Min	Max	Avg. ± st. dev.
Salinity	33.8	38.8	38.0 ± 0.9
Temperature	13.30	20.90	15.82 ± 2.56
SiO_4 (μg/L)	3.43	379.56	41.74 ± 60.13
PO_4 (μg/L)	0.03	4.06	0.71 ± 1.13
OP (μg/L)	0.15	2.63	1.70 ± 0.46
TIN (μg/L)	7.96	71.68	25.33 ± 19.72
ON (μg/L)	2.43	131.22	34.65 ± 20.52
DOC (mg/L)	0.72	1.05	0.87 ± 0.09
POC (mg/L)	0.01	0.19	0.05 ± 0.03
SAS_T (mg/L)	0.026	0.078	0.045 ± 0.015
SAS_{diss} (mg/L)	0.027	0.076	0.045 ± 0.013
CuCC (nmol Cu^{2+}/L)	24.0	480.0	134 ± 139
Log K_{app} (L/nmol Cu^{2+})	7.0	9.0	7.8 ± 0.5

Table 4
Correlation coefficients (R) and statistical significance (p) between selected parameters.

Correlated parameters	R	p
DOC vs. SAS	0.890	<0.0001
DOC vs. PO_4	−0.701	<0.05
DOC vs. NO_3	−0.745	<0.05
DOC vs. ON	0.557	<0.05
DOC vs. OP	0.735	<0.05
POC vs. ON	0.409	<0.05
POC vs. OP	0.602	<0.05
DOC vs. sal.	−0.758	<0.05
ON vs. sal.	−0.483	<0.05
OP vs. sal.	−0.521	<0.05

biological processes, geomorphology and water mass dynamics, also stressing the dominance of lateral advection in the area of South Adriatic. In our case the advection of the LIW in May 2009 brought inorganic nitrogen and phosphorus to the area of South Adriatic thus influencing the biological productivity there.

All our values for DOC, POC, SAS and CuCC in the Albanian coastal waters are significantly lower than determined in the North Adriatic (Plavšić et al., 2009a), suggesting that the intrusion of LIW brings seawater masses with low DOC and POC having for the consequence also the lower concentrations of SAS and CuCC. Complexing capacities are around 100 nM, which are the values characteristic for a pristine area in the Adriatic, e.g. Krka River estuary (Plavšić et al., 2009b), although some higher values are measured at A200 and A900 stations. The higher values of complexing capacity coincide in general with the higher concentrations of ON, pointing to the nitrogen atoms in organic ligands as a significant type of binding site for copper ions. N-polymeric material concentrations obtained in these samples are in the range of the concentrations obtained for the North Adriatic seawater samples (Strmečki et al., 2010).

5. Conclusions

The case study in May 2009 is the first comprehensive study of the physical and chemical compositions most notably those of the organic matter, across the most remarkable frontal zone in the southern Adriatic Sea, in which Albanian shelf riverine plume waters come into contact with the Southern Adriatic Pit environment. The results point to the area influenced by the ingression of LIW with high salinity value of 38.7, which brings inorganic nutrients (TIN and P-PO_4) and low concentrations of organic matter evidenced through low DOC and POC concentrations. The amount of the newly produced organic matter in the area was also low—as observed through low concentrations of SAS and CuCC. The nitrogen atoms in organic ligands appear to be a significant type of binding site for copper ions. Concentrations of DOC, POC, SAS and CuCC were much lower than usually recorded for the North Adriatic seawater in the late spring. The measurable influence of the inflowing Albanian rivers is observed from the strong inverse dependance of DOC concentrations on salinity.

Acknowledgement

The authors are indebted to the Norwegian Cooperation Programme on Research and Higher Education with the Countries on the Western Balkans; Project: Marine science and coastal management in the Adriatic, Western Balkan: An education and research network (2006–2009) and its Norwegian leader Prof. Paul Wassmann. We thank Prof. Aleko Miho from Faculty of Natural Sciences and Prof. Spase Shumka from Agricultural Faculty, University of Tirana, Albanian colleagues on the project, for their kind help in organization of the sampling. The support of the Croatian Ministry of Science, Education and Sports through the project "Nature of the organic matter, interaction with traces and surfaces in environment" (No. 098-0982934-2717) is acknowledged. We are grateful to the Editor and the reviewers on their efforts to improve the manuscript.

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ORGANIC MATTER CHARACTERIZATION AND DISTRIBUTION IN THE LAKE SHKODRA/SKADAR AND THE BUNA/BOJANA RIVER, ALBANIA: A CASE STUDY IN MAY 2009

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ABSTRACT

The Lake Shkodra - River Buna wetland complex (Albania) is included in Ramsar sites, and is one of the most important on the Adriatic coast. Dissolved organic carbon (DOC), particulate organic carbon (POC), surface active substances (SAS), copper complexing capacity (CuCC), and polymeric organic material containing nitrogen atoms (N-POM) were measured in the area. DOC concentrations were in the range 0.335-4.535 mg C L^{-1}, while POC was in the range 0.010-4.147 mg C L^{-1}. SAS concentrations expressed as equiv. of Triton-X-100 were in the range 0.083-0.302 mg L^{-1} . CuCC values were in the range 110-758 nM Cu^{2+}.The measured concentrations were increased only for certain sites (e.g. lagoon site, B1), where the highest DOC, POC and SAS values were measured. At these sites, polymeric organic material (N-POM) was measured. Normalized surfactant activity values (NSA) determined showed that the organic material present in this aquatic system is similar in adsorption properties to the model fulvic acid and protein albumin.

KEYWORDS: Shkodra /Skadar Lake, Buna /Bojana River, organic matter characterization; electroanalytical techniques

1. INTRODUCTION

The concentrations of the dissolved organic carbon (DOC) and particulate organic carbon (POC) in natural waters determine the total concentrations of the aquatic organic matter. A large part of the aquatic organic matter exhibits the property of surfactant activity, and is named surface-active substances (SAS) [1]. SAS accumulate on different phase boundaries (air/water; water/sediment; water/living or non-living suspended particles) influencing the structure and physico-chemical properties of these interfaces and mediating the processes of mass and energy transfer [1]. Surfactant activities of different classes of organic matter as representative for organic matter present in aquatic systems have been determined [2, 3]. Clear evidence of surfactant production by different phytoplankton species based on laboratory and field experiments is also available [4, 5]. A combination of general parameters (DOC and POC) and SAS gives the information about both content as well as the reactivity of organic matter in a particular aquatic system [6, 7].

Metal complexation by inorganic ligands in water (ocean, estuaries, freshwater) is well studied whereas less is known about speciation of metal ions in the presence of organic ligands [8]. With the development of a number of sensitive and selective metal speciation techniques like electrochemical techniques,also metal-organic interactions have been studied [9,10]. Copper is the mostly studied metal ion [11, 12] as it forms very stable organic complexes and is an essential metal ion [8, 13]. Its complexation to organic ligands in all aquatic systems, with the exception of deep ocean water, is >99% [13]. Catalytic and surface activity of nitrogen-containing polymeric organic material (N-POM) could be also analyzed by electrochemical technique of constant current chronopotentiometric stripping analysis (CPSA). Recently, CPSA proved to be a suitable method for determination of low concentrations of N-polymeric compounds in seawater by measuring “presodium” catalytic peak “H” [14].

Our research was performed in May 2009, on the area of the Shkodra/Skadar Lake and the Buna/Bojana River. The area of investigation is the wetland area encompassing «old Drini river»- i.e. the area of former Drini river flow which due to the several interventions in the area (building of dams, errosion, and loading of sediments) has partially changed the flow course. The scope of our research was to determine the concentration and distribution of organic matter in the area with the Buna/Bojana River (river with highest discharge rate in the area) to the southeast Adriatic shelf water. The Adriatic southeast coastal area is an eutrophic area that is strongly affected by freshwater inputs from the Buna/Bojana River system [15].

Dissolved organic carbon (DOC), particulate organic carbon (POC), surface active substances (SAS), copper

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* Corresponding author

complexing capacity (CuCC) and polymeric organic material containing nitrogen (N-POM) due to hydrological situation in late spring were measured. This is the first research of the freshwater system in this area of Albania regarding the organic matter characterization and distribution.

2. MATERIALS AND METHODS

2.1. Study area

Albania is rich in water resources including lakes, rivers, springs, and lagoons, with a high quantity of available water. Albanian rivers are characterized by the total annual mean flow of 1308 m^3 s^{-1}, which corresponds to an annual water volume of $42.3x10^9$ m^3. The rivers are mainly fed by precipitation (69%) and show a typical Mediterranean regime, with seasonal variation in the flow-rate and high flow from October to May [16, 17].

During the past decades, mining, enrichment and metallurgy industries, as well as organic products and wastes have produced high quantities of solid and liquid wastes, often dumped on river banks or directly into rivers. Some natural characteristics of Albania like geographical (high slopes), pedological, climatological (high precipitation amount) as well as some human impacts (forest mismanagement and gravel mining) have given rise to high erosion rates, and solid matter (TSS) in all rivers is because of that a crucial problem.

The investigated area is the most important wetland system along the Adriatic Sea, and one of the best preserved in the Mediterranean [18]. Its habitat is distinguished about the richness of breeding and refuge habitats for flora and fauna, especially for fishes and waterbirds (after World Database on Protected Areas; http://sea.unepwcmc.org/wdpa/index.htm). Along the Albanian coast, there are extended three wetlands of international importance (Ramsar convention): Butrinti (13500 ha), Karavasta Lagoon (20000 ha), and Lake Shkodra with the River Buna (49562 ha) [19].

The Buna delta has the characteristics of a shovel delta [20], such as the Ebro delta and, in part, the Po delta. The Po in its lower course transports mostly sand whereas, during heavy floods, the Buna transports a lot of gravel too. This type of delta grows by lateral accumulation and the separation of shallow lagoon lakes and pools. This can be seen, in particular, in the eastern half of the Bojana-Buna delta over the last 100 years. The process is related to a strong coastal influence (dune and lagoon development stages). Due to the massive reduction of bed load and suspended load following the construction of the dams in the upper Drini basin, the delta is today more and more eroded by the coastal regime. Together with reduced discharges of the rivers and the slight raising of sea level due to climate change, the erosion phase will be intensified [20]. In Fig. 1, the sampling stations are denoted. One sampling area includes the Shkodra Lake and the Buna River (B15, B8, B7, B5), and the other is the area of Drini River (B2, B3, B4, B14) and the two lagoons (B1, B6).

2.2. Analytical methods

2.2.1. DOC and POC determination

For DOC and POC determination, samples were collected directly from the Niskin samplers in dark 1.3-L bottles, previously washed with chromic-sulfuric acid and rinsed with organic free water (Milli Q water) and water samples. The filtration was performed immediately after sampling (Whatman GF/F filters, pore size 0.7 µm). Filtered samples for DOC analysis were collected in duplicates in 22-ml glass vials washed with chromic-sulfuric acid, rinsed with Milli-Q water and combusted for 4 h at 450 ^oC. The samples were preserved with mercury chloride (10 mg/L) and stored at +4 ^oC in the dark until analysis. After collection of the DOC subsamples, GF/F filters were rinsed with a few ml of Milli-Q water to remove salts from the filter and stored in liquid nitrogen at -80 °C until POC analysis. The DOC concentrations were analyzed in duplicate using the sensitive high temperature catalytic oxidation (HTCO) method [21]. A Model TOC-V_{CPH} (Shimadzu) with platinum on silica catalyst and nondispersive infrared (NDIR) detector for CO_2 measurements was used. Samples acidified with hydrochloric acid (pH 2) were purged with organic free air for 10 min prior to analysis to remove inorganic carbonate fraction. DOC concentrations were calculated by subtracting the measuring system and Milli-Q water blanks. Potassium hydrogen phthalate as a standard was used. The concentration was calculated as an average of three to five replicates. The average instrument and Milli-Q blank correspond to 0.03 mg/L (n=32), and the reproducibility was high (1.6 %). POC was analyzed with a solid sample module SSM-5000A associated with a Shimadzu TOC-V_{CPH} carbon analyzer calibrated with glucose. After acidification with hydrochloric acid (2M) to remove inorganic carbonate fraction, the filters were folded in an alumina ceramic sample boat and dried at 50 ^oC for 12 h. The prepared samples were burned in a flow of oxygen at 900 ^oC. The CO_2 produced was detected by the NDIR detector. POC concentrations were corrected on the basic of blank filter measurements. The average filter blank including instrument blank corresponded to 0.005 mg/L. The reproducibility obtained for the glucose standard was high (≤3 %).

2.2.2. Copper complexing capacity (CuCC) measurements

The experiments were performed on an electrochemical system consisting of a 663 VA-Stand (Metrohm, Herisau, Switzerland) connected via an IME663 module to a computer-controlled µ-Autolab instrument (EcoChemie, Utrecht, The Netherlands). The working electrode was a static mercury drop electrode (SMDE, drop surface area 0.52 mm^2). The reference electrode was a double-junction Ag/AgCl (3 M KCl) electrode, and the counter electrode was a glassy carbon rod. The solutions were stirred during the deposition step of measurements. Potential of deposition was -0.6 V vs. Ag/AgCl ref. electrode with the depo-

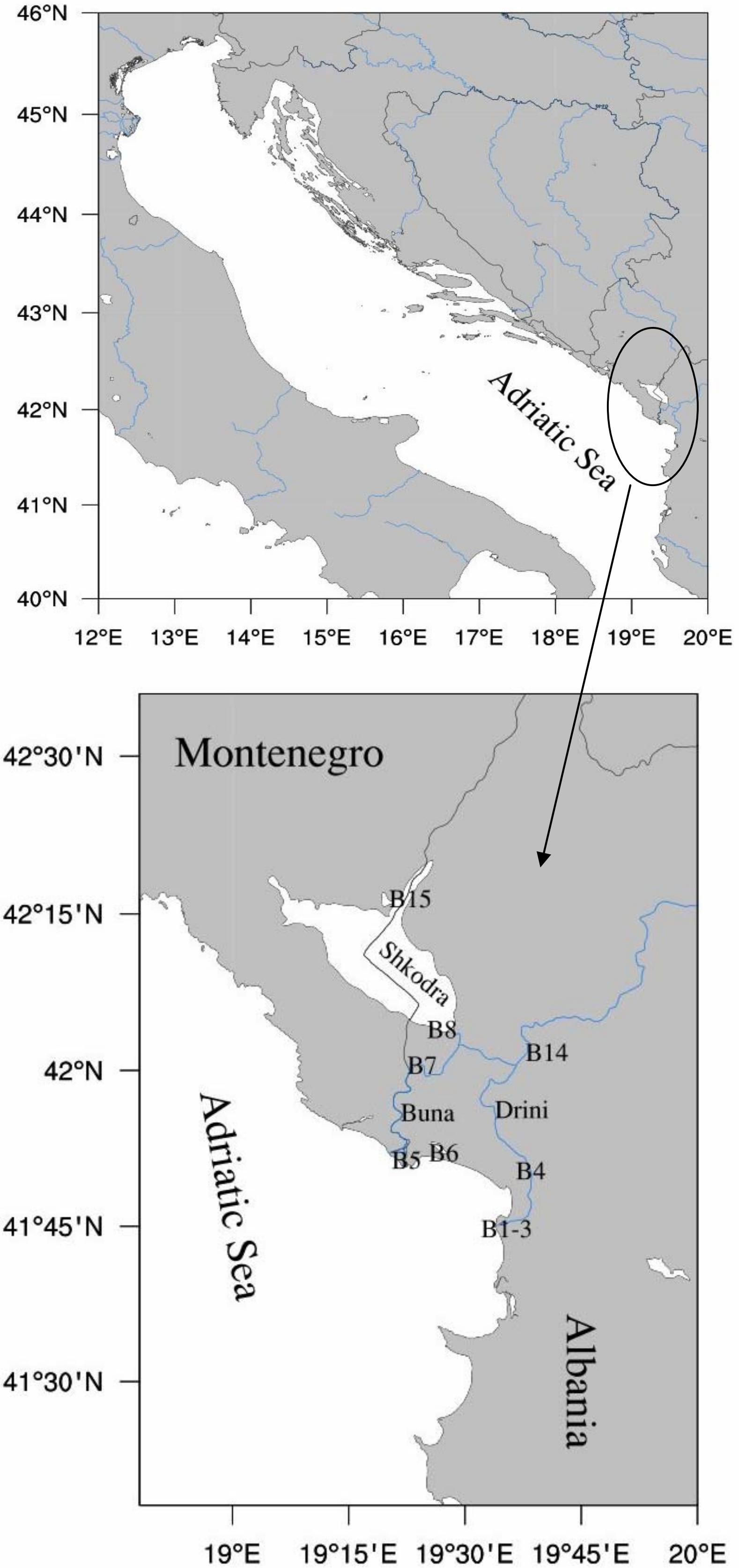

FIGURE 1 - Map of the Adriatic Sea with inserted area of sampling stations in the Shkodra Lake and the Buna River, Albania. The sampling stations were: B1, B2, B3, B4, B5, B6, B7, B8, B14 and B15.

sition time of 60 s. The complexing capacity was determined in non-filtered seawater samples after thawing deep frozen samples (-20 °C) within one month after sampling. The reproducibility of the method is $\pm 2X10^{-9}$ M Cu^{2+} from which the detection limit equal to $6X10^{-9}$ M Cu^{2+} can be calculated. Determination was performed by the direct titration method of the sample with increasing amounts of copper ions, and their electrochemical response was measured by the method of differential pulse anodic stripping voltammetry (DPASV) [22, 23]. Total Cu ion concentrations were determined in UV-irradiated (for 24 h) and acidified samples. To obtain complexing capacity values and conditional stability constant, titration data are linearly transformed assuming 1:1 metal to ligand complexes [24, 25]. The equation used for calculation is: [Cu]/[CuL] = [Cu]/CuCC + 1/KCuCC, where Cu is the copper ions detected by anodic stripping voltammetry, CuL is the copper ion bound in a complex with ligand L, CuCC is the total concentration of binding ligands (i.e. complexing capacity), and K is the apparent stability constant. The plot of [Cu]/[CuCC] vs. [Cu] yields a straight line with a slope of 1/CuCC and intercept 1/KCuCC.

2.2.3. SAS determination

Surface active substances were analyzed electrochemically by a.c. voltammetry [6] using a Metrohm 797 VA Computrace instrument. A three-electrode cell system was used: hanging mercury drop electrode (HMDE), as a working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and platinum electrode as the counter electrode. The deposition potential of -0.6V vs. Ag/AgCl ref. electrode and deposition time of 30 s controlled by stirring were applied. Surfactant activity was expressed in terms of surfactant equivalents of the non-ionic surface active compound Triton-X-100 (MW=600 mg/L), with detection limit of 0.01 mg/L and reproducibility of 3%. Surface active substances were determined in both non-filtered (SAS_T, total, i.e. dissolved + particulate) and filtered (SAS_{diss}, dissolved) samples immediately after sampling. Normalized surfactant activity (NSA) values were calculated by dividing the concentration of SAS in mg/L equiv. of Triton-X-100 with the DOC in mg C L^{-1} [6].

2.2.4. N-containing polymeric material (N-POM)

Measurement conditions for electrochemical constant current potentiometric stripping analysis (CPSA) method were as follows: accumulation potential E_a = -0.6 V and time of accumulation t_a = 60 s, with stirring, constant reduction current I = -1 µA and maximum time of measurement = 5 s. CPSA measurements were performed on unfiltered samples, in the presence of oxygen, while instrument and cell were as in CuCC determination. The results were expressed as the equivalents of the model polymer substance i.e. protein human serum albumin (HSA, Sigma, USA, MW = 67 kDa) and/or as equivalents of N atoms present in HSA taking into account the 15.7 % of N content in HSA [26] .

CuCC and N-POM were determined at the same time after thawing the deep-frozen nonfiltered samples. Samples were analyzed within one month after sampling.

3. RESULTS

All the results are summarized in Table 1. The average concentrations determined for all the parameters (DOC, POC, SAS_{diss}, and CuCC) were lower for the area of Shkodra Lake and the Buna River (B15, B5, B7, B8), while in the Drini River area (B2, B3, B4, and B14) and, especially, in the lagoons (B1, B6), the determined average concentrations were higher. DOC and POC concentrations were measured also for the stations B14A and B15A (not denoted in Fig. 1., which are situated a few 100 m upstream of stations B14 and

TABLE 1 - Salinity, temperature, pH, DOC, POC, SAS $_{diss}$, CuCC, logaritmic value of apparent stability constant for copper complexation (log $K_{app)}$ and N-POM for all stations measured.

	S	T (^{0}C)	pH	DOC mgC/L	POC mgC/L	SAS $_{diss}$. equiv.mg/L T-X-100	CuCC nM	logK_{app}	N-POM equiv µg/L HSA
The Shkodra Lake, The Buna River									
B15	0	-	8.02	1.363	0.453	0.139	432	9.2	0.0
B8	<1	21	8.30	0.947	0.134	0.082	320	9.0	0.0
B7	<1	16	7.87	1.031	0.230	0.077	302	9.2	0.0
B5	<1	15	7.32	0.954	0.180	0.051	-	-	0.0
Old Drini									
B14	0	-	8.78	0.619	0.225	-	678	8.4	0.0
B4	<1	22	8.15	1.090	0.274	0.127	758	8.2	10.8
B3	21	23	8.04	1.446	0.498	0.132	490	7.6	31.5
B2	2	22	7.69	1.470	0.517	0.153	473	8.3	10.5
Lagoons									
B1 (Kune-Vain)	14	25	8.71	4.535	4.147	0.172	446	8.0	17.4
B6 (Vilun)	17	26	8.52	3.119	0.615	0.153	110	7.0	0.0

- not measured

B15). The measured values were for B14A: DOC was 0.553 mg C/L and POC was 0.161 mg C/L; for B15A: DOC was 0.335 mg C/L and POC was 0.010mg C/L. These are very low values characteristic for a pristine systems at the eastern coast of the middle Adriatic like the karstic Krka River [27].

Part of the Drini area and lagoons are influenced by the intrusion of seawater, which could be observed from the salinity values measured there (Table 1.).

There exists a correlation between different parameters with a statistical significance. DOC is correlated with POC for stations B1, B2, B3, B4, B6 and B14 with a correlation coefficient of R^2= 0.842. In Table 1, the values for SAS $_{diss}$ are quoted as there are very small differences in the SAS concentrations determined in filtered and unfiltered samples. Values for SAS_{diss} were used for calculation of the normalized surfactant activity (NSA) as presented in Fig. 2. DOC vs. SAS_{diss} values are presented together with the straight lines which represent the relationship for SAS and DOC for selected model substances: (1) nonionic surfactant Triton-X-100; (2) polysaccharide Dextran-T-500; (3) protein-albumine; (4) fulvic acid, and (5) microbial polysaccharide xanthan. It can be observed that most of the results for the samples are close to the lines for albumine/fulvic acid and xanthan, which is to be expected for the unpolluted natural waters [28]. In Fig. 3, the frequency distribution of NSA for Albanian coastal seawater samples (data are from [29]) and Albanian freshwater samples (the Buna/Bojana river and Shkodra/Skadar lake - this paper) are presented. It can be observed that Albanian freshwaters have the NSA frequency distribution in a higher-value range which indicates that the materials determined there have a more hydrophopbic character than the samples from the Albanian coastal sea (measured at the same time as the freshwater samples in May 2009), which showed higher frequency distribution for lower NSA values, pointing to the more hydrophylic material in Albanian coastal sea, probably of autochtonous origin.

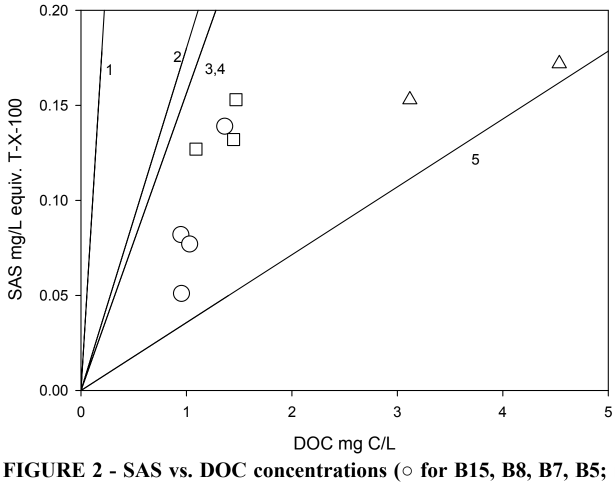

FIGURE 2 - SAS vs. DOC concentrations (○ for B15, B8, B7, B5; □ for B2, B3, B4; and Δ for B1, B6,). Lines correspond to different model substances; no. 1: nonionic surfactant Triton-X-100; no 2: model polysaccharide Dextran-T-500; no. 3: model fulvic acid, no. 4: protein-albumin; no. 5: microbial polysaccharide xanthan.

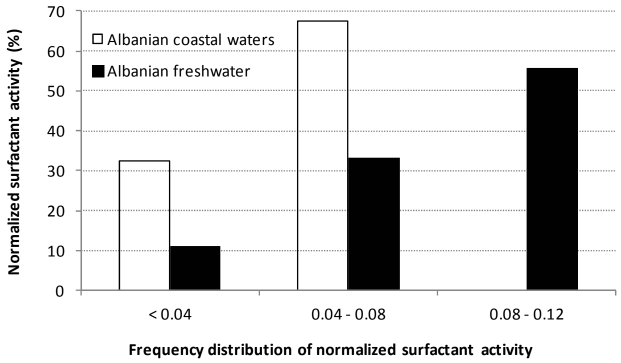

FIGURE 3 - Frequency distribution of normalized surfactant activity values for the freshwaters' and Albanian's coastal seawater samples.

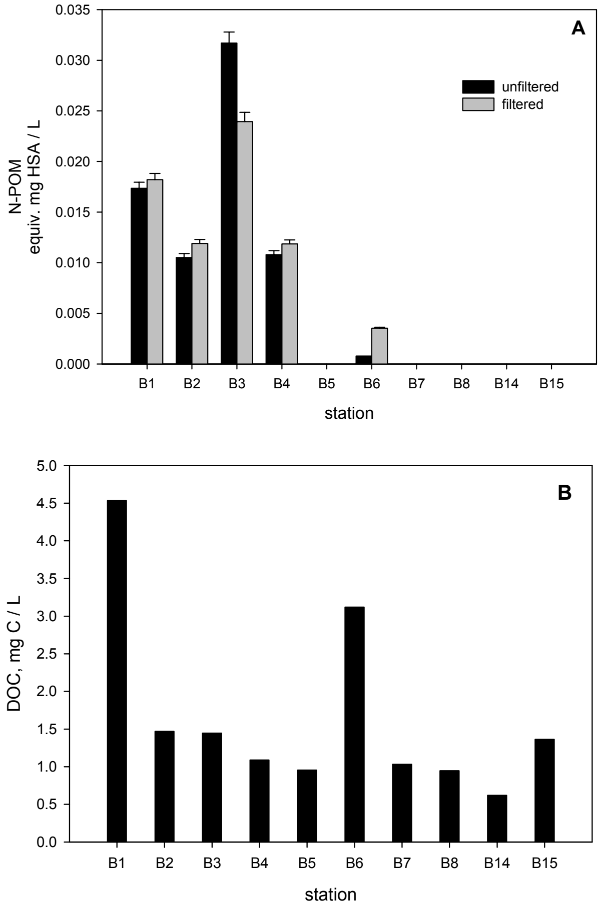

FIGURE 4 - A) N-POM concentrations for all the stations for filtered and unfiltered samples; B) DOC concentrations measured on the sampling stations B1-B15.

In the area of the Drini River and the lagoons (at B1, B2, B3, B4 and at B6, where the concentration was at the limit of detection), the polymeric organic material containing nitrogen atoms (N-POM) has been measured [26, 29], while in the area of Shkodra lake and the Buna River (stations B5, B7, B8 and B15), such organic material was not detected (Fig. 4A). N-POM has been measured in non-filtered and filtered samples (Fig. 4A). Practically, at all stations concentrations of N-POM did not differ sigificantly between filtered and nonfiltered samples (Fig. 4A). In Fig. 4B, the DOC concentrations for the stations are presented.

Usually, higher DOC concentrations measured mean that also higher N-POM concentrations [26, 29] were measured as well. In Albanian samples, this was not the case, meaning that their N-POM was not the main component in organic matter with high DOC concentrations.

Complexing capacity values were in the range 110-758 nM, which is higher than for the karstic Krka River [30], but comparable to the results obtained for the Kotor Bay, the area strongly influenced by freshwater imput [31]. Concentrations of copper ions were significantly correlated with DOC for the Shkodra Lake and the Buna River (R^2= 0.9168) which means that the loading of metal ions to the water is connected with the concentration of organic matter in the system. The concentrations of copper ions in the area were in the range 2-9 nM, with the only exception at station B1 (lagoon Kune) where it was 13 nM. At B1 station, for all the parameters, the highest concentrations were measured.

4. DISCUSSION

DOC, POC, CuCC and SAS concentrations in the samples were not high, especially regarding DOC and POC concentrations for the area of Shkodra Lake and the Buna River. The Buna River in the southeastern area of Adriatic and the Po River in the northwestern Adriatic area account for more than one third of the freshwater entering the coastal area in their respective area [15]. The median DOC concentration in the Po River in the period 1995-2007 was 2.24 mg C/L [32], and in the Buna River, a maximum of 1.36 mg C/L (and three other DOC concentrations were even lower, app. 1 mg C/L) was measured which means that the Po River is contributing more to the overal DOC budget in the Adriatic Sea than the Buna River. Also the type of organic material was different in the Albanian coastal seawater samples than in the fresh water samples visible from the NSA frequency distribution (Fig. 3). Nevertheless, the measurable influence of the Albanian rivers was observed in Albanian coastal waters from the inverse dependence of the DOC concentrations and salinity data [29]. Also, in the sampling station which was the closest to the Albanian shore, a very high concentrations of silicate was measured (up to 380 µg/L; [29]). The results for NSA, for the freshwater samples, point to the type of organic matter which regarding its adsorption properties resembled those of model fulvic acid and/or model for proteinaceous organic matter like albumine, which gave the same line for NSA [27]. NSA for B1 and B6 samples, which are lagoon samples, are closer to the line for microbial polysaccharide xanthan, which means that such a type of material could be present, indicating biological activities and the influence of the seawater intrusion there. In the coastal sea, the lower values for NSA were detected also corresponding to the low NSA values for model polysaccharide xanthan.

CuCC values were similar to the ones determined in the closed Kotor Bay [31], while log K values were all quite high (9.0-9.2) especially in the Shkodra Lake and in the Buna River samples, which could point to the ligands with high affinity for binding copper ions [8].

Statistically significant correlations between DOC and POC denote that transformation reactions between DOC and POC are prominent in the area. It was revealed that floodplain interactions increase DOC concentrations, alter dissolved organic matter compositions, and reduce nitrogen loading [33]. Polymeric organic material (N-POM) is mainly in colloidal phase which passes through the pores of 0.7-µm GF/F filters used for filtration. This was observed through almost the same concentration of N-POM measured in filtered and unfiltered samples. The presence of the organic matter which could complex copper ions is of great significance as it is known that the most toxic form of metal ions is that of free metal ions, while complexed metal ions are usually not bioavailable [12]. Recently, the metal ions in the sediments of the area have been measured [34], and they did not show increased values (except for Ni) and could be classified as background or unpolluted. The other rivers in Albania like Mati, Ishmi, Shkumbini and Sumani have been investigated to a higher extent [16, 17]. The concentration of copper ions in water samples in the above-mentioned rivers were determined to be much higher, between 43 nM and 153 nM. Nutrient concentrations in these Albanian rivers were determined to be: for $N\text{-}NO_3$, the range was 0.51-1.44 mg/L; for $N\text{-}NO_2$, it was 13.6-278.5 µg/L; for $N\text{-}NH_4$, it was 0.24-6.64 mg/L; and for $P\text{-}PO_4$, it was 5-417 µg/L. These values for nutrients are comparable to other river systems in Europe. In the Shkodra Lake, on the sampling stations in the Montenegrian part of the lake, mean total phosphorus (TP) concentrations of surface samples ranged from 4 to 54 µg/L. Mean total nitrogen concentrations ranged from 0.15 to 1.28 mg/L [35]. Chlorophyll *a* concentrations ranged from 0.12 to 39.78 µg/L with a yearly average of 5.9 µg/L [35]. According to Vollenweider and Kerekes [36], this average chlorophyll *a* value classify the Shkodra Lake as being mesotrophic [35]. Later on, the Shkodra Lake was classified to be eutrophic due to the new measurements of chlorophyll *a* concentrations and due to the presence of phytoplankton communities which become dominant in the lake on the sampling sites in Montenegro [37]. Regarding the trophy valences of the bioindicator species of diatoms in the Lake Shkodra, measured at sampling points on the Albanian site of the lake, the highest number of diatoms belong to oligo-mesotrophic and tolerant groups, which shows a good situation of the lake for sustaining life [38].

One parameter, total suspended solids (TSS) measured in Albanian rivers, is very high (38-108.9 mg/L). This is enormously above the concentrations recommended by European Water Framework Directive (WFD) [39] of 25 mg/L. Only 4% of all river water samples in Albania had

TSS levels below 25 mg/L [16, 17]. This is because of very high errosion rates for the rocks in the area, being mainly composed of silica material [20]. That is the reason while very high concentrations of silicate (up to 380 µg/L) in the seawater close to the Buna River estuary were determined [29]. For the investigated area of the Skhodra Lake, the Buna river and the old Drini area, there are no published data for the measured parameters related to organic carbon content and distribution.

5. CONCLUSIONS

It is important to preserve the sensitive watershed area which will help to prevent damage to biodiversity and humans, and help to retain the original beauty of the landscape. The Albanian territory is important for the water supply on the Eastern Adriatic coast. Sustainable watershed management in the area would guarantee the fulfillment of related tasks on a regional and international level. Further measurements there would be of importance as in comparison to other rivers in Albania (e.g. Ishmi, Fani, Tirana, Lana, Semani, Shkumbini), the area of Shkodra Lake and the Buna River as well as that of Drini River showed relatively low level of human impact. Although, the wastes from mining and metallurgy were dumped in the area, the concentrations of copper ions in the water were generally low. The organic matter (DOC, POC, SAS, CuCC, N-POM)measured there did not show high concentrations.The transformation of the organic matter was measured through the correlation between DOC and POC, and the presence of the N-POM on wetland and lagoon area. Elevated DOC and POC concentrations were measured in the area of lagoons (station B1) which, in the case of metal ions dumped in the area, could have a beneficial role, being able to bind metal ions in a form of organic complexes which are less toxic to biota. These studies could serve as a platformn to raise the awareness regarding the importance of monitoring and preserving such environmentally important sites.

ACKNOWLEDGEMENT

The authors are indebted to the Norwegian Cooperation Programme on Research and Higher Education with the Countries on the Western Balkans; Project: Marine science and coastal management in the Adriatic, Western Balkan: An education and research network (2006-2009) and its Norwegian leader Prof. Paul Wassmann. We thank Prof. Aleko Miho from Faculty of Natural Sciences and Prof. Spase Shumka from Agricultural Faculty, University of Tirana, for their kind help in organization of the sampling. The support of the Croatian Ministry of Science, Education and Sports through the project “Nature of the organic matter, interaction with traces and surfaces in environment” (No. 098-0982934-2717) is acknowledged.

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Received: November 15, 2012
Accepted: January 31, 2013

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