Water Workshop 2023

Hemijski aspekti kvaliteta voda za rekreaciju i u bazenima za kupanje

Dr Jelena Molnar Jazić, vanredni profesor

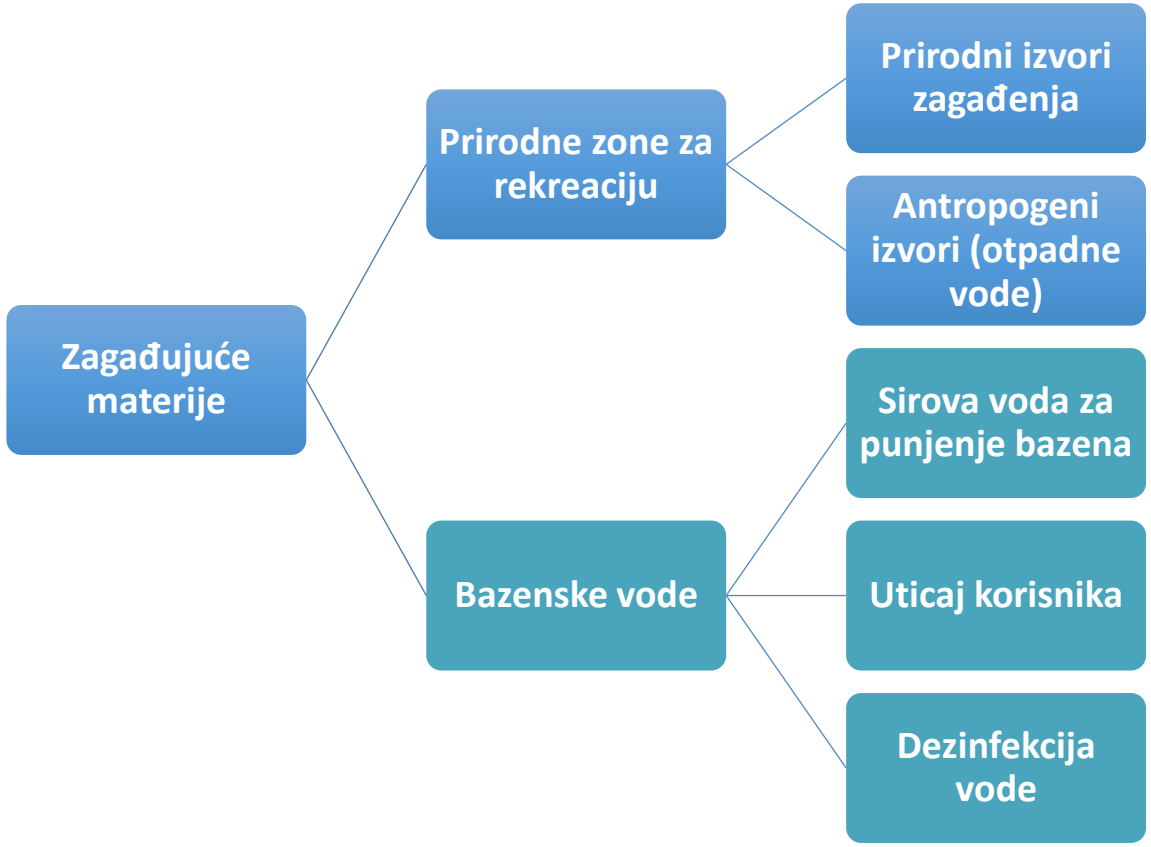
Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Departman za hemiju, biohemiju i zaštitu životne sredine

Email: jelena.molnar@dh.uns.ac.rs

20-22. Septembar 2023. Novi Sad

OSNOVNI PARAMETRI KVALITETA VODE ZA REKREACIJU

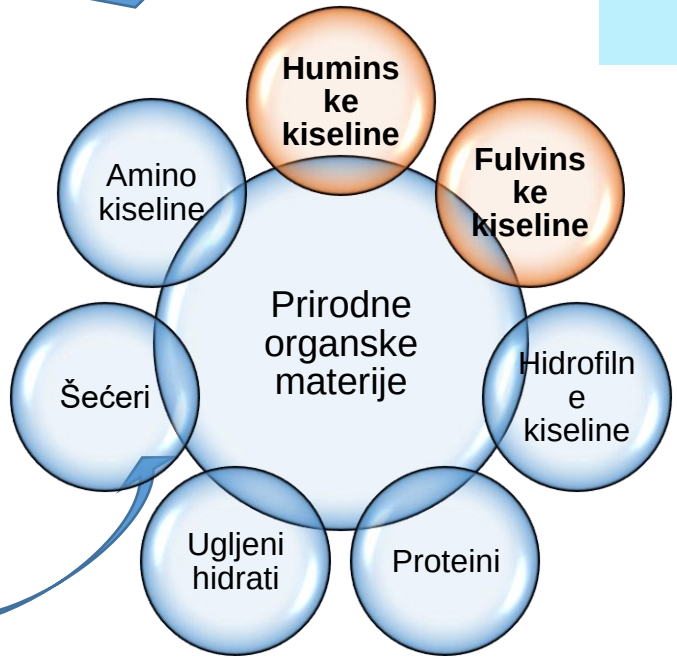
- pH (6,5-8,5)
- Mutnoća
- Salinitet
- Temperatura
- Sadržaj rastvorenog kiseonika (80%)
- Sadržaj organskih materija
- Organoleptičke karakteristike – indikatori pojave zagađenja



PRIRODNE I HEMIJSKE SUPSTANCE U PRIRODNIM ZONAMA ZA REKREACIJU

- **Organski mikropolutanti:**
  - **Prioritetne supstance i supstance na listi praćenja (2013/39/EU)**
  - **Emergentne supstance – CECs**

Interna (autohtona)



Eksterna (alohtona)

HEMIJSKE SUPSTANCE u prirodnim zonama za rekreaciju

- Farmaceutska sredstva
  - antibiotici, analgetici i antiinflamatorni lekovi, β-blokatori i regulatori masnoće
- Sredstva za ličnu higijenu
- Hemikalije koje se primenjuju u industriji i poljoprivredi
  - Pesticidi, PAHs, plastifikatori, PCB, polihlorovani dibenzo-p-dioksini/furani, perfluorovana jedinjenja (PFAS)
- Mikro- i nanoplastika

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC (DECISION (EU) 2020/1161)

- Metaflumizon
- Amoksicilin
- Ciprofloksacin
- Trimetoprim
- Venlafaksin and O-desmetilvenlafaksin
- Dimoksistrobin
- Famoksadon
- Klotrimazol
- Flukonazol
- Mikonazol
- Imazalil
- Ipkonazol
- Metkonazol
- Penkonazol
- Prohloraz
- Tebukonazol
- Tetrakonazol

NORMAN List of Emerging Substances

Algal toxins	Gasoline additives	Personal care products / Biocides
Biocide tranformation products	Industrial chemicals	Personal care products / Food additives
Biocides	Industrial chemicals / Biocides	Pharmaceuticals
Bio-terrorism / Sabotage agents	Industrial chemicals / Flame retardants	Plant protection products
Disinfection by-products (drinking water)	Lubricants / Flame retardants	Plant protection products / Biocides
Disinfection by-products (drinking water) / biocides	Moth repellent / Antimicrobial agent	Plant protection products/Biocides
Disinfection by-products (drinking water) / Flame retardants	Other	Plasticisers
Drugs of abuse	Perfluoroalkylated substances and their transformation products	Plasticisers / Flame retardants
Flame retardants	Personal care products	Surfactants
Food additives	Personal care products	Trace metals and their compounds

Kandidati za 4. “Watch list” (JRC Technical Report, 2022)

Substance/group Name	CAS Number	Use	PNEC	Matrix
Azoxystrobin	**131860-33-8**	**Fungicide used as PPP and biocide**	**0.2 µg/l(1)**	**Water**
Clindamycin	**18323-44-9**	**Human medicine** **Antibiotic (lincosamides)**	**0.044 µg/l(2)**	**Water**
Diflufenican	**83164-33-4**	**Herbicide used as PPP**	**0.01 µg/l(1)**	**Water**
Fipronil	**120068-37-3**	**Insecticide**	**0.00077 µg/l(1)**	**Water**
		Biocidal and veterinary uses		
Metformin and its transformation product guanylurea	**657-24-9 and 141-83-3**	**Pharmaceutical** **Type 2 diabetes treatment**	**156 µg/l(1)** **100(2)**	**Water**
Ofloxacin	**82419-36-1**	**Human medicine** **Antibiotic (fluoroquinolones)**	**0.026 µg/l(3)**	**Water**
Sunscreen agents	**70356-09-1 (avobenzone)**	**UV filters**	**3 µg/l(4)**	**Water**
	6197-30-4 (octocrylene)		**0.266 µg/l(5)**	
	131-57-7 (oxybenzone)		**0.67 µg/l(5)**	
Cefalexin	15686-71-2	Human medicine Antibiotic (cephalosporins)	0.08 µg/l(6)	Water
Free cyanide	57-12-5 (CN-); 74-90-8 (HCN)	Industrial and biocide	0.26 µg/l(7)	Water

List of the most suitable WL candidate substances, fulfilling the selection criteria, modified following comments from MS and Stakeholder groups (after the WG Chemicals meetings held on 10th February and 4th May 2022, and the SCG meeting on 17th May 2022). In bold, the seven substances finally identified for inclusion in the 4th Watch List. The table shows for candidate substances the group/class, CAS number, use, PNEC value and matrix (environmental compartment). PPP: Plant Protection Product.

PPCPu bazenskim vodama

PPCP	Konc. (ng/l)	Zemlja
Benzofenon-1	<0.1-1.2	Španija
	Nd-4.0	Kina
Benzofenon-3	<0.1-15.17	Španija
	Nd-134	Kina
	1.86-1178.9	Poljska
Benzofenon-8	<0.3-21.6	Španija
	49.9-226.9	Poljska
4-hidroksibenzofenon	Nd-81.5	Kina
Propil paraben	Nd-266	Kina
Izopropil paraben	Nd-440	Kina
Butil paraben	Nd-49.2	Kina
Metil paraben	0.16-872	Kina
Etil paraben	Nd-110	Kina
p-hidroksibenzoeva kiselina	Nd-1122	Kina
1H-benzotriazol	0.94-520	Kina
	<0.2-18.8	Španija
5-hloro-1H-benzotriazol	Nd-400	Kina
5-metil-1H-benzotriazol	Nd-50	Kina
	<0.3-3.40	Španija

PPCP	Konc. (ng/l)	Zemlja
Triklosan	Nd-96	Kina
Ibuprofen	16.1-197	Italija
	16-83	Australija
	<1.39-171.25	Španija
Ketoprofen	12.6-127	Italija
	<0.55-360.05	Španija
Kafein	~500	US
	20-1540	Australija
	Nd-39.08	Kina
	<0.69-13.64	Poljska
Karbamazepin	<0.01-1.42	Španija
	3.67-51.44	Poljska
	0.1-5.4	Italija
Atenolol	<0.01-0.62	Španija
	0.03-0.2	Italija
Hidrohlorotiazid	<0.61-903	Španija
	0.3	Italija
Sulfametoksazol	<0.13-6.42	Španija

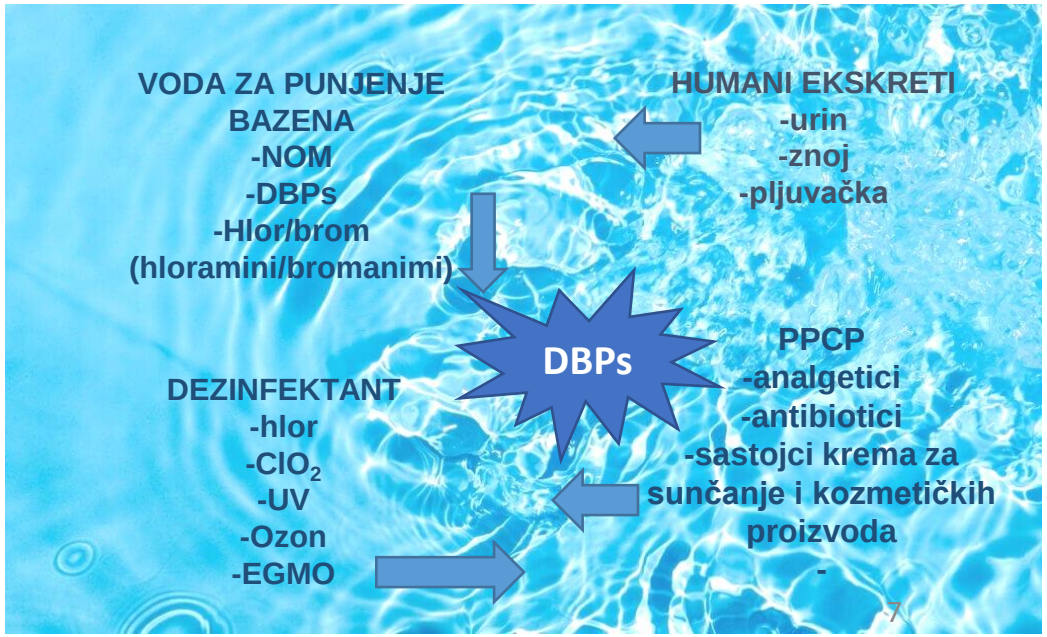
Prekursori dezinfekcionih nusproizvoda u bazenskim vodama

Organski DBPs prekursori + Neorganski DBPs prekursori + Dezinfektant = Reguli-sani i emerge-ntni DBPS

- POM (karakteristike sirove vode),
- Uticaj kupača:
  - čestice sa kože,
  - pljuvačka,
  - znoj, urin (N-DBPs),
  - određeni mikropolutanti – PPCP

Bromid
Jodid

Hlor
Ozon
Ozon/hlor
UV

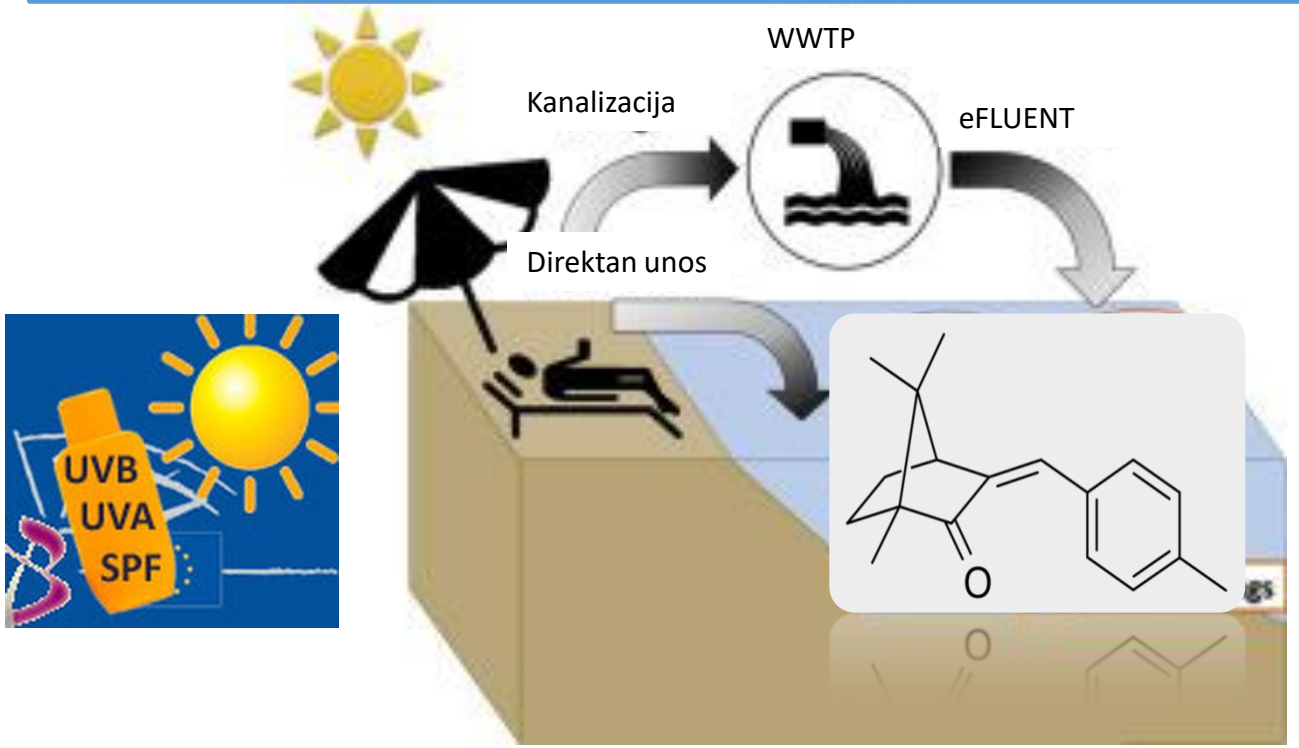


Emergentne supstance kao prekursori DBPs

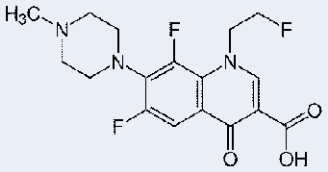
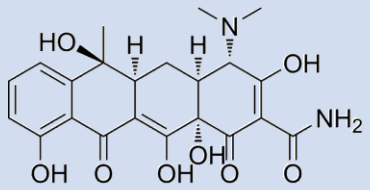
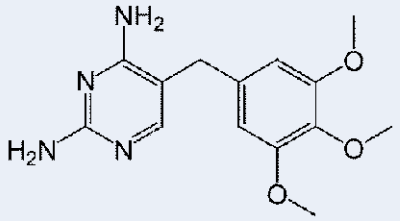
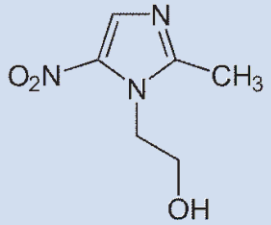
- UV filteri
  - benzofenon-3 (HAA)
  - benzofenon-4 (HAA)
  - 3-(4-metilbenziliden)kamfor (HAA)
  - 2,4-dihidroksibenzofenon (HAA)
  - Dioksibenzon (HAA)
  - Avobenzon (preko 60 DBPs)
  - 2-etilheksil-4-metoksicinamat (HAA)
  - Oktokrilen
- IR3535
- Kafein
- Bisfenol A (hloramin: THM, HAA, HAN)

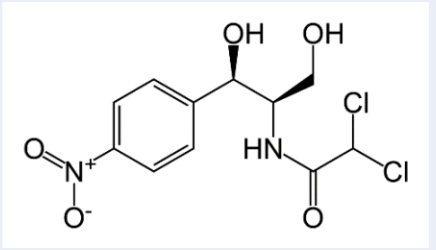
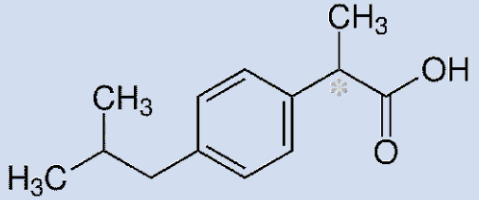
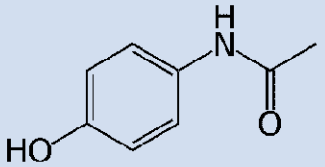
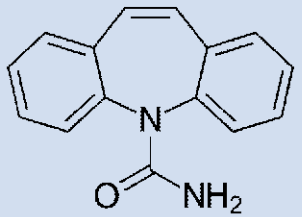
✓ Prema NORMAN-u su polutanti koji trenutno nisu obuhvaćeni rutinskim monitoring programima na evropskom nivou, a koji su potencijalni kandidati za buduće regulative u oblasti voda, u zavisnosti od njihove ekotoksičnosti, odnosno ponašanja u životnoj sredini

✓ NOMRAN lista broji preko hiljadu CEC, uključujući njihove metabolita i transformacione proizvode.



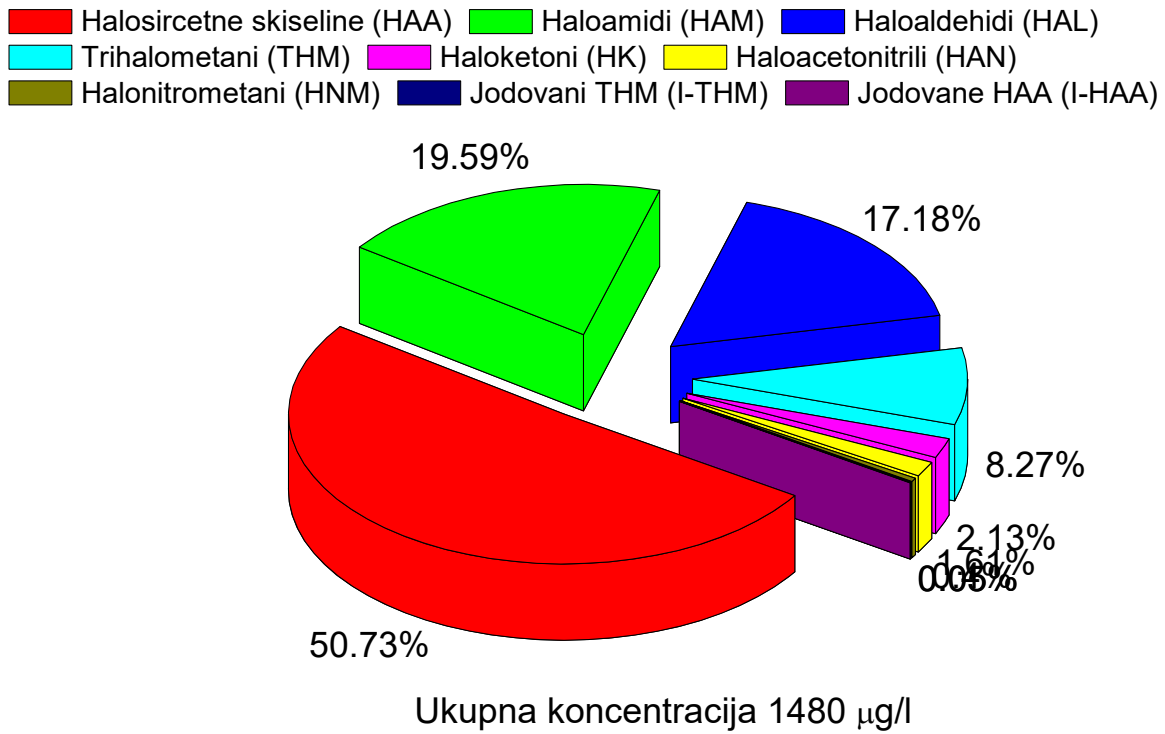
Farmaceutici kao prekursori DBPs

FARMACEUTICI	HEMIJSKA STRUKTURA	DEZINFE-KTANT	POTENCI-JALNI DBP
Enoksacin		ClO_2	HAA, HAN, THM, HK, HAL
Fleroksacin		hlor ili ClO_2	THM, HAA, HAN
Tetraciklini		hlor ili hloramin	TCM, DCAcAm, DCAN, TCM
Trimetoprim		UV/hlor	TCM, CH, DCAN, TCNM
Metronidazol		hloramin	TCM, DCAcAm, TCAcAm, DCAN

FARMACEUTICI	HEMIJSKA STRUKTURA	DEZINFE-KTANT	POTENCI-JALNI DBP
Hloramfenikol		UV/hlor	MCNM, DCNM, TCNM
Ibuprofen		UV/hlor	TCM, CH, 1,1,1-TCP, 1,1-DCP, DCAA, TCAA
Paracetamol		hloramin	TCM, DCAN, DCAcAm, TCAcAm
Karbamazepin		UV/hlor	TCM, DCAA, TCAA, DCAN, TCNM

HAL-haloacetamidi; HAN-halonitrometani; TCM-hloroform; DCAcAm-dihloracetamid; TCAcAm-trihloracetamid

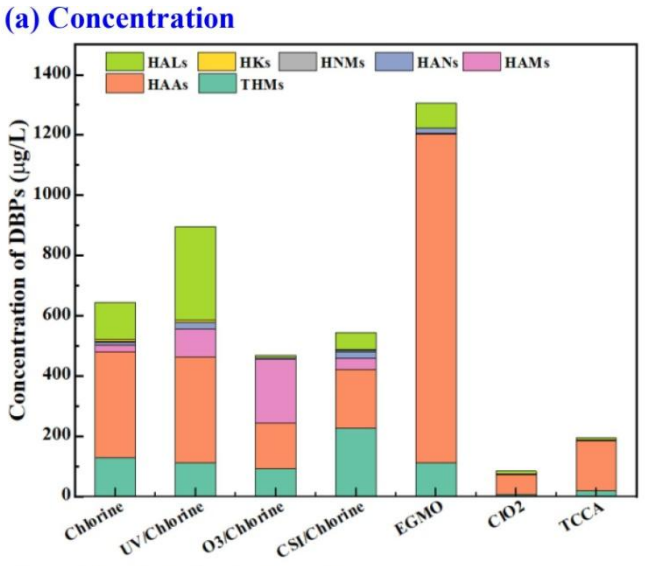
DBPs u bazenskim vodama – različite strategije dezinfekcije

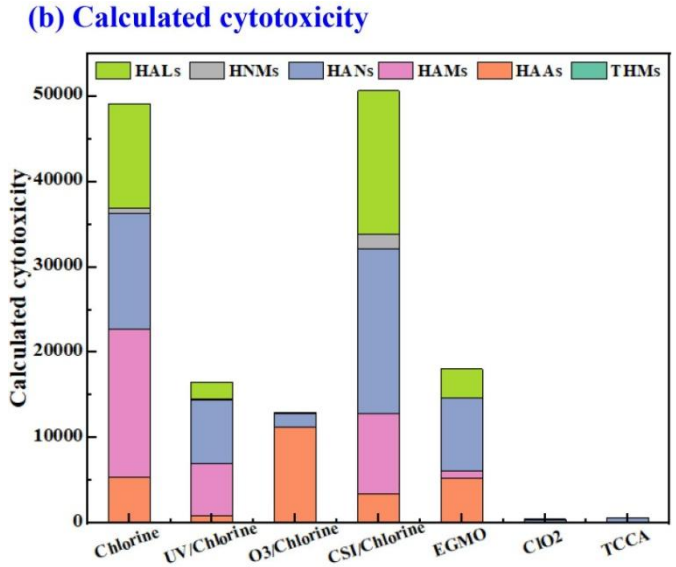


Ukupna koncentracija 1480 μg/l

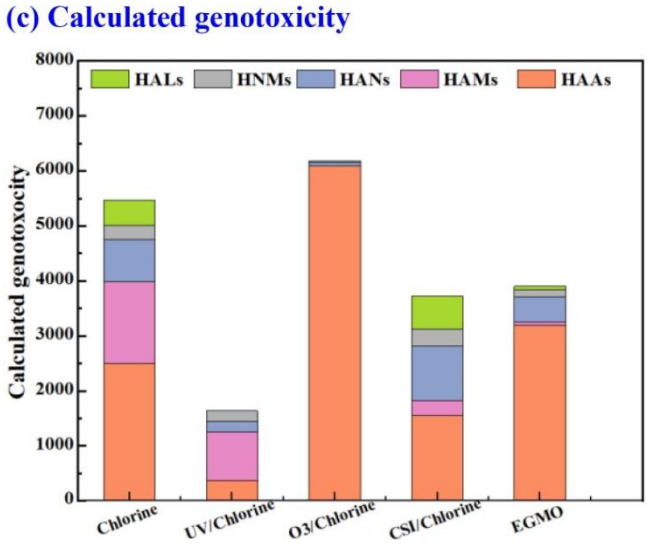
Koncentracija emergentnih DBP u bazenskim vodama u svetu (Qui et al., 2023)

EGMA > UV/hlor > Hlor > Cu-Ag joni/hlor > O_3/hlor > TCAA > ClO_2





- Hlor
- UV/hlor
- O_3/hlor
- Cu-Ag joni/hlor
- Elektrohemijski generisan mešoviti dezinfektant
- Hlor-dioksid
- Trihlorizocijanurinska kiselina



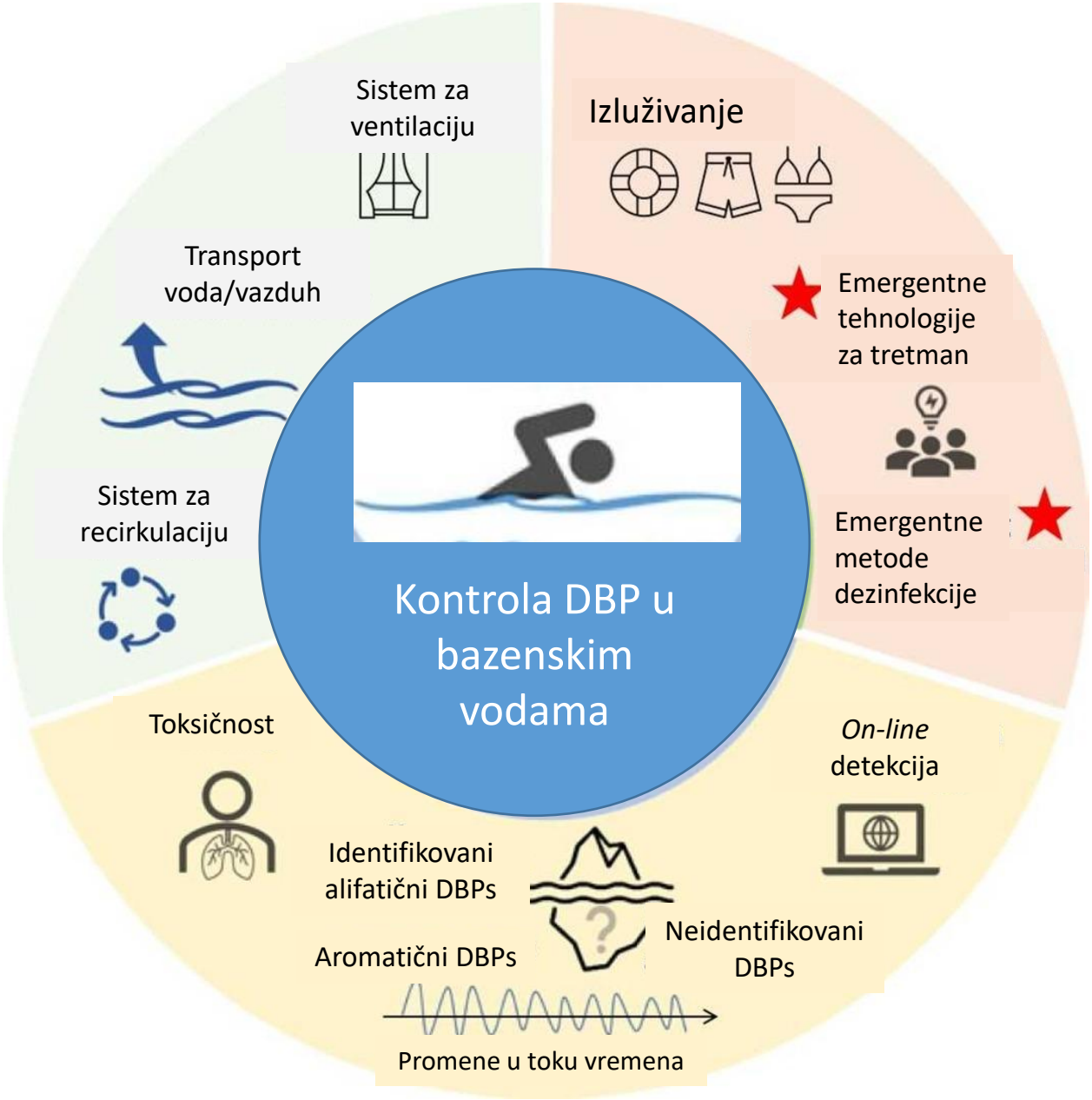
Parametri pokazatelji bazenske vode (*"Sl. glasnik RS", br. 30/2017 i 97/2017*)

Parametri	Vrednost	Merna jedinica
Mutnoća[1]	≤5	NTU
Hlorid	≤300	mg/l
Utrošak $KMnO_4$	≤20	mg/l
pH[2]	6,5-7,8	/
Slodobni rezidualni hlor[3]	0,1-1,0	mg/l
Trihalometani (ukupni)[4]	≤0,1	mg/l
Hlor-dioksid[5]	≤0,4	mg/l
Stabilizator-cijanurična kiselina[6]	30-50	mg/l
Bromati[7]	≤0,01	mg/l

[1]Vrednost za mutnoću bazenske vode koja potiče iz prirodnog izvora podzemne vode može biti i veća; [2]Ne odnosi se na bazensku vodu koja poseduje medicinske i terapeutske indikacije. [3]Izuzetno se može u ograničenom vremenskom periodu dozvoliti vrednost slobodnog rezidualnog hlora do 1,2 mg/l pri temperaturi bazenske vode do 32 ºC. U slučaju da je temperatura bazenske vode veća od 32 ºC, slobodni rezidualni hlor može da ima vrednost 2±1 mg/l. [4]Ispituje se po indikacijama u zatvorenim bazenima, u slučaju dezinfekcije vode hlornim preparatima;[5]Ispituje se ako se za dezinfekciju vode koristi hlordioksid. [6]Dozvoljena je primena u otvorenim bazenima i ispituje se ako se za dezinfekciju koriste preparati na bazi cijanurata. [7]Ispituje se ako se za dezinfekciju vode koristi ozon.

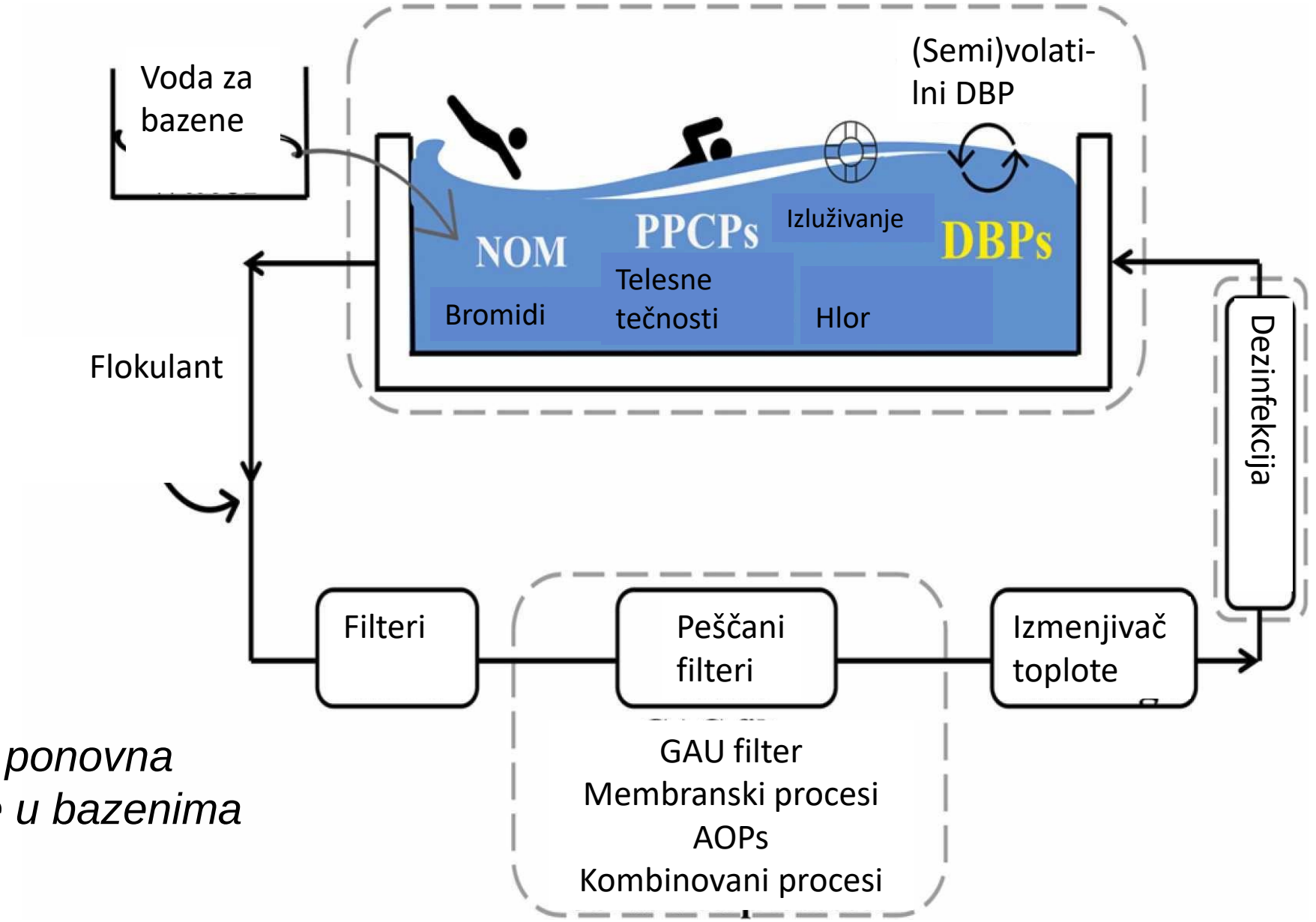
Smernice za sadržaj THM u bazenskim vodama u svetu

Zemlja	MCL (µg/l)
Nemačka	20
Švajcarska	30 (bazeni u zatvorenom prostoru)
Danska	25 ili 50
Francuska	100
Velika Britanija	100
Finska	100
Belgija	100 (TCM)
WHO	100
Poljska	100
Kina	200



Strategija kontrole DBPs u bazenskim vodama

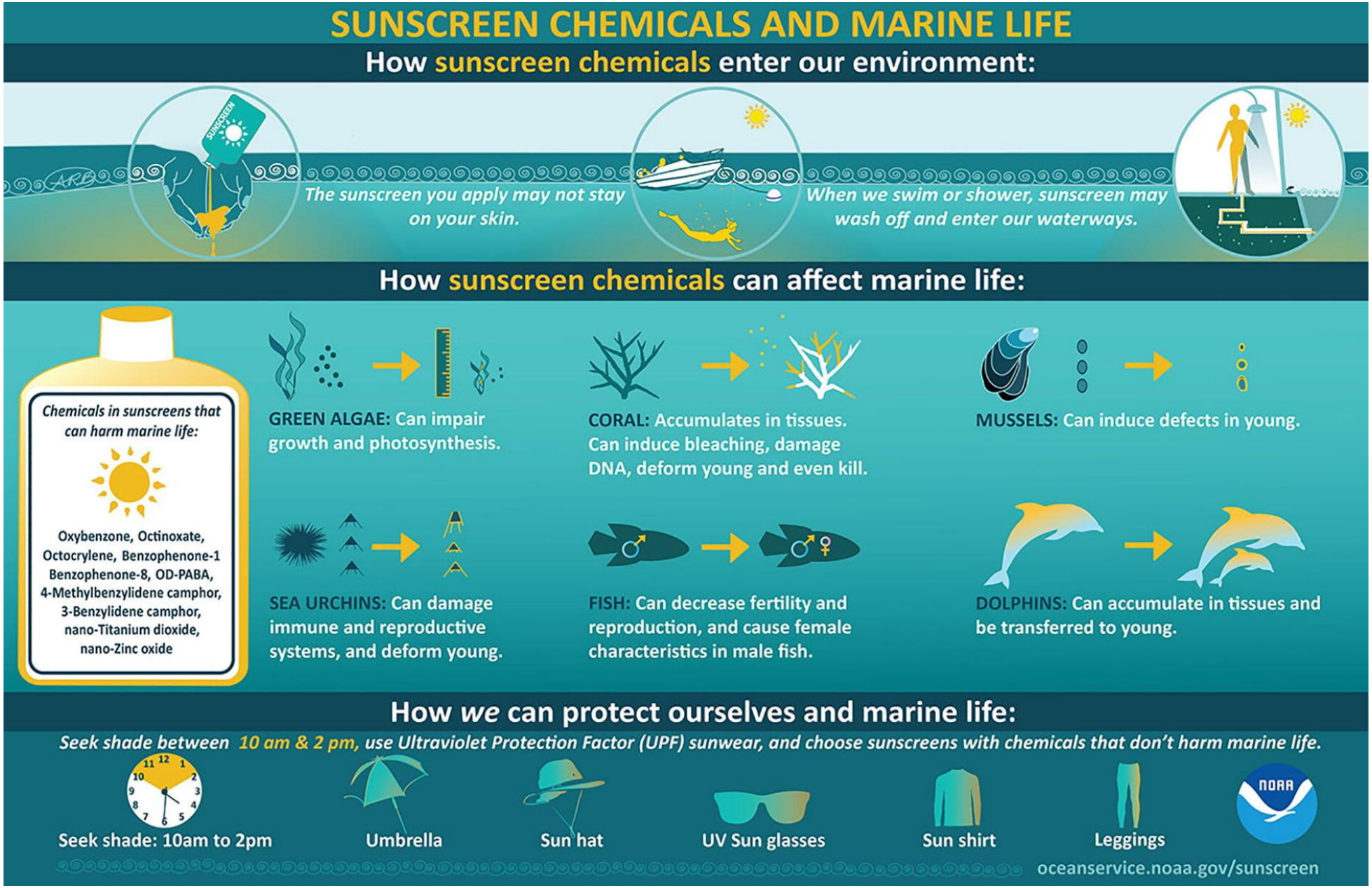
- Direktno uklanjanje formiranih DBP
- Sprečavanje formiranja DBP
- Unapređenje zakonskih regulativa iz ove oblasti



Recirkulacija i ponovna upotreba vode u bazenima

Formiranje i migracija DBP u bazenima. Procesi za kontrolu sadržaja DBP.

UMESTO ZAKLJUČKA



(*NOAA's National Ocean Service Sunscreen Infographic*)