

# WP4

## Activity progress

AdSWiM | PP 4 | Federico Girolametti

GA and SC Meeting | On line meeting | 14 December 2021

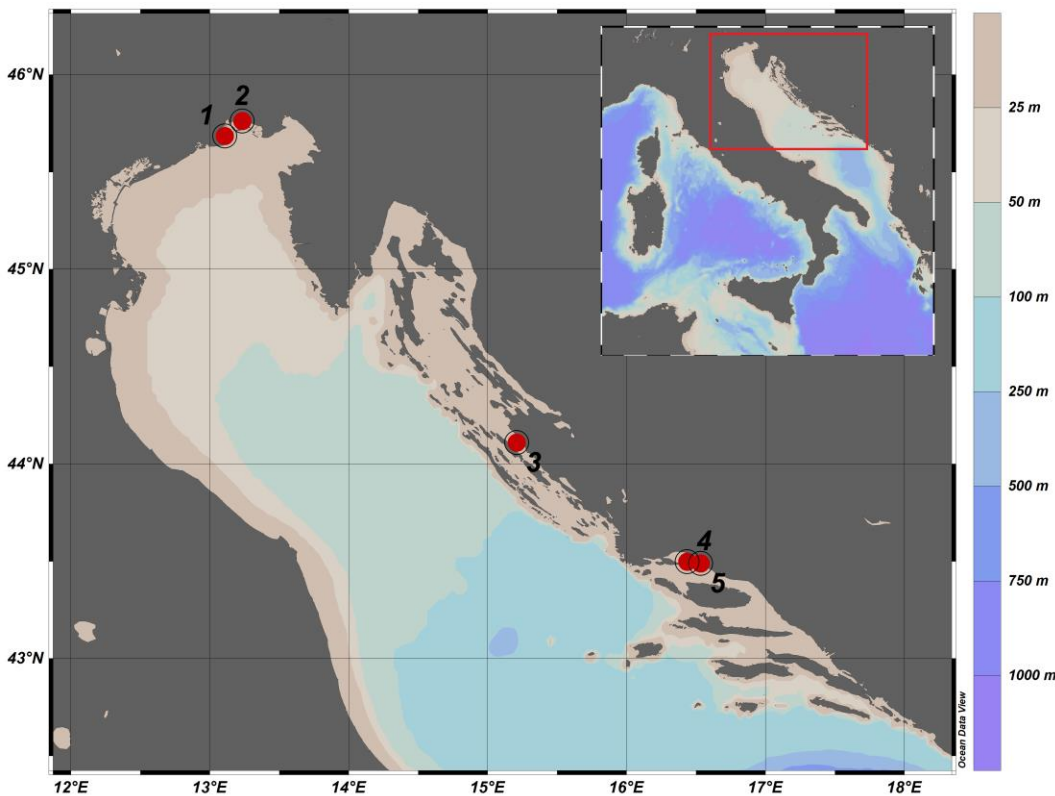
# OUR PRINCIPAL TASK IN WP4

Innovative solutions in analytical, microbiological controls  
and to treat urban wastewaters (UWW)

## 4.2 IAMD (Innovative Analytical Methods/ Devices)\_Nutrients and trace elements

Activities	PP	Project GANTT
<b>Measurements of nutrients and trace elements in relationship with master hydrological variables (A4.2.1)</b>	<b>UnivPM</b>	Aug 2019-Dec 2021

# Sampling stations



## ❑ Marano Lagoon (ITA) (metals/nutrients)

1. Lignano Sabbiadoro DP

2. San Giorgio di Nogaro DP

## ❑ Zadar (HR) (metals)

3. Zadar Upov Centar DP

## ❑ Split (HR) (metals)

4. Katalinica brig DP

5. Stupe DP

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2019	Marano L.				X	X		X	X		X		
	Zadar							X		X		X	
	Split							X					
2020	Marano L.				X	X	X	X		X	X		
	Zadar				X	X	X	X	X	X			
	Split		X			X	X	X		X			

## Metals

### Sample treatment and analyses



#### Storage

- -20°C
- PE decontaminated bottles



#### Laboratory

- Clean room laboratory ISO 14644-1 Class 6, with areas at ISO Class 5 under laminar flow.



#### Filtration

- Decontaminated polysulfone filtration apparatus
- Mixed cellulose esters (MCE) membrane



#### Mineralization

- MARS-6
- HCl UPA



#### Analysis

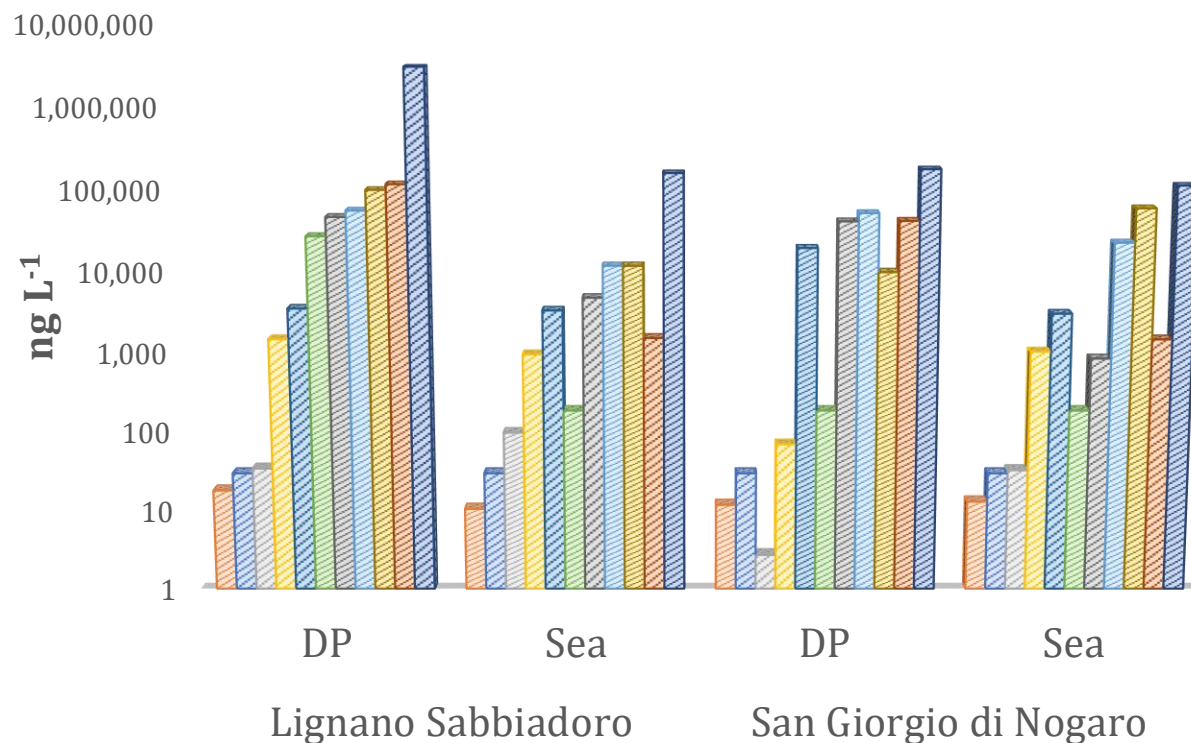
- AFS TITAN 8220
- High purity  $\text{NaBH}_4$
- Calibration curve



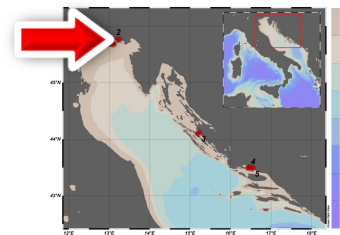
#### CRM

- NASS-6
- SLEW-3
- DORM-2
- QC3163

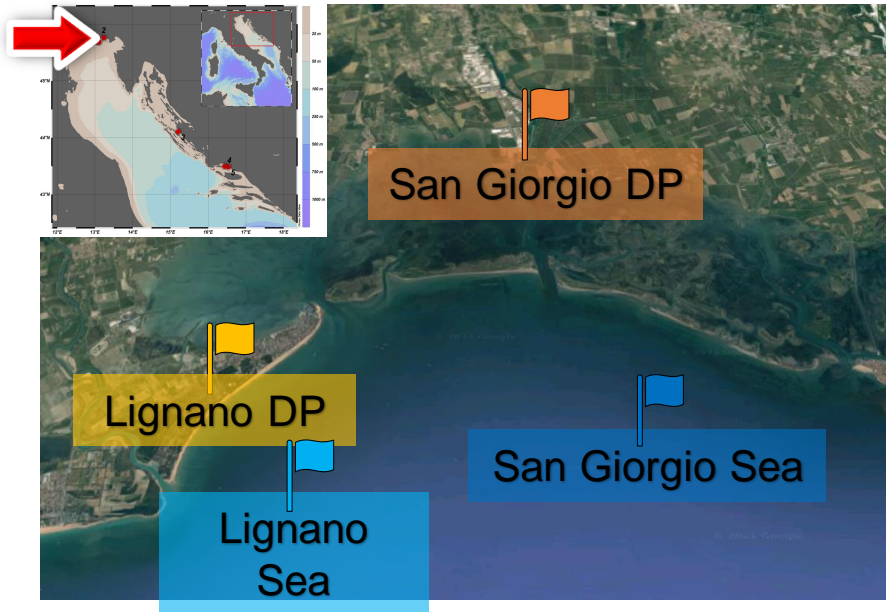
**Hg** < Pb < **Cd** < **As** < Cr < Cu < Zn < Ni < Mn < Fe < Al



Legend: Hg, Pb, Cd, As, Cu, Cr, Zn, Ni, Fe, Mn, Al



- All values below the legal limit, except for Al in Lignano DP.
- Difference between DP and seawater only for Cr, Cu, Zn, Ni, Mn, Fe, and Al.
- A further investigation for Hg, Cd and As seasonal trend.

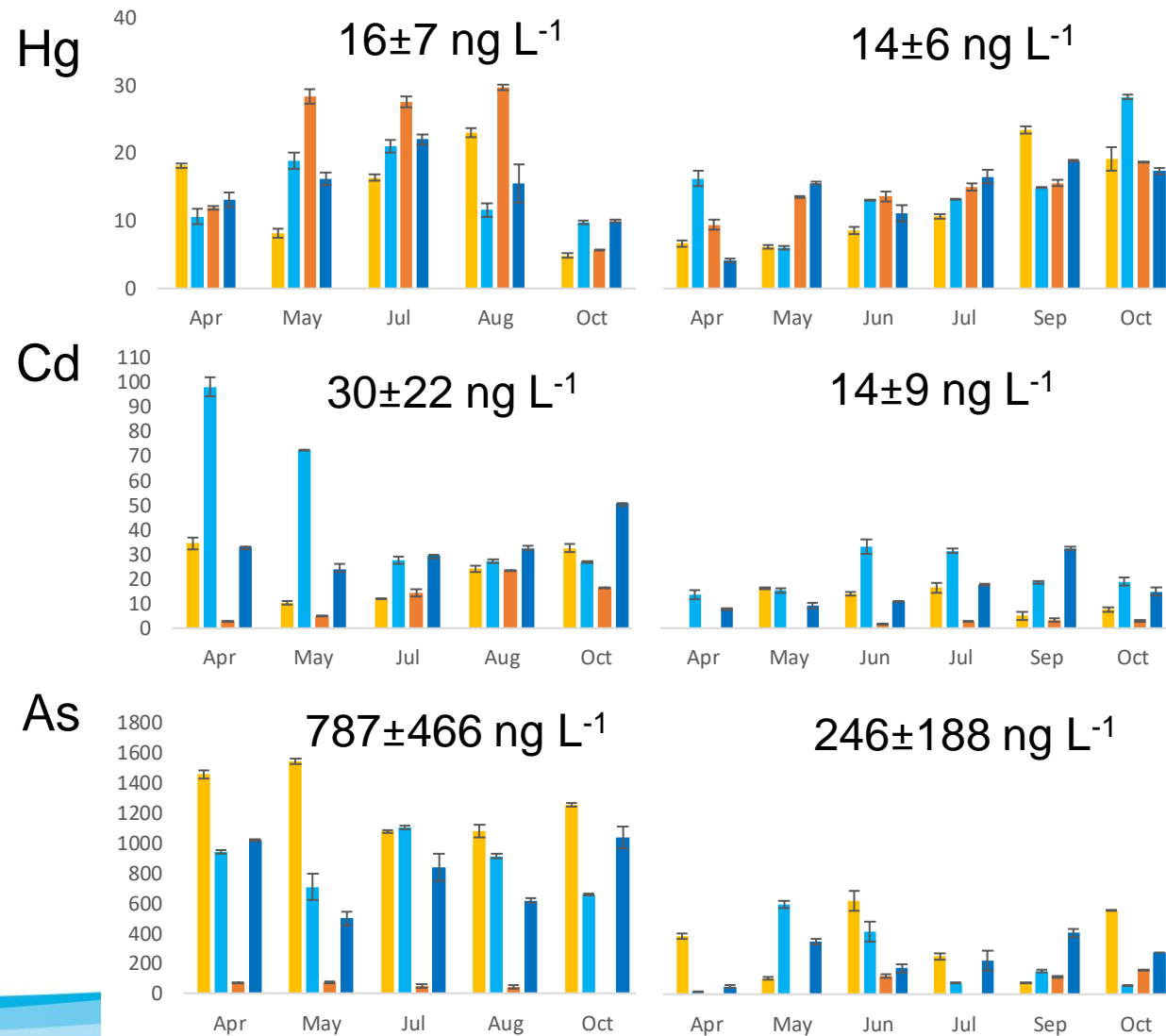


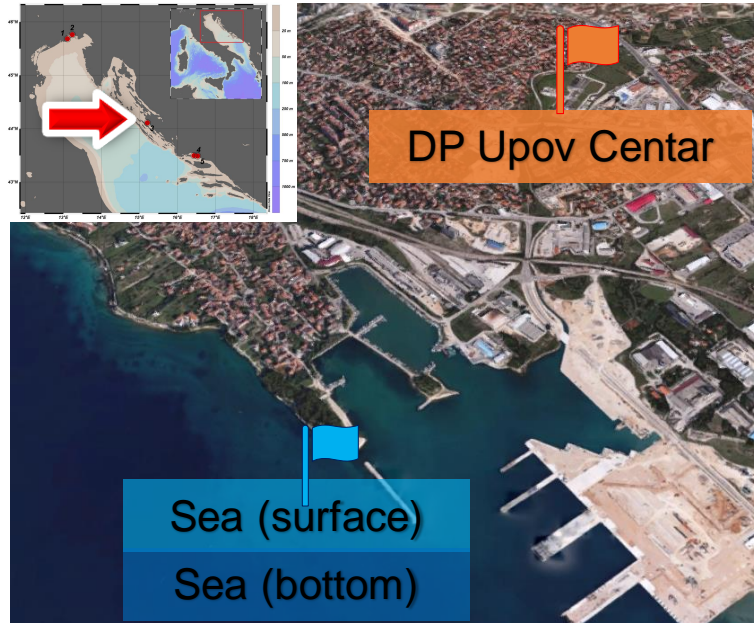
- Values below limits.
- No dilution effect (Cd and As lower in San Giorgio DP).
- Cd and As lower in 2020.

LIMITS	DP ( $\mu\text{g L}^{-1}$ )	Sea ( $\mu\text{g L}^{-1}$ )
Hg	5	0.07
Cd	20	0.45
As	500	5

## 2019

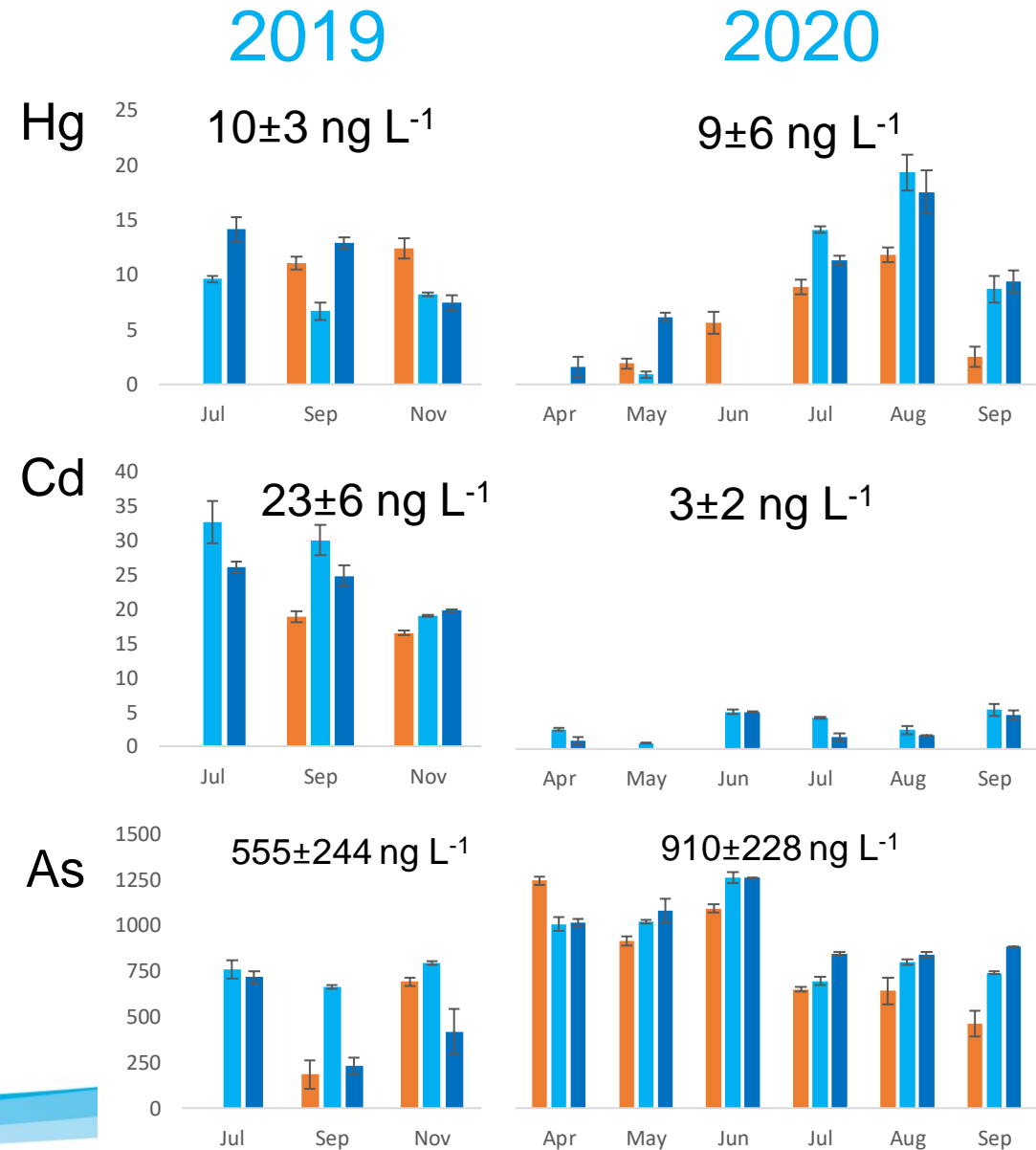
## 2020

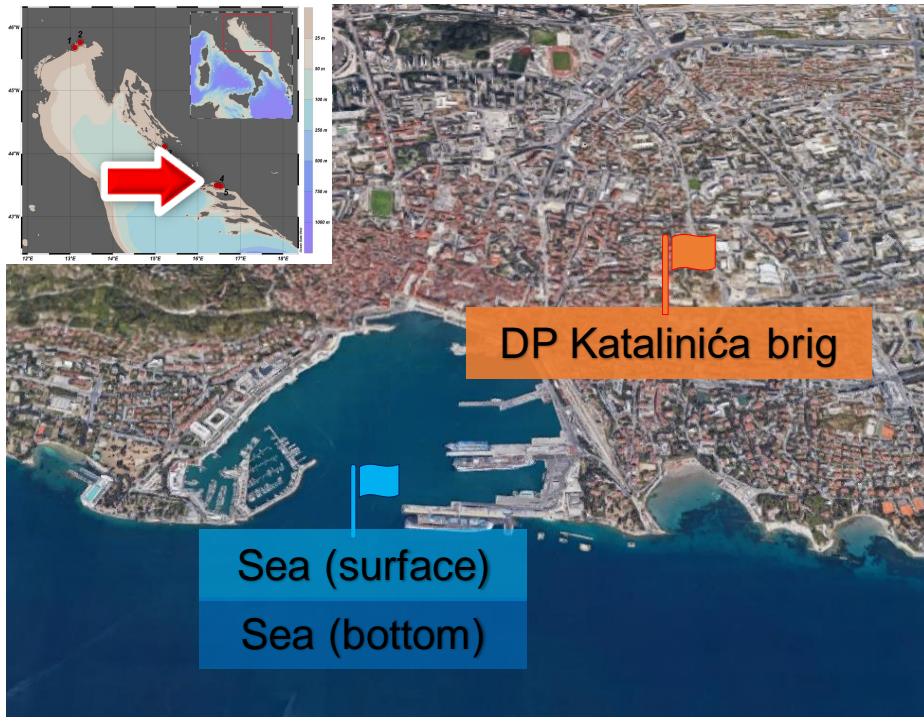




LIMITS	DP ( $\mu\text{g L}^{-1}$ )	Sea ( $\mu\text{g L}^{-1}$ )
Hg	5	0.07
Cd	20	0.45
As	500	5

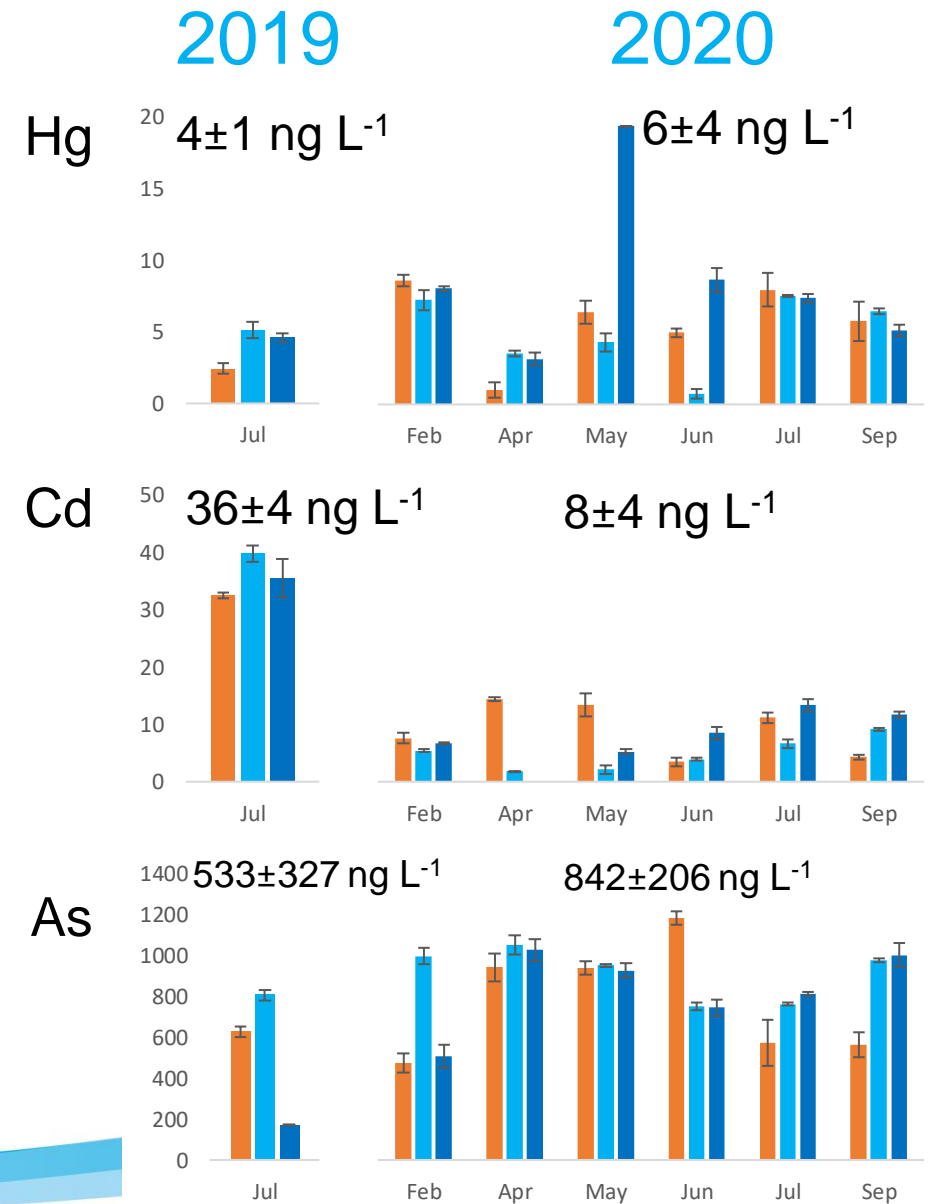
- Values below limits.
- No dilution effect.
- Cd lower in 2020 (DP always  $<\text{LOD}$ ).
- No difference with depth.

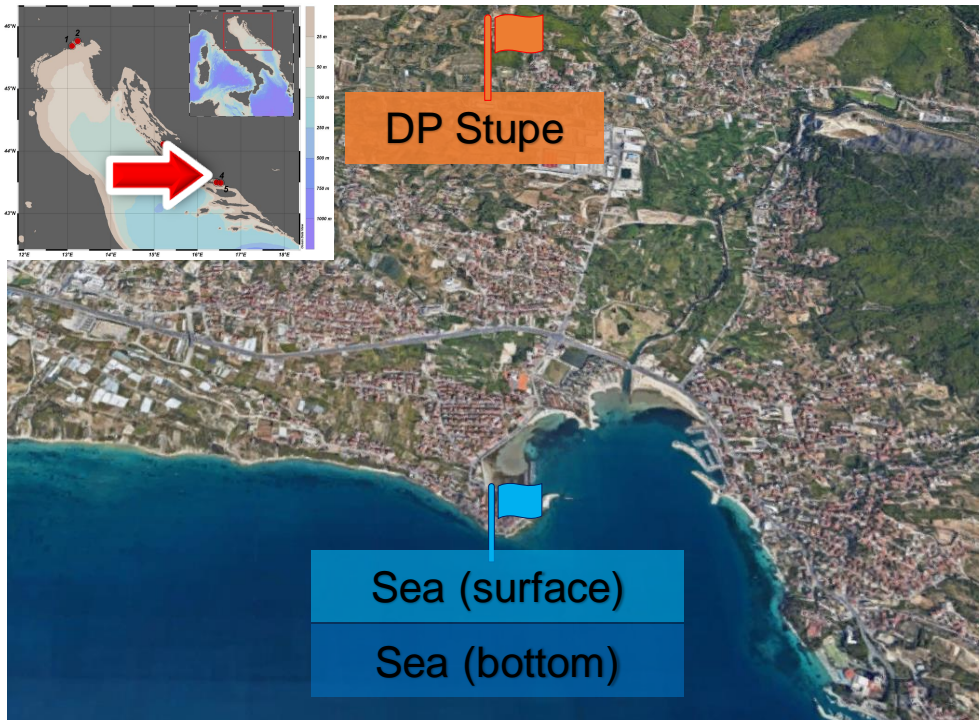




- Values below limits.
- No dilution effect.
- Cd lower in 2020.
- No difference with depth.

LIMITS	DP ( $\mu\text{g L}^{-1}$ )	Sea ( $\mu\text{g L}^{-1}$ )
Hg	5	0.07
Cd	20	0.45
As	500	5





- Values below limits.
- Dilution effect in Cd 2020.
- Cd lower in 2020.
- No difference with depth.

LIMITS	DP ( $\mu\text{g L}^{-1}$ )	Sea ( $\mu\text{g L}^{-1}$ )
Hg	5	0.07
Cd	20	0.45
As	500	5

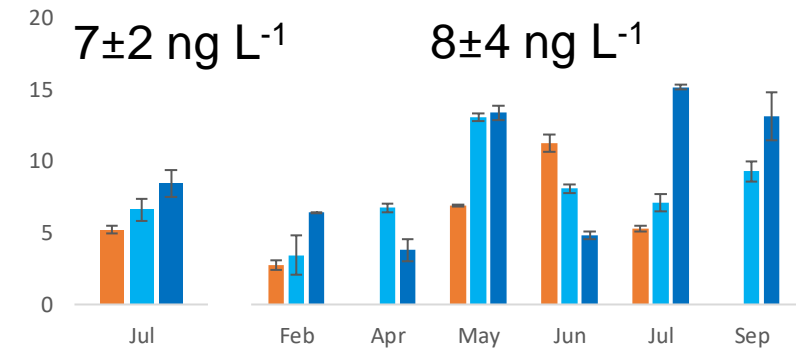
Hg

2019

$7 \pm 2 \text{ ng L}^{-1}$

2020

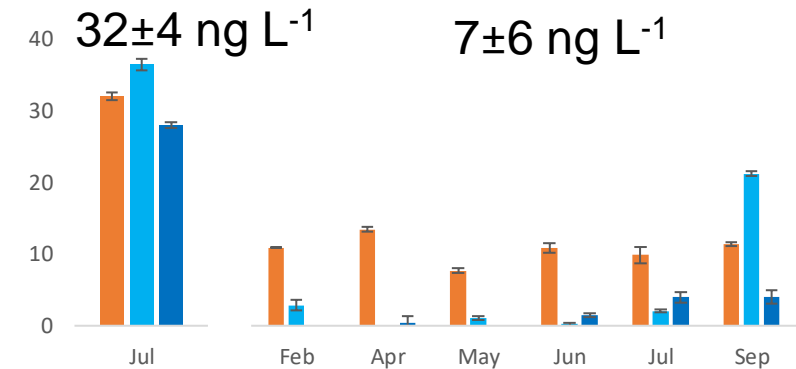
$8 \pm 4 \text{ ng L}^{-1}$



Cd

$32 \pm 4 \text{ ng L}^{-1}$

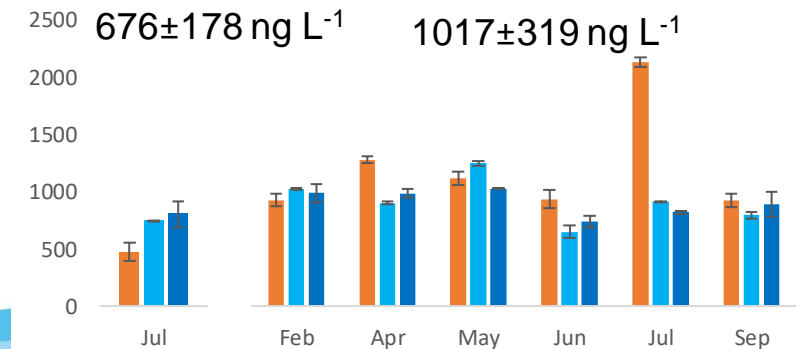
$7 \pm 6 \text{ ng L}^{-1}$

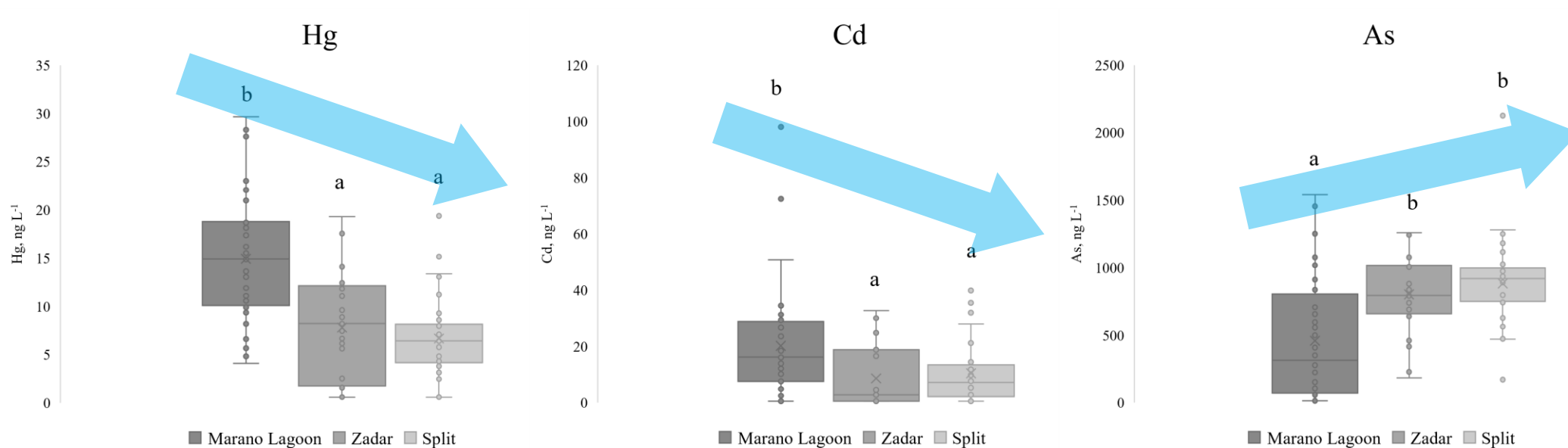


As

$676 \pm 178 \text{ ng L}^{-1}$

$1017 \pm 319 \text{ ng L}^{-1}$

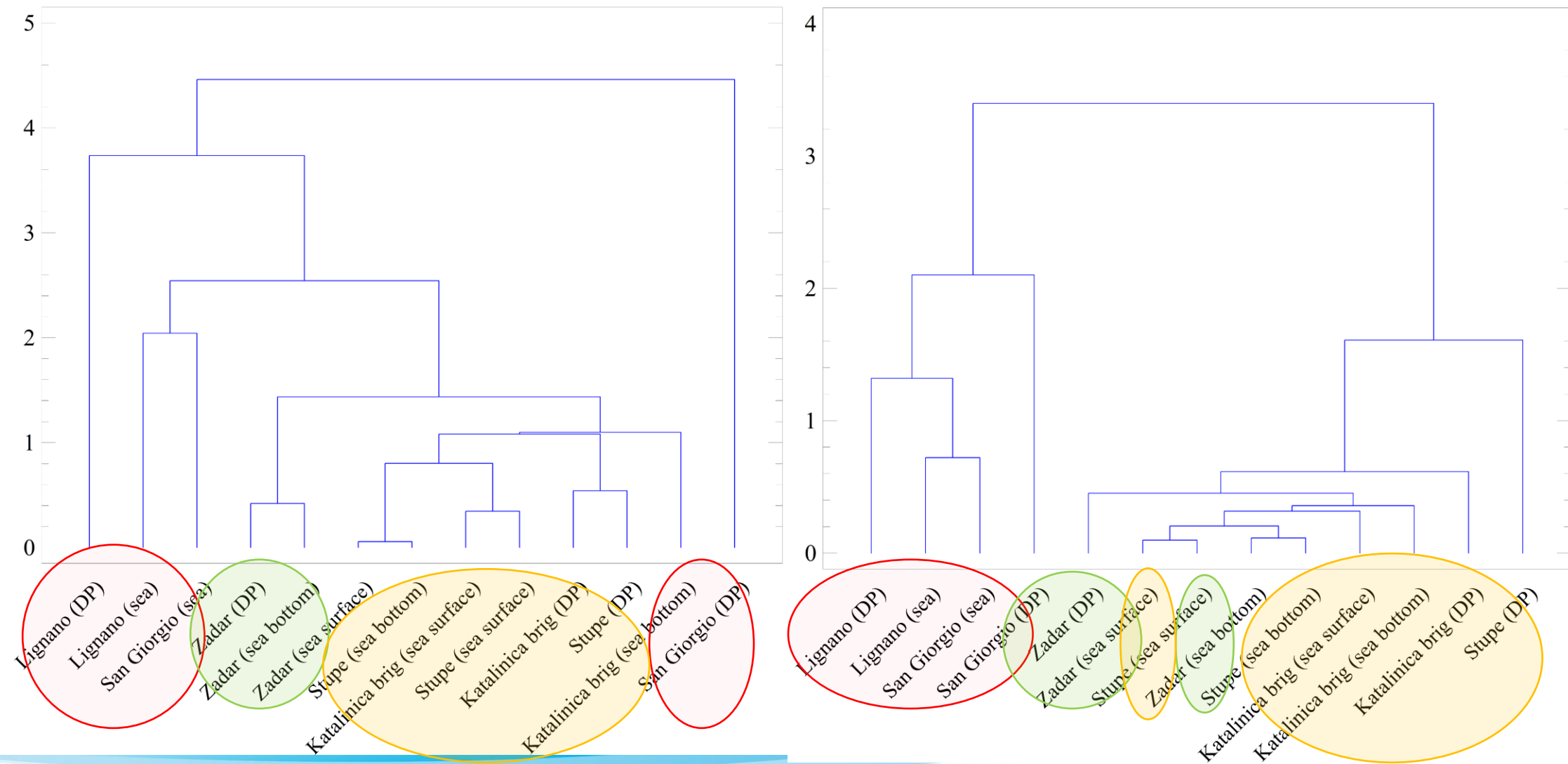




- Hg statistically higher in Marano Lagoon (decrease from North to South)
- Cd statistically higher in Marano Lagoon (decrease from North to South)
- As statistically higher in Zadar and Split (increase from North to South)

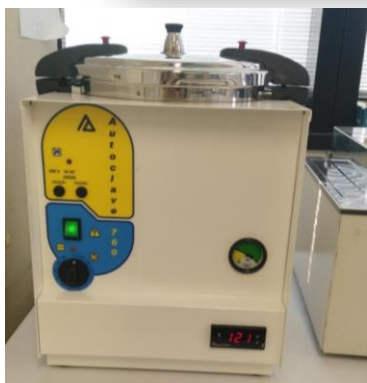
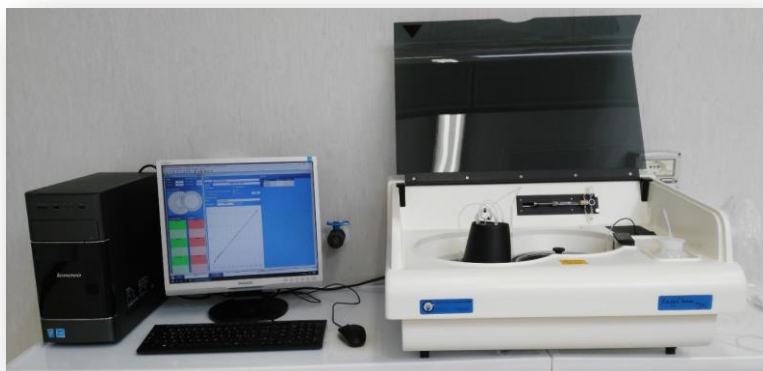
2019

2020



## Nutrients

### Sample treatment and analyses



Persulfate digestion  
(Langner and Hendrix, 1982)

$$\begin{array}{c} \text{P-P}_{\text{tot}} \\ \downarrow \\ \text{P-P}_{\text{tot}} - \text{P-DIP} = \text{P-DOP} \end{array}$$

#### Nitric Nitrogen $\text{N-NO}_2$

Ref. United States Environmental Protection Agency (EPA) Method # 354.1  
Nitrogen, Nitrite (Spectrophotometric)

#### Nitrous Nitrogen $\text{N-NO}_3$

Ref. National Environmental Methods Index 9171 Nitrate via V(III) reduction

#### Ammoniacal Nitrogen $\text{N-NH}_3$

Ref. APHA Standard Methods for the Examination of Water and Wastewater 4500-NH3  
G – Automated Phenate Method

#### Silicon as Silicates $\text{Si-SiO}_2$

Ref. APHA Standard Methods for the Examination of Water and Wastewater 4500-SiO2  
D. Molybdosilicate Method

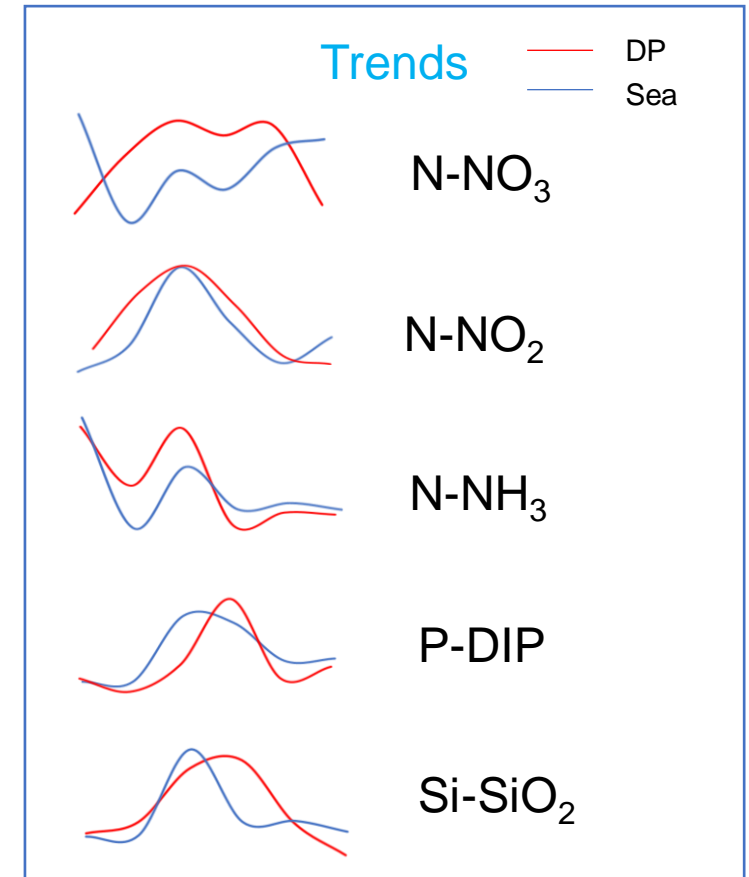
#### Orthophosphate $\text{P-PO}_4$ P-DIP

Ref. International Standard Organization 15923-1 Water quality.  
Determination of selected parameters by discrete analysis systems.  
Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with  
photometric detection

QC3179 - Simple Nutrients in Seawater

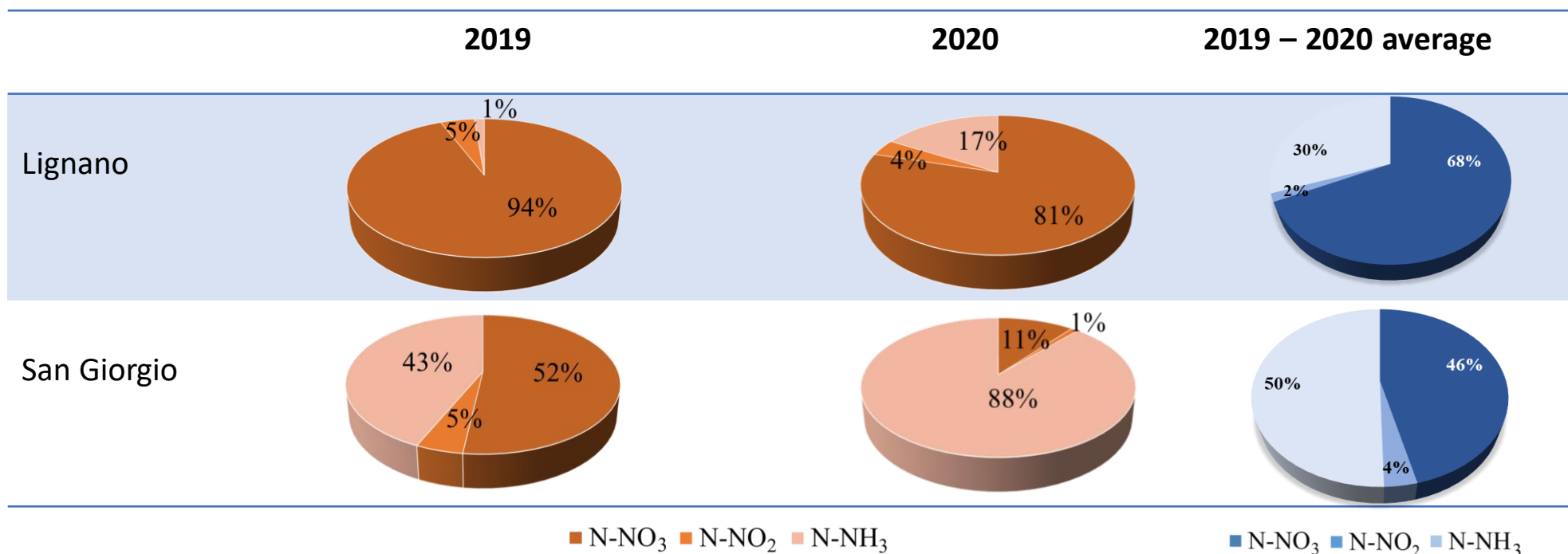
## General results and trends (nutrients)

$\mu\text{mol L}^{-1}$	P-P <sub>tot</sub>		P-DIP		N-NO <sub>2</sub>		N-NO <sub>3</sub>		N-NH <sub>3</sub>		Si-SiO <sub>2</sub>	
	min	max	min	max	min	max	min	max	min	max	min	max
2019 - DP outflow samples	6.4	78.1	4.15	57.02	0.98	59.34	1.38	445.5	0.5	88.3	88	206.6
Average	28.90		21.30		11.1		189.5		16.8		142.7	
2020 - DP outflow samples	4.03	78.80	1.43	73.06	0.4	86.02	0.2	503.8	1.4	295	26.3	253.6
Average	22.84		18.6		10.9		142		114.9		100.87	
2019 - Sea samples	0.4	1.6	0.011	0.025	0.03	0.08	0.3	7.6	0.4	2.5	1.4	10.9
Average	0.82		0.015		0.05		2.06		0.93		4.24	
2020 - Sea samples	0.43	2.35	0.011	0.045	0.06	0.27	0.4	3.2	0.5	5.1	4.07	10.7
Average	1.38		0.018		0.13		1.71		1.71		6.44	
Dilution: DP/Sea 2019	35.1		1468		233		92		18		33	
Dilution: DP/Sea 2020	16.6		1018		85		83		35		16	



- ✓ All values below the legal limit (except one for N-NO<sub>2</sub>)
- ✓ Similar trends between DP and Sea (except for N-NO<sub>3</sub>)

## Dissolved Inorganic Nitrogen distribution



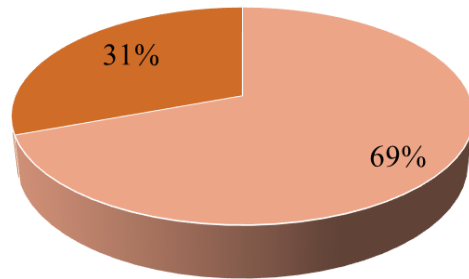
**DP**

- ✓ Differences between the two DPs
- ✓ Differences between the years
- ✓ Increment on Ammoniacal nitrogen concentrations

**Sea**

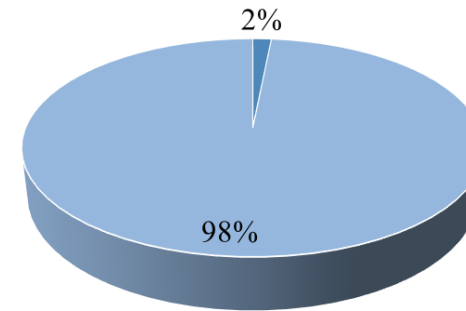
- ✓ No differences between the sea sites
- ✓ The increment on ammoniacal nitrogen levels in 2020 led to a different DIN distribution

## Dissolved phosphorus distribution



■ DIP ■ DOP

DP (average between 2019 and 2020)	DIP	Ptot
Lignano DP	$28.9 \pm 7.4 \mu\text{M}$	$37.4 \pm 9.3 \mu\text{M}$
San Giorgio DP	$11.0 \pm 15.5 \mu\text{M}$	$14.3 \pm 15.7 \mu\text{M}$



■ DIP ■ DOP

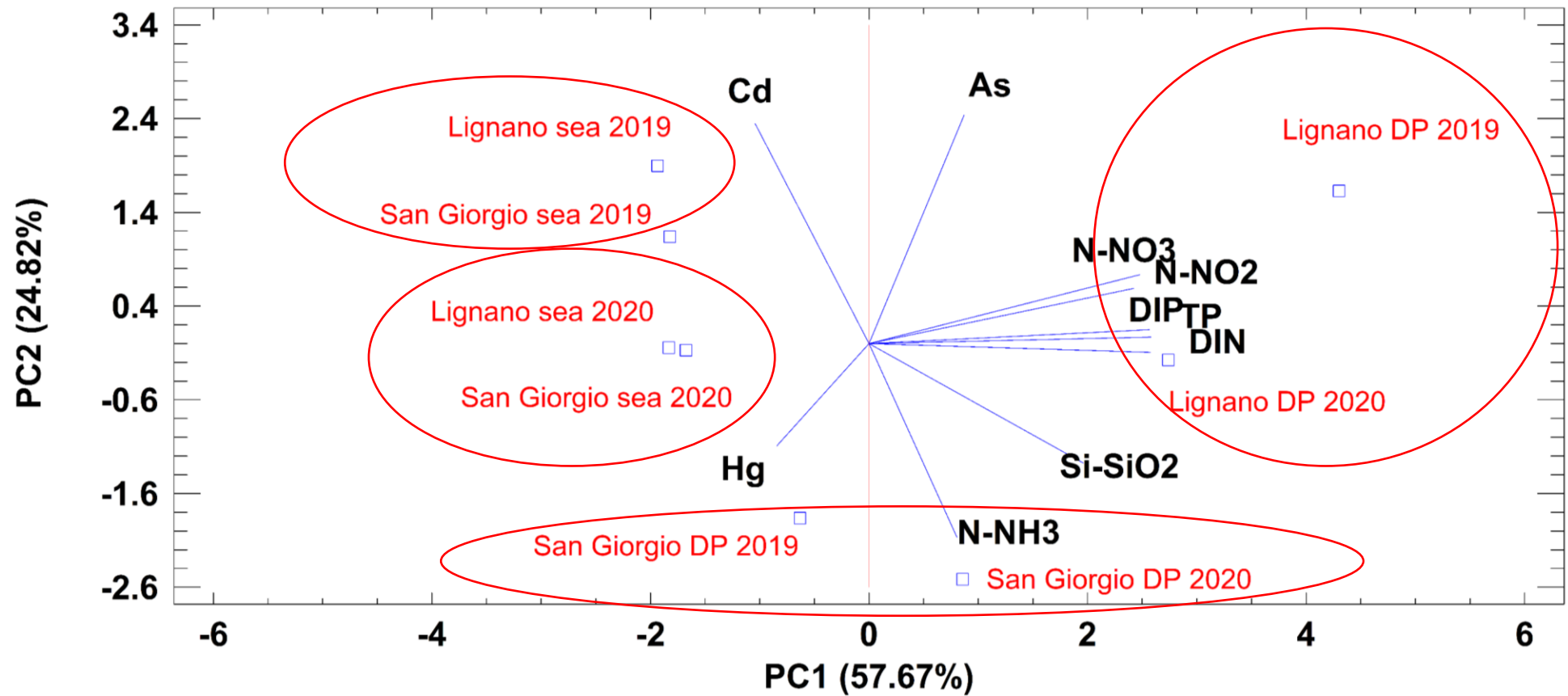
Sea (average between 2019 and 2020)	DIP	Ptot
Lignano Sea	$0.0140 \pm 0.005 \mu\text{M}$	$1.05 \pm 0.55 \mu\text{M}$
San Giorgio Sea	$0.019 \pm 0.011 \mu\text{M}$	$1.20 \pm 0.61 \mu\text{M}$

- ✓ No difference between sea sites
- ✓ Lignano's DP P concentrations are 2.6 times higher than San Giorgio
- ✓ From DP to Sea the DIP-DOP distribution changes drastically

# Dataset (D 4.2.3)






Salvataggio automatico		null		Cerca (ALT+X)		GIROLAMETTI FEDERICO					
File		Home		Inserisci		Layout di pagina		Formule		Dati	
Revisione		Visualizza		Guida		Commenti		Condividi			
Numero		%		000		Formattazione condizionale		Inserisci			
Formatta come tabella		Stili cella				Microb. parameters				Metals	
Sampling station		CTD parameters		Nutrients							
Date/time		Site		Type		Depth		Month		Year	
Temperature		Salinity		Density		Turbidity		pH		Total suspended solids 105 °C	
Suspended solid		Dissolved oxygen		Sat O2%		Redox potential		BOD <sub>5</sub>		COD(Cr)	
Ammoniacal Nitrogen (N-NH <sub>3</sub> )		Nitrous Nitrogen (N-NO <sub>2</sub> )		Nitric Nitrogen (N-NO <sub>3</sub> )		Dissolved Inorganic Nitrogen (DIN)		Total nitrogen (TN)		Total Phosphorus (TP)	
Orthophosphate (P-PO <sub>4</sub> )		Silicates (Si-SiO <sub>2</sub> )		Chl a		TOC		Pseudomonas aeruginosa		Escherichia coli	
Enterococci		Dissolved Mercury									
30/07/2019		ZD-UC-DP		DP		/		7		2019	
13/09/2019		ZD-UC-DP		DP		/		9		2019	
07/11/2019		ZD-UC-DP		DP		/		11		2019	
22/04/2020		ZD-UC-DP		DP		/		4		2020	
18/05/2020		ZD-UC-DP		DP		/		5		2020	
18/06/2020		ZD-UC-DP		DP		/		6		2020	
27/07/2020		ZD-UC-DP		DP		/		7		2020	
26/08/2020		ZD-UC-DP		DP		/		8		2020	
29/09/2020		ZD-UC-DP		DP		/		9		2020	
31/07/2019		SP-KB-DP		DP		/		7		2019	
27/02/2020		SP-KB-DP		DP		/		2		2020	
23/04/2020		SP-KB-DP		DP		/		4		2020	
28/05/2020		SP-KB-DP		DP		/		5		2020	
26/06/2020		SP-KB-DP		DP		/		6		2020	
22/07/2020		SP-KB-DP		DP		/		7		2020	
21/09/2020		SP-KB-DP		DP		/		9		2020	
31/07/2019		SP-ST-DP		DP		/		7		2019	
27/02/2020		SP-ST-DP		DP		/		2		2020	
23/04/2020		SP-ST-DP		DP		/		4		2020	
28/05/2020		SP-ST-DP		DP		/		5		2020	
26/06/2020		SP-ST-DP		DP		/		6		2020	
22/07/2020		SP-ST-DP		DP		/		7		2020	
21/09/2020		SP-ST-DP		DP		/		9		2020	
30/04/2019		Lignano DP		DP		/		4		2019	
26/05/2019		Lignano DP		DP		/		5		2019	
27/06/2019		Lignano DP		DP		/		6		2019	
17/07/2019		Lignano DP		DP		/		7		2019	
23/08/2019		Lignano DP		DP		/		8		2019	
08/10/2019		Lignano DP		DP		/		10		2019	
27/04/2020		Lignano DP		DP		/		4		2020	
27/05/2020		Lignano DP		DP		/		5		2020	
24/06/2020		Lignano DP		DP		/		6		2020	
23/07/2020		Lignano DP		DP		/		7		2020	
02/09/2020		Lignano DP		DP		/		9		2020	
01/10/2020		Lignano DP		DP		/		10		2020	
30/04/2019		San Giorgio DP		DP		/		4		2019	
26/05/2019		San Giorgio DP		DP		/		5		2019	
27/06/2019		San Giorgio DP		DP		/		6		2019	
17/07/2019		San Giorgio DP		DP		/		7		2019	
29/08/2019		San Giorgio DP		DP		/		8		2019	

# Principal component analysis (PCA) metals and nutrients



A PCA with microbiological and CTD data is in progress

# Description\_Activities\_4.2

Deliverables	State of art	
<ul style="list-style-type: none"> <li>Report of seasonal trend of the checked parameters on the IT/HR coast (D 4.2.1)</li> <li>Nutrients 2019/2020 (D 4.2.1) ~1000 analyses</li> <li>Metals 2019/2020 (D 4.2.1) ~1000 analyses</li> <li>Statistical analysis on results (D 4.2.1)</li> <li>Dataset (D 4.2.3)</li> </ul>	<p>Done</p> <p>Done</p> <p>Done</p> <p>Done</p> <p>Done</p>	    

All deliverables have been achieved in time

# Conclusions

## Principal results

- ✓ All values below the legal limit
- ✓ Strong dilution effect for nutrients, but not for metals (always low)
- ✓ DPs' activity does not influence seawater quality

## Research activities

- ✓ **2 scientific papers** published
- ✓ **3 scientific papers** in progress (*Water journal*)
- ✓ **5 communications** at scientific congresses and **2 thesis**

## Future perspectives

- ✓ **Urea** determination as quality indicator
- ✓ **PMEase** determination (to investigate the possibility of some algae to use organic P as substrate of growth)

Both analyses have to be done on fresh sample

# Polytechnic University of Marche

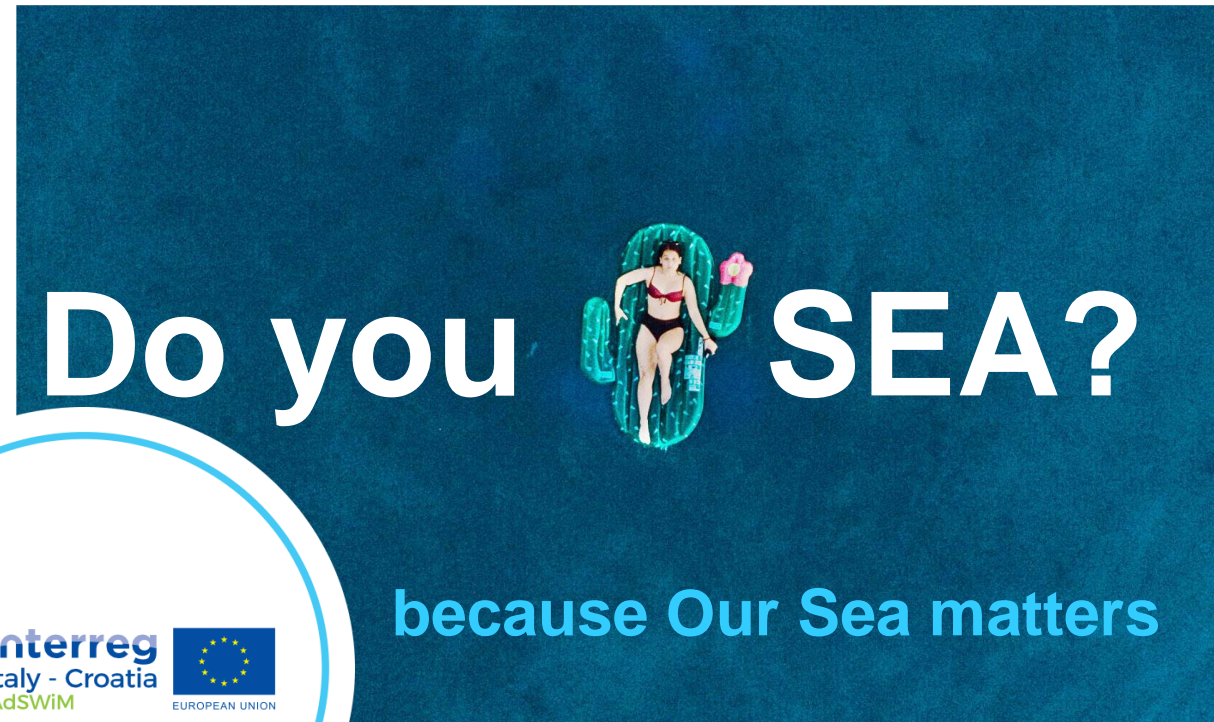
## PP4 | Anna Annibaldi

 Via Brece Bianche

 a.annibaldi@univpm.it

 +390712204981

 [www.italy-croatia.eu/adswim](http://www.italy-croatia.eu/adswim)



ZAVOD ZA JAVNO ZDRAVSTVO ZADAR

