Development of marine sediment quality guidelines for evaluation of heavy metals contamination in Croatia

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Aim

- The main aim of the presented research was to define sediment standards for selected heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, As, Pb) for protection of marine environment from excessive pollution.
- Defining standards and proposing Sediment Quality Guidelines (SQG) for selected metals taking different environmental categories in account would be the first such attempt in Croatia.

Introduction

- Most important tool for the assessment of the marine environmental quality are Sediment Quality Guidelines (SQGs).
- Quality of sediments are crucial for evaluating pollution trends (positive and negative). SQGs are a vital tool for determining the sediment quality.
- The hypothesis that a concentration threshold could be identified for chemicals in sediments below which aquatic life was not harmed was first proposed in the early 1970s by the USEPA and US Army Corps of Engineers.
- Unlike soils, sediments are constantly diluted with freshly precipitated material. Therefore it is possible to obtain better sediment quality in time only by introducing protective environmental measures, no remediation is needed.
- Here we propose Croatian SQGs for several chemical elements based on the sediment geochemical maps developed for the Croatian coastal sediments screening purposes (>700 sediment samples analysed for K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb by EDXRF)*.
- This is the first attempt to define Croatian SQGs for toxic elements in marine sediments together with a brief analysis of the environmental quality according to different types of the marine environment and human activities.

*Obhođaš, J.,Valković V., A. Kutle (2010): Atlas of Sediments (Croatia's Coastal Region and Islands), NGO "Lijepa naša", Zagreb. ISBN: 978-953-97044-3-6 (*in Croatian*)

SQGs used around the world

Numerous SQGs have been established since the 1980s, each **incorporating different criteria**, factors and approaches to try and account for the varied conditions in which sediment contamination occurs. Generally, these approaches can be divided into **two main categories**:

1.) **Empirical relationships** - based on contamination or background enrichment evaluation, or based on toxic studies

2.) **Theoretical relationships** (equilibrium partitioning, EqP) to describe bioavailability of contaminants.

SQG Category	Approach	Developers
Theoretical	Equilibrium Partitioning	Di Toro, Mahony et al. (1991) Di Toro, Zarba et al. (1991) Ankley et al. (1996) NYSDEC (1998) Di Toro and McGrath (2000)
Empirical	Screening-Level Concentration	Persaud et al. (1993) Von Stackelberg and Menzie (2002)
Empirical	Effects Range-Low (ERL) and Effects Range-Median (ERM)	Long et al. (1995) USEPA (1996)
Empirical	Threshold-Effects Level (TEL) and Probable-Effects Level (PEL)	MacDonald et al. (1996) Smith et al. (1996) USEPA (1996)
Empirical	Apparent-Effects Threshold (AET)	Barrick et al. (1988) Ginn and Pastorok (1992) Cubbage et al. (1997)
Empirical	Consensus-Based Evaluation	Swartz (1999) MacDonald, DiPinto et al. (2000) MacDonald, Ingersoll et al. (2000)
Empirical	Logistic Regression Modeling (LRM)	Field et al. (1999, 2002)

- **Empirical SQGs** are generally used for heavy metals and arsenic, but may incorporate other contaminants like organics.
- Several empirical approaches have been published. They differ in the way they determine the threshold effects, but many are quite similar. These approaches include the **effects range approach** (Long and Morgan 1991; Ingersoll et al. 1996), **effects level approach** (Smith et al. 1996; Ingersoll et al. 1996), **apparent effects threshold approach** (Cubbage et al. 1997), **and screening level concentration approach** (Persaud et al. 1993).

These approaches generally set two threshold levels - **one below which effects rarely occur**:

- the lowest effect level (**LEL**),
- threshold effect level (**TEL**),
- effects range low (**ERL**),
- minimal effect threshold (**MET**),
- and threshold effect concentration (**TEC**),

and **one above which effects are likely to occur**:

- the severe effect level (**SEL**),
- probable effects level (**PEL**),
- effect range median (**ERM**),
- toxic effect threshold (**TET**),
- and probable effect concentration (**PEC**).

- The predictive capabilities of these guidelines leave great uncertainty in the “grey” region of contaminant concentrations that lie between the thresholds.

Overview of the three main groups of numerical SQGs and their calculation methods (EDS ¼ effect data set, NEDS ¼ no-effect data set

Approach	Acronym	Complete term	Calculation method
NS&T- or NOAA-approach	ER-L	Effects Range Low	10th percentile EDS
	ER-M	Effects Range Median	50th percentile EDS
FDEP-approach	TEL	Threshold Effect Level	15th percentile EDS x 50th percentile NEDS
	PEL	Probable Effect Level	50th percentile EDS x 85th percentile NEDS
EC & MDDEP-approach	REL	Rare Effect Level	15th percentile EDS x 15th percentile NEDS
	OEL	Occasional Effect Level	50th percentile EDS x 50th percentile NEDS
	FEL	Frequent Effect Level	85th percentile EDS x 85th percentile NEDS

Extreme effect sediment quality guidelines for metals (mg/kg)

SQG	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference
TET	17	3	100	86	170	1	61	540	a
SEL[1]	33	10	110	110	250	2	75	820	a
CB PEC	33	4.98	111	149	128	1.06	48.6	459	a
SQO Netherlands Intervention	55	12	–	190	530	10	–	720	b
Flanders RV Z[2]	174	6	267	126	0.8	221	174	1057	c
Extreme Elevated Stream Sediments[3]	28	20	60	200	100	0.3	–	300	d

SQG, Sediment quality guideline; TET, toxic effect threshold; SEL, severe effect level; CB, Consensus Based; PEC, probable effect concentration; SQO, Sediment Quality Objective; RV, Reference Value; SQAL, Sediment Quality Advisory Level; ANZECC, Australian and New Zealand Environment and Conservation Council

[1] Same as Ontario Ministry of Environment Screening Level Guidelines[b]

[2] Reference values and class limits for rivers in Flanders; <X class 1, <Y class 2, <Z class 4, >Z class 5

[3] Classification of Illinois Stream Sediments

[a] MacDonald et al. 2000b

[b] ANZECC 1997

[c] De Cooman et al. 1999

[d] Classification of Illinois Stream Sediments

[e] Swartz 1999

Classification of Illinois Stream Sediments

[i] Hyland et al. 1999

[f] Chapman et al. 1999

[g] De Cooman et al. 1999

[h] Shiga Prefecture 2001

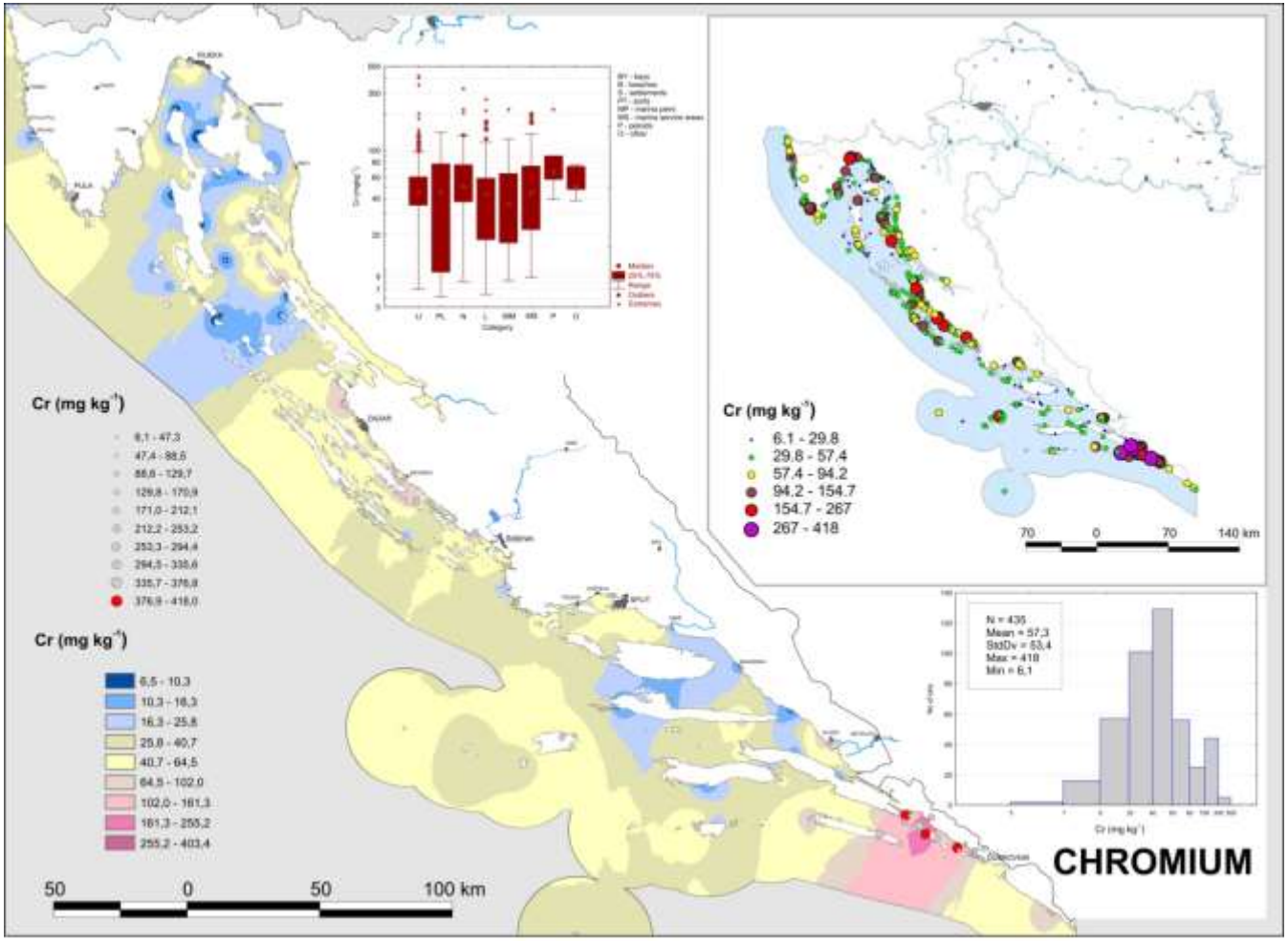
[i] Classification of Illinois Stream Sediments

Results

- Sediments samples collected for screening purposes were designated by categories (**bay, beach, settlement, port, marina pier, marina service area, peloids, and estuaries-brackish water)** in order to obtain a quick overview of the range of concentrations in relation to different marine environments and human activities.
- Atlas of Sediments for Croatia's Coastal Region and Islands contain distribution maps of K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb.
- SQGs have been evaluated for the elements Cr, Mn, Fe, Ni, Cu, Zn, As, Pb.
- In long term monitoring of sediments in marinas it has been noticed that concentrations of Fe, Cu, Zn, As and Pb increase with time.
- This can be related to antifouling paints that are used to prevent boats from fouling.
- Elevated concentrations of Mn in sediments found along the middle Croatian Littoral are related to abounded fero-alloy industry.
- Other anthropogenic sources of Cr, Mn, Fe, Ni, Cu, Zn, As, Pb in coastal sediments of the Croatian Littoral are sewage discharges and agricultural activities.
- Elements like As and Cr are naturally elevated in Croatian coastal sediments. Sediments in the vicinity of the volcanic islands have elevated concentrations of many heavy metals. Therefore, it is essential to distinguish between natural and anthropogenic concentrations in order to define meaningful SQGs.

Chromium (Cr)

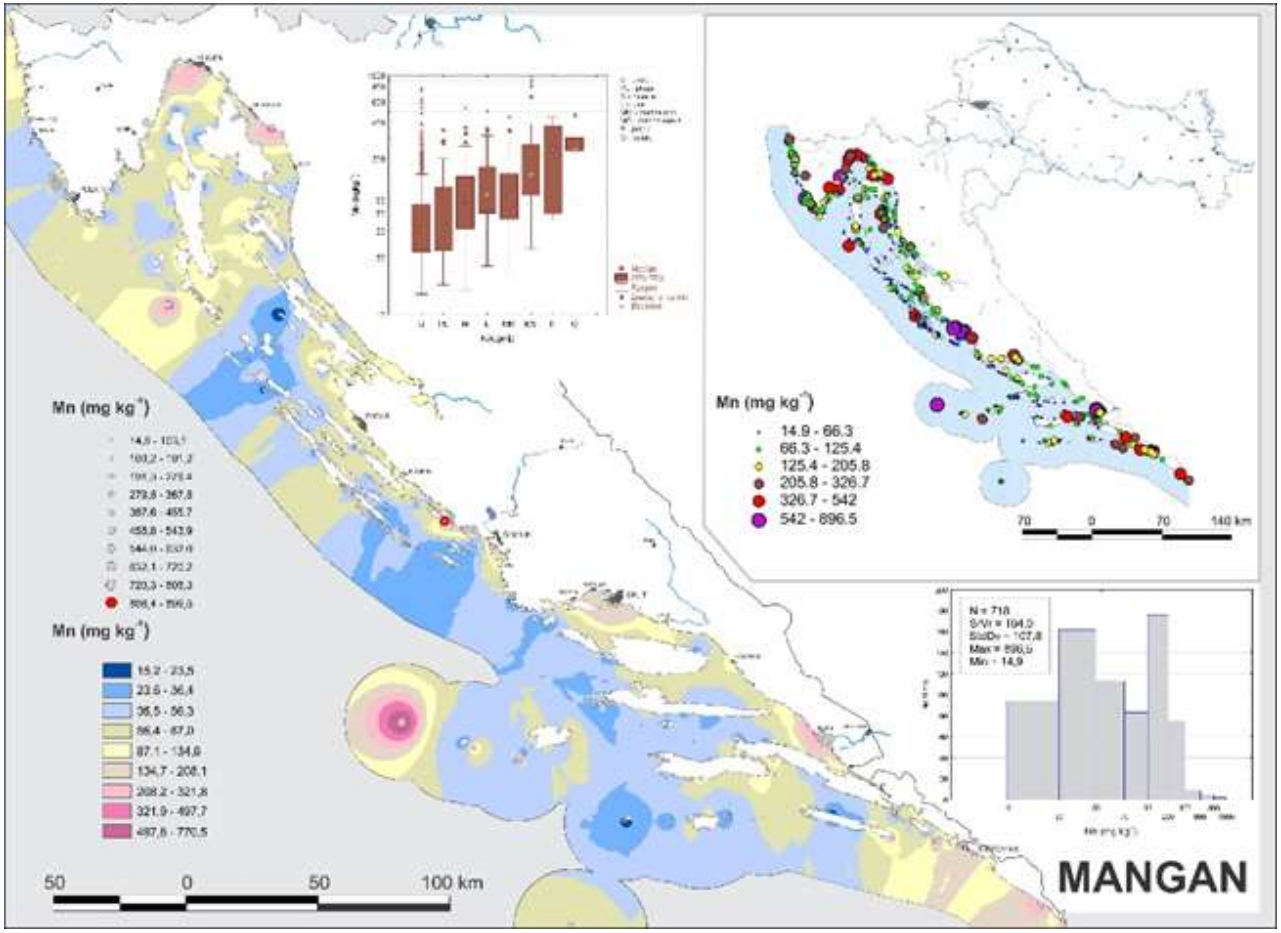
The highest levels were measured in the Elafiti cove and on the Island of Koločep. The elevated values are found along the Croatian south coast including the Isands of Šipan and Jarnjak, the Ston cove and at the southern part of the Island of Mljet.



Range (mg kg^{-1})	6.1 - 418								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	57.8 ± 57.8	44.7 ± 38.9	70.0 ± 58.1	52.8 ± 49.5	47.8± 39.5	62.3 ± 53.4	90.3 ± 66.1	57.3 ± 16.7	57.3± 53.4

Manganese (Mn)

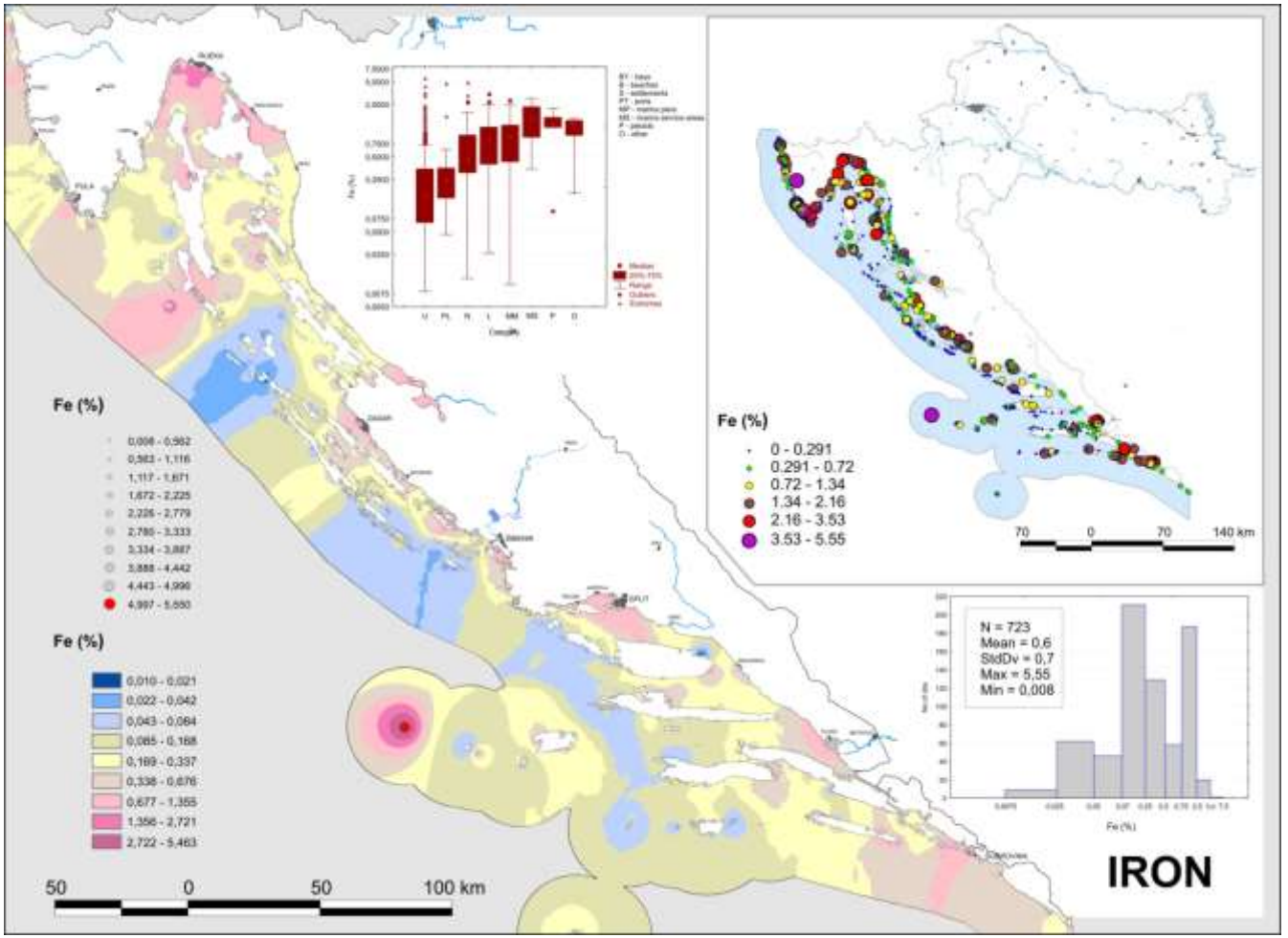
The highest levels were measured on the Island of Murter in the ACI marina “Jezera” in the service area. High concentrations were also found on the Island of Jabuka, in the vicinity of the cities of Split, Šibenik and Rijeka, on the Island of Susak and in Novi Vinodolski.



Range (mg kg^{-1})	14.9 - 896.5								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	79.8 ± 94.9	94.8 ± 90.5	118.8 ± 88.9	130.0 ± 90.9	117.1 ± 77.6	215.8 ± 187.8	236.1 ± 146.8	292.8 ± 99.9	104.0 ± 107.8

Iron (Fe)

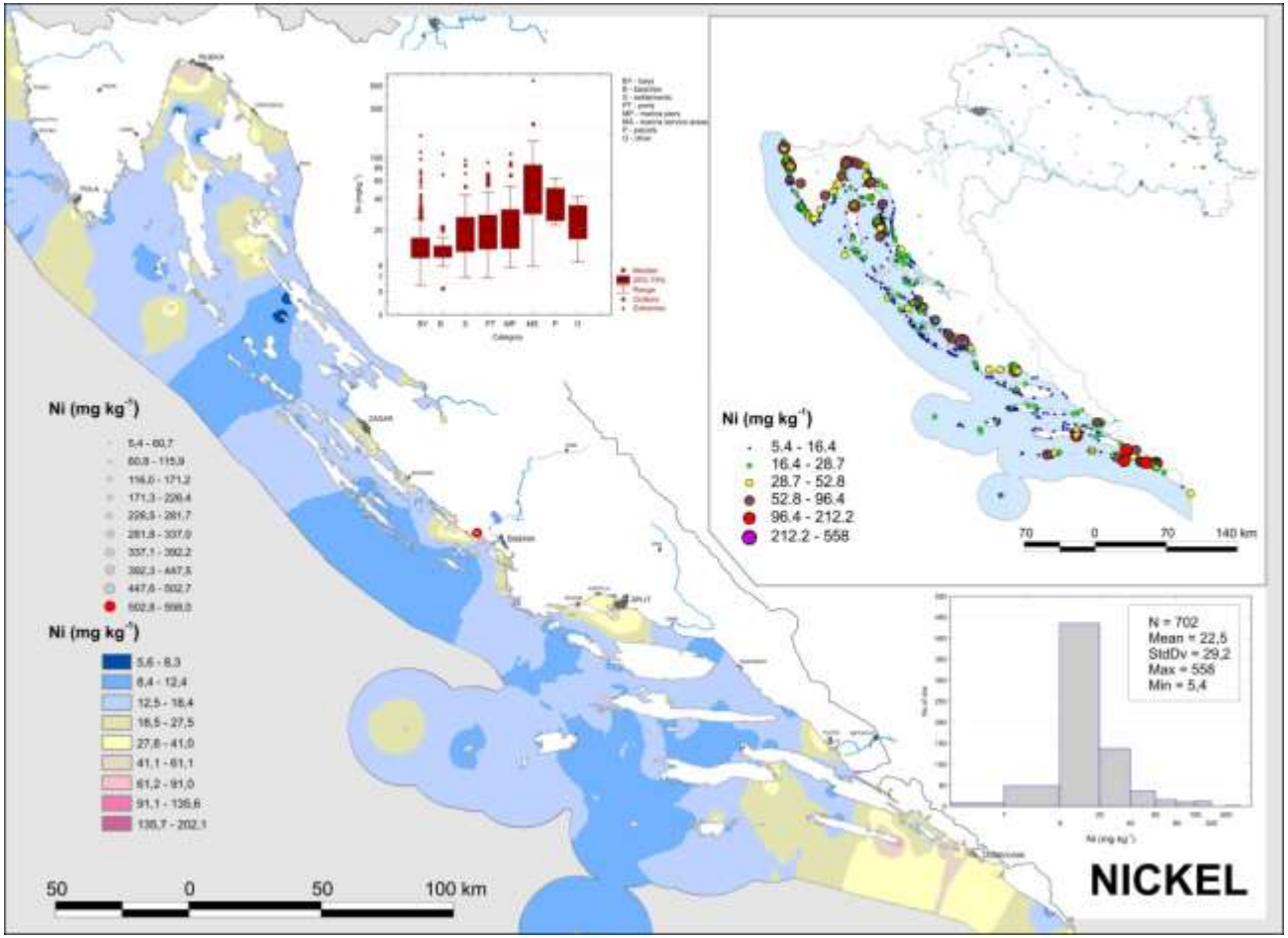
The highest values were measured on the Island of Jabuka. In all larger cities on the coast like Pula, Rijeka, Zadar, Šibenik, Split, Ploče and Dubrovnik, elevated concentrations were found. Higher concentrations were also measured in marina service zones, in peloids and sediments of brackish waters, on the Island of Susak and in the village Seline.



Range (%)	0.008 - 5.55								
Average values ± SD (%)	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	0.3 ± 0.6	0.5 ± 0.9	0.8 ± 0.8	0.8 ± 0.7	1.0 ± 0.7	1.6 ± 0.8	1.4 ± 0.7	1.1 ± 0.6	0.6 ± 0.7

Nickel (Ni)

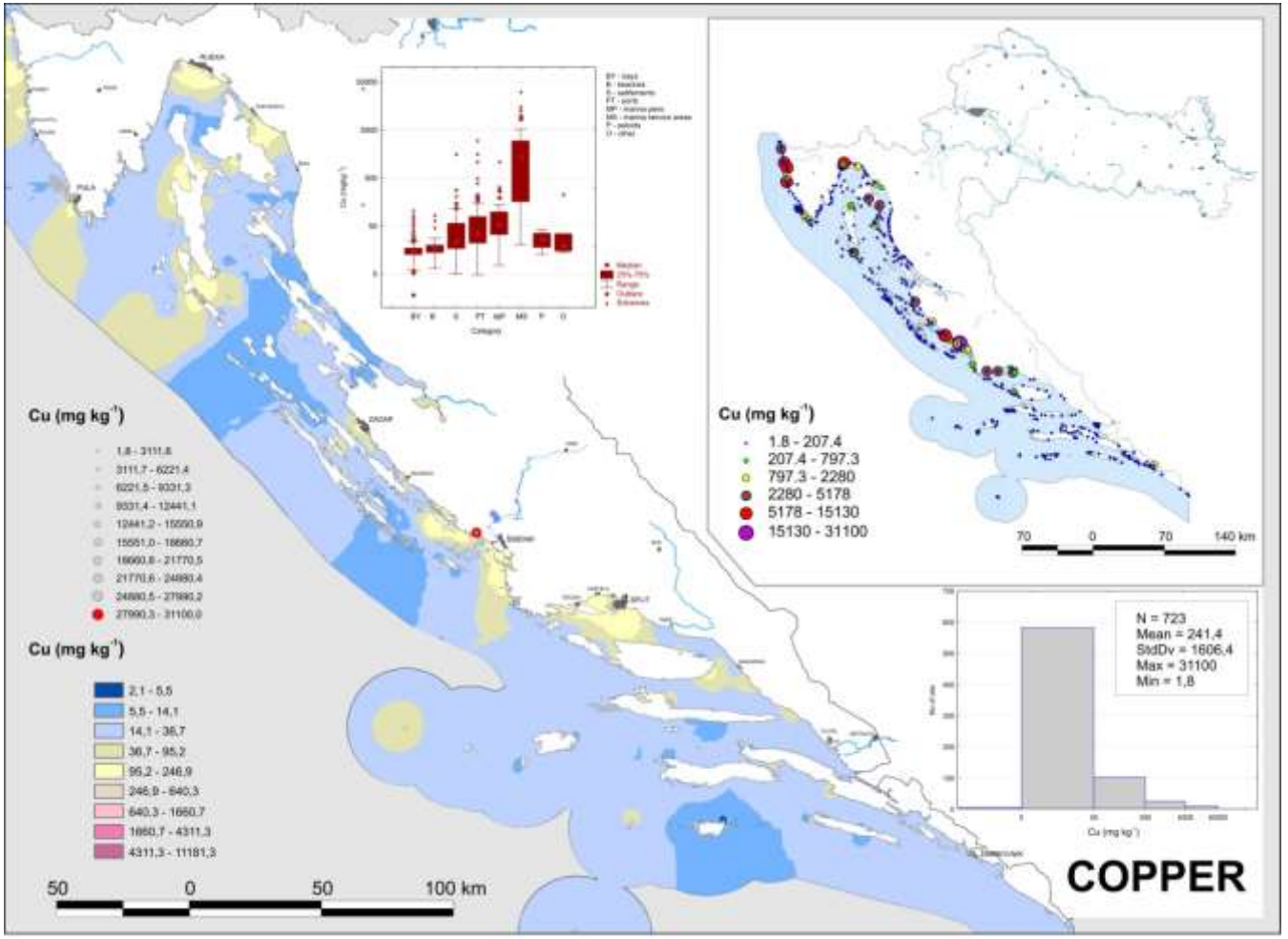
The highest levels were measured in the marina ACI Vodice in the service zone. Higher concentrations were found on the coast line near larger cities such as Pula, Rijeka, Zadar, Šibenik, Split, Ploče and Dubrovnik, and in marina service zones. Somewhat elevated concentrations were also found in peloids and on the Island of Jabuka, village Seline and in the Dubrovnik region (south part of the Island of Mljet, Ston cove, islands Lopud and Koločep).



Range (mg kg^{-1})	5.4 - 558								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	16.3 ± 13.6	18.4 ± 21.9	23.9 ± 18.5	23.8 ± 16.3	25.3 ± 19.3	71.7 ± 89.7	36.6 ± 14.9	24.5 ± 13.3	22.5 ± 29.2

Copper (Cu)

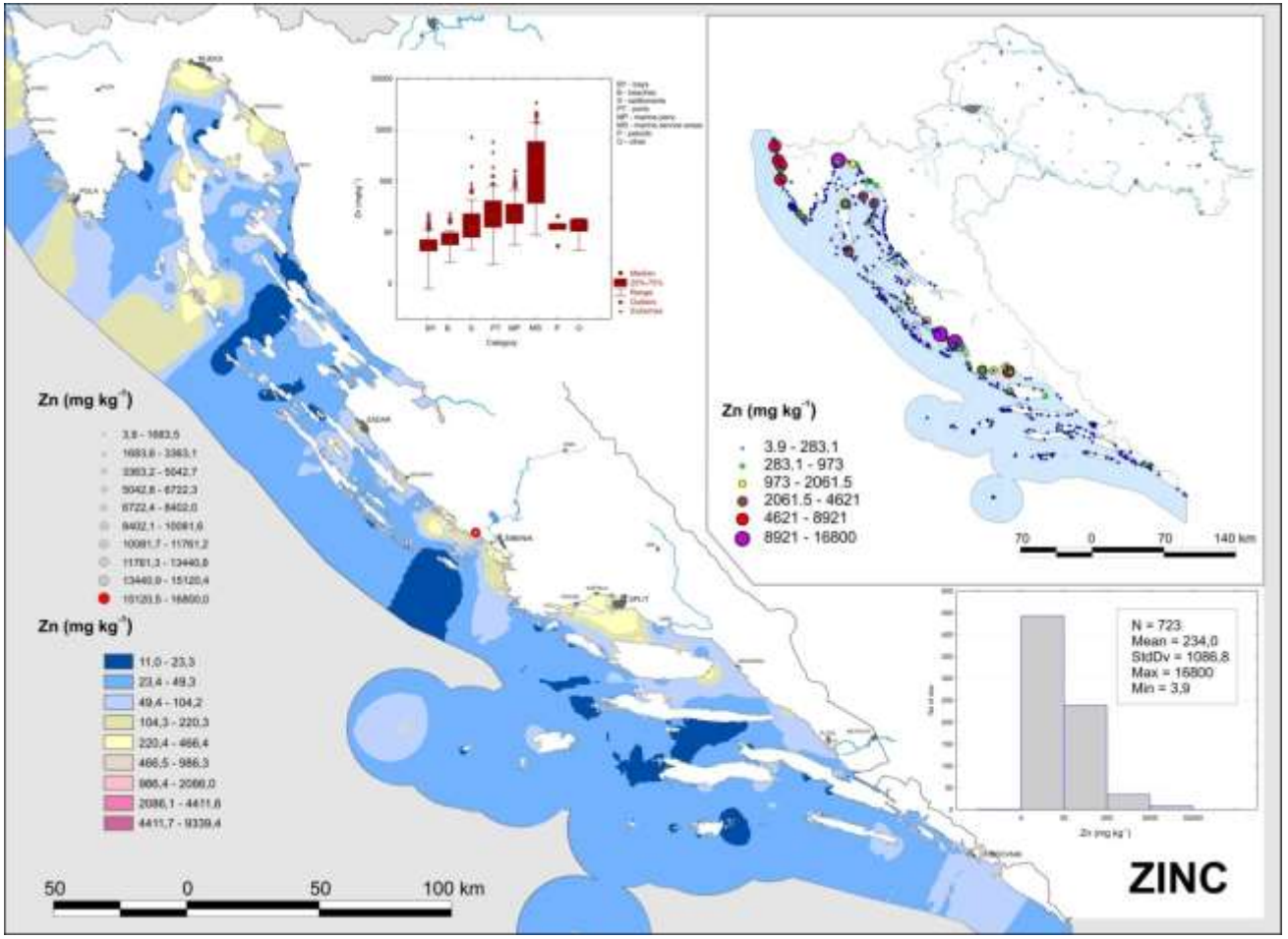
The highest levels were found in the marina ACI Vodice in the service zone. Higher concentrations were found on the Island of Sušac.



Range (mg kg^{-1})	1.8 - 31,100								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	16.4 ± 9.1	19.5 ± 11.6	71.2 ± 190.9	121.7 ± 374.5	90.4 ± 139.0	3 448.9 ± 5 816.8	26.5 ± 10.3	61.2 ± 91.3	241.4 ± 1 606.4

Zinc (Zn)

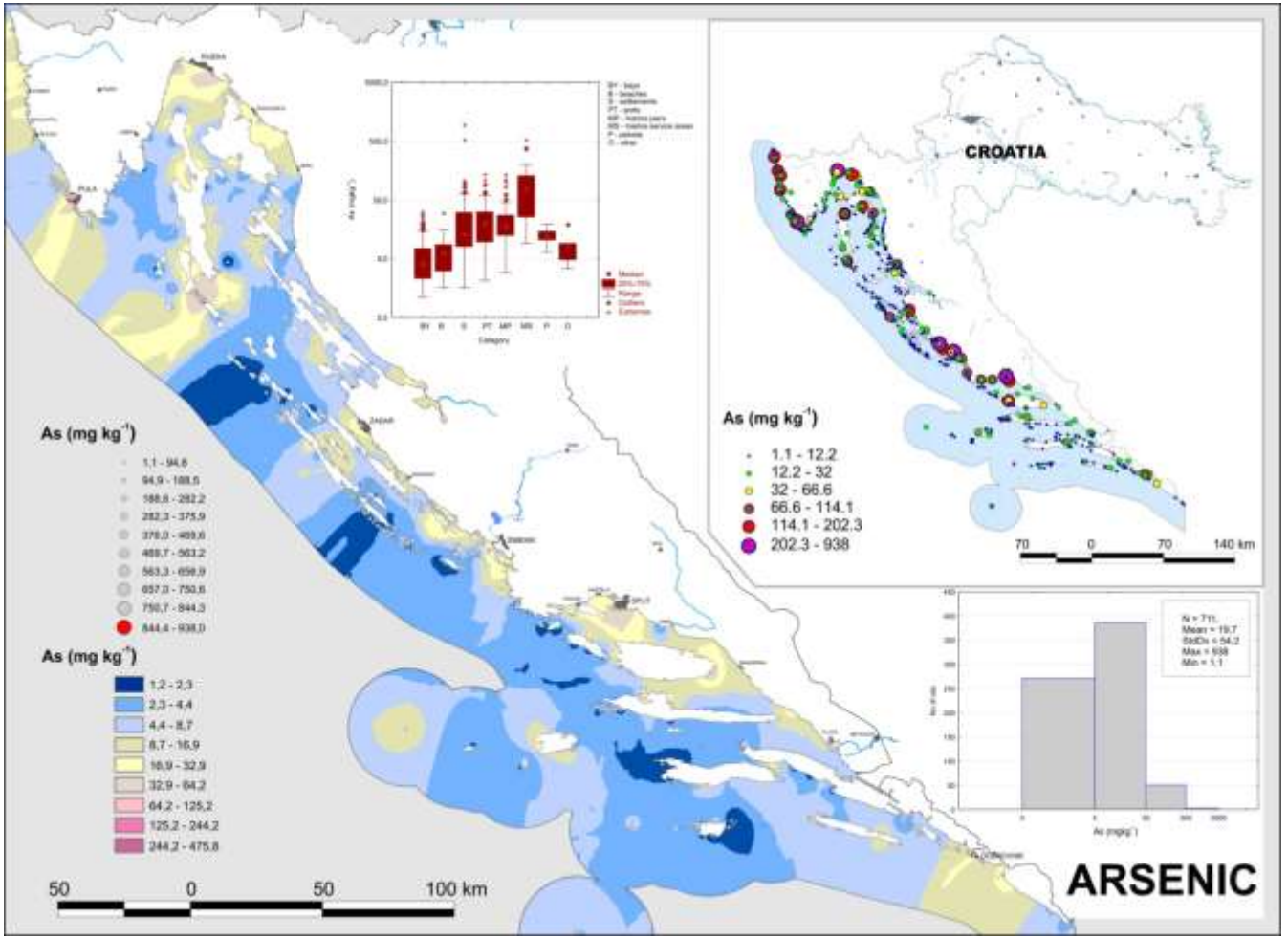
The highest levels were found in the marina ACI Vodice in the service zone. Generally, significantly elevated concentrations are found in marina service zones. Higher zinc concentrations were measured on the Island of Jabuka.



Range (mg kg^{-1})	3.9 - 16,800								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	31.6 ± 17.3	41.1 ± 25.0	161.3 ± 435.1	205.9 ± 368.3	175.2 ± 172.0	2 687.5 ± 3 677.0	63.9 ± 22.5	66.4 ± 29.5	234.0 ± 1 086.8

Arsenic (As)

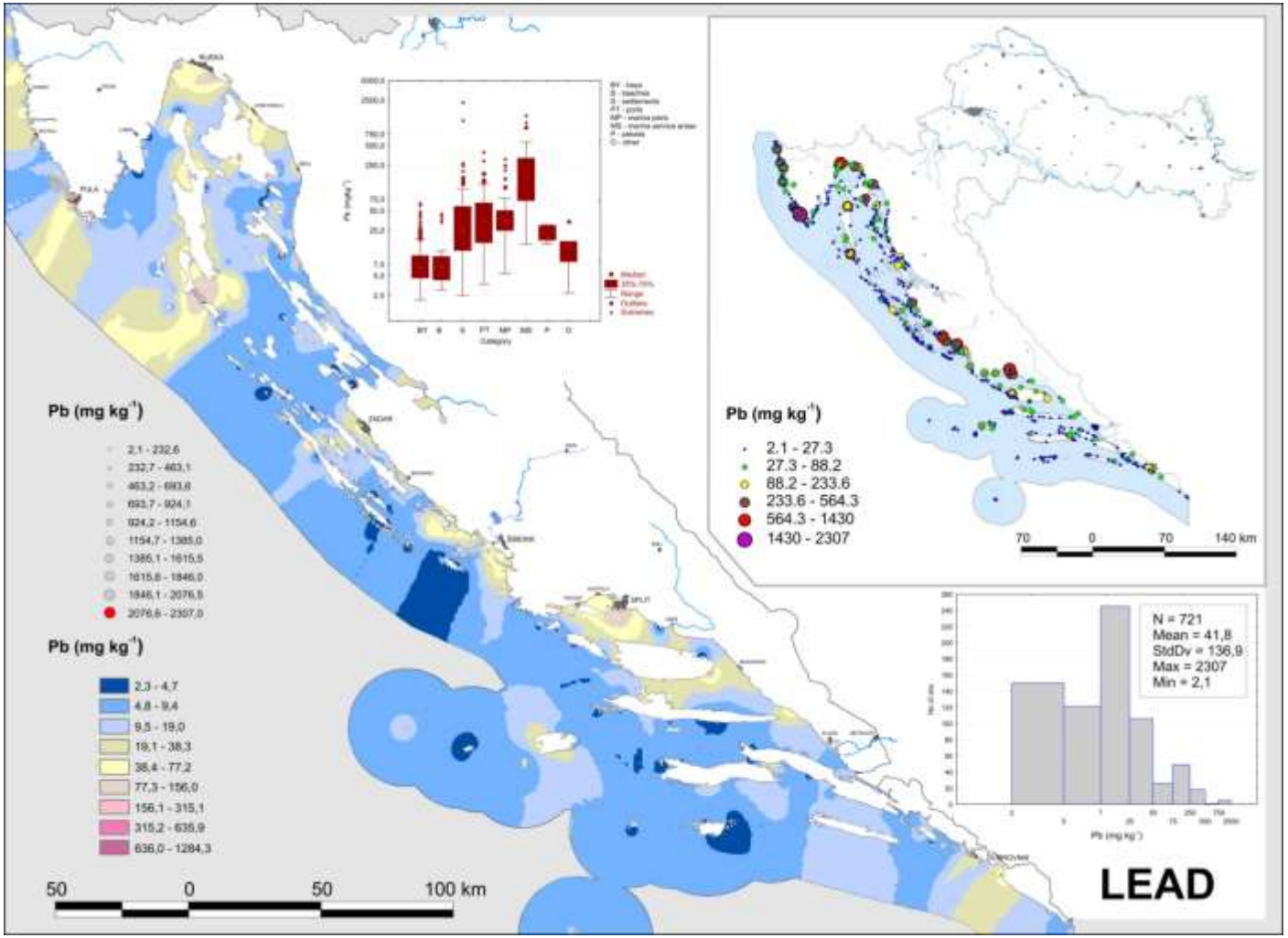
The highest concentration levels were measured near the city of Pula. Generally, significantly elevated concentrations are found in marina service zones. Higher arsenic concentrations were measured at the Island of Jabuka.



Range (mg kg^{-1})	1.1 - 938								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	5.9 ± 5.2	7.2 ± 6.1	45.1 ± 129.6	25.9 ± 23.2	25.5 ± 24.8	101.8 ± 107.9	12.5 ± 4.0	9.0 ± 6.1	19.7 ± 54.2

Lead (Pb)

The highest concentration levels were measured in the bay of the city of Pula. Generally, significantly higher concentrations are found in marina service areas.



Range (mg kg^{-1})	2.1 - 2,307								
Average values ± SD (mg kg^{-1})	Bay	Beach	Settlement	Port	Marina pier	Marina service area	Peloids	Estuaries	Total
	9.0 ± 8.0	11.1 ± 12.4	100.3 ± 315.0	52.7 ± 61.8	52.8 ± 58.3	258.3 ± 298.3	21.1 ± 6.0	15.4 ± 11.8	41.8 ± 136.9

Proposal for SQGs in Croatia

- SQGs were evaluated based on screening data of natural (background) and pollution values in Croatian coastal sea sediments and after comparing them to other available SQGs.

- Proposed Croatian coastal sea SQGs are classified into four (4) classes:

- **Class I – clean sediments;**
- **Class II – small contamination (allowed disposal in sea waters);**
- **Class III – contaminated material (disposal in sea waters allowed with mandatory monitoring);**
- **Class IV – highly contaminated material (not allowed for disposal in sea waters).**

Class I: Clean material

Background values of selected metal contaminants obtained for Bays & Beaches

Contaminant	Bays Mean± Std.D	Background val. Mean± 3 x Std.D
Cr	58±58	232
Mn	80±95	365
Fe	0,35±0,57	2,0
Ni	16±14	58
Cu	16 ± 9	43
Zn	32 ±17	83
As	6 ± 5	21
Pb	9 ± 8	33

Classes 2-4: Contaminated material

The sum of mean values and 3 st.dev. for Cr, Mn, Fe, Ni, Cu, Zn, As, Pb

Class II: 95 % percentile for Settlements, Ports, Marina pier
Class III: Marine service area – 75% percentile for very skewed distribution of Cu and Zn)
(Class IV: Marine service area – the whole distribution or 95% percentile for very skewed distribution of Cu and Zn)

Category	Cr (mg/kg)	Mn (mg/kg)	Fe (%)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)
Settlements	244,3 N =47	378,5 N =67	3,2 N =67	79,4 N =64	643,9 N =67	1466,6 N =67	433,9 N =66	1045,3 N =67
Port	201,3 N =79	402,7 N =88	3 N =89	72,7 N =87	1245,2 N =89	1310,8 N =89	95,2 N =89	238,1 N =89
Marina pier	284,8 N =52	349,9 N =69	3,1 N =69	83,2 N =67	507,4 N =69	691,2 N =69	99,9 N =69	227,7 N =69
Marina service area	222,5 N =35	779,2 N =42	5 N =42	340,8 N =41	20899,3 N =42	13718,5 N =42	425,5 N =42	1153,2 N =42

Other – Peloids and Estuaries

Category	Cr (mg/kg)	Mn (mg/kg)	Fe (%)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)
Peloids	288,6 N =6	676,5 N =7	3,5 N =7	81,3 N =7	57,4 N =7	131,4 N =7	24,5 N =7	39,1 N =7
Estuaries	107,4 N =5	592,5 N =5	2,9 N =5	64,4 N =5	335,1 N =5	154,9 N =5	27,3 N =5	50,8 N =5

Proposed Croatian preventive SQGs

Sediment Class	Cr (mg/kg)	Mn (mg/kg)	Fe (%)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)
Class I: clean material Bay and Beaches – whole distribution	<235	<365	<2	<60	<45	<85	<25	<35
Class II: small contamination Settlements, Ports, Marina Piers – 95th percentile and Marinas service areas – 95th percentile (Mn)		365-670	2-3	60-75	45-210	85-370	25-100	35-260
Class III: contaminated material Marinas service areas – 75th percentile (Cu and Zn) and the whole distribution *		670-800	3-5	75-350	210-3000	370-3000	100-430	260-1200
Class IV: highly contaminated material Marinas service areas – above 75th percentile (Cu and Zn) and above the whole distribution *		>800	>5	>350	>3000	>3000	>430	>1200

* Outliers excluded

Portuguese SQGs for dredged material

Sediment Class	Cr (mg/kg^{-1})	Mn (mg/kg^{-1})	Fe (%)	Ni (mg/kg^{-1})	Cu (mg/kg^{-1})	Zn (mg/kg^{-1})	As (mg/kg^{-1})	Pb (mg/kg^{-1})
Class 1: clean material Disposal: aquatic and beaches	< 50	-	-	< 30	< 35	< 100	< 20	< 50
Class2: traces of contamination Disposal: aquatic environment	50 - 100	-	-	30 - 75	35 - 150	100 - 600	20 - 50	50 - 150
Class3: small contamination Disposal: aquatic mandatory monitoring	100 - 400	-	-	75 - 125	150 - 300	600 - 1500	50 - 100	150 - 500
Class 4: contaminated material Disposal: waste disposal site on land	400 - 1000	-	-	125 - 250	300 - 500	1500 - 5000	100 -500	500 - 1000
Class 5: highly contaminated material Disposal: special treatment	> 1000	-	-	> 250	> 500	> 5000	> 500	> 1000

Comparison of Portuguese SQGs and Croatian proposed SQGs

- Croatian SQGs are primarily developed to prevent further trend of significant pollution increase.
- Portuguese SQGs are developed for dredged material disposal.
- Concentrations of Cr are naturally elevated in Croatian coastal sediments. The highest values were measured in natural environment, therefore no protective SQGs were proposed with respect to Cr in Croatia.
- Small contamination (and therefore allowed for disposal at sea with no monitoring) has been determined on similar levels for Croatia/Portugal SQGs(in mg/kg): Ni – 75/75, Cu – 210/150, Zn 370/600, As 100/50 and Pb – 260/150.
- It has to be notified that sediments Class I and II of the Croatian SQGs include majority (> 95%) of all coastal sediments. These SQGs are primarily designed to protect these environment for further increase of the pollution. The rest of 5% percent are mostly industrial sites, and thus highly consumed by human activities. These locations should be under the mandatory monitoring in order to prevent the excessive pollution.

Conclusion

- This is **first attempt to define Croatian SQGs** for Cr, Mn, Fe, Ni, Cu, Zn, As, Pb as potentially toxic elements in marine sediments according to different types of the marine environment and human activities.

- The purpose was to **set a baseline for future analysis** of trends in contamination levels in sediments and for **improving the knowledge of ways in which pollution occurs** in Croatian coastal sediments. This is necessary for **proposing strategies and actions** that will ensure that levels of contaminants will not significantly increase in long term period.

- The proposed Croatian SCGs for sediments are **based on the background values and distribution of contaminants concentrations** along the Croatian Littoral covering **different environmental categories.**

- It has to be notified that the SQGs used alone can be misinterpreted and should always be **evaluated in conjunction with additional information** about the environment.

Thank you for your attention!