

Supplementary Materials for the manuscript

Trace metal partitioning in the salinity gradient of the highly stratified estuary: A case study in the Krka River estuary (Croatia)

Saša Marcinek^{1,*}, Ana Marija Cindrić¹, Jasmin Pađan¹ and Dario Omanović^{1,*}

¹Ruđer Bošković Institute, Center for Marine and Environmental Research, 10000 Zagreb, Croatia

*Correspondence: smarcin@irb.hr and omanovic@irb.hr

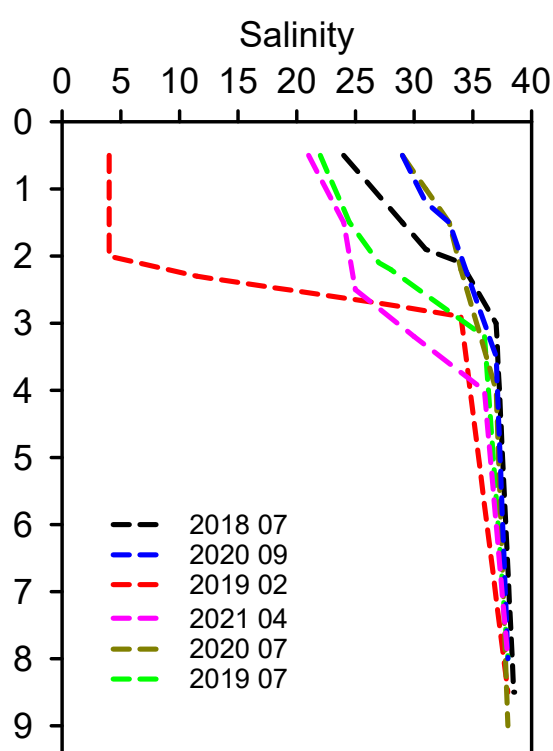


Figure S1. Vertical salinity profiles during the time of the samplings as indicated in the legend.

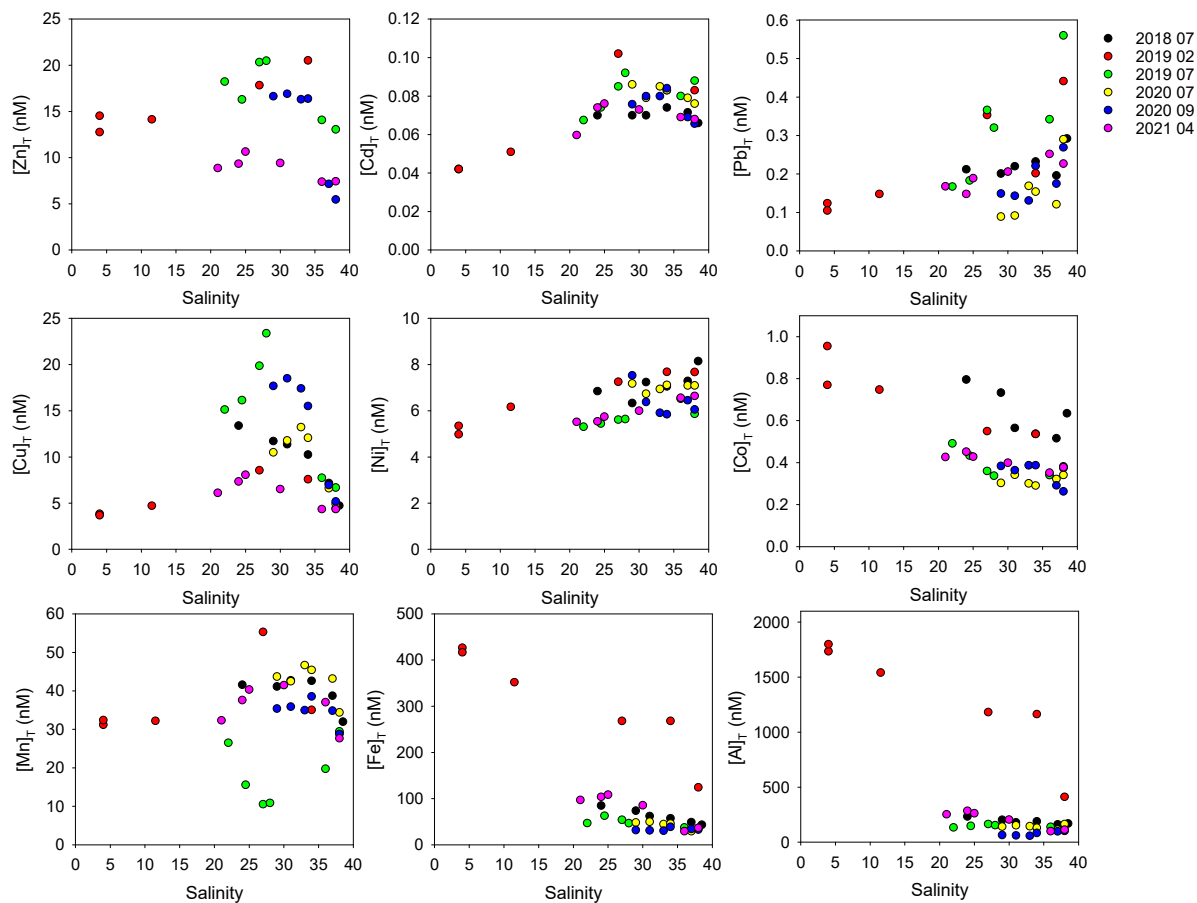


Figure S2. Concentrations of studied trace metals in the total fraction (unfiltered sample) in relation to salinity.

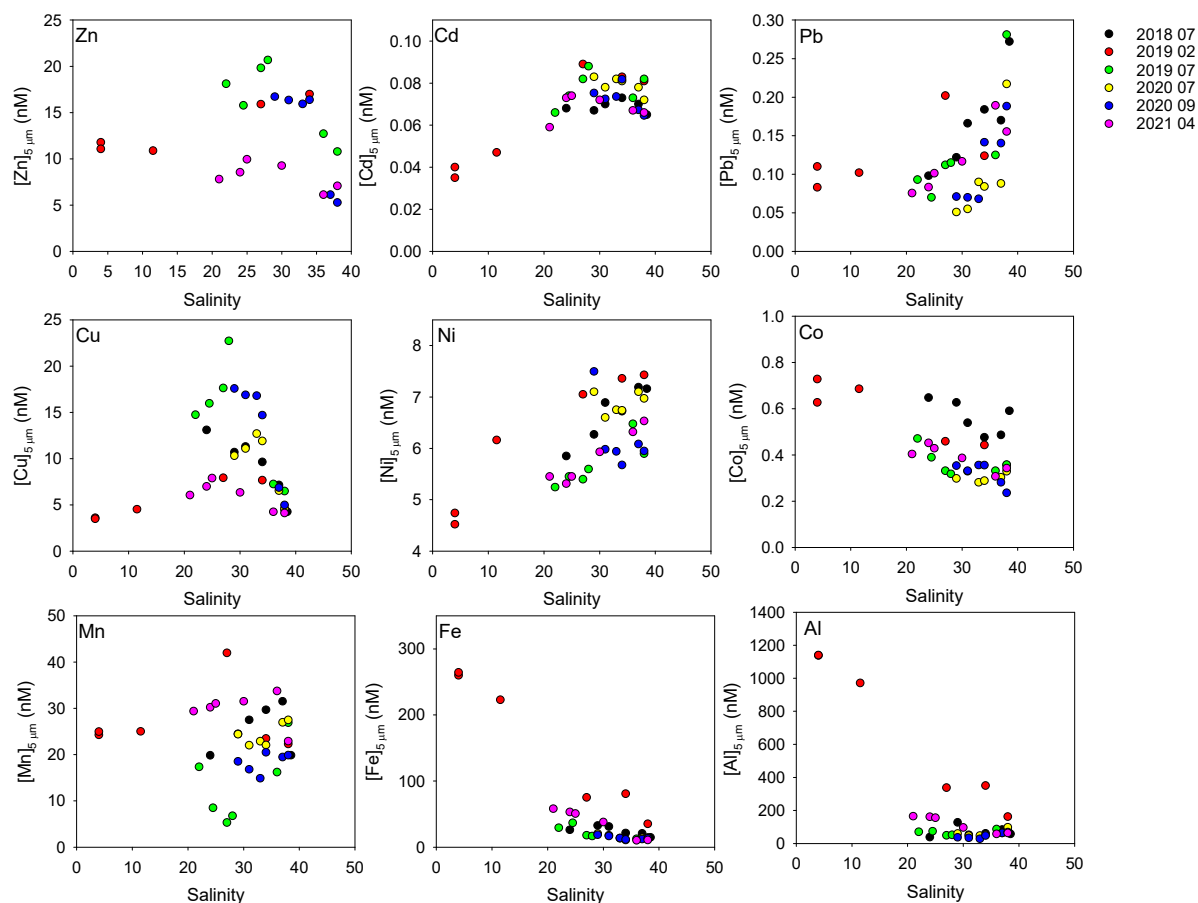


Figure S3. Concentrations of studied trace metals in < 5 μm fraction in relation to salinity.

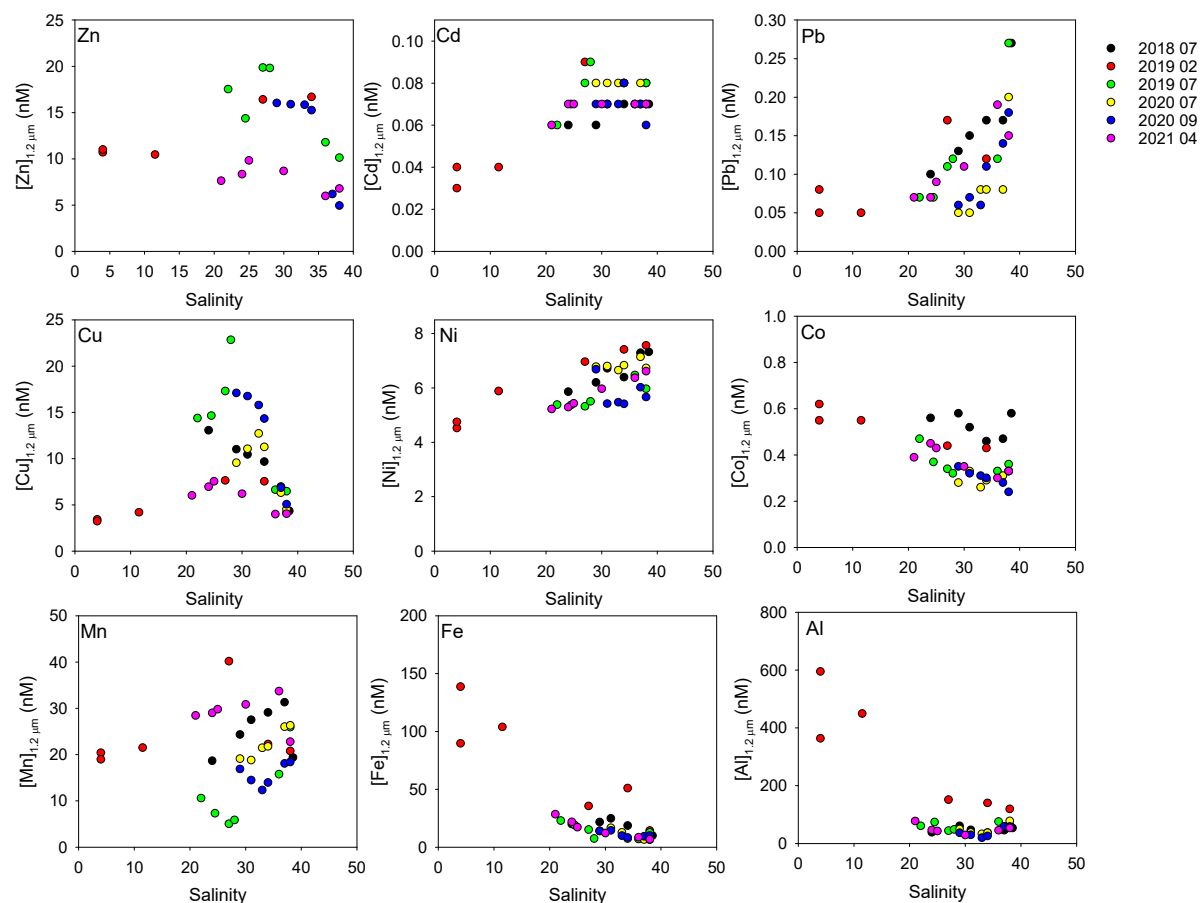


Figure S4. Concentrations of studied trace metals in < 1.2 μm fraction in relation to salinity.

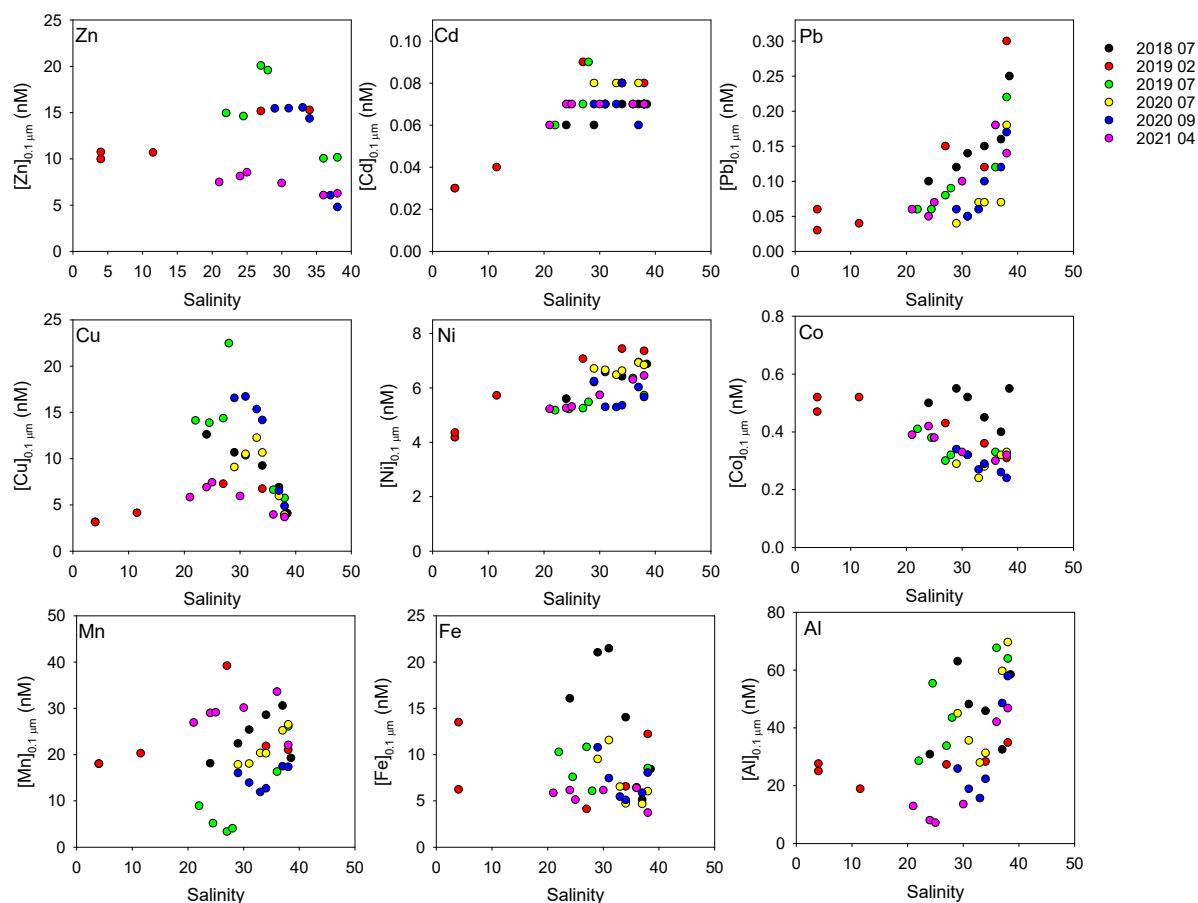


Figure S5. Concentrations of studied trace metals in $< 0.1 \mu\text{m}$ fraction in relation to salinity.

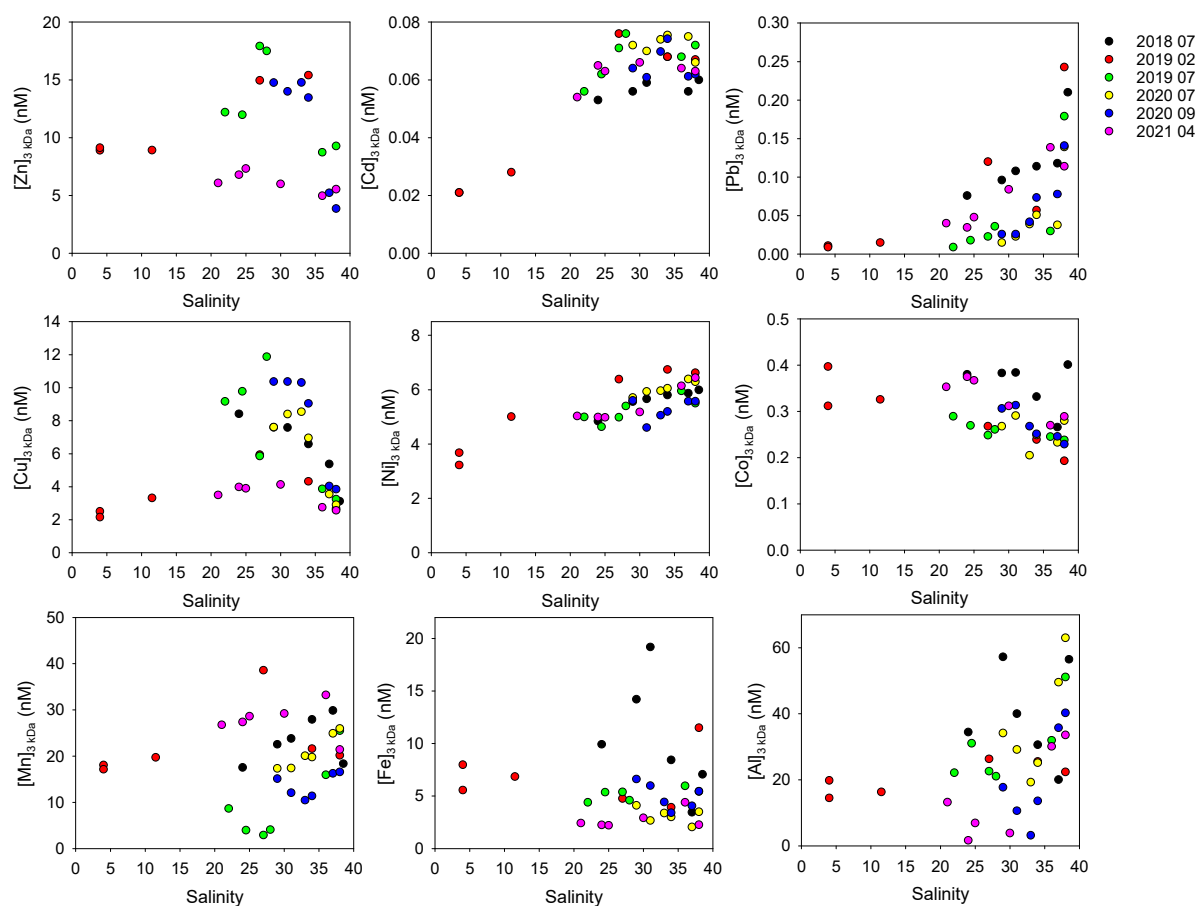


Figure S6. Concentrations of studied trace metals in truly dissolved fraction (< 3 kDa) in relation to salinity.

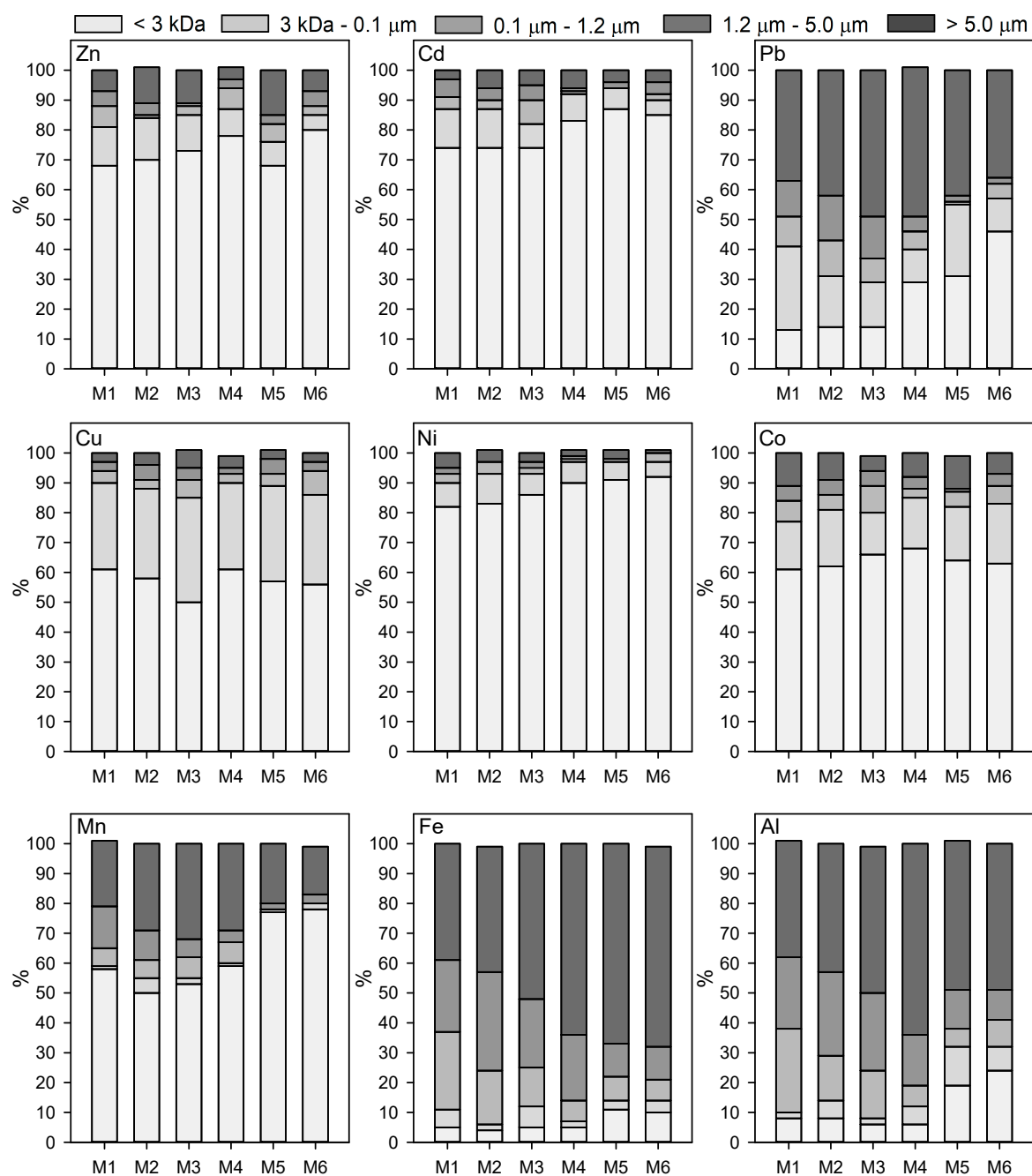


Figure S7. Average percentages of studied trace metals (samplings with FWL characterised by salinity < 25) in each size fraction (as indicated in the figure) at each depth (M1 – M6).

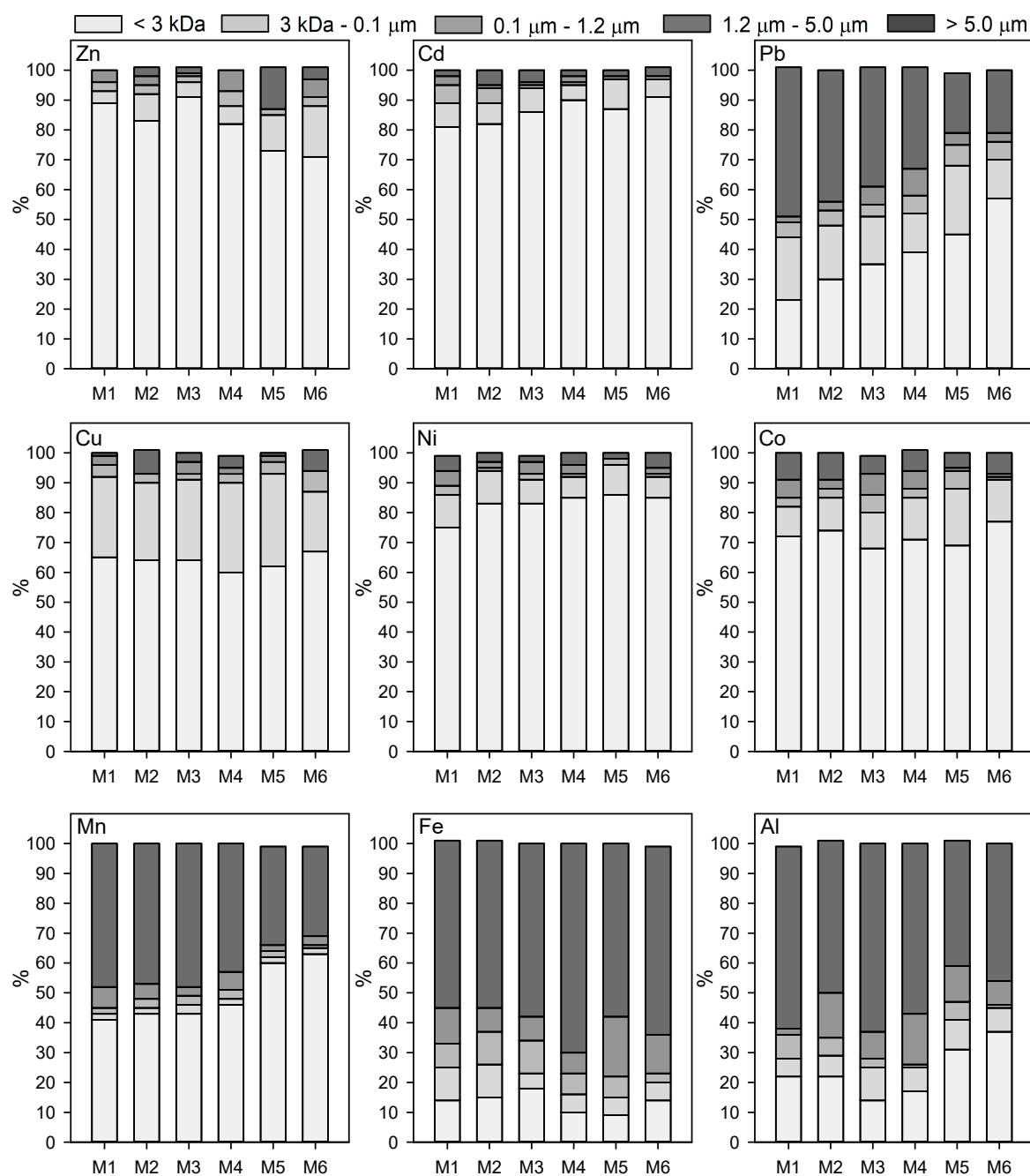


Figure S8. Average percentages of studied trace metals (samplings with FWL characterised by salinity > 25) in each size fraction (as indicated in the figure) at each depth (M1 – M6).

Table S1. Percentage of colloidal metal fraction in the dissolved phase - comparison between various coastal areas.

Trace metal	Colloidal size	Colloid%	Study area	Reference
Pb	3 kDa – 0.1 μm	37%	Krka River estuary	This study
	1 kDa – 0.2 μ m	Up to 42%	Guandang River estuary	(Lu et al., 2020)
	1 kDa – 0.2 μ m	31%	Coast of North Yellow Sea	(Lu et al., 2019)
	1 kDa – 0.2 μ m	< 14%	Xin'an River estuary	(Lu et al., 2020)
	5 kDa – 0.2 μ m	94%	Penzé estuary	(Waeles et al., 2008)
Fe	3 kDa – 0.1 μm	37%	Krka River estuary	This study
	100 kDa – 0.4 μ m	87%	Venice Lagoon	(Martin et al., 1995)
	5 kDa – 0.2 μ m	7.6%	Gulf of Trieste	(Klun et al., 2019)
	10 kDa – 0.2 μ m	84%	San Francisco Bay – low salinity region	(Sañudo-Wilhelmy et al., 1996)
	10 kDa – 0.2 μ m	40%	San Francisco Bay – high salinity region	(Sañudo-Wilhelmy et al., 1996)
Al	3 kDa – 0.1 μm	31%	Krka River estuary	This study
	5 kDa – 0.2 μ m	1.5%	Gulf of Trieste	(Klun et al., 2019)
	10 kDa – 0.2 μ m	84%	San Francisco Bay – low-salinity region	(Sañudo-Wilhelmy et al., 1996)
	10 kDa – 0.2 μ m	< 10%	San Francisco Bay – high-salinity region	(Sañudo-Wilhelmy et al., 1996)
Mn	3 kDa – 0.1 μm	4%	Krka River estuary	This study
	10 kDa – 0.2 μ m	< 20%	San Francisco Bay	(Sañudo-Wilhelmy et al., 1996)
	5 kDa – 0.2 μ m	7%	Gulf of Trieste	(Klun et al., 2019)
Cu	3 kDa – 0.1 μm	32%	Krka River estuary	This study
	5 kDa – 0.2 μ m	20%	Gulf of Trieste	(Klun et al., 2019)
	20 nm – 0.45 μ m	~30%	Loire estuary	(Dulaquais et al., 2020)
	1 kDa – 0.2 μ m	< 23%	Xin'an River estuary	(Lu et al., 2020)
	1 kDa – 0.2 μ m	< 24%	Guandang River estuary	(Lu et al., 2020)
	1 kDa – 0.2 μ m	< 51%	Coast of North Yellow Sea	(Lu et al., 2019)
	10 kDa – 0.2 μ m	< 20%	San Francisco Bay	(Sañudo-Wilhelmy et al., 1996)
	5 kDa – 0.2 μ m	94%	Penzé estuary	(Waeles et al., 2008)
	300 kDa – 0.4 μ m	~70%	Ob estuary	(Dai and Martin, 1995)
Co	3 kDa – 0.1 μm	18%	Krka River estuary	This study
	1 kDa – 0.45 μ m	19%	Galveston Bay	(Wen et al., 1999)
	0.015 – 0.2 μ m	Up to 86%	Amazon and Pará River estuaries – low-salinity region	(de Carvalho et al., 2021)
	0.015 – 0.2 μ m	Down to 16%	Amazon and Pará River estuaries – high-salinity region	(de Carvalho et al., 2021)
Zn	3 kDa – 0.1 μm	9%	Krka River estuary	This study
	5 kDa – 0.2 μ m	1%	Gulf of Trieste	(Klun et al., 2019)
	10 kDa – 0.2 μ m	< 3%	San Francisco Bay	(Sañudo-Wilhelmy et al., 1996)
	1 kDa – 0.45 μ m	91%	Galveston Bay	(Wen et al., 1999)
Cd	3 kDa – 0.1 μm	9%	Krka River estuary	This study
	5 kDa – 0.2 μ m	1%	Gulf of Trieste	(Klun et al., 2019)
	10 kDa – 0.2 μ m	< 1%	San Francisco Bay	(Sañudo-Wilhelmy et al., 1996)
	1 kDa – 0.2 μ m	Up to 17%	Guandang River estuary	(Lu et al., 2020)
	1 kDa – 0.2 μ m	Up to 20%	Xin'an River estuary	(Lu et al., 2020)
	100 kDa – 0.4 μ m	34%	Venice Lagoon	(Martin et al., 1995)
	> 0.4 nm – 0.45 μ m	37%	Fal estuary	(Braungardt et al., 2011)
	1 kDa – 0.2 μ m	Up to 51%	Coast of North Yellow Sea	(Lu et al., 2019)
	1 kDa – 0.45 μ m	44%	Galveston Bay	(Wen et al., 1999)
Ni	3 kDa – 0.1 μm	12%	Krka River estuary	This study
	5 kDa – 0.2 μ m	4%	Gulf of Trieste	(Klun et al., 2019)
	10 kDa – 0.2 μ m	< 2%	San Francisco Bay	(Sañudo-Wilhelmy et al., 1996)
	1 kDa – 0.45 μ m	36%	Galveston Bay	(Wen et al., 1999)
	0.015 – 0.2 μ m	Up to 38%	Amazon and Pará River estuaries – low-salinity region	(de Carvalho et al., 2021)
	0.015 – 0.2 μ m	-	Amazon and Pará River estuaries – high-salinity region	(de Carvalho et al., 2021)

- Benoit, G., Oktay-Marshall, S.D., Cantu, A., Hood, E.M., Coleman, C.H., Corapcioglu, M.O., Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar. Chem.* 45, 307–336. [https://doi.org/10.1016/0304-4203\(94\)90076-0](https://doi.org/10.1016/0304-4203(94)90076-0)
- Braungardt, C.B., Howell, K.A., Tappin, A.D., Achterberg, E.P., 2011. Temporal variability in dynamic and colloidal metal fractions determined by high resolution in situ measurements in a UK estuary. *Chemosphere* 84, 423–431. <https://doi.org/10.1016/j.chemosphere.2011.03.050>
- Dai, M.-H., Martin, J.-M., 1995. First data on trace metal level and behaviour in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia. *Earth Planet. Sci. Lett.* 131, 127–141. [https://doi.org/10.1016/0012-821X\(95\)00021-4](https://doi.org/10.1016/0012-821X(95)00021-4)
- de Carvalho, L.M., Hollister, A.P., Trindade, C., Gledhill, M., Koschinsky, A., 2021. Distribution and size fractionation of nickel and cobalt species along the Amazon estuary and mixing plume. *Mar. Chem.* 236, 104019. <https://doi.org/10.1016/j.marchem.2021.104019>
- Dulaquais, G., Waeles, M., Breitenstein, J., Knoery, J., Riso, R., 2020. Links between size fractionation, chemical speciation of dissolved copper and chemical speciation of dissolved organic matter in the Loire estuary. *Environ. Chem.* 17, 385. <https://doi.org/10.1071/EN19137>
- Klun, K., Falnoga, I., Mazej, D., Šket, P., Faganeli, J., 2019. Colloidal Organic Matter and Metal(loid)s in Coastal Waters (Gulf of Trieste, Northern Adriatic Sea). *Aquat. Geochemistry* 25, 179–194. <https://doi.org/10.1007/s10498-019-09359-6>
- Lu, Y., Gao, X., Chen, C.T.A., 2019. Separation and determination of colloidal trace metals in seawater by cross-flow ultrafiltration, liquid-liquid extraction and ICP-MS. *Mar. Chem.* 215, 103685. <https://doi.org/10.1016/j.marchem.2019.103685>
- Lu, Y., Gao, X., Song, J., Chen, C.T.A., Chu, J., 2020. Colloidal toxic trace metals in urban riverine and estuarine waters of Yantai City, southern coast of North Yellow Sea. *Sci. Total Environ.* 717, 135265. <https://doi.org/10.1016/j.scitotenv.2019.135265>
- Martin, J. -M, Dai, M. -H, Cauwet, G., 1995. Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). *Limnol. Oceanogr.* 40, 119–131. <https://doi.org/10.4319/lo.1995.40.1.0119>
- Sañudo-Wilhelmy, S.A., Rivera-Duarte, I., Russell Flegal, A., 1996. Distribution of colloidal trace metals in the San Francisco Bay estuary. *Geochim. Cosmochim. Acta* 60, 4933–4944. [https://doi.org/10.1016/S0016-7037\(96\)00284-0](https://doi.org/10.1016/S0016-7037(96)00284-0)
- Waeles, M., Tanguy, V., Lespes, G., Riso, R.D., 2008. Behaviour of colloidal trace metals (Cu, Pb and Cd) in estuarine waters: An approach using frontal ultrafiltration (UF) and stripping chronopotentiometric methods (SCP). *Estuar. Coast. Shelf Sci.* 80, 538–544. <https://doi.org/10.1016/j.ecss.2008.09.010>
- Wen, L.S., Santschi, P., Gill, G., Paternostro, C., 1999. Estuarine trace metal distributions in Galveston Bay: Importance of colloidal forms in the speciation of the dissolved phase. *Mar. Chem.* 63, 185–212. [https://doi.org/10.1016/S0304-4203\(98\)00062-0](https://doi.org/10.1016/S0304-4203(98)00062-0)