Risk sources due to metals in the Danube floodplain

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Fluvial systems such as the Lower Danube River System provide a wide array of resources and services to the socio-economic systems (Vadineanu et al., 2001). However, some of the services, such as the retention of pollutants can impinge on the resources production, by lowering their quality trough transfer and accumulation of pollutants. For instance, after a retention of metals in a particulate form (Neagoe et al., 2001), dissolved metals (Zn, Cr, Cd) may be exported from the alluvial islands of the Danube floodplain (Iordache, 2002); fish in the Danube river were found to have metal concentrations higher than accepted in human health regulations (Iordache et al., 2000), possibly related to the mentioned export. The retention of pollutants, when too intensive, can also negatively influence services such as species diversity maintenance. There are no direct proofs of this, but Neagoe et al. (2000) found excessive levels of Cr, Mn, Ni, Zn as well as, surprisingly, deficit level of Cu in plants of the Danube floodplain, with possible effects on the plant populations and tropho-dynamic modules. Thus, some metals might be a source of risk by affecting resources and, indirectly, the human health, as well as by affecting services provided by the floodplain ecological systems. In this context, the purpose of our study was to characterize the distribution of metals with different mobility in the soil/sediment of the floodplain in order to find a possible explanation of the reported distribution patterns of metals in flood water and plants. This can be important because of two reasons: firstly, it would indirectly confirm the already existing findings about environmental risks, and secondly, by providing information about the mechanism at the origin of the risks, it might suggest pathways of controlling the metals behavior, if needed.

Materials and Methods

The study site was Fundu Mare Island, a complex island located in the Danube floodplain. Three ecosystem types were considered: forested levee (station H2), forested depression (H3), and marsh (H4). Table 1 provides a short characterization of the sampling sites. The soil was sampled from the 0-8 cm top layer (a layer), excepting for station H2, where a deeper layer (40-48 cm depth) was also sampled (layer b). The number of sample units was ten. After sampling the soil was sieved to less than 2mm, air dried and extracted for the metal content using a combination of the methods provided by Asami et al. (1995) and BCR (1988). The following metal fractions were characterized: easily exchangeable (EE), carbonate-associated (C), easily reducible oxide-associated (ERO), moderately reducible oxide-associated (MRO), organic matter-associated (OM), extractable with aqua regia (AR). Extractions were performed with an end-over-end shaker, and, in the case of the last fraction, with a microwave digestion system

(PerkinElmer–AntonPaar). The extraction scheme is presented in table 2. Metals were analyzed with a F- and GF-AAS (Perkin-Elmer 300 and 600). The analyzed metals were Cr, Cu, Fe, Mn, Ni, Pb and Zn. Percent distribution of metals in each fraction was computed with regard to the concentration in aqua-regia extract (total metal concentration, with complete matrix destruction, was not assessed). Testing of the differences between average concentration in different ecosystems was done using the t-test for independent samples.

Table 1 Characterization of the sampling stations (with distinction between a and b soil layers, where appropriate).

Parameter / Station	H2	H3	H4
Ecosystem type	levee	depression	marsh
Direct anthropogenic impact	low	none	none
Average water level (cm)	-208	26	63
Min water level (cm)	-400	-150	-150
Max water level (cm)	80	210	260
Water speed when flooded	low	low or stagnant	low or stagnant
Soil type	silty sand	silt	clay
Top soil humidity (%, annual average)	30.2	44.6	43.2
Top soil pH (annual average)	7.51	7.19	7.19
Redox potential in soil at 5 cm (mV, annual average)	360	108	54
Loss on ignition (%, average)	9.89a (3.04b)	11.81	10.50
Cation exchange capacity (meq/100g d.w., average)	38.86	44.04	43.30
Soil humidity at sampling moment (%, average)	24.57a (12.49b)	35.56	40.99
pH at sampling moment (average)	7.90a (8.04b)	7.93	7.85
S-SO4 at sampling moment (ppm, average)	232.02a (237.80b)	170.70	251.62
N-NH4 at sampling moment (ppm, average)	0.83a (0.29b)	0.69	2.46
N-NO2 at sampling moment (ppm, average)	0.097a (0.146b)	0.583	0.881
N-NO3 at sampling moment (ppm, average)	22.231a (2.607b)	2.906	3.182

Table 2 The extraction method.

Step	Analytical sample	Extraction solution	Name of extract
1	Air dried soil	0.05 M $CaCl_2$, 8h	easily exchangeable
2	Residual to step 1	2.5% v/v Ac-OH, 24h	carbonate-associated
2	Residual to step 2	0.1 M $K_4P_2O_7$, 8h	organic matter- associated
4	Residual to step 3	0.1 M NH_2OH*HCl, pH 2, 12h	easily reducible oxide-associated
5	Residual to step 4	0.1 M $C_2O_4(NH_4)_2$, pH 3, 24h	moderately reducible oxide- associated
By difference between full extract in aqua regia and the other fractions			extractable with aqua regia

Results and Discussions

Table 3 presents the concentrations of metals in fractions with different mobility. One can remark that AR concentrations are higher in depression and marsh than in levee (excepting for Mn), and that all concentrations decrease with the depth in the levee (excepting for Ni). Most of the statistically significant differences (table 4) are in the case of AR concentrations; differences in EE concentrations occur especially in the case of Fe, Mn, and Zn; differences in the fractions associated to carbonates occur in the case of Zn and Pb. Cu, Zn, Pb, Fe and Pb in ERO fraction significantly differ between depths in the levee, as well as between the levee and the depression and marsh. Significant differences of MRO and OM fractions occur for all metals.

Table 3 Metals concentrations (ppm) in the soil of the studied ecosystems.

H2a		AR	Sum of Fr.	EE	C	ERO	MRO	OM
Cr	Media	88.08	6.55	0.10	0.30	0.33	3.93	1.90
	DS	*9.34*	*0.45*	*0.04*	*0.14*	*0.16*	*0.56*	*0.47*
Cu	Media	89.96	63.30	0.56	9.31	0.97	21.71	30.75
	DS	*13.09*	*13.23*	*0.17*	*4.96*	*0.24*	*3.83*	*11.42*
Fe	Media	29134.40	4451.03	2.75	19.37	307.98	3837.36	283.57
	DS	*3705.82*	*286.64*	*0.74*	*9.50*	*108.33*	*238.09*	*52.92*
Mn	Media	766.60	615.37	8.79	87.49	366.24	113.21	39.63
	DS	*92.24*	*48.08*	*2.55*	*20.95*	*28.09*	*23.07*	*8.43*
Ni	Media	71.46	22.39	0.17	4.00	3.54	8.81	5.87
	DS	*10.69*	*3.44*	*0.12*	*1.66*	*0.93*	*1.53*	*1.30*
Pb	Media	45.36	30.54	1.16	4.76	2.57	4.21	17.84
	DS	*7.39*	*5.24*	*0.73*	*1.58*	*0.94*	*2.08*	*4.86*
Zn	Media	189.34	127.47	0.86	53.00	18.53	38.94	16.14
	DS	*26.26*	*15.75*	*0.37*	*10.51*	*3.12*	*7.22*	*4.24*
H2b		Total*	Sum of Fr.	EE	C	ERO	MRO	OM
Cr	Media	68.69	4.50	0.08	0.34	0.20	2.81	1.07
	DS	*12.93*	*1.63*	*0.04*	*0.12*	*0.11*	*1.39*	*0.41*
Cu	Media	42.31	26.94	0.36	7.22	0.54	10.05	8.77
	DS	*10.69*	*10.13*	*0.14*	*2.65*	*0.11*	*3.98*	*4.81*
Fe	Media	23444.80	4179.23	1.99	24.02	456.15	3522.04	175.03
	DS	*4243.69*	*1373.09*	*0.82*	*7.24*	*229.78*	*1199.50*	*79.10*
Mn	Media	667.68	464.96	7.87	95.98	260.48	83.06	17.57
	DS	*102.05*	*129.73*	*3.10*	*21.72*	*85.17*	*31.92*	*5.75*
Ni	Media	86.40	26.62	0.15	6.58	3.54	13.03	3.32
	DS	*8.97*	*6.19*	*0.04*	*1.45*	*0.84*	*4.97*	*0.75*
Pb	Media	22.91	14.15	0.81	3.52	1.12	2.43	6.27
	DS	*6.08*	*5.34*	*0.24*	*1.36*	*0.35*	*1.36*	*3.17*
Zn	Media	93.89	58.40	0.58	30.33	6.41	16.17	4.92
	DS	*14.90*	*11.84*	*0.11*	*8.45*	*1.94*	*4.58*	*1.81*
H3a		Total*	Sum of Fr.	EE	C	ERO	MRO	OM
Cr	Media	113.84	7.78	0.10	0.39	0.38	3.65	3.25
	DS	*5.39*	*1.82*	*0.03*	*0.08*	*0.14*	*0.96*	*1.16*
Cu	Media	105.77	76.83	0.67	10.17	0.49	25.30	40.19
	DS	*6.00*	*17.76*	*0.31*	*2.54*	*0.17*	*9.53*	*8.44*
Fe	Media	39036.00	6603.56	10.44	23.50	457.22	5583.75	528.65
	DS	*2738.49*	*2006.46*	*3.35*	*3.40*	*72.35*	*1931.50*	*121.81*
Mn	Media	611.95	383.91	8.86	84.76	195.35	72.97	21.97
	DS	*79.81*	*80.86*	*4.33*	*19.33*	*64.34*	*27.36*	*5.47*
Ni	Media	91.52	31.44	0.24	4.74	3.30	16.23	6.93
	DS	*7.82*	*4.59*	*0.14*	*1.34*	*1.11*	*3.40*	*1.57*
Pb	Media	70.11	48.32	1.51	7.42	1.75	8.28	29.35
	DS	*4.46*	*5.42*	*0.93*	*1.73*	*0.84*	*4.35*	*6.16*
Zn	Media	214.90	142.92	3.91	81.98	15.07	28.51	13.45
	DS	*13.78*	*17.12*	*1.75*	*13.25*	*1.85*	*9.52*	*4.72*
H4a		Total*	Sum of Fr.	EE	C	ERO	MRO	OM
Cr	Media	107.64	8.46	0.13	0.38	0.31	3.31	4.33
	DS	*7.00*	*1.34*	*0.05*	*0.05*	*0.15*	*0.33*	*1.12*
Cu	Media	103.59	81.10	0.67	9.70	0.57	26.91	43.26
	DS	*7.64*	*13.24*	*0.31*	*2.69*	*0.17*	*1.51*	*12.18*
Fe	Media	37043.60	6953.47	22.11	23.89	749.39	5674.71	483.36
	DS	*3608.47*	*277.66*	*7.47*	*5.62*	*133.40*	*239.35*	*165.89*
Mn	Media	718.84	514.24	16.17	105.95	266.39	96.87	28.86
	DS	*125.85*	*95.21*	*6.42*	*35.64*	*54.47*	*18.33*	*8.22*
Ni	Media	82.26	29.40	0.20	4.10	4.73	13.78	6.58
	DS	*3.87*	*3.13*	*0.11*	*0.69*	*2.00*	*1.22*	*2.02*
Pb	Media	63.27	43.32	1.12	7.03	1.09	6.94	27.14
	DS	*4.77*	*5.03*	*0.57*	*2.46*	*1.36*	*0.86*	*2.85*
Zn	Media	191.96	123.06	3.77	69.38	14.75	22.11	13.05
	DS	*13.94*	*22.06*	*2.12*	*17.14*	*1.02*	*1.30*	*4.01*

Table 4 Degree of statistical significance of the differences of metal and other parameters in the soil of studied ecosystems (t-test, *, **, *** = significant at level 0.05, 0.01, and 0.001).

	H2a/H2b	H2a/H3a	H2a/H4a	H3a/H4a
Cu AR	***	**	*	NS
Zn AR	***	*	NS	**
Pb AR	***	***	***	**
Ni AR	**	***	**	**
Cr AR	**	***	***	**
Fe AR	**	***	***	NS
Mn AR	*	**	NS	*
Cu EE	*	NS	NS	NS
Zn EE	*	***	***	NS
Pb EE	NS	NS	NS	NS
Ni EE	NS	NS	NS	NS
Cr EE	NS	NS	NS	NS
Fe EE	*	***	***	***
Mn EE	NS	NS	**	**
Cu C	NS	NS	NS	NS
Zn C	***	***	*	NS
Pb C	NS	**	*	NS
Ni C	**	NS	NS	NS
Cr C	NS	NS	NS	NS
Fe C	NS	NS	NS	NS
Mn C	NS	NS	NS	NS
Cu ERO	***	***	***	NS
Zn ERO	***	**	**	NS
Pb ERO	***	NS	*	NS
Ni ERO	NS	NS	NS	NS
Cr ERO	NS	NS	NS	NS
Fe ERO	NS	**	***	***
Mn ERO	**	***	***	*

	H2a/H2b	H2a/H3a	H2a/H4a	H3a/H4a
Cu MRO	***	NS	**	NS
Zn MRO	***	*	***	*
Pb MRO	*	*	**	NS
Ni MRO	*	***	***	*
Cr MRO	*	NS	**	NS
Fe MRO	NS	*	***	NS
Mn MRO	*	**	NS	*
Cu OM	***	*	*	NS
Zn OM	***	NS	NS	NS
Pb OM	***	***	***	NS
Ni OM	***	NS	NS	NS
Cr OM	**	**	***	*
Fe OM	**	***	**	NS
Mn OM	***	***	*	*
sand (%)	*	*	***	NS
silt + clay %	*	*	***	NS
Humidity %	***	***	***	**
LOI (% in dry soil)	***	NS	NS	NS
pH	NS	NS	NS	NS
N-NH_4	NS	NS	*	*
N-NO_2	NS	*	**	NS
N-NO_3	NS	NS	NS	NS

Table 5 presents the percent distribution of metals in the assessed fractions. One can remark that:

- the percentages are in the domain mentioned in the scientific literature (Barona et al., 1994, BCR, 1998, Ngiam and Lim, 2001, Rouset and Loez-Sanchez, 2001, Nome et al., 2001, Dollar et al., 2001);
- Fe, Mn and Zn percentages in forms easily transferable to surface water and plants (EE) increases from levee to forested depression and to marsh, whereas the Pb percent in the same form decreases on this gradient; Cu percentages in forms easily transferable to plants is not much lower than the percent of other metals, suggesting that the reported apparent deficiency Cu levels in plants (Neagoe et al., 2000) is not due to low Cu levels in soil, but to other mechanisms (for instances the fact that Fe, with high concentrations in the floodplain, table 3, might reduce Cu absorption from soil solution by plants – Kabata Pendias and Pendias, 1992);
- Mn percentages as ERO decreases on the mentioned gradient, as well as the percent of Cr, Cu, Pb and Zn associated to Mn oxides;
- Cr percentage decrease on the gradient also in the case of MRO (a fraction dominated by Fe oxides);

- Cr, Cu, Fe and Pb percentage as OM increases on the same gradient.
- In the levee the percentages of metals in ERO and OM form decreases with the depth (excepting for Cu and Fe), and the percentages of the C form increases for all metals.

The distribution of metals in EE and ERO fractions in the soil of forested depressions and marshes suggests that a transfer is possible to floodwater and plants especially in the case of Fe, Mn, and Zn, and less in the case of Cr (which shows high affinity for organic matter). However, Neagoe et al. (2000) reports that Cr concentrations in emergent macrophytes of the depression and marshes are relatively high (4-10 ppm) compared to concentrations in the levee vegetation (2-3 ppm), suggesting that a mobilization of Cr from the soil of the depression and marshes takes place, and possibly through this mechanism also occur a further transfer (during plants decomposition) to flood water.

Table 5 Percent distribution of metals in fractions with different mobility in the soil of the studied ecosystems. Grey cells indicate cases where there is a significant variation with the depth (in the levee) or on the gradient levee – depression – marsh.

Station	Metal	Sum of Fr.	EE	C	ERO	MRO	OM
Cr	H2a	*7.44*	0.11	0.34	0.37	4.46	2.16
	H2b	*6.55*	0.11	0.50	0.29	4.08	1.56
	H3a	*6.83*	0.09	0.34	0.33	3.21	2.86
	H4a	*7.86*	0.12	0.35	0.29	3.07	4.02
Cu	H2a	*70.36*	0.62	10.35	1.08	24.13	34.18
	H2b	*63.68*	0.85	17.06	1.27	23.76	20.74
	H3a	*72.64*	0.64	9.62	0.46	23.92	38.00
	H4a	*78.29*	0.64	9.37	0.55	25.97	41.76
Fe	H2a	*15.28*	0.01	0.07	1.06	13.17	0.97
	H2b	*17.83*	0.01	0.10	1.95	15.02	0.75
	H3a	*16.92*	0.03	0.06	1.17	14.30	1.35
	H4a	*18.77*	0.06	0.06	2.02	15.32	1.30
Mn	H2a	*80.27*	1.15	11.41	47.77	14.77	5.17
	H2b	*69.64*	1.18	14.37	39.01	12.44	2.63
	H3a	*62.73*	1.45	13.85	31.92	11.92	3.59
	H4a	*71.54*	2.25	14.74	37.06	13.48	4.01
Ni	H2a	*31.34*	0.24	5.60	4.95	12.33	8.22
	H2b	*30.81*	0.18	7.61	4.10	15.09	3.84
	H3a	*34.36*	0.27	5.18	3.61	17.74	7.57
	H4a	*35.74*	0.24	4.98	5.75	16.76	8.00
Pb	H2a	*67.32*	2.55	10.50	5.67	9.28	39.33
	H2b	*61.74*	3.52	15.38	4.89	10.60	27.36
	H3a	*68.91*	2.16	10.59	2.50	11.81	41.87
	H4a	*68.48*	1.78	11.11	1.72	10.97	42.90
Zn	H2a	*67.32*	0.45	27.99	9.79	20.56	8.53
	H2b	*62.20*	0.62	32.30	6.82	17.22	5.24
	H3a	*66.50*	1.82	38.15	7.01	13.27	6.26
	H4a	*64.11*	1.97	36.14	7.68	11.52	6.80

Conclusions

- The distribution of metals in EE and ERO fractions in the soil of depression and marshes ecosystems suggests a possible transfer of Fe, Mn, and Zn, in the flood water;

- Cr transfer to floodwater might take place rather mediated by plants.
- Cu levels in forms easily transferable to plants is not much lower than the percent of other metals, suggesting that the recorded apparent deficit in plants is not due to low Cu levels in soil, but rather to other mechanisms.

Summary

Existing data shows that there could be an indirect human health risk, as well as an ecological risk, in the Danube floodplain due to metals. The arguments for this are: relatively high concentrations in flood water and fish, high concentrations of metals in plants in certain ecosystems, as well as low (deficit) concentration certain metals in plants in other ecosystem types. The objective of the study was to characterize the distribution of metals with different mobility in soil/sediment in order to find a possible explanation of the distribution patterns of metals in flood water an plants. To do this we used a sequential extraction method followed by AAS. The metals distribution in the soil of levees, swamps and marshes/shallow lakes confirmed that the metals with high concentration in water could have as a source the soil (either directly or through rooted macrophytes), but the deficit found in some plants can not be explained by the fact that those metals are more strongly immobilized in the ecosystem soil than other metals.

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