Joint Danube Survey 2

icpdr International Commission for the Protection of the Danube River
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Summary report on the determination of the inorganic composition of the JDS-2 sediment samples by JRC

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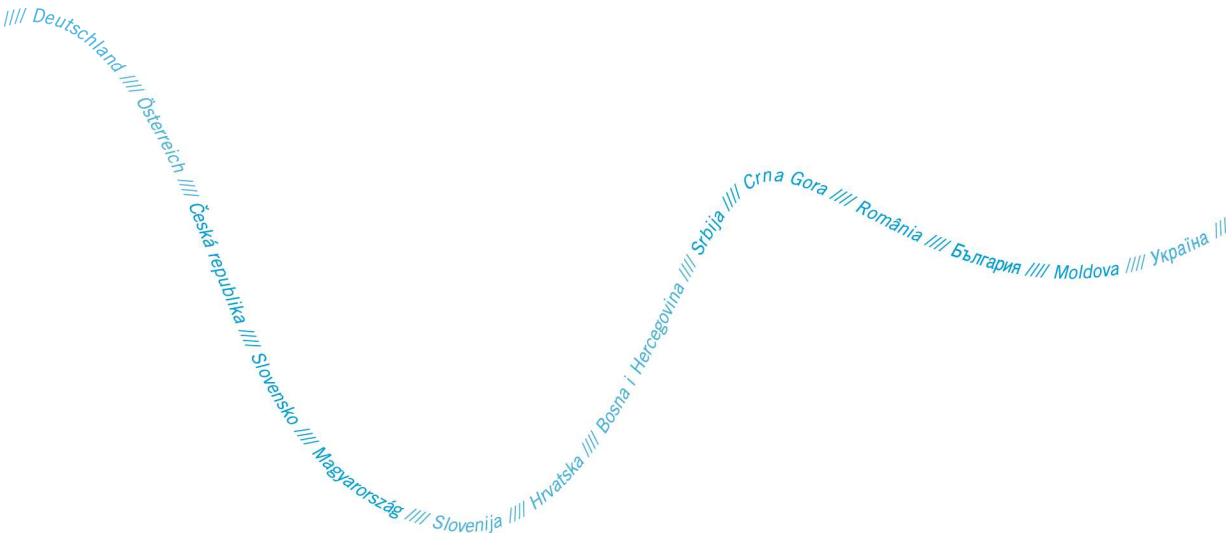

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Table of content

1 Introduction 4

2 Methods 4

2.1Samples and sample pre-treatment 4
2.2WDXRF Analyses 4
2.3Hg Analyses 5

3 Results 6

4 Conclusions 9

1 Introduction

River sediments constitute complex and difficult analytical samples. They play a fundamental role in the distribution of toxic compounds in aquatic systems and in the evaluation of the current state and the course of changes taking place in the environment. For an understanding of the occurring processes as well as for proper understanding of underlying geo-chemical process, information on major and minor element patterns are very useful.

To this end, all sediment samples stemming from the second Joint Danube Survey were analyzed by means of wave-length dispersive X-ray fluorescence spectrometry (WDXRF) for the elements silicium (Si), Calcium (Ca), Potassium (K), Iron (Fe), Magnesium (Mg), Titanium (Ti), Sulfur (S), Phosphorus (P), Chlorine (Cl), Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Manganese (Mn), Chromium (Cr), Sodium (Na), Aluminium (Al), Vanadium (V), Cobalt (Co), Arsenic (As) and Cadmium (Cd). In addition to these major and minor elements, Mercury (Hg) was determined using solid-sampling cold-vapour atomic absorption spectrometry (SS-CVAAS).

The data reported here require a careful chemometric analyses in order to better understand the underlying dynamics. However, the data set covers all sediments sampled over a distance of 2600 km 2600 from Germany to the Black see. As such it is a unique a valuable data set, which elucidates the geomorphology of the Danube system.

2 Methods

2.1 Samples and sample pre-treatment

In total 148 ssediment samples were obtained on both side of the river were dispatched to the premises of the JRC at Ispra, Italy. Upon arrival, the samples were dried for 24 hours in an oven at a temperature not exceeding 40°C. Upon completion, each sample was ground using an planetary mill equipped with agate-zirconia milling vessels (Fig 1). Each sample was ground for ca. 5 min. The resulting powder was then transferred to pre-cleaned HDPE sample containers until further processing (Fig. 2).

For Hg analysis, no further treatment was necessary. For WDXRF measurements, samples were pelletised using a hydraulic press (Herzog). For this purpose, ca. 2 g of samples were placed in special XRF sample containers. A pressure of 20 t/cm^2 was applied for 20 sec, resulting into a solidified pellet ready for analyses by means of WDXRF.

2.2 WDXRF Analyses

The measurements were carried out on a Bruker-AXS® SRS-3400 X-ray fluorescence spectrometer equipped with four analysing crystals, a Rh-anode end-window X-ray tube (75 lm Be window) and 4 kW maximum power. The spectrometer is controlled by an external PC using the 241

manufacturer's software SPECTRAplus®. The calibration was built using the following certified reference materials of soils and sediments: BCR-141, BCR-141R, BCR-142, BCR-142R, BCR-143, BCR-143R, BCR-144, BCR-144R, BCR-145, BCR-145-R, BCR-146, BCR-146R, BCR-277, BCR-280, BCR-320, CANMET- SO1, CANMET-SO2, CANMET-SO3, CANMET-SO4, NIST-SRM-2704, NIST-SRM-2709, NIST-SRM-2710, NIST-SRM-2711, IAEA-SOIL-7.

It has to be stressed that in some cases the availability of certified values is limited. In those cases, the most justified indicative value reported by the certification report was used. Even in this case the sum of certified + indicative elements concentrations normally does not yield 100%: therefore a matrix correction based on fixed alphas calculated by empirical regression methods has to be applied. The elements for which the used characteristic lines energies are, on an energy scale, beyond the Fe Ka (6.4 keV) have been matrix-corrected using Rh Ka Compton scattered tube line as an internal standard.

All measurements were run under repeatability conditions, i.e. in one analytical run. Given the significant size and mass of test portion in relationship to the grain size after milling, only one test portion was analysed per laboratory sample.

2.3 Hg Analyses

For the mercury analysis an Advanced Mercury Analyser (AMA-254, made by ALTEC and distributed by LECO) was used. This technique uses a direct atomic absorption cold-vapour method with gold amalgamation (Bartha et al., 1996; ISO/CD 17852). The analysis was performed in solid samples without any further sample preparation. As stock solutions of mercury, a single-element standard solution for AA (1 l/ml) from Carlo Erba, and a single element AS standard solution Fluka (1000 mg/l) were used. Calibration standard solutions were made by stepwise dilution of these stock solutions. Final acid concentration was 10 ml/l sulphuric acid (Merck, ''Suprapur''). The concentrations of calibration solutions in dosing of 100 µl are as follows: 5, 10, 20, 50, 100, 200 and 500 ng/100 µl solutions. Pure O_2 was used as carrier gas. Calibration curves were verified using the following certified reference materials: BCR-141R (0.25 ± 0.02 mg/kg Hg), BCR-143R (1.10 ± 0.07 mg/kg Hg), RTH-953 (1.84 ± 0.22 mg/kg Hg).

3 Results

The summary results of obtained on the sediments are briefly compiled hereafter. Besides mean values and standard deviation, 25-, 50-, 75- and 90 percentiles were calculated. Data obtained for the River Danube are compared to the respective summary findings obtained on samples taken from the tributaries. Data are displayed without discussion. This will be done in the full report.

Table 1 Summary findings mercury

Mercury	Danube	Tributaries
Mean	0,29	0,25
Standard Deviation	0,22	0,13
Minimum	0,01	0,08
Maximum	1,42	0,47
Median	0,25	0,26
25-Percentile	0,13	0,14
75-Percentile	0,36	0,36
90-Percentile	0,47	0,41
data are in mg/kg dw		

Table 2 Summary findings silicon

Silicon	Danube	Tributaries
Mean	23,07	25,78
Standard Deviation	2,50	1,69
Minimum	16,51	23,15
Maximum	28,81	28,70
Median	23,86	26,11
25-Percentile	20,63	24,43
75-Percentile	25,17	26,88
90-Percentile	25,88	27,79
data are in wgt% dw		

Table 3 Summary findings calcium

Calcium	Danube	Tributaries
Mean	6,63	3,71
Standard Deviation	2,54	1,83
Minimum	1,75	1,04
Maximum	14,66	7,77
Median	6,50	3,45
25-Percentile	4,59	2,47
75-Percentile	8,72	4,97
90-Percentile	9,70	5,63
data are in wgt.% dw		

Table 4 Summary findings potassium

Potassium	Danube	Tributaries
Mean	1,96	2,13
Standard Deviation	0,23	0,21
Minimum	1,24	1,74
Maximum	2,49	2,42
Median	1,96	2,15
25-Percentile	1,86	1,97
75-Percentile	2,09	2,29
90-Percentile	2,27	2,38
data are in wgt.% dw		

Table 5 Summary findings iron

Iron	Danube	Tributaries
Mean	4,17	4,69
Standard Deviation	0,85	0,58
Minimum	2,09	3,62
Maximum	10,07	5,39
Median	4,18	4,80
25-Percentile	3,77	4,40
75-Percentile	4,64	5,08
90-Percentile	4,97	5,24
data are in wgt.% dw		

Table 6 Summary findings magnesium

Magnesium	Danube	Tributaries
Mean	2,20	1,40
Standard Deviation	0,66	0,27
Minimum	0,84	0,94
Maximum	3,62	1,85
Median	1,95	1,38
25-Percentile	1,66	1,23
75-Percentile	2,75	1,56
90-Percentile	3,20	1,78
data are in wgt.% dw		

Table 7 Summary findings titanium

Titanium	Danube	Tributaries
Mean	0,47	0,53
Standard Deviation	0,08	0,05
Minimum	0,26	0,46
Maximum	0,68	0,60
Median	0,47	0,51
25-Percentile	0,40	0,50
75-Percentile	0,54	0,57
90-Percentile	0,58	0,59

data are in wgt.% dw

Table 8 Summary findings sulphur

Sulphur	Danube	Tributaries
Mean	0,12	0,13
Standard Deviation	0,12	0,10
Minimum	0,01	0,03
Maximum	1,30	0,43
Median	0,10	0,10
25-Percentile	0,07	0,07
75-Percentile	0,13	0,15
90-Percentile	0,17	0,19

data are in wgt.% dw

Table 9 Summary findings phosphorus

Phosphorus	Danube	Tributaries
Mean	0,11	0,13
Standard Deviation	0,02	0,06
Minimum	0,07	0,07
Maximum	0,24	0,33
Median	0,11	0,11
25-Percentile	0,10	0,10
75-Percentile	0,12	0,14
90-Percentile	0,13	0,18

data are in wgt.% dw

Table 10 Summary findings chlorine

Chlorine	Danube	Tributaries
Mean	0,010	0,013
Standard Deviation	0,003	0,009
Minimum	0,006	0,007
Maximum	0,026	0,046
Median	0,009	0,012
25-Percentile	0,008	0,009
75-Percentile	0,011	0,013
90-Percentile	0,013	0,015

data are in wgt.% dw

Table 11 Summary findings lead

Lead	Danube	Tributaries
Mean	75,51	89,67
Standard Deviation	38,99	37,84
Minimum	39,00	41,00
Maximum	393,00	195,00
Median	63,00	97,00
25-Percentile	55,00	61,50
75-Percentile	85,00	98,50
90-Percentile	102,00	113,80

data are in mg/kgdw

Table 12 Summary findings zinc

Zinc	Danube	Tributaries
Mean	243,21	309,80
Standard Deviation	135,90	135,69
Minimum	102,00	105,00
Maximum	1070,00	509,00
Median	190,00	289,00
25-Percentile	159,00	222,50
75-Percentile	295,00	425,00
90-Percentile	390,40	481,60

data are in mg/kgdw

Table 13 Summary findings copper

Copper	Danube	Tributaries
Mean	187,77	122,53
Standard Deviation	1178,93	116,46
Minimum	28,00	44,00
Maximum	13666,00	525,00
Median	74,00	88,00
25-Percentile	64,00	68,00
75-Percentile	89,00	132,00
90-Percentile	123,00	144,80

data are in mg/kgdw

Table 14 Summary findings nickel

Nickel	Danube	Tributaries
Mean	91,18	124,00
Standard Deviation	33,14	64,39
Minimum	0,00	71,00
Maximum	254,00	245,00
Median	86,00	99,00
25-Percentile	71,00	80,50
75-Percentile	106,00	156,00
90-Percentile	131,80	223,20

data are in mg/kgdw

Table 15 Summary findings manganese

Manganese	Danube	Tributaries
Mean	1079	1496
Standard Deviation	281	432
Minimum	530	906
Maximum	2472	2459
Median	1027	1405
25-Percentile	903	1261
75-Percentile	1222	1658
90-Percentile	1371	2040
data are in mg/kgdw		

Table 16 Summary findings chromium

Chromium	Danube	Tributaries
Mean	146	184
Standard Deviation	33	39
Minimum	65	144
Maximum	250	283
Median	140	172
25-Percentile	120	158
75-Percentile	172	206
90-Percentile	182	229
data are in mg/kgdw		

Table 17 Summary findings sodium

Sodium	Danube	Tributaries
Mean	0,709	0,634
Standard Deviation	0,115	0,086
Minimum	0,325	0,533
Maximum	1,144	0,818
Median	0,699	0,602
25-Percentile	0,643	0,571
75-Percentile	0,787	0,672
90-Percentile	0,838	0,772
data are in wgt.%dw		

Table 18 Summary findings aluminium

Aluminium	Danube	Tributaries
Mean	7,60	8,10
Standard Deviation	0,92	0,76
Minimum	4,54	6,82
Maximum	9,86	9,09
Median	7,68	8,25
25-Percentile	7,07	7,67
75-Percentile	8,24	8,71
90-Percentile	8,61	8,98
data are in wgt.%dw		

Table 19 Summary findings vanadium

Vanadium	Danube	Tributaries
Mean	108	126
Standard Deviation	20	13
Minimum	52	103
Maximum	166	144
Median	111	123
25-Percentile	94	117
75-Percentile	122	140
90-Percentile	130	142
data are in mg/kg dw		

Table 20 Summary findings cobalt

Cobalt	Danube	Tributaries
Mean	19,4	24,5
Standard Deviation	6,2	6,0
Minimum	8,0	15,0
Maximum	67,0	34,0
Median	19,0	25,0
25-Percentile	15,0	20,0
75-Percentile	22,0	29,0
90-Percentile	25,0	31,0
data are in mg/kg dw		

Table 21 Summary findings arsenic

Arsenic	Danube	Tributaries
Mean	61,1	69,7
Standard Deviation	23,1	9,4
Minimum	0,0	49,0
Maximum	272,0	81,0
Median	59,0	73,0
25-Percentile	53,0	64,5
75-Percentile	68,0	77,0
90-Percentile	74,8	78,2
data are in mg/kg dw		

Table 22 Summary findings cadmium

Cadmium	Danube	Tributaries
Mean	9,4	10,4
Standard Deviation	2,6	3,0
Minimum	0,0	5,0
Maximum	21,0	15,0
Median	9,0	10,0
25-Percentile	8,0	8,5
75-Percentile	11,0	12,5
90-Percentile	13,0	14,0
data are in mg/kg dw		

4 Conclusions

The data presented are to be seen in a broader sense. In some cases, observed sediment concentrations re abnormal and require a further investigation. In most cases typical geo-chemical background concentrations, which can for instance observed in soil, are observed. Data for trace elements in low concentrations are of indicative character only.