UNDP/GEF Danube Regional Project

Preparation of Reference Materials for Analytical Quality Control in the Water Laboratories

Report on Homogeneity Tests of the First Sediment Reference Material

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LIST OF CONTENT

A. PROJECT OBJECTIVES

Objective: Ensure the reliability and comparability of monitoring results during the implementation of the transnational water quality monitoring (TNMN) in the Danube river basin (DRB) by providing appropriate reference materials (RM) for analytical quality Control (AQC).

Outputs: Ensure availability of homogenous reference samples (RM), as AQC sample, for analyzing specified pollutant characteristics in water and sediment. The RMs shall be available for performance testing (intercalibration) and intra-laboratory quality control.

This project output will assist DRB-countries to control the water quality monitoring results by reference samples in their laboratories and to ensure sustainable quality work as well as to improve their working quality as needed.

Implementation of the project will ensure the continuity of the quality assurance activities in the DRB which have been developed and maintained since 1995 in the frame of different projects supported from different financial sources, e.g. individual countries, PHARE programme and the ICPDR.

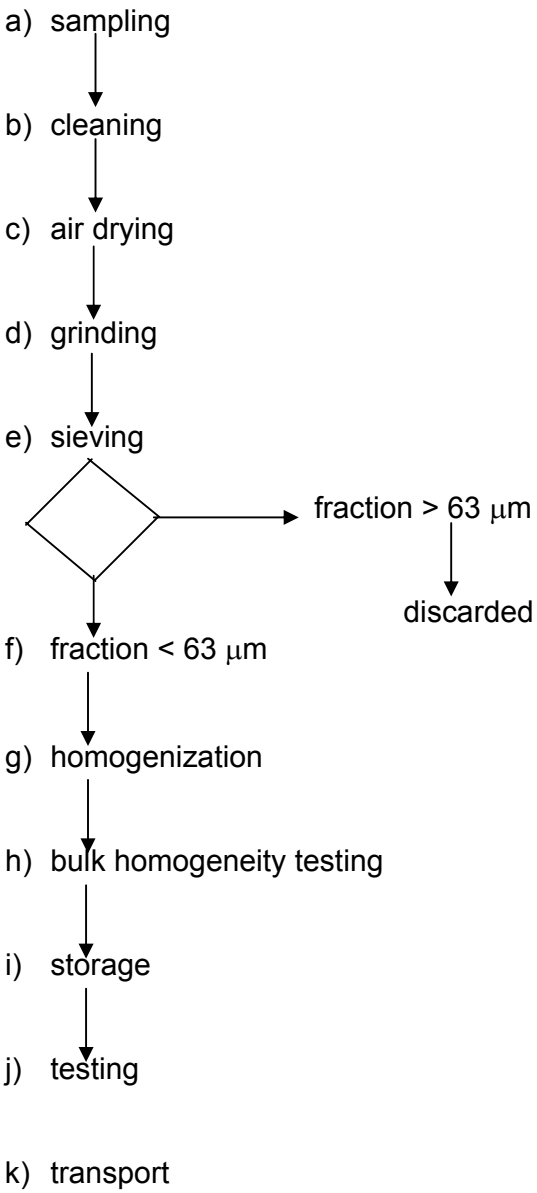
B. APPROACH OF WORK IN LINE WITH THE REQUIRED SERVICE

In line with the Work Program of the MLIM Expert Groups, there is a need to ensure and maintain the analytical quality control measures in the water laboratories in the DRB as a basic requirement of the quality assurance in the trans-national monitoring. This Project provides significant quantities of water and sediment RMs:

Sediment RMs:
based on earlier experience concerning the problem of determination of the different river quality characteristics the target determinands include nutrients, i.e. nitrogen and phosphorus forms, heavy metals, as well as selected determinands to characterize organic contamination, e.g. total organic carbon (TOC), chlorinated hydrocarbons, ((DDT, HCB, HCH (α-, β-, γ-), PAHs (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indenopyrene, benzo(g,h,i)perylene (Borneff PAHs)).

The compounds of interest in the sediment RMs will be in the range of concentrations found in Danube sediments.

In the case of sediment reference materials all the preparation steps and tests are specified. The procedure for producing powdered RMs is the following:



C. HOMOGENIZATION

Homogenization of sediment (fraction < 63 μm) was carried out by a special equipment in VITUKI. The time of homogenization at a constant rotating speed was five days.

D. HOMOGENEITY TESTING

1. Bulk homogeneity test

During production, sub-samples were taken from the bulk material to control the homogeneity on three heavy metals: copper, lead, nickel, using a relatively fast and accurate method (atomic absorption spectrometric method). The test results were used as indicators of successful bulk homogenization.

Randomly selected four sub-samples were tested. Each sub-sample was analyzed in five replicates. The results of bulk homogenization tests can be seen in **Table 1**.

Table 1. Results of the first homogenization

Replicate sample	Sample-1			Sample -2		
	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)
/1	45,20	33,00	32,00	45,80	34,40	32,50
/2	45,40	35,40	31,90	46,20	35,20	32,90
/3	46,10	38,60	33,00	45,40	37,30	31,90
/4	45,40	37,50	31,30	46,20	37,20	32,40
/5	45,10	37,60	31,30	45,80	37,30	31,30
Minimum	45,10	33,00	31,30	45,40	34,40	31,30
Maximum	46,10	38,60	33,00	46,20	37,30	32,90
Median	45,40	37,50	31,90	45,80	37,20	32,40
Average	45,44	36,42	31,90	45,88	36,28	32,20
SD	0,39	2,24	0,70	0,33	1,38	0,62
Replicate sample	**Sample-3**			**Sample -4**		
/1	45,80	35,30	31,30	45,20	35,40	32,80
/2	45,70	36,80	31,30	45,40	38,00	31,30
/3	45,10	35,30	31,90	46,20	35,60	32,00
/4	45,70	37,80	32,00	45,80	37,20	31,90
/5	46,10	37,30	31,30	45,30	37,50	31,40
Minimum	45,10	35,30	31,30	45,20	35,40	31,30
Maximum	46,10	37,80	32,00	46,20	38,00	32,80
Median	45,70	36,80	31,30	45,40	37,20	31,90
Average	45,68	36,50	31,56	45,58	36,74	31,88
SD	0,36	1,15	0,36	0,41	1,17	0,60

As the analytical results indicated inhomogeneity, a repeated homogenization was necessary.

2. Specific homogeneity test

After the repeated homogenization specific homogeneity both for between-units and within-unit was tested.

Between-units homogeneity

It was necessary to check – using a reasonable number of samples – if the differences between-units stay within acceptable limits.

The selected analytical method was atomic absorption spectrometric method, which was applied under the best repeatable conditions: all samples were measured on the same day, with the same instrument, by the same operator, against the same calibrates.

Five representative replicate samples were selected from each bottle in order to verify their homogeneity. All the representative samples were analyzed by VUVH and VITUKI as well.

Within-unit homogeneity

Within-unit homogeneity was calculated from the five replicates per bottle (unit).

The analytical results are presented in Table 2-7. The analytical data summarized in **Table 2, 4, 6** originate from VUVH, while analytical results in **Table 3, 5, 7** originate from VITUKI.

Table 2. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Cu (mg/kg)	Cu mg/kg)	Cu (mg/kg)	Cu (mg/kg)		
/1	46,85	46,45	45,49	45,89		
/2	45,13	46,04	45,86	46,94		
/3	45,93	46,16	45,32	46,65		
/4	45,63	45,95	45,95	45,46		
/5	45,89	46,66	46,05	45,99		
Minimum	45,13	45,95	45,32	45,46	45,13	**Minimum**
Maximum	46,85	46,66	46,05	46,94	46,94	**Maximum**
Median	45,89	46,16	45,86	45,99	45,94	**Median**
Average	45,89	46,25	45,73	46,19	46,01	**Average**
SD	0,63	0,30	0,31	0,60	0,46	**SD**
RSD (CV_w)	1,36	0,64	0,69	1,30	1,00	**RSD (CV_b)**
U_w	0,43	0,20	0,22	0,41	0,32	**U_b**
CV_w+U_w	1,80	0,84	0,90	1,71	1,31	**CV_b+U_b**
CV_w-U_w	0,93	0,44	0,47	0,89	0,68	**CV_b-U_b**

Table 3. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Cu (mg/kg)	Cu (mg/kg)	Cu (mg/kg)	Cu (mg/kg)		
/1	45,20	45,80	45,80	45,20		
/2	45,40	46,20	45,70	45,40		
/3	46,10	45,40	45,10	46,20		
/4	45,40	46,20	45,70	45,80		
/5	45,10	45,80	46,10	45,30		
Minimum	45,10	45,40	45,10	45,20	45,10	**Minimum**
Maximum	46,10	46,20	46,10	46,20	46,20	**Maximum**
Median	45,40	45,80	45,70	45,40	45,55	**Median**
Average	45,44	45,88	45,68	45,58	45,65	**Average**
SD	0,39	0,33	0,36	0,41	0,38	**SD**
RSD (CV_w)	0,86	0,73	0,80	0,91	0,82	**RSD (CV_b)**
U_w	0,27	0,23	0,25	0,29	0,26	**U_b**
CV_w+U_w	1,13	0,96	1,05	1,20	1,08	**CV_b+U_b**
CV_w-U_w	0,59	0,50	0,54	0,62	0,56	**CV_b-U_b**

Table 4. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Ni (mg/kg)	Ni (mg/kg)	Ni (mg/kg)	Ni (mg/kg)		
/1	34,83	36,97	34,74	34,84		
/2	35,90	35,72	35,02	35,23		
/3	36,19	36,19	35,15	35,43		
/4	36,37	36,39	35,12	35,04		
/5	36,00	36,15	35,32	34,54		
Minimum	34,83	35,72	34,74	34,54	34,54	**Minimum**
Maximum	36,37	36,97	35,32	35,43	36,97	**Maximum**
Median	36,00	36,19	35,12	35,04	35,56	**Median**
Average	35,86	36,28	35,07	35,02	35,56	**Average**
SD	0,60	0,45	0,21	0,34	0,40	**SD**
RSD (CV_w)	1,68	1,25	0,61	0,98	1,13	**RSD (CV_b)**
U_w	0,53	0,40	0,19	0,31	0,36	**U_b**
CV_w+U_w	2,21	1,65	0,80	1,30	1,49	**CV_b+U_b**
CV_w-U_w	1,15	0,86	0,42	0,67	0,77	**CV_b-U_b**

Table 5. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Ni (mg/kg)	Ni (mg/kg)	Ni (mg/kg)	Ni (mg/kg)		
/1	33,00	34,40	35,30	35,40		
/2	35,40	35,20	36,80	38,00		
/3	38,60	37,30	35,30	35,60		
/4	37,50	37,20	37,80	37,20		
/5	37,60	37,30	37,30	37,50		
Minimum	33,00	34,40	35,30	35,40	33,00	**Minimum**
Maximum	38,60	37,30	37,80	38,00	38,60	**Maximum**
Median	37,50	37,20	36,80	37,20	37,20	**Median**
Average	36,42	36,28	36,50	36,74	36,49	**Average**
SD	2,24	1,38	1,15	1,17	1,49	**SD**
RSD (CV_w)	6,15	3,81	3,15	3,18	4,07	**RSD (CV_b)**
U_w	1,94	1,20	1,00	1,01	1,29	**U_b**
CV_w+U_w	8,09	5,01	4,15	4,19	5,36	**CV_b+U_b**
CV_w-U_w	4,20	2,60	2,16	2,18	2,78	**CV_b-U_b**

Table 6. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Pb (mg/kg)	Pb mg/kg)	Pb (mg/kg)	Pb (mg/kg)		
/1	31,18	31,10	30,67	30,95		
/2	30,51	30,95	30,72	31,44		
/3	30,46	30,89	31,00	31,68		
/4	30,37	30,99	30,62	31,65		
/5	30,79	31,62	30,95	31,35		
Minimum	30,37	30,89	30,62	30,95	30,37	**Minimum**
Maximum	31,18	31,62	31,00	31,68	31,68	**Maximum**
Median	30,51	30,99	30,72	31,44	30,86	**Median**
Average	30,66	31,11	30,79	31,41	30,99	**Average**
SD	0,33	0,30	0,17	0,29	0,27	**SD**
RSD (CV_w)	1,07	0,95	0,56	0,94	0,88	**RSD (CV_b)**
U_w	0,34	0,30	0,18	0,30	0,28	**U_b**
CV_w+U_w	1,41	1,25	0,73	1,23	1,16	**CV_b+U_b**
CV_w-U_w	0,73	0,65	0,38	0,64	0,60	**CV_b-U_b**

Table 7. Results of homogeneity test

Replicate sample	Bottle-1	Bottle-2	Bottle-3	Bottle -4		
	Pb (mg/kg)	Pb (mg/kg)	Pb (mg/kg)	Pb (mg/kg)		
/1	32,00	32,50	31,30	32,80		
/2	31,90	32,90	31,30	31,30		
/3	33,00	31,90	31,90	32,00		
/4	31,30	32,40	32,00	31,90		
/5	31,30	31,30	31,30	31,40		
Minimum	31,30	31,30	31,30	31,30	31,30	**Minimum**
Maximum	33,00	32,90	32,00	32,80	33,00	**Maximum**
Median	31,90	32,40	31,30	31,90	31,90	**Median**
Average	31,90	32,20	31,56	31,88	31,89	**Average**
SD	0,70	0,62	0,36	0,60	0,57	**SD**
RSD (CV_w)	2,18	1,91	1,13	1,87	1,78	**RSD (CV_b)**
U_w	0,69	0,61	0,36	0,59	0,56	**U_b**
CV_w+U_w	2,87	2,52	1,49	2,47	2,34	**CV_b+U_b**
CV_w-U_w	1,49	1,31	0,78	1,28	1,21	**CV_b-U_b**

E. EVALUATION OF HOMOGENEITY

The coefficients of variation (relative standard deviation) were obtained from the between-unit and within-unit homogeneity tests (CV_B and CV_W respectively).

Their respective uncertainties U_{CV}, are defined as follows:

$U_{CV} \approx CV/\sqrt{2n}$, where n = number of replicates.

No inhomogeneity is detected when the uncertainty ranges of the two coefficients of variation overlap, or when
$CV_B \pm U_{CV}$, and $CV_W \pm U_{CV}$ show overlap.

Variation coefficients and uncertainties are also presented in *Table 2-7* based on copper, nickel and lead analytical results.

The evaluated values from between-unit and within-unit homogeneity test are summarized in **Table 8**.

The bolded values inside the range ($CV_B \pm U_{CV}$) indicate the homogeneity of sediment RM and it is plotted in **Fig. 1-3.**

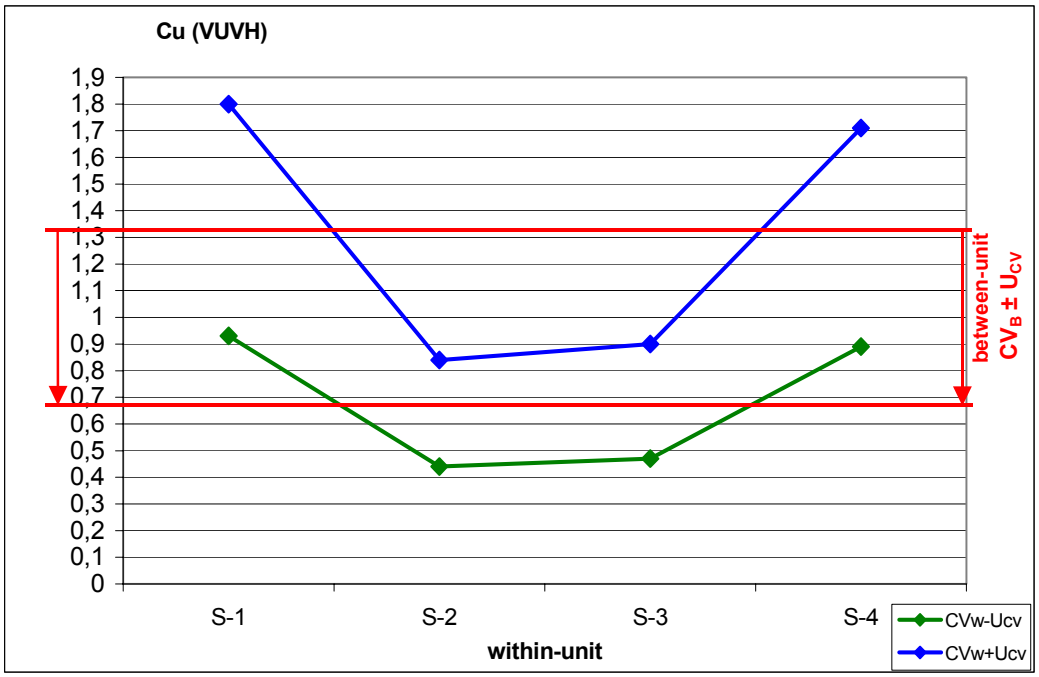
The requirement of homogeneity – namely the uncertainty ranges of the two coefficients of variation shall be overlapped – is achieved.

Table 8. Evaluation of homogeneity test results

Copper					
VUVH			VITUKI		
$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$		$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$	
0,68-1,31	w_1	***0,93***-1,80	***0,56-1,08***	w_1	***0,59***-1,13
	w_2	0,44-***0,84***		w_2	0,50-***0,96***
	w_3	0,47-***0,90***		w_3	0,54-***1,05***
	w_4	***0,89***-1,71		w_4	***0,62***-1,20

Nickel					
VUVH			VITUKI		
$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$		$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$	
0,77-1,49	w_1	***1,15***-2,21	***2,78-5,36***	w_1	***4,20***-8,09
	w_2	***0,86***-1,65		w_2	2,60-***5,01***
	w_3	0,42-***0,80***		w_3	2,16-***4,15***
	w_4	0,67-***1,30***		w_4	2,18-***4,19***

Lead					
VUVH			VITUKI		
$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$		$CV_B \pm U_{CV}$	$CV_W \pm U_{CV}$	
0,60-1,16	w_1	***0,73***-1,41	***1,21-2,34***	w_1	***1,49***-2,87
	w_2	***0,65***-1,25		w_2	***1,31***-2,52
	w_3	0,38-***0,73***		w_3	0,78-***1,49***
	w_4	***0,64***-1,23		w_4	***1,28***-2,47



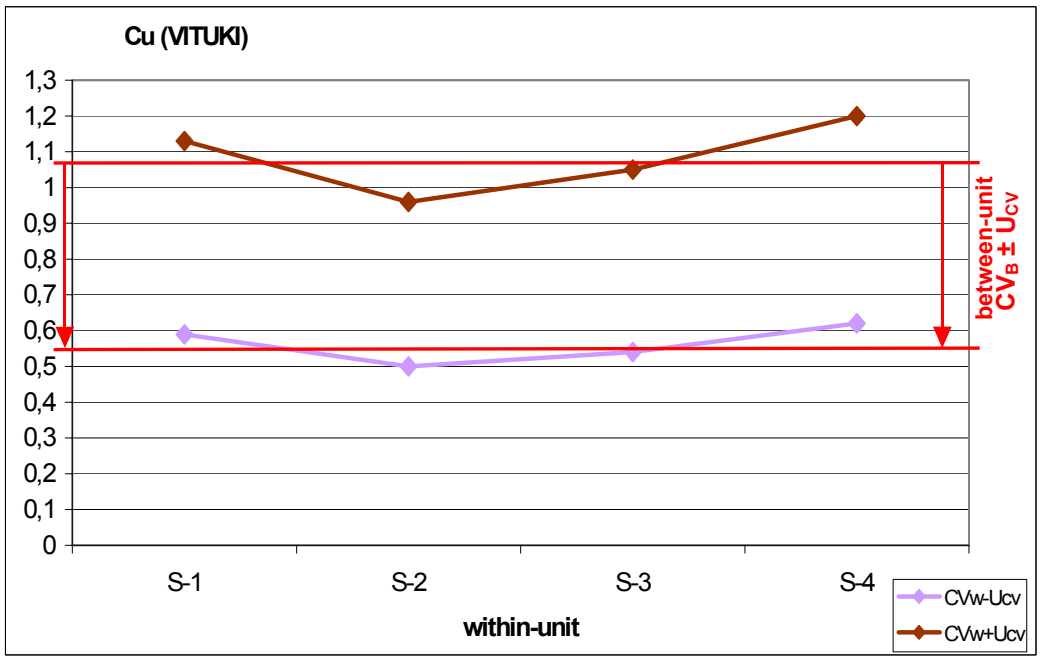
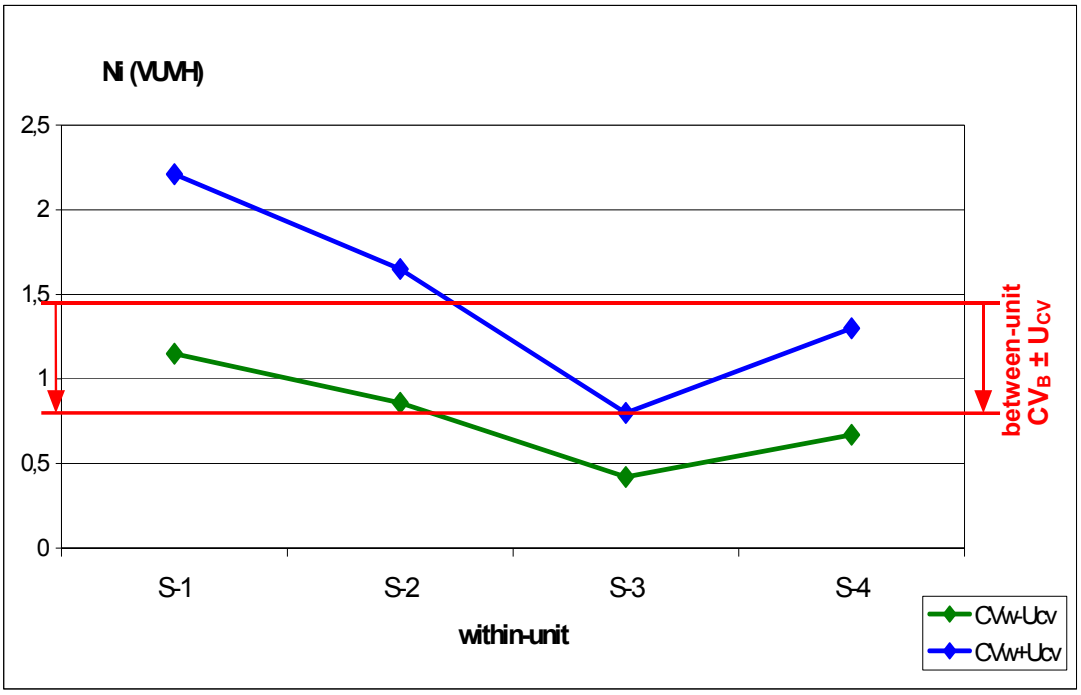


Figure 1. Graphical representation of homogeneity of sediment RM



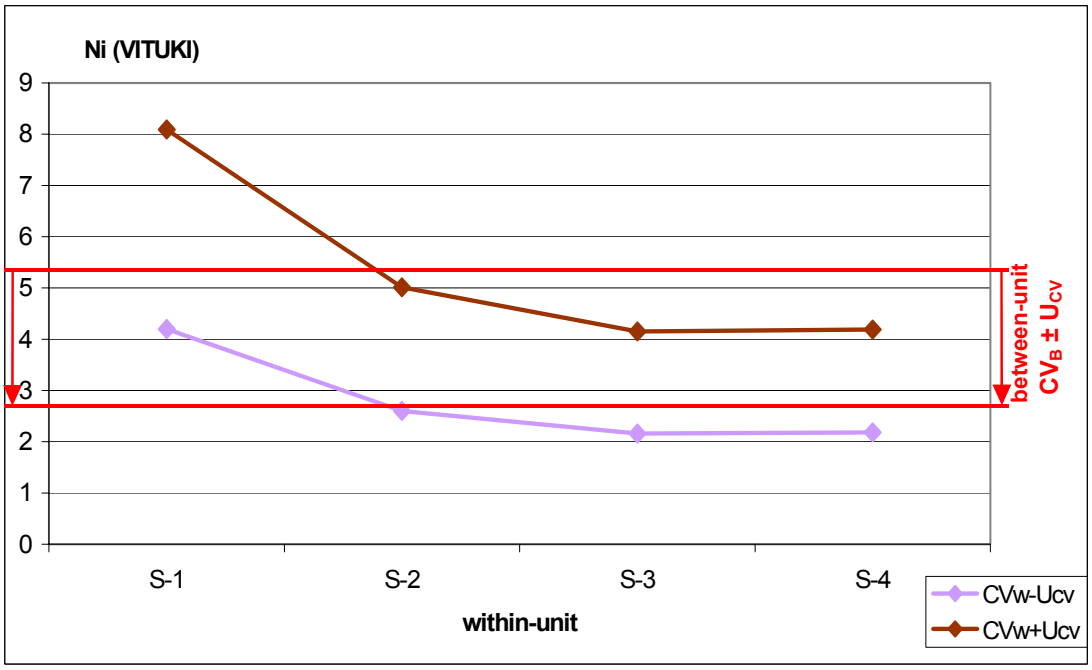
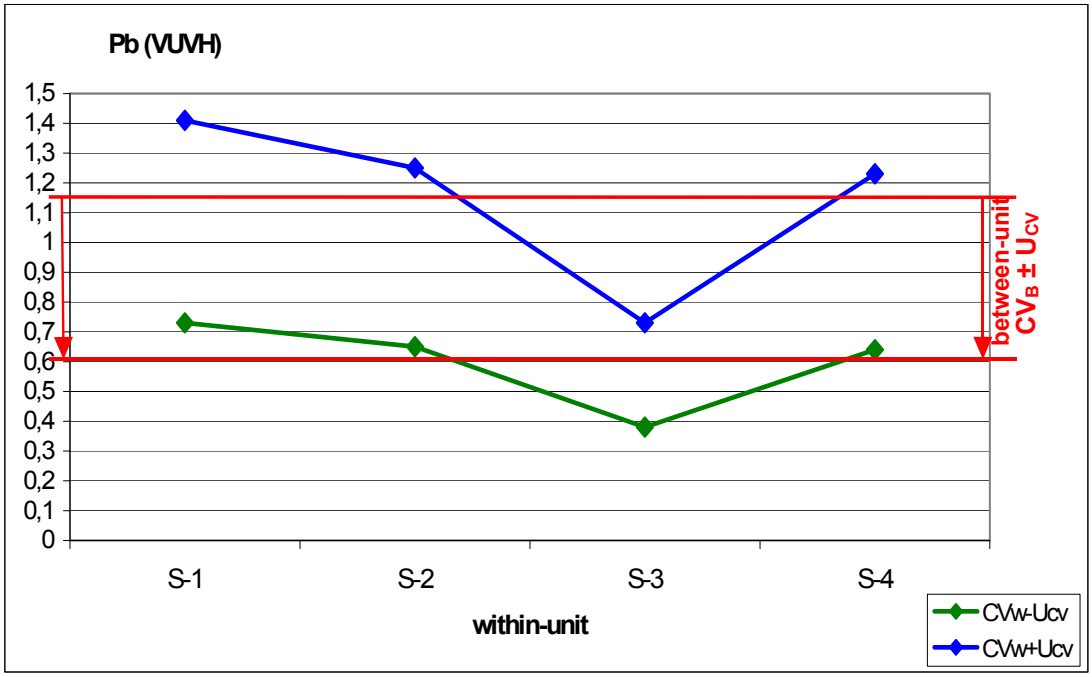


Figure 2. Graphical representation of homogeneity of sediment RM



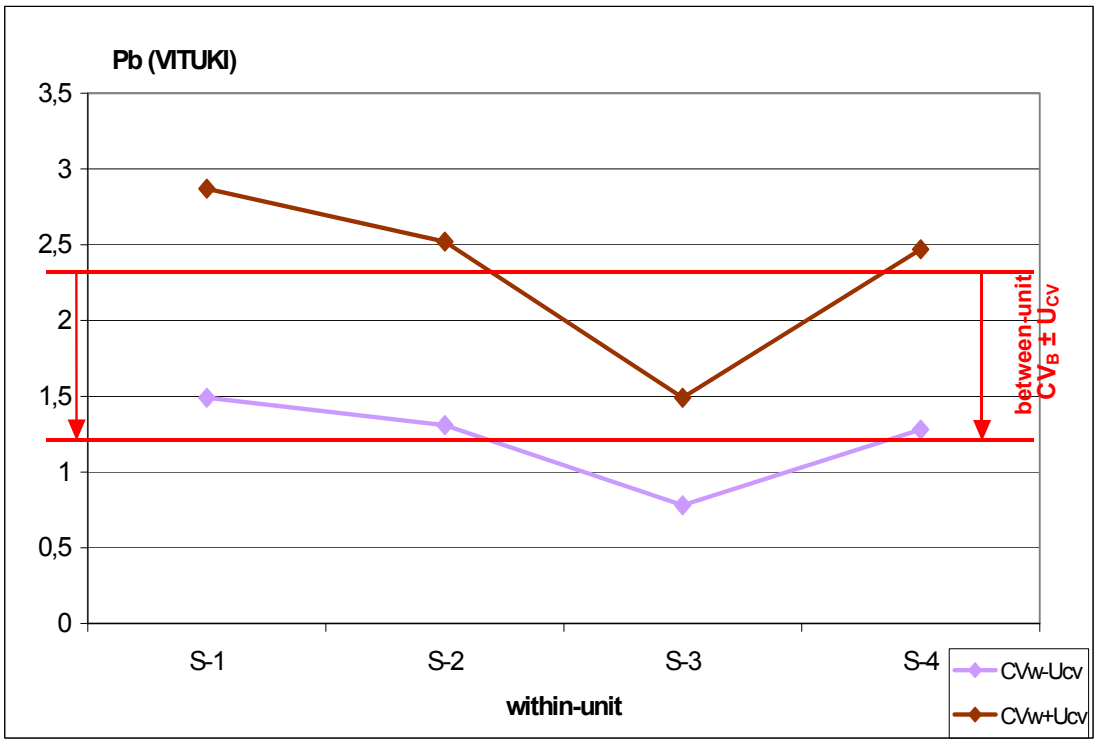


Figure 3. Graphical representation of homogeneity of sediment RM

F. PROGRESS OF WORK

The Project goes forward according to the work plan (Annex 2: paragraph E). The first set of the water RMs prepared for nutrients (ammonium-N, nitrate-N, phosphate-P, total P) and heavy metals (cadmium, copper, chromium, lead, mercury, nickel, aluminum arsenic) were delivered in August.

To prepare the first set of sediment RMs bulk sediment was collected in the Danube. The sediment was processed according to the flow chart of sediment RM preparation (cleaning, drying, grinding, sieving and homogenization). After homogenization bulk homogeneity test was carried out. As the analytical results did not show homogeneity this step was repeated again. After the second homogenization the sediment was bottled and between- and within-units homogeneity tests were carried out. As the evaluated results of homogeneity tests showed homogeneity, the sediment RMs were delivered together with water RMs.

The reference material samples have been prepared and tested according to the "Practical Manual for Production of Laboratory Reference Materials" as well as ISO Guide 34, 1996. Quality system guidelines for the production of reference materials. Ibid.

Budapest, 29/08/2003

Dr. Jolan Schneider
team leader