Kemijski inštitut Ljubljana Slovenija

National Institute of Chemistry Slovenia

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Proficiency testing of wastewater sampling: What can we learn?

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Laboratory for Environmental Sciences and Engineering

http://www.ki.si

- **Basic and applied research**
  - **Environmental catalysis (water purification, energy production)**
  - **Metrology in chemistry (environment)**
  - **Wastewater treatment technologies**
  - **Sludge treatment**
  - **Ecotoxicology**
  - **Process engineering**
- **National and EU projects**
- **Industrial projects**
- **Training and education (diplomas and Ph.D. theses)**

Metrology in Chemistry

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- **Holder of the national standard in the scope of the SI unit mol, based on designation of MIRS**
  - Field of measurements: environment (water)
- **MIRS/KI - Designated institute**
  - Quality system approved by EURAMET TC-Quality in 2006
  - Calibration and measurement capabilities (CMC) approved by EURAMET TC-Metrology in Chemistry, SC – Inorganic Chemistry in February 2010
- **National PT provider – Wastewater** (Slovenian Environmental Agency)
- **Accreditation according to ISO/IEC 17025** (since 2001)
- **EU and national projects**

Interlaboratory comparisons

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NIC
Laboratory for Environmental Sciences and Engineering

ILC - Wastewater sampling
- **Started in year 2012**
- **One round per year**
- **20 labs from Slovenia**
- **Technical meeting**

ILC - Wastewater
- **Started in year 2000**
- **Two rounds per year**
- **50 labs from Slovenia, Croatia and other countries**
- **Technical meeting**

http://mpp.ki.si

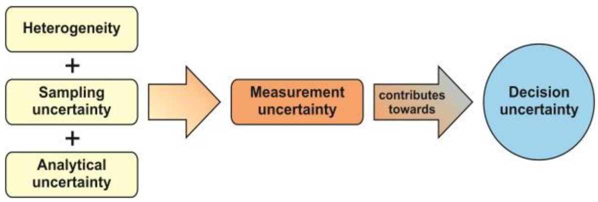
ISO/IEC 17043

eptis

www.eptis.bam.de

Decision chain and uncertainty

http://www.ki.si



- Make measurements more reliable (and the management decision based upon them).
- Integrate sampling into the the rest of the measurement process – take a more holistic approach.
- Organize PT in wastewater sampling in order to compare validated protocols.

Wastewater sampling targets

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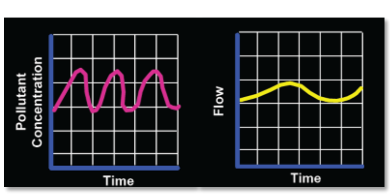
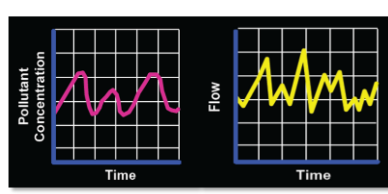
- Investigations related to specific control limits (industrial wastewater).
- Supervision of inlet to wastewater treatment plants for optimization of the wastewater treatment process.
- Surveillance of the outlet from an industry or wastewater treatment plant related to allowable limits.
- Supervision of treatment processes.





Sampling of wastewater

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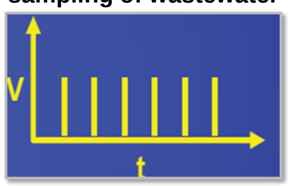
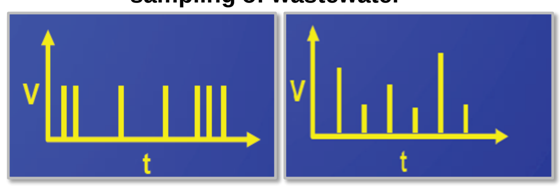
ISO standard describes: manual sampling and automatic sampling.

The principle of using automatic equipment is that the sampler takes a series of discrete samples at fixed intervals that are held in individual containers.

Time proportional sampling of wastewater



Flow proportional sampling of wastewater



*** ISO 5667-10 Water quality – Sampling Part 10: Guidance on sampling of wastewaters**

Overview chart

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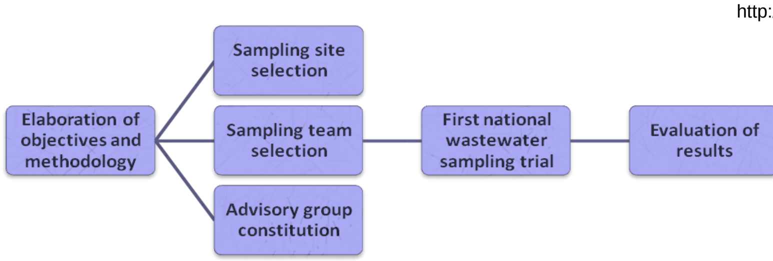

Sampling sites selection

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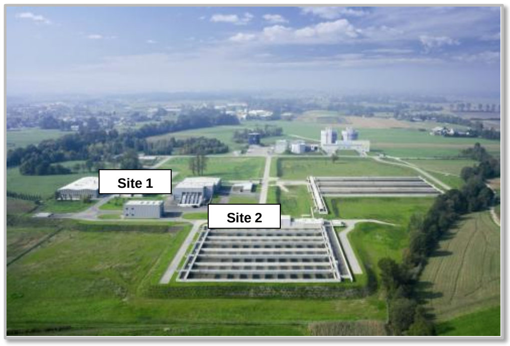

Central Wastewater Treatment Plant Ljubljana

Preliminary tests started in 2010 at both candidate sites to choose for a trial the most convenient one. Wastewater analyses were carried out for the whole year in order to establish the concentration level of target compounds and spatio-temporal homogeneity.

Wastewater analyses

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	Sampling site 1					
	Mean	Median	SD	Min	Max	N
pH, /	7.60	7.58	0.14	7.35	7.90	32
SS, ml L^{-1}	18.8	18.0	7.9	1.9	48.0	33
TSS, mg L^{-1}	414	398	138	126	884	33
COD, mg L^{-1}	395	369	92	247	635	15
BOD_5, mg L^{-1}	432	430	108	184	674	26
TOC, mg L^{-1}	227	222	50.7	173	325	8
NH_4^+-N, mg L^{-1}	37.7	38.7	8.4	17.9	55.3	33
N_{Kjel}, mg L^{-1}	55.1	54.4	11.3	26.7	75.3	33
NO_2^--N, mg L^{-1}	< 0.1					33
NO_3^--N, mg L^{-1}	< 0.5					33
P_{tot}, mg L^{-1}	11.3	11.3	2.43	6.6	16.14	33
PO_4^{3-}-P, mg L^{-1}	4.64	4.47	1.68	2.3	12.2	29
SO_4^{2-}, mg L^{-1}	30.9	30.9	1.0	25.2	35.6	21
Cl^-, mg L^{-1}	132	132	10.5	125	104	21
HCO_3^-, mg L^{-1}	469	465	17.4	450	490	16

SD: Standard deviation
N: Number of measurements during the year

Sampling site

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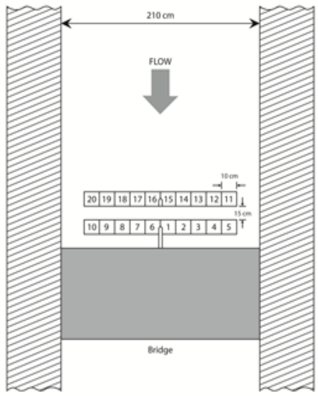

- **The sampling site was prepared in advance for all participants.**
- **Micro locations of participants were determined by organizers.**

Experimental set-up

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- **The participants used 6 hour time-proportional sampling, but they were allowed to follow their own sampling protocols.**
- **The monitoring consisted of both field (pH value, temperature) as well as laboratory measurements (ammonium nitrogen, BOD_5, COD, TOC, TSS and sulphate ion).**
- **All acquired samples were also analyzed at NIC in order to minimize the analytical impact on global uncertainty.**

Used sampling methods

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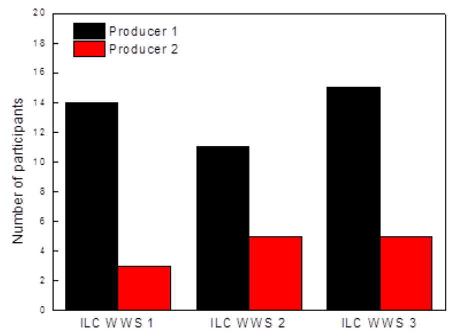
Sampling team	Sampling method
S01	Time-proportional sampling
S02	Time-proportional sampling
S03	Time-proportional sampling (4 × 300 mL h^{-1})
S04	Time-proportional sampling (200 mL / 9 minutes)
S05	Time-proportional sampling
S06	Time-proportional sampling (400 mL / 15 minutes)
S07	Time-proportional sampling (take off of 24 samples of 200 mL in 6 hours)
S08	Time-proportional sampling
S09	Time-proportional sampling (500 mL / 15 minutes)
S10	Time-proportional sampling (50 mL / 6 minutes)
S11	Time-proportional sampling
S12	Time-proportional sampling (take off a sample every 15 minutes); no sample cooling
S13	Time-proportional sampling
S14	Time-proportional sampling
S15	Time-proportional sampling (250 mL / 15 minutes)
S16	Time-proportional sampling (300 mL / 10 minutes)
S17	Time-proportional sampling (take off a sample every 15 minutes)

The participants used various commercially available sampling equipment with different principles of sample collection. All used devices had adjustable time interval between discrete samples from 5 minutes to 1 hour.



Measurements of pH value and temperature

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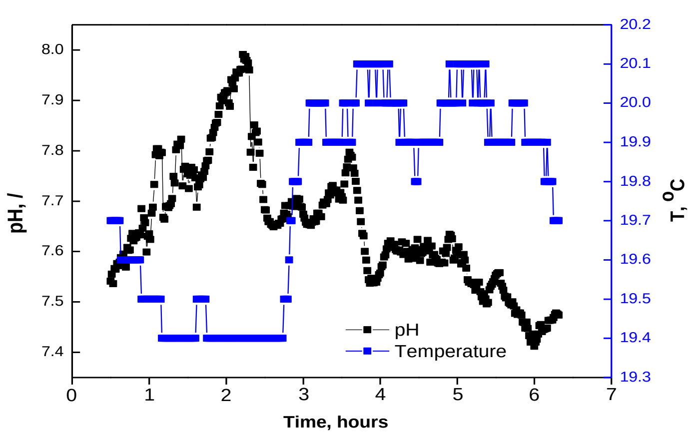

ILC WWS 3

Mean
pH = 7.65
T = 19.8 °C

The pH value and temperature were continuously measured during the trial by placing probes 20 cm below the water level at the sampling site.

Results of field measurements

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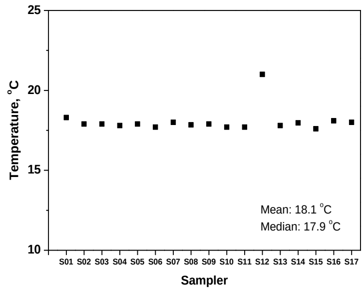
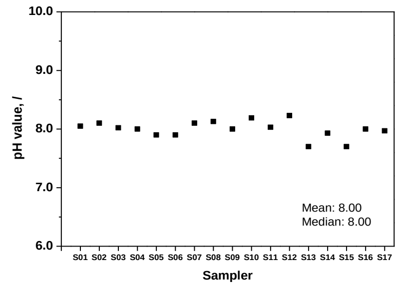
ILC WWS 1





Analytical measurements

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ILC WWS 1	COD, TSS, sulphate ion
ILC WWS 2	Ammonium nitrogen, BOD_5, COD, TOC
ILC WWS 3	Ammonium nitrogen, COD, sulphate ion, TOC

- **Sampling variation can be studied by making analytical measurements.**
- **All samples were analyzed together under randomized repeatability conditions by using a high accuracy method.**

Sample preparation

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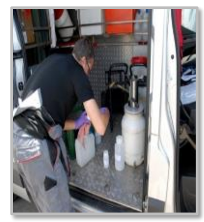
Composite sample → Sample A → Sample A-COD (addition H_2SO_4)

Composite sample → Sample B → Sample B-COD (addition H_2SO_4)



Homogenisation, preservation and sub-sampling were performed by participants following their own protocols and equipment.

NIC was in charge to supply bottles for sample storage and to assure transportation to its laboratory, in order to minimize global uncertainty.

Results - ILC WWS 1

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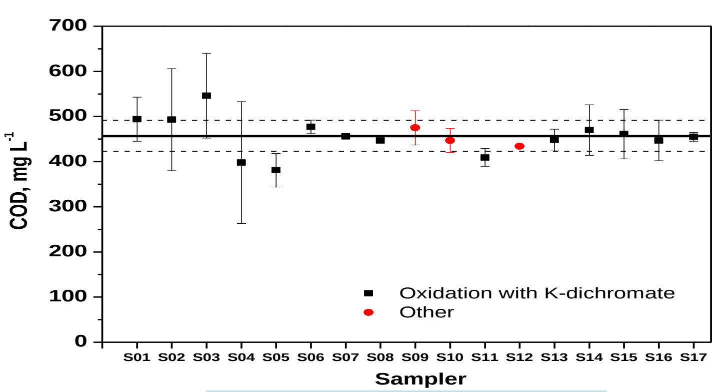

Mean	455 mg L^{-1}
Median	455 mg L^{-1}
Number of results	17
Standard deviation	38.7 mg L^{-1}
Robust standard deviation	29.6 mg L^{-1}
Result range	381 to 546 mg L^{-1}

Results of reported values and measurement uncertainties of analyses performed in laboratories. Results of reference measurements are demonstrated as reference values (solid lines) together with evaluated analytical measurement uncertainty (dashed lines).

Results - ILC WWS 1

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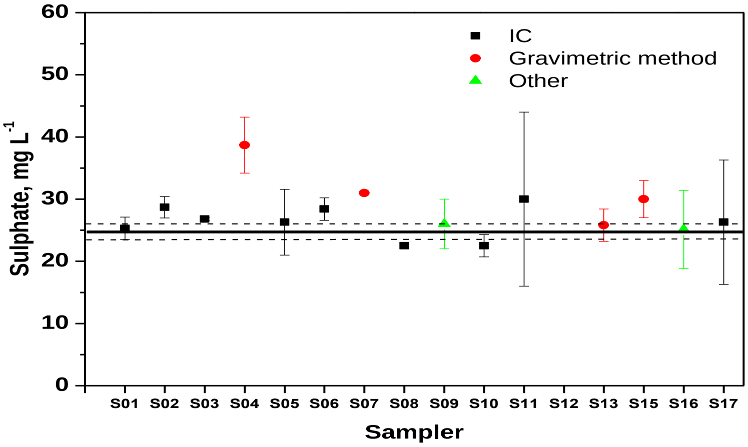

Mean	28.2 mg L^{-1}
Median	26.6 mg L^{-1}
Number of results	16
Standard deviation	2.70 mg L^{-1}
Robust standard deviation	2.96 mg L^{-1}
Result range	22.5 to 38.7 mg L^{-1}

Results - ILC WWS 1

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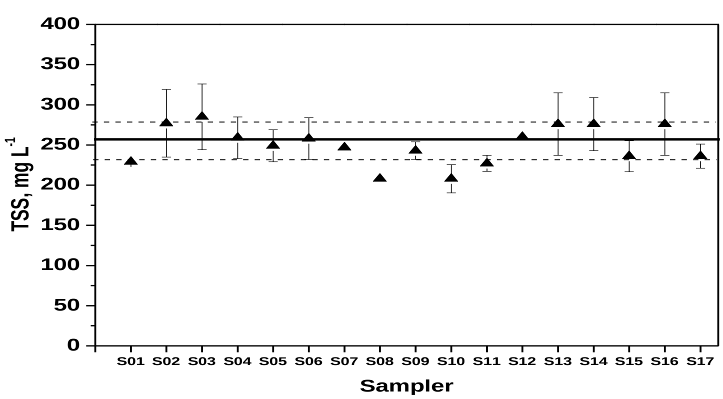

Mean	250 mg L^{-1}
Median	249 mg L^{-1}
Number of results	17
Standard deviation	23.9 mg L^{-1}
Robust standard deviation	29.6 mg L^{-1}
Result range	208 to 285 mg L^{-1}

Measurement uncertainty of reference measurements

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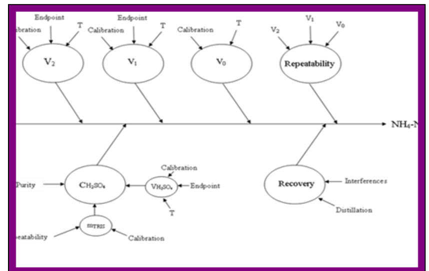

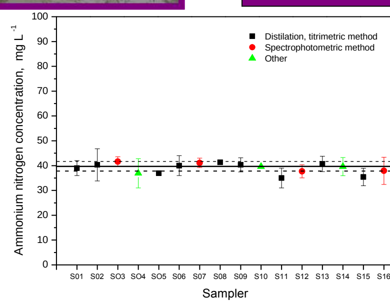

ILC WWS 2

Performance scoring

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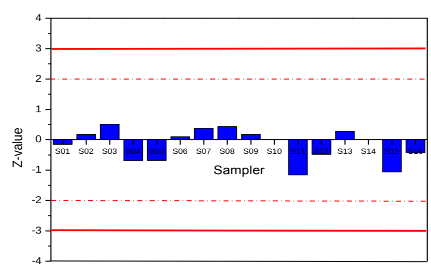
$$z_i = \frac{(x_i - X_A)}{\sigma_p}$$

The standard deviation for proficiency σ_P is best equated with the uncertainty regarded as fit for purpose.



ILC WWS 1 COD
($\sigma_P = 10\ \%\ X_A$)

The scoring must take into account the heterogeneity of the sampling target and the contribution of the analytical uncertainty, both of which should not observe the contribution from the sampling itself.

Measurement uncertainty

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The most complete information about the precision of sampling protocols can be obtained from the SPT, which should involve a sufficient number of experienced samplers (n ≥ 8) and enough typical targets with an appropriate range of analyte concentrations.

$$U_{global} = \sqrt{U^2_{sampling} + U^2_{analysis}}$$

To establish the uncertainty, we decided to focus on the reproducibility (CV_R) standard deviation (expanded uncertainty k=2 is given as 2 × CV_R).

Comparison of results

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ILC WWS 1

	Samples A				Samples B			
	Mean, mg L^{-1}	Median, mg L^{-1}	SD, mg L^{-1}	N	Mean, mg L^{-1}	Median, mg L^{-1}	SD, mg L^{-1}	N
COD	455	455	38.7	17	455	457	21.4	17
Sulphate	27.6	26.3	4.00	15	24.9	24.9	0.77	17
TSS	250	249	23.9	17	260	256	12.8	17

SD: Standard deviation
N: Number of measurements

Measurement uncertainty

	U_{global} (k=2), %	$U_{analytical}$ (k=2), %	$U_{sampling}$ (k=2), %
COD	17.0	9.41	14.1
TSS	19.1	9.84	16.3
Sulphate	29.0	6.18	28.3

U: Expanded uncertainty

Variability between reported results

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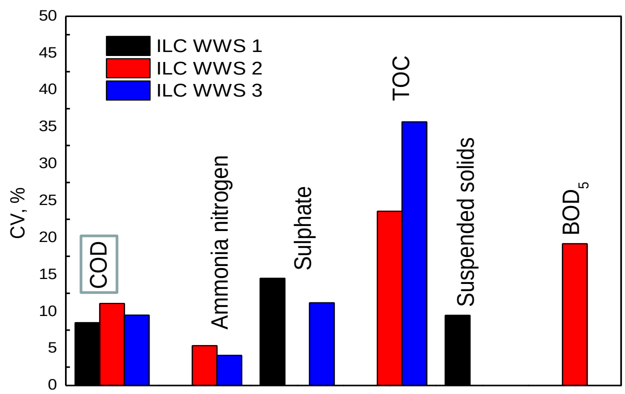

Similar values of the variability between reported results of participants were observed.

Conclusions

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The scope of the exercises was to obtain a realistic picture of wastewater sampling, which was performed on a real sampling site, additionally settled in order to reduce an impact of sampling site on the measurement uncertainty.

The largest sampling uncertainty (i.e. 28 %) was observed in the case of sulphate concentration that resulted in global measuring uncertainty as high as 29 %.

Further PTs will be conducted on a regular basis, in which the used methodology for measuring uncertainty evaluation will be upgraded with other approaches.

Acknowledgements

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