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A project implemented by a Consortium  
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# **Annex IV**

## **Assessment of the chemical Analysis Quality Control of the Joint Field Survey Samples**





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**Assessment of the Chemical Analysis Quality Control of the Joint Field Survey Samples**

Each country's results were reviewed by the NKEC, who visited their analytical laboratories in order to audit the results. This analysis audit entailed selecting certain samples, focusing on a number of individual results and checking them at all levels to ensure that the correct analytical procedures, quality control and quality assurance procedures were applied.

These audits were also used as training exercises for the national laboratories' managers to undertake their own internal audits in future. Many of the countries suffered from incomplete quality assurance procedures. However the audit of the JFS analysis by the NKEC had highlighted these problems and focused on these issues in his training missions with recommendations for improvements for the next JFS. All countries assured the Project that they would be able to correct any omissions by the next JFS and make the recommended improvements. If there should be any further problems the NKEC would be available to provide extra on line support.

The following results were found for each country:

***Armenia***

The JFS analysis was carried out by the Environmental Impact Monitoring Centre (EIMC) laboratory and the following quality control were noted when the NKEC carried out the audit/training in October 2013:

- i.) Staff Training records-were available however should be improved by ensuring that there is record of the date and results the analyst obtained during the training for each parameter.
- ii.) Shewhart Control Charts were not produced for the JFS analysis. However following further training submitted by the NKEC, these control charts were initiated by the new QC Department and were currently fully operational.
- iii.) Method Validations had not been undertaken prior to the JFS. However the UK Method Validation software AQC99 was installed and senior staff were trained on this operation by the NKEC. Therefore it is anticipated that the method validations should be ready for the next JFS.
- iv.) Dedicated Instrument log books to record the analytical equipment's performances were previously not used and therefore unavailable for JFS. However it is anticipated that the new AQC department will establish this for the next JFS.
- v.) Standard Operating Procedures were previously not used and therefore unavailable for JFS. However it is anticipated that the new AQC department will establish this for the next JFS.



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An audit was also carried on the sampling procedures and the following issues were noted:

- i.) The Leading Specialist from the Water Monitoring Department had not been fully trained to calibrate the on-site monitoring sonde. Training was submitted during the NKEC mission and EIMC assured the Project that in future the sonde sensors would be calibrated prior to sampling. A log book should be established to record this.
- ii.) Some of the sampling bottles were not quite correct as some of the large plastic containers had air gaps in the handles. It was recommended that apart from the bacteriological and pesticide samples, there should be no air gaps in the bottles when filled with the water sample.
- iii.) It was recommended that the on site DO readings could be checked in the laboratory by taking samples in dedicated 250 ml glass bottles with ground glass stoppers.
- iv.) The air temperature should be measured
- v.) as should the cooler box for transportation.
- vi.) Qualitative odour tests could be undertaken as described in the Project Physico-Chemical Sampling Manual.
- vii.) The procedure for taking sediment samples was observed and it was recommended that a mechanical grabber should be procured and used to obtain more representative samples.

### **Azerbaijan**

Azecom/National Environmental Monitoring Department (NEMD) of the Centre for Environmental Pollution Monitoring of the Ministry of Ecology and Natural Resources of the Azerbaijan Republic

The analysis for the JFS samples was carried out by Azecom Laboratory, which sub- contracted the general chemical parameter analysis to NEMD.

The following initial quality assurance issues were noted at NEMD during the NKEC mission in October 2013.

- i.) Initially there was a mismatch between the results of supplied by the NEMD laboratory and those submitted to the Project,
- ii.) The limits of detection (LOD) results were incorrect as this concept was not fully understood and further training was submitted.
- iii.) No AQC results were undertaken.

Owing to these problems the NKEC had submitted extra training. NEMD assured the Project that these issues would be resolved and in-future the analysis for the next JFS the correct report would be submitted.

Other issues included:



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- i.) Sampler Records were reviewed and the completed proformats on the samples were satisfactory but could be improved by including the number and type of bottles as shown in the Project Physico-Chemical Sampling Manual.
- ii.) Staff Training records were not available and it was recommended that a system should be established.
- iii.) Method Validations were not available for the JFS but full training using the donated software AQC99 was carried out during the latest NKEC mission for Nitrite. Therefore this should be carried out for all analyses prior to the next JFS.
- iv.) There was no Instrument log book to check the performance of the equipment; this will be applied in the next JFS.
- v.) Ideally the laboratory instruments should be checked and maintained by the manufacturer on a yearly basis. However it is recognized that the department has limited funds to do this. Therefore it was recommended to apply a pragmatic approach by undertaking simple instrumental checks e.g. measure the wavelength calibration using standard dichromate solutions and to review the instrument responses recorded in the log book on a 6 monthly basis. The date of this and the next check could be recorded on a small label attached to the instrument, so all staff should be aware of the instrument's condition.
- vi.) Standard Operating Procedures (SOPs) were yet to be fully initiated, however this would be an ideal task for the newly proposed AQC department.

The on-site sampling training and audit was undertaken at Kurdakhani Lake and the following issues were noted:

- i.) Apart from the bacteriological and pesticide samples, there should be no air gaps in the bottle.
- ii.) The DO readings could be checked in the laboratory by taking samples in dedicated 250 ml glass bottles with ground glass stoppers.
- iii.) The air temperature should be measured as should the cooler box for transportation.
- iv.) Further information recorded regarding the environment such as the excessive foam and litter on the banks of the sampling point.
- v.) Qualitative odour tests undertaken as described in the Project Physico-Chemical Sampling Manual.

### **Belarus**

#### Republican Centre for Analytical Control of Environmental Pollution

Republican Centre for Analytical Control of Environmental Pollution (RCACEP) analysed the heavy metals and pesticides and the rest of the parameters (General Chemical) were analysed by the two other regional laboratories:

Mogilov Regional laboratory of Analytical Control (14 samples) &  
Minsk Regional Laboratory of Water Quality & Soil Pollution.



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Two samples were selected to be audited:

- 1) No 11 Vyazma River Drut type 6 DDT <0.000022 mg/l, which was analysed by GLC with capillary column and ECD detector. All the correct documentation was submitted viz.: Chromatograph, Shewhart Chart, Method validation, and training records of analysts.
- 2) No 7 Tereshkoviichi River Ut Trype 5 for Lead 0.0002, which was analysed by ICP/MS. All the correct documentation was submitted viz.: Emission report for all metals for the sample Method validation, and training records of the analysts.

The laboratory was nationally accredited and, as far as could be seen, their documentation was of a good international standard. The RCACEP was responsible for ensuring that all their subsidiary laboratories also had satisfactory AQC procedures in place. Therefore it can be assumed and that the other laboratories involved in the analysis of the JFS samples had equally good AQC systems, this was also confirmed in previous missions

The following minor recommendations were made by the NKEC:

- i.) The Shewhart Charts' action and warning limits should be constructed before the analysis is undertaken, not after.
- ii.) Standard Operating Procedures may need to be developed.
- iii.) In future the analytical results should be submitted with the associated AQC results and should be submitted not only as a proforma, but also collated in a spreadsheet.

An audit/training of the water sampling at the Svisloch River a sub tributary of the Dnieper, at Korolystshevichy Bridge was undertaken by the NKEC on 5<sup>th</sup> December 2013.

The sampling was carried out well though the following recommendations were made:

- i.) The general chemistry samples' plastic containers could not be completely filled leaving an air gap in the handle, which could affect the analytical results. It was recommended that these should be replaced by bottles that can be completely filled with no air gaps.
- ii.) It would be useful to undertake EC analysis on site as this analysis can change in storage.

The NKEC also provided advice and training on the three type of sampling quality controls viz.:

- i.) Duplicate sampling;
- ii.) Field Blanks &
- iii.) Spikes recovery samples.

It was recommended that the controls i) and ii) should be applied in the next JFS.

## **Georgia**

### The National Environmental Agency (NEA) of Georgia

The analyses for most of the parameters were undertaken by NEA which were audited by the NKEC in September 2013, and the following issues were noted:

- i.) Sampler Records were submitted showing a completed proforma on the sample and were satisfactory.



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- ii.) The chain of custody was submitted but could be improved by including the number and type of bottles as shown in the Project Physico-Chemical Sampling Manual.
- iii.) Staff Training records were available but should be improved by ensuring that there is a record of the training date and results that the analyst obtained during the training for each parameter.
- iv.) Similarly there should be a training record for the water sampler. The audit of the water sampling proved useful, as it clarified the procedures for sampling of total and dissolved metals.
- v.) The record of results were satisfactory but in-future the results should be saved on the computer together with the calibration curve.
- vi.) AQC results were analysed separately from the samples. It was recommended that in-future the AQC standard should be included with every batch of 10 analytical samples and analysed with the samples.
- vii.) The Method Validation was carried out during the NKEC mission for Ammonia; however in-future NEA should carry this out for all main analyses.
- viii.) There was an instrument log book but this should be improved by recording the response of the top calibration standard (e.g. NH<sub>4</sub> -1.5mg/l) to check the state of the equipment.
- ix.) Ideally the spectrophotometer should be checked and maintained by the manufacturer on a yearly basis. However it was recognized that the department had limited funds to do this. Therefore it was recommended to apply a pragmatic approach by checking in-house the wavelength calibration using standard dichromate solutions. Also to review the instrument responses recorded in the log book on a 6 monthly basis. The dates of these checks could be noted on a small label attached to each instrument.
- x.) Analytical Methods were satisfactory but the ammonia standards were out of date (2008 & 2011) and the Standard Operating Procedures (SOP) should be produced for this method and at least for all the other important parameters.

The water sampling also audited on 25<sup>th</sup> September whilst sampling from Tibilisi Sea Lake and it was recommended that:

- i.) Apart from the bacteriological and pesticide samples, there should be no air gaps in the bottle.
- ii.) The DO readings could be checked in the laboratory by taking samples in dedicated 250 ml glass bottles with ground glass stoppers.
- iii.) The air temperature should be measured as should the cooler box for transportation.
- iv.) Further information recorded regarding the environment such as the excessive foam and litter on the edge of the lake.
- v.) Qualitative odour tests undertaken as described in the Project Physico-Chemical Sampling Manual.



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The staff were trained in taking replicates, field blank and on the theory of the spiked matrix quality controls.

These issues will be addressed in future sampling including the sampling for the next JFS.

### **Moldova**

#### The State Hydromet Services, (SHS).

Most of the chemical samples were analysed by Hydromet (SHS) and the audit was carried out on 22<sup>nd</sup> November 2013.

The audit training of JFS results focused on the iron results and Alpha HCB- organochlorine pesticide.

Most aspects of quality control were fine though there were issues that needed addressing:

- 1) The SOPs for the some of the analysis had not been written, only the Gost standards were available. It was recommended that the SOPs should be completed at least for the important parameters ready for the next JFS.
- 2) AQC analysis were undertaken but it was noted that there were different systems for logging these results it was recommended that these systems should be rationalised into one system by the new AQC manager.
- 3) The results of submitted for the JFS did not include the AQC results only replicate tests and not the Shewhart Control results. It was recommended that next time these AQC results should be included in the JFS results.
- 4) It was recommended to place labels on analytical equipment indicating the dates the routine maintenance had been carried out in a clearer position so that the analyst would be easily reminded.

The audit and training of the water sampling was undertaken in at Westmurka Reservoir, near Kishner Gate at the sampling platform. The following issues were noted:

- i. The pesticide bottles were not ideal, as they had large mouth, with a screw top lid. Such bottles could suffer from high evaporation losses of volatile components and also it was difficult to avoid air being trapped in the bottle.
- ii. Three bottles used preservatives: e.g. Sodium Hydroxide (NaOH) for phenol analysis, Chloroform (CHCl<sub>3</sub>) for nutrient parameters, and Sulphuric Acid H<sub>2</sub>SO<sub>4</sub> for petroleum products. It was recommended that with the last two sample bottles these should be washed with the sample before adding the reagents on site.
- iii. These three bottles were 1L amber glass bottles stored un-capped. It was recommended that in future they are stored with their caps on to prevent dust contaminating them. Also the caps had fragile cardboard inserts, which had been damaged by the corrosive preservatives. In fact many of these were so damaged that the actual tin plate lid was corroding. It was recommended that all these caps should be replaced by plastic caps or with new caps with Teflon inserts.



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- iv. Large 2L plastic sampling containers were used to take the other water samples. These were also not ideal, as it was impossible to prevent air being trapped in the vessel and thus contaminating the sample. It was recommended that alternative bottles should be used.
- v. One of the samplers smoked during the sampling audit, ideally this should not be allowed, as the smoke particles could contaminate the samples, especially the organic ones. It was recommended that the samplers should be advised about this problem.

There were four sediment samplers, two were grabbers, which appear to function well. The other two were core samplers- one could be operated manually and the other one could be used remotely. This latter one may only be suitable for taking marine samples. It was recommended that all these could be investigated further in future JFSs.

### **Ukraine**

The NKEC audited the JFS results of two pilot regions in Ukraine in November 2013 viz.: Kiev for the Upper Dnieper river basin and Chernitzvi for the Prut river basin. In each region two different organisations were responsible for the analysis for the JFSs samples.

#### Upper Dnieper River Basin

##### Water Basin-Ukraine Geological Company

This company undertook the analysis of six parameters for the JFS surface water samples.

The NKEC noted that the company ideally needed to update their chromatography methods for the OCPs using capillary columns rather than packed columns. Furthermore it was noted that no Shewhart charts and method validations had been undertaken for the analyses. A training course was presented on 27<sup>th</sup> November so that they should be able to undertake these AQC procedures prior to the next JFS.

##### Dnieper River Basin Management Council (Vyshhorod) (BUVR)

It was stated that following the previous training by the Project about 50% of the analysis applied the internal analytical quality control charts; this is an excellent direction for the department and the project.

Following the audit a number of gaps in quality assurance were identified and the following recommendations for improved supporting information were submitted:

- i.) Some staff training records-were available, however these should be improved by ensuring that there is record of the date and results the analyst obtained during the training for each parameter.
- ii.) Shewhart Control Charts should be further developed for all the main analysis.
- iii.) Method Validations may not have been being carried yet. However customised training was submitted and this procedure should be developed for the next JFS.
- iv.) Ideally a new QC Department should be established to progress the quality assurance and control procedures.



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- v.) An instrument log book should be used to record the response of the top calibration standard for the analytical instruments to check the equipment performance.
- vi.) Standard Operating Procedures need to be prepared- hopefully this could be initiated by a new QC department, if established.

### The Prut River Basin

#### Prut & Dniester River Basin Management Council Chernitzvi BUVR

Following the previous AQC training by the Project, there were five parameters in which internal quality control (Shewhart) charts were applied using customised software from Romania, which appeared to work well.

The AAS method using flame atomisation for some of the heavy metals required further validation research to confirm the LOD. The other alternative recommendation was to use another AAS accessory called furnace atomisation.

To address the gaps noted and to ensure the quality assurance procedures would be improved for the next JFS, the following recommendations were submitted:

- i.) Some of the Staff Training records these maybe available however these should be improved by ensuring that there is record of the date and results the analyst obtained during the training for each parameter.
- ii.) Shewhart Control Charts should be further developed for all the main analysis.
- iii.) Method Validations had not been being carried out. However as training was submitted, then this procedure should be developed for the next JFS.
- iv.) An Instrument log book was required to record the response of the top calibration standard for the analytical instruments to check the state of the equipment.
- v.) Standard Operating Procedures need to be prepared.

#### The Research Centre of Preventative Toxicology, Food & Chemical Safety of the Public Health Ministry of Ukraine

This Research Centre undertook the analysis of Arsenic and the OCP analysis for the River Prut JFS Samples. This laboratory had been internationally accredited with ISO 17025 for about three years.

One Surface Prut water JFS sample was audited, #4865/873-10 SW Prut sample 1 Prutets-Yablunitskiy River for the following parameters:

Arsenic <0.01µg/l Spectrophotometric Method  
HCB <0.0061 µg/l – used capillary GLC

All supporting information for the audit was submitted and it was recommended that this laboratory could be used as a model or local Project training centre. It was also recommended that links via a technical working group should be established between BUVR and the research centre so that BUVR could be assisted with their quality controls and methods.