



Twinning Project - SR 2005/IB/EN/01 Capacity Building of the Directorate for Water

between the Ministry of Agriculture, Forestry and Water Management of Serbia and the
German Ministry for Environment, Nature Conservation and Nuclear Safety

Component 2: Support for the upgrading of the water monitoring system

Sub-Component 2.1. Enhancing monitoring system and laboratory capacity

Activity 2.1.6 “Technical implementation plan for enhancing laboratory equipment and capacity ”

Activity 2.1.7 “Training of laboratory staff processing/handling of samples and analytical techniques”

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Twinning Project “Capacity Building of the Directorate for Water”
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Project Activity 2.1.6

“Technical implementation plan for enhancing laboratory equipment and capacity”

I. Method

The works under this activity concentrated and focused on the laboratories of the Republic Hydrometeorological Service of Serbia (RHMS) as this institution is the competent institution for surface water and groundwater by law in Serbia. Although focussing on RHMS for this project the experts also visited laboratory installations of the Institute of Public Health of Belgrade, the Institute for Public Health of Serbia “Dr. Milan Jovanovic Baturt and the Water Control Department of the Belgrade Waterworks.

The laboratory of RHMS is a subdivision of the division “Environmental Protection Sector”.

The laboratory is split into the two departments:

- Instrumental department
- Wet chemistry department

First objective was to get an overview about the capabilities to fulfil several requirements of the Water Framework Directive according to the chemical parameters (e.g. Priority list of Annex X). In detailed the following items were discussed with the Serbian experts:

- the working capacity of the laboratories
- the quality and quantity of the equipment
- the conditions of the building
- the infrastructure in which the laboratory is integrated.

II. Current concept of the laboratory tasks:

Serbian government requests from RHMS laboratory to perform systematic water quality monitoring of surface water and ground water in shallow aquifer, in certain dynamic and certain profiles. RHMS is also obliged by accidental pollutants of groundwater and surface water to sample and assess the water quality and issue an opinion to the Ministry of Agriculture.

The laboratory must be integrated into the planning of all monitoring activities since these require laboratory capacity.

It might be a vision for the future that RHMS will be responsible to advise the Serbian government in urgent questions relevant for the aquatic environment as well as rivers and groundwater. Currently the laboratory is analysing thousands of water samples of inorganic and organic standard parameters. The analysis of these samples binds 100 % of personal capacity. Therefore, time is very limited for innovation, establishing/developing new analytical methods and to adequately advise the government in emerging environmental issues.

III. Laboratory staff

Current situation

In total 18 persons are working in the chemical laboratory, including the head of the laboratory. 2 chemists for metal analysis, 1 engineer of technology and 1 chemical engineer for basic parameters, 2 chemists for organic analysis, 1 chief (physical chemist) for instrumental laboratory, 2 biologists, 8 technicians, 1 head of laboratory. One position of the chief for wet chemistry and one for a technician are vacant. The laboratory is accredited for certain parameters to the ISO Norm 17025.

Skills of the staff

The staff showed that they are very well educated to fulfil their main tasks according to measure a high number of water samples for sum parameters, metals, nutrients and routine organic parameters. A deficit can be seen in running the new instruments due to missing training courses on WFD parameters. Due to the history of the institute the skills for inorganic parameters are higher than for organic parameters. Therefore, even more training courses than carried out under activity 2.1.7, are recommended for the staff involved in the analysis of the organic parameters.

Necessary staff in future

The existing staff is not large enough to attend the upcoming monitoring requirements in future and needs upgrading in numbers.

In order to fulfill the tasks of monitoring of the biological quality elements (BQEs) by RHMS the necessary equipment and what is more important staff with academic formation is necessary. Only this will guarantee that the upcoming issues of a harmonization of the monitoring programme according to the WFD as envisaged by Serbia (see strategy under activity 2.1.2 and the monitoring programme of the Kolubara River developed under project activity 1.2.3) can be provided in future. At least four specialized biologists (for the elements

fish, macro invertebrates, macrophytes and phytoplankton) are necessary to attend the monitoring needs in future.

The water quality department of RHMS and the laboratory will face the development of adequate assessment methods for the corresponding BQEs.

IV. Taking and storage of water samples

Most of the samples are supplied by the Hydrology Division of the same institution to the laboratory. The laboratory has no influence on the date of sampling and delivering. There is obviously no procedure for transporting the samples in a proper way. Because of this, the samples have no clear history, when they arrive in the laboratory.

The sample storage does not represent the common technical state of the art. Especially the possibility for cooling and darkening the room at the central sample storage is missing. This has to be modified first, the draft of the field handbook developed under activity 2.1.5 offers guidance for this.

The sampling process can by no means be separated from the laboratory section, analysis and sampling has to be organized from one hand in order to guarantee an efficient and save approach. Sampling and analysis should be preferably in one hand. If this is not possible, the handling of the samples should be clearly described and commonly organised and planned. In any case the storage of the water samples should be improved in case of the following parameters: all organic contaminants, nutrients and sum parameters. For instance enabling a storage temperature of 5°C and the darkness of the room for all organic parameters as well as nutrients and sum parameters is essential.

If this is not encouraged the invested time and effort into analysing such samples is per se scientifically questionable.

The provision of an adequate number of staff to organize the necessary collection of samples is a “sine qua non” condition in order to provide sound and reliable results.

The number of staff has to be derived from the sampling effort in future under consideration “*Strategy for the redesign of the monitoring programme for groundwater and surface water in Serbia*” (see for more information report to activity 2.1.2 of this project). As the new strategy was used for planning a future monitoring within the Kolubara river catchment area for surface water and groundwater experiences derived can be used to estimate the number of

staff and funds necessary in future. The pilot experience will also provide an overview of the “what” and “how much” to measure in future and to estimate the effort.

V. Laboratory equipment

Instrumental equipment recently provided by the EU

- GC/MSD with EI, purge and trap, twister
- GC/ECD & NPD
- Several photometers
- FTIR spectrometers
- Freeze drying machine
- Milli Q devices
- LC/MS
- ICP/MS
- AAS with graphite furnace, AAS (hydride system)
- 2 microwave devices

The lab personal is currently not able to run all these new instruments meaning to use the full potential properly and training seminars described under activity 2.1.7 were delineated with the Serbian partners and described below.

Va. Appropriateness of the instrumental equipment for chemical parameters

Metals, sum parameters

The instrumentation is totally up to date and fulfils all requirements needed to measure the parameters listed in the WFD.

Anions

Photometric methods are used for anions such as PO₄³⁻, Cl⁻, NO₃⁻. The high number of filtrated water samples would make it possible, that they could be analyzed by help of Ion-Chromatography in a more effective way.

Organic parameters

Analysis of water and sediment samples for non polar organic compounds content - organochlorine and organophosphorus pesticides, PCBs, PAHs, phenols, triazine herbicides in water and sediment are carried out in accordance with international standards after EPA

methods, by liquid-liquid extraction and by detection and quantification with help of ECD, FID, NPD, ATD, FPD detectors since 1985 (and they are as such accredited), and from 2007 also the MSD detector is in use for this purpose.

GC/MS Agilent Technologies was obtained from the EAR mid-2006 and it is already in use for measuring of content of the following parameter: organochlorine pesticides, PCBs, PAHs, phenols, triazine herbicides.

The analysis of priority list-compounds is already included and it will be in routine application after the new systematic monitoring program is adopted.

Total Petroleum Hydrocarbons content is also being measured from 1986 in water and sediment, according to the method EPA 418.3, by liquid-liquid extraction and IR detection, and from the 2004 also by FT-IR detection.

The international intercalibration tests (Wituki, Hungary) which is continuously being carried out several times per year since 2002 show that the analytic works in this area is satisfactory concerning all criteria given.

The results of water and sediment analysis for organochlorine pesticides content, PCBs, PAHs, triazine herbicides in the framework of the project JDS-2 (August-September 2007) show full compliance with the results of european laboratories in charge for this type of analysis.

Lipophilic compounds such as PCBs, organochlorines can be analyzed in the water phase by GC/MS or GC/ECD and PAHs by GC/MS or LC/MS. The polar pesticides such as triazines and phenyl urea herbicides can be analyzed by LC/MS/MS or after derivatization by GC/MS.

A major deficit can be seen for the analysis of polar compounds which will be crucial for the revised priority list of Annex X and those specific pollutants (e.g. pharmaceuticals) currently in the lists for river basins for the ecological status. Due to inappropriate sensitivity, the LC single MS provided by the EU will not allow to measure those polar compounds in low concentrations. **Therefore, it is strongly recommended to enlarge the equipment for organic analysis by an LC tandem MS. That would help to measure also polar emerging compounds and will reduce the time of the sample preparation.** The existing LC single MS can only be used for analysis in accidental cases with higher concentrations.

V.b Appropriateness of the instrumental equipment for biological parameters

In order to fulfill the tasks of monitoring of the biological quality elements by RHMS the necessary equipment and what is more important staff with academic formation is necessary. Only this will guarantee that the upcoming issues of an harmonization of the monitoring programme according to the WFD as envisaged by Serbia (see strategy under activity 2.1.2 and the Monitoring programme of the Kolubara River developed under project activity 1.2.3)

can be provided in future. At least four specialized biologists and equipment work places etc. (for the elements fish, macro invertebrates, macrophyta and phytoplankton) are necessary to attend the monitoring needs in future.

VI) Infrastructure of the laboratory

Rooms and infrastructure

The room conditions and infrastructure should be improved in some cases. The capacity of the fume-hood in the room with the micro-wave digestion equipment seems to be insufficient and has to be enlarged. In general, the size and the conditions of the rooms are appropriate for the given tasks.

Furthermore the capacity of the fume-hood in the room with the micro-wave digestion equipment seems to be insufficient and the room and digestors are not in function from the start.

Accreditation according to ISO EN 17025

The laboratory is accredited according to the ISO EN 17025 by the accreditation body of Serbia (ATS). A survey is made every year by this institution. After five years re-accreditation is carried out.

Analytical quality assurance

The laboratory controls its own analytical results external by participation in inter comparison tests and internal by measuring international certified standards for a set of representative parameters. As a further step in intensifying AQS the implementation of control charts can be recommended.

Laboratory information and management system (LIMS)

The data produced by the different analytical devices are collected and reported without any LIMS. Taking into account the high number of samples the laboratory has to run, a LIMS is strongly recommended. This could help to give a better overview about the results and their combinations and avoids mistakes which can occur during manually data-transfer (this issue is addressed in details under project activity 2.2.3).

VII. Further general considerations

Since the standard parameters can be easily sub-contracted to external labs we recommend to significantly reduce the number of samples analyzed for the standard parameters and to

concentrate the work more on emerging issues. The quality of sub-contracted work can be confirmed by a parallel analysis of 10% of the samples by the RHMS laboratory. With the free capacity the RHMS laboratory will be able to develop methods for emerging pollutants such as new pesticides, pharmaceuticals, hormones, perfluorinated compounds, biocides etc. That will enable the laboratory to advise the government in all these topics. Furthermore, it is suggested to integrate diploma and PhD students in order to develop new methods and to use the new instruments.

The suggested shift in the laboratory concept will set the laboratory in the position to participate in European projects as a partner. Via EU research projects the RHMS laboratory can receive extra money for consumables and to hire temporary staff. With that respect we recommend to enlarge the co-operation with international laboratories and that the laboratory scientists of RHMS participate on international meetings at least once the year.

Project Activity 2.1.7

“Training of laboratory staff processing/handling of samples and analytical techniques”

1. Method

Under project activity 2.1.7 four training seminars directed to the laboratory of the Republic Hydrometeorological Service of Serbia (RHMS) in the field of instrumental trace analytical techniques were agreed with and organized the Serbian partner.

The seminars aimed of enhancing the knowledge of the staff for instrumental analytics in the operating the modern and donated laboratory equipment of the EC. Thus was done in the concept that the powerful and modern equipment could be used appropriately. The seminars were held of German experts in the following field:

2 Seminars upon the use of application of liquid chromatography and mass spectrometry for the analysis of polar substances in water (LC/MS) (Date 22.10.-26.10.2007 and from 21.07.-25.07.2008)

The presence of polar substances in water is becoming prominent environmental issue. This is also reflected in the Annex 10 „Priority Substance list“ of the Water Framework Directive. The analytics for such compounds require the development of adequate methods to detect such substances. For this reason this issue was addressed by the given seminars.

Both seminars were held by the STE Mr. Dirk Loeffler who is a specialist in this type of analysis and works for the Federal Institute BFG (Bundesanstalt für Gewässerkunde) /Koblenz. The seminar focused on running calibration runs with polar standard substances and necessary essential preparatory steps for running the equipment. The second seminar addressed advanced aspects of analysis of polar compounds of water and sample preparation in the lab. Isotope (not radioactive) marked standard substances are essentially necessary for a sound calibrating and the estimation of recovery rates and very difficult to purchase, since the customs procedure are long lasting and represent a barrier. For an efficient laboratory process this is a must in future. Otherwise all effort i.e. the results produced become questionable.

Evaluation

At the end of the seminar it was checked that the analyzed standards could be traced with adequate accuracy meaning that the elaborated laboratory method is successfully applied, but will need further development by routine and practice. The existing LC/MS equipment is not convenient and efficient for the analysis of a highly complex matrix represented by surface water, where many disturbing compounds could be found. The provision of one Tandem LC-MS equipment would be of substantial help. Otherwise the analytical possibilities remain technically limited.

1 Seminar upon the use of oil spill identification with the help of gas chromatography and mass spectrometry (GC/MS) (Date 23.06. - 27.06.2008)

Oil spill by accidents or illegal discharge are an issue of serious concern in Serbia, more important when they are occurring on the Danube a becoming a trans boundary issue. It is often difficult or impossible to trace its origin or the relevant polluter.

STE Gerhard Dahlmann held a five day training seminar with the laboratory staff of RHMS and introduced the Serbian colleagues into the analytical techniques. the method provides tools to identify and match oil spills by „fingerprint matching“ of gas chromatograms which could be compared with data base results containing reference material of worldwide petrol extraction wells or with suspicious polluters. Within this seminar a standard laboratory method was established for the laboratory of RHMS.

Evaluation

At the end of the seminar it was checked that the analyzed standards could be traced with adequate accuracy meaning that the elaborated laboratory method is successfully applied, but will need further development by routine and practice. The methods were developed that GC/MS results can be potentially interchanged between institutions in future and discussed among competent experts without sending any water samples.

1 Seminar upon multi-element analysis with the use of induced couple plasma and mass spectrometry (ICP/MS) (Date 28.07-01.08.2008)

The new ICP-MS equipment allows the simultaneous measuring of heavy metals and elements within one analytical cycle. The operation of the machine is complex and requires deep knowledge of its software. The German expert Ms. Raue introduced the Serbian colleagues into the operation of the equipment by „teaching at the machine“ as all other German experts of the other seminars did. The German expert installed additional software which facilitates the handling of data as excel files, as this was not done before when the

machine was delivered by the manufacturer. The seminar comprised the calibrating of the machine, the measuring and verification of blind values, the checking of the adequacy of the ambient of the machine (which is not satisfactory) as well as measuring certified standards to check for the plausibility of values measured after the training to place. This working approach was also applied in the complementing seminars at RHMS.

Evaluation

At the end of the seminar it was checked that the analyzed standards could be traced with adequate accuracy meaning that the elaborated laboratory method is successfully applied, but will need further development by routine and practice. Concerning the ambient (room) in which the machine is standing it seems probable that the room is not suitable since results produced from blind values, that the room is contaminated with heavy metals which disturbs successful measurements at ultra trace level. Room modification is urgently necessary.

2. General observations/recommendations derived from the works carried out under activities 2.1.6 and from 2.1.7 after the seminars took place

- **Without developing the appropriate collecting of water samples (done in responsibility of the laboratory) which guarantees the quality of the sample and a sound logistic chain all analytical effort should be interrupted in order to save time and effort.** For addressing these short comings the Twinning project has developed a handbook which gives the necessary organizing hints concerning the sampling logistics (see field handbook developed under activity 2.1.5).
- **It is important to stress that the laboratory is severely understaffed and that more persons especially for the taking of samples must be integrated in the laboratory works.**
- Until the sampling deficits are „healed“ the spared time and capacity of the laboratory could be used meanwhile by the staff to gain experience with the use of the instrumental analytical equipment.
- In order to fulfill the tasks of monitoring of the biological quality elements by RHMS the necessary equipment and what is more important staff with academic formation is necessary.

- During the training seminars it became clear that the ordering and availability of consumables and elementary supply of chemicals is a weak point within the organization of the RHMS laboratory. According to the Serbian partners the funds available for maintaining the equipment are not appropriate.
- Isotope (not radioactive) marked standard substances are essentially necessary for sound calibrating and the estimation of recovery rates are not available and nearly impossible to purchase, since the purchasing them is a problem as described above! For an efficient laboratory process this is a must in future. Otherwise all efforts i.e. the produced results become questionable.
- A smooth and well developed supply of standard laboratory material is not given. This is a considerable hindering barrier for providing cost efficient analytics. Relatively cheap consumables are not or only limitedly available.
- The procurement process for purchasing and providing consumables must be modified and streamlined.
- Without the use of internal standards (due to lack of provision of such standards) the measurement respective the results are questionable or cannot be validated.
- The staff involved in analytics is overburdened with analysis (with questionable results, since the sampling of the samples and the logistic chain until the sample arrives in the lab is full of deficits and reflects the bottleneck for reliable results).
- Time should be provided to the very qualified and motivated staff of RHMS for developing the corresponding methods in time.