DISTRIBUTION OF THE SEDIMENT FILL AND ASSOCIATED POLLUTANTS IN BĂBENI RESERVOIR, OLT RIVER, VÂLCEA, ROMANIA

G.V. UNGUREANU^{(1)(#)}, V. BOIAN⁽¹⁾, GHEORGHE OAIE⁽²⁾, ŞTEFAN SZOBOTKA⁽²⁾, DAN SECRIERU⁽²⁾, J. DOMINIK⁽³⁾, J.-L. LOIZEAU⁽³⁾, R. MIHAIESCU⁽⁴⁾

(1) University of Bucharest, Faculty of Geology and Geophysics, Romania
(2) National Institute for Marine Geology and Geoecology - GeoEcoMar Bucharest, Romania
(3) University of Geneva, Institute F.-A. Forel, Switzerland
(4) University "Babes-Bolyiay" Cluj-Napoca, Faculty of Environmental Sciences, Romania
(#) Corresponding author: gigi_ungureanu@yahoo.com

Abstract: Băbeni reservoir is situated on the Olt River, near the chemical platform Rm.Valcea. A large amount of sediments has been deposited since the dam building, 30 years ago. A great role was played by the tributaries Bistrița and Topolog that flow into Băbeni reservoir. Both rivers built important deltas filling the reservoir. Grain-size distribution is in accordance with the evolution of the filling process. Most sediments present great concentrations of heavy metals. The mercury stands out with very high values, up to 8 µg/g. Other metals with concentrations higher than the norms are Ni, Cu and Cr. Cleaning the site is an expensive challenge.

Key words: Sediment fill, Reservoir, Mercury, Industrial pollution

INTRODUCTION

The Olt River is the largest and the longest Romanian tributary of the Danube River: 615 km long with a catchment area of 24 050 km², and a mean water discharge of 160 m³/s. Human impact here is possibly the most serious among all rivers in Romania. Only in its middle and lower reaches, 19 dams and reservoirs have been constructed in the last 30 years along with bank modification. The combined surface of the reservoirs is 21 484 ha with a water volume of 1 753 million m³. The river flow is regulated by the hydroelectric plants according to the need for electricity. The full control of water flow implies the control of sediment load and settling. All this completely alters the natural transport of river water and sediments. Moreover, frequent resuspension of bottom sediments in the upper part of reservoirs occur when filling the reservoirs previously emptied to attenuate the floods.

Băbeni reservoir is situated downstream the city of Rm. Vâlcea, as part of a chain of multipurpose reservoirs: industrial water supply, power generation and flood protection (Fig.1). The contour dams were built mainly on the western bank. Sediments deposited in the Băbeni reservoir are transported by the Olt River and by three of its tributaries: Govora, Bistrița, and Topolog. Many Olt sediments are retained in the upstream reservoirs. The environmental state of the entire area is heavily impacted by the chemical industrial platform that is situated upstream and evacuates effluents into the reservoir. Past and present industrial activity in the region of Rm Vâlcea.

The region of Rm Vâlcea has a high concentration of industrial companies, a lot of them being placed on the industrial platform from the right bank of Olt River (Fig. 1). Two chemical plants are of special interest: "Uzinele Sodice Govora" and OLTCHIM Rm. Vâlcea. The first one is a chlor-alkali plant established in 1955 which became the largest chemical plant of its type in the country. It has discharged a large amount of effluents containing chlorinated compounds which deteriorate water quality and may potentially have serious impact on aquatic life. A considerable discharge of suspension increases turbidity. Although settling ponds and sludges exist, the fine suspension is evacuated to the Olt River, downstream of the Govora reservoir. In the last few years, some technological processes and production of several substances were abandoned during an important restructuring of the production



Fig. 1 Location map of the study area. Sampling sites from the field campaigns from 2005 and 2006 are shown. Source of satellite image – Google

profile. Nowadays, the plant produces lime, Na hydroxide, Na sulphide, detergents, Na silicate and Na carbonate and bicarbonate.

Since 1968, the OLTCHIM Rm Vâlcea plant has been an important source for many types of pollutants due to a wide range of produced chemicals, both inorganic and organic substances. Heavy metals and organic compounds, such as pesticides, HCH, chlorine residues of various types are the main types of pollutant. Even though, during the recent years, this plant has diminished or even stopped the production of hazardous products and also switched to non pollutant technologies, remnant effects of historical pollutant accumulation exist.

Several studies concentrated on the pollution with organic compounds of the Olt River (Toader *et al.*, 1998, 2000a, 2000b, 2000c, 2000d) but virtually nothing is published on the heavy metal problem in the area. The silting up problem of Romanian reservoirs was tackled by Radoane and Radoane (2005) but in a very general manner, with no insights on the processes that contributed to the sediment filling. Garcia *et al.* (2007, 2008) and Ungureanu *et al.* (2007) recognized the importance of Hg pollution in Băbeni area and tried to explain how the mercury reached the system and what is the potential risk for the environment of high concentration of this toxic metal.

The aim of this paper is to evaluate sedimentation in the Băbeni reservoir and its possible environmental consequences.

METHODS

Present day bathymetry was obtained from acoustic measurements on profiles of the water depths, by using a Garmin 238 GPS Sounder, with an operating frequency of 200 KHz (Fig. 2). Digital records have been corrected for water temperature and salinity. The depth has been converted to bottom elevation using the water level recorded by the dam water gauge. All morphological comparison with the predam situation was done using a detailed topographic survey done for the purpose of the dam design.

Water and sediment samples were collected from the Băbeni and Govora reservoirs as well as from the Topolog river and waste-water effluents into the Olt river. The Băbeni reservoir receives the strongest impact from the industrial waste-water, therefore most samples were collected from here. Topolog river was selected to determine the local geochemical background because its basin is devoided of industrial activity and the geological setting is similar to the Olt river. Sediment samples were taken in 2005 using a 5 cm diameter light gravity corer that penetrated 45 cm in Băbeni reservoir and 56.5 cm in Govora reservoir. Surficial sediments were also sampled using a van Veen bodengreifer in 2005 and 2006. Both equipments were operated manually from a small boat. Water suspensions were sampled using Alpha-Laval centrifuge in a continuous flux. After splitting the core tubes, the cores were subsampled for laboratory analyses, including sedimentological and chemical analyses. The subsampling was done considering the lithology of the cores; 23 sediment samples were collected from the Băbeni core, only 19 being collected from the Govora core.

Seventeen chemical components including CaCO₃, TOC, Fe₂O₃ (total), TiO₂, MnO, Rb, Co. Ni. Ba, Sr, Cu, Pb, Zn, Cd, Cr, V and Zr were analyzed by using titration, flame and electrothermal atomic absorption and X-ray fluorescence analytical methods. Titration methods were used for analyzing CaCO₃ and total organic carbon.

Co, Cu, and Pb were analyzed by flame atomic absorption spectrometry, using a slotted tube atom trap for Cu and Pb to enhance analytical sensitivity, and Cd by electro-thermal atomic absorbtion spectrometry on a Pye Unicam SOLAAR 939E double beam absorption spectrophotometer with deuterium lamp background correction. A wet digestion technique consisting of boiling with concentrated nitric acid was used to solve the trace elements. After drying, the residue was heated to dryness with concentrated hydrochloric acid, solved in diluted hydrochloric acid and brought to 50 ml. Factory recommended parameters and optimizing procedures were used for setting up the analytical system. The system was calibrated with a series of standard solutions prepared from spectral pure metals. The analytical results represent the means of three consecutive readings; residual standard deviations were usually less than 2% for FAAS and less than 5% for FTAAS determinations.

Fe₂O₃ (total), TiO₂, MnO, Rb, Ni, Ba, Sr, Zn, Cr, Zr and V were analyzed by X-ray fluorescence spectroscopy on a VRA - 30 XRF sequential spectrometer, fitted with a X-ray tube with wolfram anode, directly on compacted powders. An analyzer crystal LiF 200 was used to select the characteristic wavelengths, measurements being done with a Na(Tl)J scintillation detector. Calibration was carried out with the help of a series of international standards kindly provided by US Geological Survey, The National Institute of Standards and Technology – USA and The National Research Council – Canada, using the relationship between concentration and the difference between the number of impulses recorded at the analytical line and the number of impulses at the background line.

Due to the reduced dimensions of the cores and the splitting of the samples between different laboratories, the quantity of one sample from the Băbeni core was too small to perform the CaCO₃ and X-ray fluorescence determinations. For the same reasons, CaCO₃ determinations could not be performed in seven more samples from the same core. The concentration of mercury was measured using a LECO AMA 254 analyzer. Major and minor components are reported as percentages; trace elements as $\mu g/g$.



Fig. 2 Location of bathymetric profiles used for morphological interpretation

RESULTS

Sediment filling

The sediment deposition was not uniform. Some depocenters can be identified by comparison betweeen the present day and the past topography (Fig. 3 A and B). The sediment fill thickness map (Fig. 3 C) shows that Topolog and Bistriţa rivers created prograding sedimentary bodies. Sediments depocenters evolved into emerged area that cover 13% of the reservoir area. The distribution of the these surfaces (Fig. 5) is a direct consequence both of the fluviatile sediment quantity and of the initial water depth. Therefore, in the shallower parts from the reservoir upstream end, are present 34% and the Bistriţa delta covers 38% of the total emerged area. Topolog River created also its own delta. Although it is greater, the Topolog delta is mostly submerged, due to the greater water depth. Another active deposition is taken place on the left bank.

The comparison between the initial morphology and the present day bathymetry as they are represented along the measured profiles (some of them represented in Fig. 4) offers hints on the way in which the sediment filling evolved and on the differences existing among various sectors of the reservoir. The profiles 13-17 (e.g. profile 15, Fig. 4) demonstrate the active erosion in the upstream end of the reservoir. The bank erosion was caused probably by the change in the flow pattern from a chanelized flow to an areal one, combined with the constantly changing water level in relation to the anthropogenic water flow control. Profiles 10-12 (e.g. profile 12, Fig. 4) are very suggestive for the way in which the sediment fill progrades downstreamwards. The sediments transported into the reservoir are deposited in the proximal area, creating a platform that advances by an abrupt prograding front towards the center of the reservoir. The old channels used by the Olt River are filled. The flattening of the bottom by sediment deposition and filling of previous existing morphological irregularities is demonstrated in the profiles 7-9 (e.g. profile 7, Fig. 4). The profiles 5 and 6 are connected at their eastern end to the Topolog delta. The large amount of sediment deposited in this area creates a strong asimetry between the two sectors (eastern and western) of the reservoir. Closer to the dam (profiles 1-4, e.g. profile 4, Fig. 4), significant deposition takes place only along the banks. In the central part some erosion is noticeable and it can be explained by the hydraulical resuspension of the material when the dam gates are opened. The longitudinal profile demonstrates that the bottom of the upper part of the reservoir has been brought to a relative constant level and emphasizes the abrupt slope of the prograding wedge southward of Topolog delta.

The Gaussian distribution of hypsometric intervals in 1978 is in accordance with the valley morphology, the confluence zone and the position of the dams that comprises a wider area in the center with an average altitude of 191.6 m (Fig. 6 B). In 2005, the distribution is totally changed (Fig. 6 A). The sediments transported by the three rivers flowing into the reservoir were deposited preferentially in front of their inlets and created a flater depositional surface that advances towards the center of the reservoir and downstreamwards. As a result, highest altitudes occupy largest areas.

The sediment thickness map (Fig. 3 C) clearly demonstrates the role played by the two tributaries, especially Topolog in filling the reservoir with sediments. Statistical distribution of the sediment thickness (Fig. 6 C) indicates that, in most instances, between 1 and 3 m of sediments have been deposited.

Sediment grainsize characteristics of bottom sediments vary according to the position within the reservoir (Fig. 7). Greater participations of sand fraction are met in the upper part of the reservoir in the vicinity of the Olt inlet. Silt dominates the sediment grain-size composition in the middle section of the reservoir, where there is a strong influence from Bistriţa and Topolog inputs. Finer sediments are deposited closer to the dam.



Fig. 3 Băbeni reservoir morphology: A – Initial topographic map (1978), B - Present-day bathymetry (2005). Emerged areas are painted black (elevation over 197 m). C – Sediment fill thickness map

HEAVY METALS IN BOTTOM SEDIMENTS

From all metals analyzed, only four (Hg, Ni, Cr, and Cu) present concentrations higher than the legal norms and are of potential danger for the environment. Distribution maps of their concentrations are shown in Fig. 8. Concentration limits admitted in sediments by Romanian environmental regulations for these elements are: $0.3 \ \mu g/g$ for Hg, $40 \ \mu g/g$ for Ni, $35 \ \mu g/g$ Cu and $100 \ \mu g/g$ for Cr.

The most dangerous is the mercury, whose concentration in bottom sediments might exceed 25 times the limit, reaching 8 µg/g. In most situations, the concentration is over 2 µg/g. Hg is widespread in Băbeni reservoir. Highest concentrations are found near the Olt inlet and in the areas with lesser sedimentary input from the Bistrița and Topolog rivers. The two deltas are made up of clean sediments from the point of view of the content in Hg.

Another widespread metal thas passes over the legal limit on large areas is Ni, whose distribution of concentrations suggests a connection with the Bistrița sediments and a correlation with the finer grain-size fraction.

Highest concentrations of Cu and Cr are clearly associated with fine sediments deposited in the lower section of the reservoir near the dam. But it is worth to mention the ressemblance of their concentration contour lines with the ones of Ni. The similar distribution of concentrations for Ni, Cu and Cr suggest an unique source and a similar behavior in the sediments.

Other metals, such as As, Cd, Pb and Zn, are not an environmental problem since the values measured of their concentration do not exceed the admitted limits.

Possible sources of the sediment pollution

There is an important question to be answered. What is the origin of polluting metals? Since there is a high risk of Hg methylation and of its subsequent entering in the food chain with potential health consequences for the surrounding population, it is very important to find out wherefrom and how the mercury has entered the system.

It is well known that mercury was and is still used in the technological processes in alkali-plants. Being a catalysator for brine electrolysis, Hg reaches easily industrial wastewaters. In the case of Rm. Vâlcea industrial platform, there is a two point input of industrial effluents to the riverine system (Fig. 9). Effluent number 1 is a mixture of industrial waste waters made up of "unpolluted" waters collected on the industrial platform, and the limpid overflow from the settling pond. The highly turbid effluent is discharged into Olt immediately downstream the







Fig. 5 Distribution of present-day emerged areas, Băbeni reservoir



G.V. Ungureanu, V. Boian, G. Oaie, S. Szobotka, D. Secrieru, J. Dominik, J-L. Loizeau, R. Mihaiescu – Distribution of the Sediment Fill and Associated Pollutants in Băbeni Reservoir

Fig. 6 Distribution of hypsometric intervals: A- 2005, B – 1978. C- distribution of sediment fill thickness



Fig. 7 Lithologic maps of bottom sediments: A – sand, B – silt, C – clay, Băbeni reservoir

Govora dam. Used technological waters are directed to a biological treatment plant and the effluent, also very turbid and numbered in this paper as effluent 2, is discharged into Govora River, a right-hand side tributary of Olt. Both effluents reach the Olt river in the section comprised between the Govora and Băbeni reservoirs. The lack of mercury in Govora sediments (Ungureanu *et al.*, 2007), points out to these 2 effluents as main suspects for the Hg input in Băbeni. The sampling of bottom sediments and of suspensions in 2005 (Fig. 1) has proven that the suspension from effluent 1 is rich in Hg (41.54 µg/g).

Conclusions

The high rate of fine and medium size sediment deposition lead to a significant sediment fill of the Băbeni reservoir. This causes difficulties in the correct exploitation of its volume, both for power generation and flood control. In this situation there are only a few options to be taken into account for the engineers in order to maintain the operational state of the reservoir. The first potential solution is the removal of the newly deposited material. This could be done partially in the cheap way named "hydraulical flushing". It consists in lowering the water level prior to a predicted high water discharge event and opening the dam gates to evacuate rapidly downstreamwards the high quantity of incoming water and associated resuspended sediments. This option must be avoided, taking into account the high Hg concentration in bottom sediments. Another option is digging out the polluted sediments, treating them and depositing them elsewhere. This second option is very expensive and creates other problems that are difficult to solve, such as finding a place for a large amount of sediments and securing the Hg extracted in the cleaning process. Taking into account that deposition is very active in Topolog and Bistrița deltas, redistributing these relatively clean sediments in order to seal the Hg might be a valid option. But no solution will be effective as long as the pollution does not stop.

Acknowledgments

The work has been financed by SNSF and SDC through the ESTROM Programme, project IB6120-107008 - Environmental assessment of the Olt River reservoirs in the region of Rm. Vâlcea: focus on suspended matter and sediments – ORSED. The team thanks the Romanian Water Authority, the Environmental Protection Agency Vâlcea and the Vâlcea District Council for all the support offered to the ORSED project.





Fig. 8 Distribution of Ni, Hg, Cu and Cr in bottom sediments of Băbeni reservoir



Fig. 9 Scheme of industrial effluents in the study area. Explanations in text

BIBLIOGRAPHY

- Garcia Bravo, A., Ancey, L., Loizeau J.-L., Ungureanu, V.G., Dominik, J., 2008. Historical record of high mercury contamination in the Băbeni reservoir (Olt River, Romania), *Environ Sci Pollut Res*, in press
- RADOANE, M., RADOANE N., 2005. Dams, sediment sources and reservoir silting in Romania, *Geomorphology*, 71 (1-2): 112-125
- TOADER C., CHITIMIEA S., PATROESCU C., 1998. Atrazin bioaccumulation in Babeni Lake biocenosis, *Revista de Chimie* 49 (11): 808-812
- TOADER C., CHITIMIEA S., PATROESCU C., 2000. HCH bioaccumulation in Băbeni Lake biocenoses, *Revue Roumaine de Chemie*, 45 (3): 285-288
- TOADER C., CHITIMIEA S., PATROESCU C., 2000. Some medium toxicity pesticides fading out of an aquatic ecosystem biotope, *Revista de Chimie* 51 (3): 233-237

- TOADER C., CHITIMIEA S., PATROESCU C., 2000. Spreading and degradation of some persistent pesticides in a hydrological regulation reservoir biota. *Revue Roumaine de Chemie* 45 (2): 197
- TOADER C., CHITIMIEA S., PATROESCU C., 2000. Spreading and degradation of some persistent pesticides in a hydrological regulation reservoir biota, *Revue Roumaine de Chemie*, 45 (2): 197-201
- UNGUREANU, V.G., SZOBOTKA, S., OAIE, G., GRACIA BRAVO, A., DOMINIK, J., LOIZEAU J.L., MIHAIESCU, R., 2007. Mercury Distribution in the Bottom Sediments of the Olt River Reservoirs, Romania, 33rd International Conference of SSCH, Tatranske Matliare, Slovakia, May, 2007