E3S Web of Conferences **1**, 10009 (2013)
DOI: 10.1051/e3sconf/20130110009

Distribution of heavy metals (Cu, Zn and Cr) in groundwater from the area of a future radioactive waste repository Saligny – Romania

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Abstract. A study of some heavy metals (Cu, Zn and Cr) concentrations in natural groundwater has been conducted, by considering samples collected from the area located in the neighbourhood of Saligny village (Cernavodă, Romania). Atomic absorption spectrometry methods with thermal and electrothermal atomization has been developed, tested and used for some heavy metals content determination. The results show various concentrations of Cu, Zn and Cr in groundwater samples.

Key words: Heavy metals, groundwater, radioactive waste repository, atomic absorption spectrometry, Romania

Introduction

The contamination of groundwater with various metal chemical species derived from anthropogenic activities is an investigation field which in the recent years made the object of intensive studies, the latter circumstance being a consequence of the corresponding high toxicological potential and of the undesirable effects exerted on the associated ecosystems, and – last but not least – of the effects exerted on the general health condition of the human communities which use the concerned water supplies (Matache et. al.,2009).

In order to determine the total copper, zinc and chromium concentrations in samples of either fresh or waste water, a multitude of analytical techniques are currently utilized, such as: spectrophotometric methods, atomic absorption spectrometry methods, inductively coupled plasma a type of atomic emission spectrometry/mass spectrometry, or electrometric technique (Cave et. al., 2000).

The low and intermediate level radioactive wastes generated by the operation and decommissioning of Cernavodă Nuclear Power Plant are planned to be disposed into a new repository located on Saligny site (Cernavodă – Romania). The repository will be near surface type, with multiple barriers, including red clay layers. The disposal of radioactive waste needs to be carried out in a manner that provides an acceptable level of safety and which can be demonstrated to comply with the established regulatory requirements and criteria.

The main objective of the present study was to evaluate the distribution of copper, zinc and chromium concentrations in groundwater from Saligny area where the low and intermediate level radioactive wastes generated at Cernavodă Nuclear Power Plant are planned to be disposed into a new future repository.

Materials and Methods

An area extending between the Danube and the Black Sea – Danube Channel, in close vicinity of the Nuclear Power Plant at Cernavodă, is being currently considered for the development of a future weakly and medium active waste repository (Saligny FWMAWR). In order to provide a characterization of the site in terms of groundwater hydrology, groundwater samples have been collected during February 2012 from 15 piezometric observation drillings and wells (Fig. 1).

When collected, water samples were filtered *in situ* by means of a Chromatography Research Supplies filtering system, provided with a manual Nalgene vacuum pump. MCE – Millipore membranes, mixed cellulose esters, of 0.45 µm porosity and of 47 mm diameter have been used for filtering. Each membrane filter was washed in ultra – pure water before the experiment and used only once. During filtration, the first 250 mL of solution were discarded, thus allowing the saturation of the membrane surface prior collecting the filtrate. Filtered water samples have been collected in HDPE Nalgene sampling bottles, and for the subsequent determination of copper, zinc and

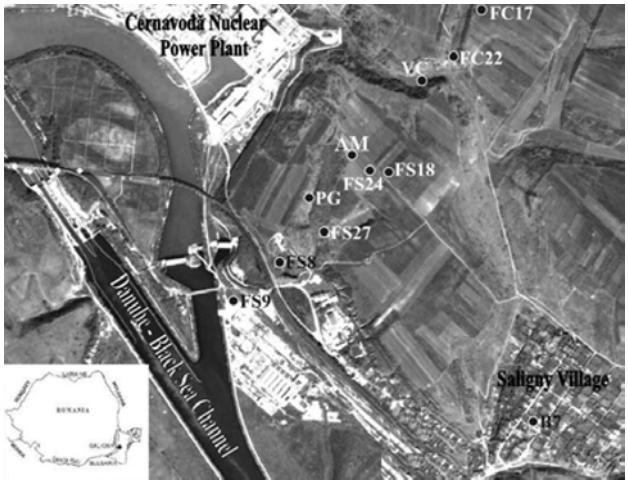

Fig. 1. Location map indicating groundwater sampling sites.

chromium they were acidified with Ultrapure® 60% nitric acid to pH 2 and stored at 4°C.

The Cu and Zn concentrations in water samples were determined in laboratory by flame – AAS (F – AAS), while the Cr concentration were determined in laboratory by graphite furnace–AAS (GF – AAS). The determinations were carried out with a Perkin-Elmer atomic absorption spectrometer, model AAnalyst 700, with deuterium arc background correction, equipped with an HGA – 800 graphite furnace, an AS – 800 autosampler (for GF – AAS) and S10 autosampler (for F – AAS). The calibration lines were traced using solutions prepared from standard solutions CertiPUR® (Merck). The methods accuracy, precision and sensitivity were tested by using the reference matters provided by Perkin – Elmer groundwater and wastewater pollution control certified reference materials (Trace Metals I – 15 elements – Part No. N9300211). All the solutions were prepared with ultra – pure water (TKA Ultra Pure System GenPure, electric resistance 18.2 MΩ×cm). The performance of the employed analytical procedures was determined according to the IUPAC ([Thompson et. al., 1999], [Thompson et. al., 2000]) (Table 1).

Results and Discussion

In Figs. 2 – 4 there are plotted the values of the heavy metals concentrations, determined for the samples collected in the February 2012. Shown in figures 2 and 4 high concentrations of copper and chromium for the groundwater samples taken from drilling AM. High concentrations of Cu can be attributed to the factthat during 2006, in drilling AM were injected copper salts for conducting hydrogeological studies. For this reason, the analytical determination of this element is not natural background concentrations.

For zinc (fig. 3), the highest concentrations are recorded in samples taken from well B7 located in the Saligny village.

Table 1. Analytical performance and validation for thermal and electrothermal AAS methods

Element		Cu	Zn	Cr
Method limit	*n*	*10*	*10*	*10*
		0.008	0.010	0.30
Precision-repetability	*n*	8 (at 0.5 mg/L)	6 (at 0.2 mg/L)	8 (at 10 µg/L)
		0.087	0.0054	0.195
Precision-reproductibility	*n*	*24* (at 0.5 mg/L)	*24* (at 0.2 mg/L)	*19* (at 10 µg/L)
		0.01	0.0132	0.618
Trueness ("bias")	*n*	*24* (at 0.5 mg/L)	*24* (at 0.2 mg/L)	*19* (at 10 µg/L)
	%	0.86	1.58	0.65
Experimental recovery	%	89.1-104.7	87.4-108.0	86.6-98.5

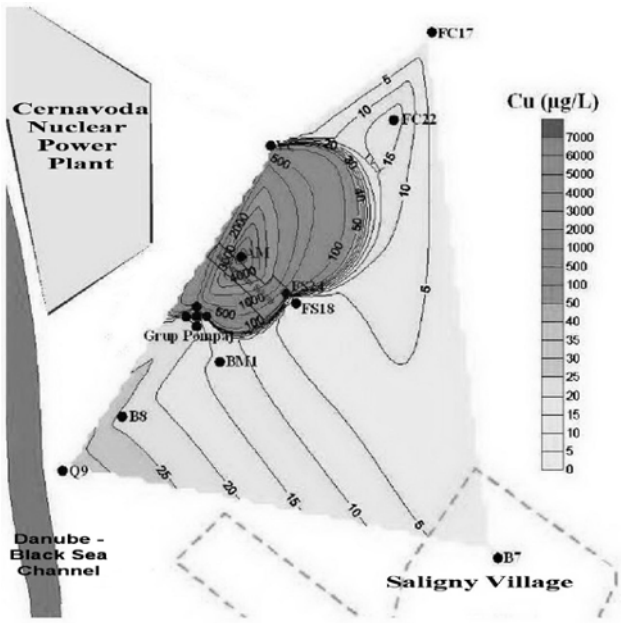

Fig. 2. Distribution of cooper concentrations in groundwater samples.

Conclusion

In order to evaluate the distribution of cooper, zinc and chromium concentrations in groundwater from Saligny area where the low and intermediate level radioactive wastes generated at Cernavodă Nuclear Power Plant are planned to be disposed into a future new repository, water samples have been collected from aquifers with distinct hydrogeological features. The atomic absorption spectrometric method with thermal and electrothermal atomization, has been employed for directly assessing the

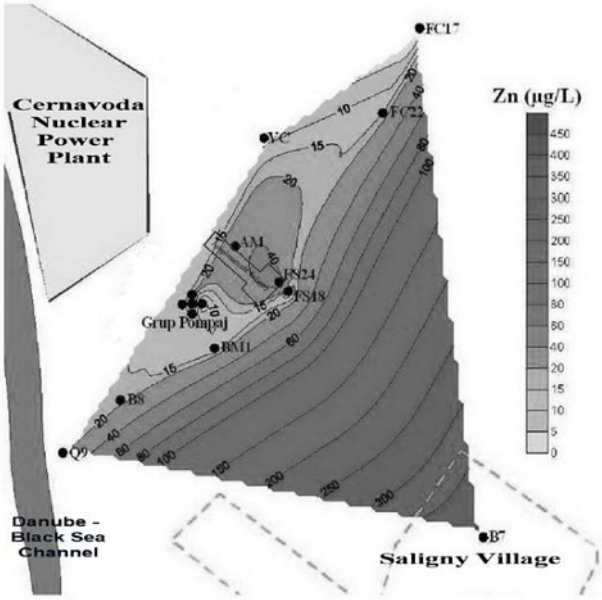

Fig. 3. Distribution of zinc concentrations in groundwater samples.

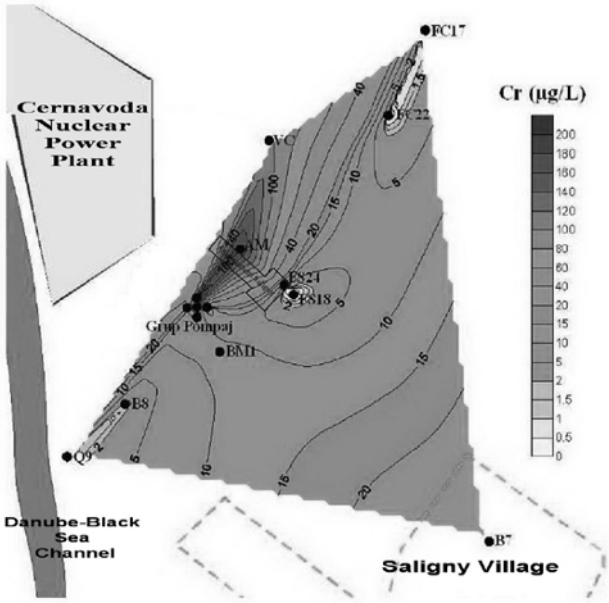

Fig. 4. Distribution of chromium concentrations in groundwater samples.

cooper, zinc and chromium content in all the samples. The results show high concentrations of Cu and Cr in groundwater samples taken from drilling AM (hosted by the Aptian formations), while for Zn high concentrations are recorded in samples taken from well B7 (hosted by the Berriasian formations).

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN– II – RU – PD – 2011 – 3 – 0081.

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