Hg ANOMALIES ON THE ROMANIAN BLACK SEA SHELF: POLLUTION OF RECENT SEDIMENTS OR HYDROCARBON STRUCTURES PATHFINDER ?

Dumitru IOANE (1), Dan SECRIERU(2)

(1) University of Bucharest, Faculty of Geology and Geophysics, 6 Traian Vuia St, Bucharest 020956, Romania
(2) National Institute of Marine Geology and Geo-ecology (GeoEcoMar), 23-25 Dimitrie Onciul St, 024053 Bucharest, Romania
Corresponding author: ioane@gg.unibuc.ro

Abstract. Samples of recent sediments collected during the "ANTARES" international scientific cruise on the Western Black Sea shelf in 1990 and 1991, have been analyzed using a high sensitivity Scintrex HGG-3 Hg spectrometer. The mercury contents displayed a large variation between very low background values and high mercurometric anomalies, the latter closely associated with the geological structures Lebada, Constanta and Callatis. The mercury anomalies are considered to derive from both anthropogenic and geological sources. The pollution with Hg organic and inorganic compounds seems to be better represented on the Lebada-Portita sector, due to its depressionary aspect and location with respect to the marine water currents along the littoral. The deep seated geological sources of Hg, that also contribute to the large mercury anomaly located in the Lebada-Portita area, include hydrocarbon accumulations and highly mineralized waters situated within the Lebada structures.

Key words: Black Sea, Romanian shelf, sediments, mercury

INTRODUCTION

Mercurometry was first mentioned as an exploration method by A.A. Saukov (1946), who studied the abundance of mercury in nature and its association with sulphide ores. During the last decades important advances have been made in studying mercury, its organic and inorganic compounds, due to the increased interest for environment and human community health protection. The Hg toxicity and the consequent environmental problems determined its inclusion on the European Community "black list" of priority pollutants (EEC, 1976).

The main source of mercury is considered to be the mantle, considering measurements on stony meteorites and inclusions in kimberlitic pipes. High quantities of mercury migrate along continental transcrustal faults or very deep faults associated with oceanic ridge systems or subduction settings. Since the mercury migration towards the surface is practically continuous, the mercurometric anomalies may locate "blind ores" or any other Hg source that is covered by thick geological formations or soils. Compact rocks such as shales or unaltered magmatic bodies and lavas may diminish the mercury migration in metallic state or vapour phase, while porous geological rocks, such as sandstones, limestones or tuffs are easily penetrated by Hg toward the surface.

The most abundant mercury bearing mineral is cinnabar (HgS), native mercury being found in base metal sulphides like sphalerite and sulpho-salts like tetrahedrite. The mercury content of rocks is usually less than a few hundred parts per billion (1 ppb = 10^{-9} grams). Soils usually contain less than 100 ppb and water less than 1 ppb mercury, while atmospheric air contains ca. 10^{-9} grams (1 ppb) per cubic meter. High contents of Hg have been noted in areas with volcanic fumaroles, hot spring gases and geothermal waters, as well as on the sediments situated in the vicinity of such sources.

For example, in the Culver-Baer mercury deposit situated in California, an association of cinnabar with petroleum, usually located along hanging walls of breccia veins was observed. Isotopic and biological marker data supported the hypothesis that these components have been derived from sedimentary sequences in response to heating and transported in gas phase. This association of petroleum with cinnabar was considered to be due to a common source and

common transport rather than to a direct geochemical link (Peabody and Einaudi, 1992).

Most mineralized waters that are associated with petroleum in various geological traps contain significant concentrations of mercury, offering good possibilities to mercurometry to be involved in oil exploration. Compared to background values, mercury content in petroleum was found to be 5 to 100 bigger, while in hydrocarbon gases it is 5 to 1000. Airborne mercurometric measurements performed at 200 m above oil accumulations in the Caspian Sea area showed anomalous levels 2 to 3 times greater than the background ones (Fursov, 1983).

Being extremely volatile, mercury can migrate toward the surface through considerable depths of overburden during tectonic activity, weathering and oxidation processes, that liberate metallic mercury or mercury vapours. In cases when anomalous contents of Hg are detected at the surface it can serve as a pathfinder for locating the sources that released mercury.

MATERIALS AND METHODS

The "ANTARES" international scientific cruise investigated the western and north-western parts of the Black Sea continental shelf during 1990. The Romanian continental shelf has been studied on a main profile that was located at distances ranging between 25 and 35 km from the shoreline, the sampling procedures being carried out in stations situated at ≈5 km intervals. This profile, trending NE-SW between the Cormoran and Corbu structures and N-S between the Constanta and Callatis structures, was intersected by three orthogonal profiles at the latitudes of Lebada, Constanta and Callatis structures. The distance between sampling stations on the orthogonal profiles was 7.5-9 km (Panin *et al.,* 1992 a, b).

Among the main sedimentological, geochemical and environmental tasks of this cruise, the collection of samples of recent sediments in the above-mentioned network of stations was one of the most important. During the 1990 cruise the primary samples were collected in all 63 stations using a large capacity Okean type grab with a sampling surface of 0.25 m^2, able to recover a 20 to 40 cm thick pack of almost undisturbed superficial sediments. A 0 to 5 cm depth surface sediment sub-sample was collected from the sediment pack with a fixed volume sampling device, for subsequent laboratory chemical analyses. All sub-samples were dried and grounded on shipboard.

Since the research on the Danube-Danube Delta-Black Sea shelf system was mostly focused on environmental purposes, it was considered that information on the mercury content of the collected samples in the Romanian Black Sea shelf area might contribute to a better understanding of the contamination of marine recent sediments with products from industrial facilities located inland and offshore, along the Danube and the Romanian Black Sea shoreline. Consequently, dried and grounded sample aliquots from 42 stations were used for mercury determinations. Offshore stations from the orthogonal profiles and a few stations from the longitudinal profile were considered as irrelevant from an environmental point of view and no samples were analysed.

The use of mercury as a pathfinder element in geological exploration or in environmental studies requires very sensitive instruments, atomic absorption techniques offering such a possibility.

To measure the mercury content of the sediments sampled on the Black Sea shelf we used a Scintrex HGG-3 mercury flameless AA spectrometer based on the "Zeeman Effect" whose sensitivity reaches 10^{-12} grams. The mercury spectrometer includes a powerful electromagnet placed around the Hg lamp, which naturally emits light having a wavelength of 2537 Angstroms. The magnet is cycled on and off, the measurement being made to differentiate total absorption at 2537 Angstroms from background absorption at the shifted wavelength. As a result of methodological studies it was considered that the most suitable measurement technique was by direct pyrolysis (Stoffers *et al.,* 1986; Ioane, 1999). Small quantities of the marine sediments samples (≈0.1 g) have been heated at 400°C in a quartz-glass tube, the readings being obtained in mV. To compensate for the eventual heterogeneity in the samples, three independent determinations were made on each sample, the results being reported in mV, both as their maximum and mean (Fig. 1).

Considering the calibration provided by the company producing the Hg spectrometer, the results may be easily transformed into values of mercury concentrations:

$$1\ mV = 10 \times 10^{-12}\ g\ Hg$$

RESULTS AND DISCUSSION

The analyzed marine samples display different characteristics as compared to continental soils, the latter usually being sampled from the B geochemical layer. The marine sediments are frequently coarse and sandy and therefore less suitable for trapping heavy metals. As a direct consequence the measurements repeatability at the same marine station was quite poor and that is why it was decided that using only mean values for a particular station may not be meaningful.

The mean and highest mV values obtained by Hg spectrometry for each marine station have been presented on the same map (Fig. 1), in the frame of geological structures revealed by geophysical exploration (Patrut *et al.,* 1982).

The anomaly contoured in the Lotus-Lebada-Sinoe-Portita area is the largest and includes sectors with high concentrations of mercury, the most important being located on the West Lebada-Lotus structures. We consider that this anomalous area cumulates mercury concentrations from two main sources, general pollution of the shelf through riverine inputs from above the marine sediments and naturally high mercury inputs from the oil accumulations situated beneath the marine sediments. It is difficult at this stage to estimate quanti-

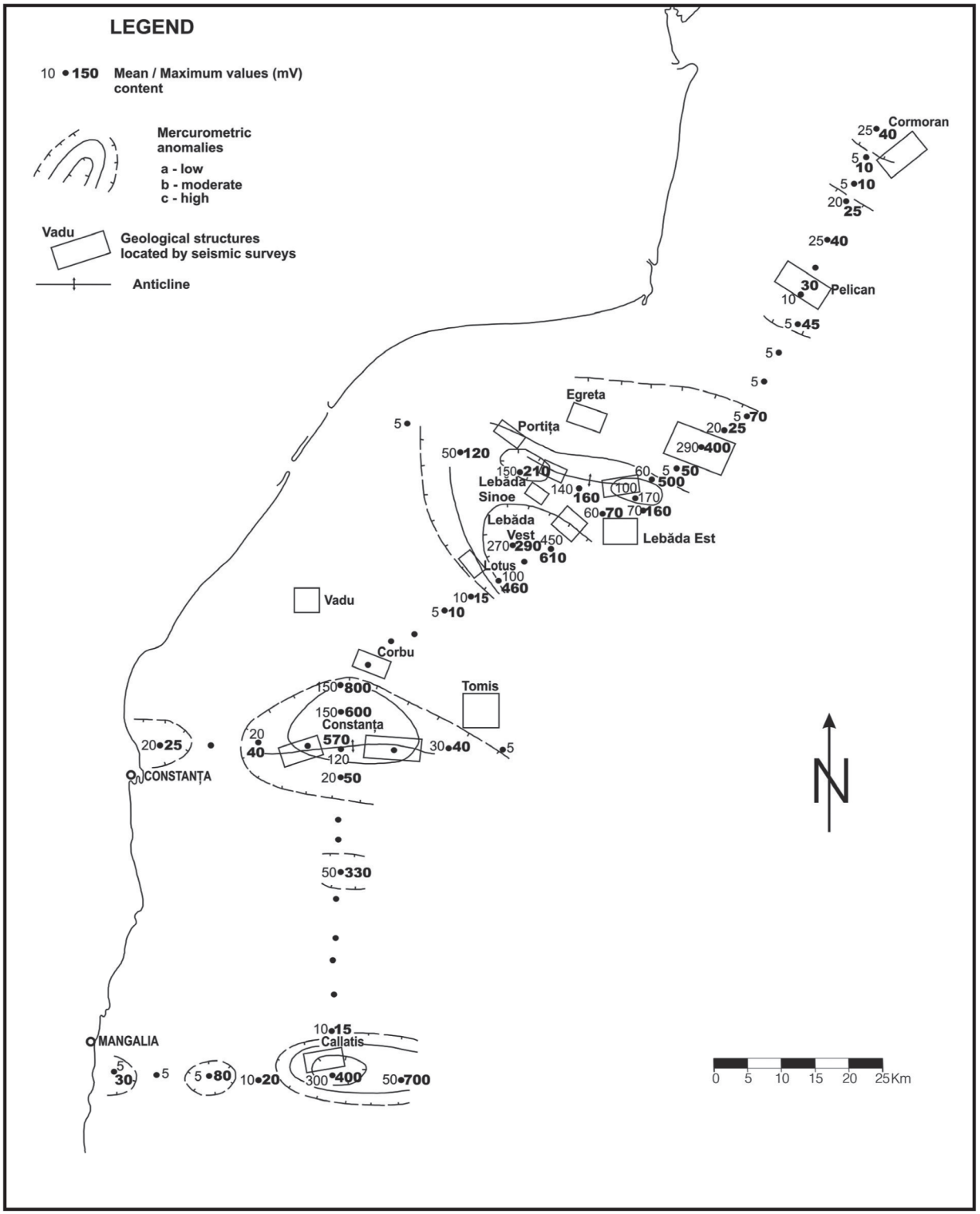

Fig. 1 Mercury concentrations (expressed as mV) in superficial sediments from the Romanian Black Sea shelf

tatively these two main contributions. A third source may be added to the previous two, a rather local pollution associated with the drilling operations and oil exploitation activities.

The anomaly contoured in the area of Constanta structure shows high Hg contents in close relation with an anticline structure revealed by geophysical surveys. We consider that highly mineralized underground waters may be the "geological" source of mercury, supplemented by an anthropogenic contribution probably related to the industrial activities in Constanta, which is also an important harbour. The anthropogenic component of the mercury anomaly seems to be higher in this area, supplementary sources needing to be taken into account: the end of the Danube-Black Sea canal and the oil refinery located in the Navodari area.

The anomaly contoured in front of the city of Mangalia seems to be strongly related to the Callatis geological structure, the small and elongated anomalous area suggesting that the anthropogenic pollution component here may be very weak as compared to the deep situated geological sources.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. Nicolae Panin and his coworkers for kindly offering the "ANTARES" marine sediments samples for performing the Hg spectrometry study.

REFERENCES

EEC, 1976, Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, Official Journal L129, 18. 05. 1976, 12 pp.

FURSOV, V.Z., 1983, Use of vapour mercury method in ore deposits exploration (in Russian), Nauka, Moscow.

IOANE, D., 1984, Testing the mercurometric method in North Dobrogea (in Romanian), Tehn. Bull, Institute of Geology and Geophysics, Bucharest.

IOANE, D., 1999, Methodological and interpretation contributions to the gravimetric, magnetic, gamma ray spectrometric and mercurometric study of ore deposits associated to the Neogene magmatism in Romania (in Romanian), Carpatica, Cluj-Napoca, pp. 174.

IOANE, D., ANDREI J., GERMAN M., 1994, On the applicability of mercurometry in hydrocarbon exploration (in Romanian), XVIIth Symp. Geophys., Abstr. Vol., Bucharest.

IOANE, D., DRAGOI D.N., 1996, Crustal faults as depicted by mercury content anomalies, An.Inst.Geol.Rom., Vol. 69, Suppl. 1, Bucharest.

McNERNEY, J., BUSECK, R.P., 1973, Geochemical exploration using mercury vapour, Econ.Geol., 68, 1313-1320.

PANIN, N., SECRIERU, D., MANOLELI D., REZNIK V., FESIUNOV O., NAZARENKO M. F., 1992, The Ecological Conditions in the NW Part of the Black Sea. A brief description of the Romanian - Ukrainian geo-ecological research in 1990 - Mediul Inconjurator, III, 1, p. 27-35, Bucuresti.

PANIN, N., SECRIERU, D., MANOLELI D., REZNIK V., FESIUNOV O., NAZARENKO M. F., 1992, The ecological condition in the N-W part of the Black Sea - Rapp. Comm. Int. Mer Medit., 33, p.146.

PEABODY, C.E., EINAUDI, M.T., 1992, Origin of petroleum and mercury in the Culver-Baer Cinnabar deposit, Mayacmas district, California, Economic Geology, Vol. 87, 1078-1103.

ROBBINS, J., 1975, Mercury as a geochemical trace element, Scintrex Technical Report, Ontario.

SCINTREX LTD, 1977, Mercury vapour analysis in exploration, Technical Report, Ontario.

STOFFERS, P., GLASBY, G. P., WILSON, C. J., DAVIS, K. R., WALTER, P, 1986, Heavy metal pollution in Wellington Harbour, New Zealand Journal of Marine and Freshwater Research, V. 20, 495-512.