

TEMPORAL AND GEOGRAPHIC VARIABILITY OF PARTICULATE METAL CONCENTRATIONS IN BRINES USED IN CRYSTALLIZATION PROCESSES FOR SALT PRODUCTION

S. P. Varnavas^{1*} and Th. Lekkas²

¹ Department of Geology, University of Patras, Patras, Greece

² Department of Environment, University of Aegean, Mytilini, Greece

Abstract

Suspended particulate matter separated during two different seasons from brine ponds of a saltworks system were analysed for Fe, Pb, Cd, Cr, Cu and Zn. It was found that during both seasons the metal concentrations were markedly high in the first ponds of the system while they decreased with decreasing distance from the crystallizers. However, the waters entering the crystallizers contained significant amounts of particulate metals. This phenomenon should be investigated further in relation to the crystallization processes and the quality of the produced salt.

Keywords : particulate metals, lagoons, eastern Mediterranean, brines.

Introduction

The Mesolongi saltworks are located on the eastern coastal zone of the inner part of the Mesolongi lagoon (1, 2, 3). The extreme environmental conditions occurring in the Etolikon lagoon, in the vicinity of the saltworks due to its physiography, combined with the input of large quantities of metals in the lagoon derived from agrochemicals and other anthropogenic sources lead to an increase of metal concentrations in the waters of the area (4).

The aim of this work was to investigate the geographic and temporal variability of particulate metal concentrations in the brine ponds through which the water passes prior to its use in the crystallizers for the production of salt. It is considered that this investigation is of great importance because it can lead to conclusions related to the quality of waters and brines used which affect the quality of the salt produced.

Methods and materials

It is noteworthy that station PS1 which is the main pumping station for the water input to the saltworks aquatic system is characterized by low concentrations of SPM. The geographic distribution of SPM shows that stations at the northern part of the aquatic system, nearer to the crystallizers, are generally characterized by higher concentrations of SPM relative to the stations in the southern part of the system.

In order to determine the geographic variability of the quality of waters used in the crystallization process for the production of salt, SPM samples obtained along the brine ponds were analyzed for Fe, Pb, Cu, Cd, Cr and Zn. For the separation of SPM, waters/brines were filtered using a vacuum pump and millipore filtering system with membrane filters of 0.45 μm pore size. The SPM material was then leached with hot 50% HCl for 3 hours and analyzed using a Perkin Elmer 2100 atomic absorption spectrophotometer. The precision was checked with replicates and the accuracy with standard samples, and were found to be below $\pm 5\%$ and $\pm 2\%$, respectively.

Results and discussions

Geographic variability of particulate metal concentrations in spring 1995.

Iron, Copper, Lead

Iron varied in SPM between 53 $\mu\text{g/g}$ and 2476 $\mu\text{g/g}$ (Table 1) with its highest value found at station PS III. At this station Fe was markedly enriched relative to all other stations. At station PS IV Fe was slightly increased relative to station PS II. At station PS VI/15 the Fe concentration was very low. Generally Fe in SPM decreased in the following order :

PS III > PS IV > PS II > PS VI/15A > PS VI/15 (the number of stations increase with decreasing distance from the crystallizers).

The concentrations of Cu varied between 2 $\mu\text{g/g}$ and 24 $\mu\text{g/g}$. The highest concentrations of Cu were observed at station PS III with equally high values found at stations PS II. Lower values were observed at stations PS IV, PSVI/15 and PSVI/15A.

It should be stressed that Pb exhibited marked enrichments in SPM, varying between 32 $\mu\text{g/g}$ and 354 $\mu\text{g/g}$. As in the case of Fe and Cu, Pb displayed its maximum concentration at station PSIII with evaluated values at station PSII and lower values at PSIV, PS VI/15 and PS VI/15A, respectively.

Cadmium, Chromium and Zinc

The distributions of Cd and Cr differ from those of the other metals since both metals show very low values at stations PS III. However, both metals exhibited high values at station PS II. Low values of Zn were observed only at stations PS VI/15A and PSVI/15.

Table 1. Seasonal variability of particulate metal concentrations in the brine ponds.

| Season | Fe $\mu\text{g/g}$ | Pb $\mu\text{g/g}$ | Cu $\mu\text{g/g}$ | Cd $\mu\text{g/g}$ | Cr $\mu\text{g/g}$ | Zn $\mu\text{g/g}$ | SPM gr/l |
|--------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|--------------|
| Spring | 53-2476 | 32-354 | 2-24 | 0-4 | 0-74 | 0-8 | 0.0015-0.724 |
| Summer | 66-3467 | 32-942 | 10-67 | 0-13 | 0-67 | 0-173 | 0.032-0.960 |

Temporal variability of particulate metal concentrations

A comparison between the particulate metal levels found in early spring and those observed in late summer 1995 showed that the later were markedly higher. However, their geographic variability in the later samples was similar to the former with the highest Fe, Cu, Pb, Cd and Zn values found at station SP III.

A comparison between the metal concentrations obtained prior to pumping with those obtained after transferring the water to the next basin (i.e. stations SPIII, SPV) showed that the waters in the basin prior to pumping have higher concentrations of particulate metals (i.e. Fe, Pb, Cd).

Geochemical Behaviour of Metals

In order to determine the geochemical behaviour of the metals studied, the correlation coefficients among their concentrations were calculated. On the basis of this analysis the following grouping of metals was observed.

i) Fe, Pb, Cu; ii) Cd, Zn.

It is implied that Pb and Cu may be associated with the Fe oxide fraction of SPM, while Cd and Zn may be contained in a different SPM fraction. Although organic carbon was not determined in the SPM, Zn and Cd may be bound to the organic fraction of SPM since they have been found to be associated with organic carbon of the sediments from other regions.

Conclusions

The present data show significant enrichments as well as geographic and temporal variability in the particulate metal levels in the brines prior to their use in crystallizers for the production of salt. Significantly higher metal concentrations were observed in summer compared to spring.

The particulate metal concentrations during both sampling periods are generally very high in the first ponds and they decrease with decreasing distance of the basins from the crystallizers. This phenomenon is very pronounced in the case of Pb. However, particulate metal concentrations remain high in the waters entering the crystallizers. This phenomenon needs further investigation as it relates to the quality of the produced salt.

References

- 1 - B.P. Company 1971 The geological results of petroleum exploration in western Greece. Institute for Geology and Subsurface Research, Special Report No 10.
- 2 - Varnavas S.P. and Lekkas T. 1988. Distribution of metals in the saltworks (salinas) of Mesolongi, Greece. Proceedings of International Conference on Heavy Metals in the Hydrological Cycles, Lisbon, 473-480.
- 3 - Varnavas S.P. and Lekkas T. 1996 Factors controlling the geochemical and crystallization Processes in marine brine ponds. *Marine Georesources and Geotechnology*, 14 : 111-141.
- 4 - Varnavas S.P. 2000. Assessing and monitoring the environmental conditions of lagoons in Western Greece. In : M.F.Price (ed.) Proceedings and Biosphere Reserve Coordinators. Unesco, MAB, Cambridge, 90-92.