STUDIES OF ENVIRONMENTAL HISTORY OF THE BALTIC AS RECIPIENT AND ESTUARY OF ELEMENTAL POLLUTANTS

I.Ahlgren, A.Bignert, B.Carell, E.Dunca, E.Kulakowsky, H.Mutvei, J.Nyström, M.Olsson, A.Seire, T.Slepukhina, O.Wahlberg, T.Westermark (1), *V.Ziuganov.*
(1) The Royal Institute of Technology, Department of Chemistry, Nuclear Chemistry, S-10044 Stockholm, Sweden.

The aim of our studies ("With rivers to the Baltic") is to elucidate the environmental history of tributing rivers and the Baltic during the last 100-200 years. These studies are based on structural and chemical analysis of mussel shells. They have been carried out at the Swedish Museum of Natural History, Stockholm (structural analysis and sampling for elemental analysis), Royal Institute of Technology, Department of Chemistry, Nuclear Chemistry, Stockholm (Neutron Activation Analysis), and Department of Radiation Sciences, Division of Biomedical Radiation Sciences, Uppsala University (μ PIXE analysis).

Outline of the studies

Several freshwater bivalve species from N Europe can be used for studies of transport of pollutans from lakes and rivers to the sea. The choise of the species depends of age, ecological parameters and availability. The freshwater species used here are *Margaritifera margaritifera*, *Unio crassus*, *U.tumidus*, *U.conus*, *U.pictorum* and *Anodonta* spp.; the brackish water species are *Macoma baltica* and *M.calcarea*; and the marine species is *Arctica islandica.*

General information about environmental conditions is obtained from the shell structure and growth rate. This information is then used for sampling for elemental analysis. 20-30 elements or more have been detected in calcium carbonate fraction of the shell by Neutron Activation Analysis and Gamma Spectroscopy. PIXE analysis give us elemental concentrations with high spatial resolution.

Shells are studied from places suspected for antropogenic influences like acid fallout, and industrial and agricultural pollution. The results are compared with shell analyses from environments less influenced by human activities. For studies of environmental changes during the last 100-200 years, shells from well dated collections of natural history museums are used.

Additional analysis, such as ICP-MS and others, have been carried out by commercial laboratories.

Recent methodological achievements

Element/time mapping in mussel shells, in combination with aquatic chemistry, makes it possible to study pH changes and oxygen depletion. The solubility constrained elements Fe, Co and Zn give rise to characteristic minima in the concentration/time direction. By using the water chemistry data to the plane concentration/pH, acidified periods in the past were detected. A case example is the River Kvarnbäcken, central Sweden, with a debut of pH decrease at about 1950 down to pH 5 and then an increase of pH by liming the source lake. The key property is the presentation of the slopes of logc/pH relation from the shell data. A comparison of measurements (W.Dickson) of pH relation for Zn showed the value to be the same, validating the mussel shell response.

The redox chemistry of Mn has been used by sedimentologists to describe the oxygen level from Mn (II). Mn analyses with PIXE show seaonal variations in shells, which are related to oxygen levels. Rare earth elements or lanthanides (Ln) are often recorded in shells. Their relative abundance is used here to identify pathways of contamination of the Baltic.

Some results

Freshwater

High acid fallout, due to air-borne S and N precipitation, was analyzed in shells from several rivers in W and central Sweden. Shells from rivers in N Sweden (Pärlälven), N Russia (Kerjet) and Kola Peninsula (Varzuga) were used as references. Shells from the latter rivers have low S and P levels, and pH values change at most 0.5 units.

Acid fallout is expected also from sulphur emitting forest industries. Shells from two areas were analyzed: the River Bollstaån from N Sweden, and rivers from W Sweden.

Fe, Zn and Co data from *Margaritifera* shells from the rivers Vramsån (210 years time span) and Höje å, Scania, S Sweden, indicate pH reductions from the last decades of the 18th century through the next decades. We interpret this as a result of oxidation of soils from wetlands and pastures exposed to air in the intense cultivation phase at that time. Elevated P and N levels were also shown in these shells.

Lowering of lakes by man have produced notable environmental effects. Our data suggest strong oxygen depletion in two cases, in the Lake Hjälmaren and Vallentunasjön in the last century. In the latter lake there is an evidence of pH reduction.

Analyses of the organic shell periostracum show much higher levels of U, Th, Ln, Zr, Hf, P, Br and Hg than the calcium carbonate shell fraction.

The Baltic

Sr and lanthanides seem to peak at Stockholm-Tallinn-S:t Petersburg latitude. In the Tallinn Bay *Macoma* shells show a high contamination of lanthanides and Fe, P and Zn in the 1970:ies, probably originated from the Lower Ordovician Dictyonema-shale. On the other hand, shells collected 1993 show reduced levels of the elements in question.

An apparent leakage of lanthanides from the Ytterby mine, Island of Resarö, E of Stockholm, occurre around the island. Six lanthanides were found in *Macoma* shells, collected 1933 close to the island. Ferns growing at the mine contained eight lanthanides at relatively high levels. Here the relative pattern of abundance is different from that in the Tallinn Bay.

Arctica shells collected from the Sounds (one of the outlets from the Baltic) did not show any significant increase of P until 1910. On the other hand, N increased from the last decades of the last century, whereas Na decreased from 1800 to 1860, and Sr increased at the same time, suggesting a salinity decrease during this period.

A *Macoma calcarea* shell (1866-1878) from the Bornholm Basin has been analyzed for Mn, Fe, P, N, Na, Sr, Ln and other elements. The temporal data and intercorrelations suggest an oxygen depletion and a higher salinity at that time.

No artificial radioactivity was found in mussel shell from Gulf of Finland, except naturally occurring radioactive U and Th including daughter Ac-228.

Support from several sponsors is gratefully acknowledged: SNV, NFR, The Swedish Council of Forestry and Agricultural Research, The C.Trygger Foundation, The Bank of Sweden Tercentenary Foundation, The Wallenberg Foundation, The Royal Swedish Acad. Sci., The Schwarz' Foundation, The Johnson Foundation, EU MAST III,