STUDY ON ORGANIC MICROPOLLUTANTS OF THE MAROS (MUREŞ) RIVER

ANNA FERGE and LÁSZLÓ SÉLLEI

Introduction

Samples from the Maros River at three sites were investigated by gaschromatograph/mass-spectrometry system (GC/MS).

Sampling sites: 1. Toplița
2. Sîntimbru
3. Makó

The sample preparations and the extraction of organic materials were completed within 24 hours after sampling.

Since we had not known anything about the sampling sites and their characteristics, the sample preparation was completed for multipurpose investigation.

It was particularly a great difficulty in the case of the sample taken at Makó because of its high contents of algae and their metabolic products which distributed the evaluation of mass spectra.

On the basis of the results, the source of the compounds cannot be identified.

Material and methods

Sample preparation

The sample preparations were carried out by means of the USEPA methods.

The extraction of materials that were present in small quantity in the water (between 0.1 and 100 g/l) was carried out from 1000 ml by the following procedure:

— Centrifugation (2000 rpm for 35 min.) was made to eliminate the interfering suspending materials.

— Adsorption of organic materials on XAD-4 resin. The water samples were run through 5 ml of resin at a rate of 30-40 ml/min. After this, the resin was rinsed by 20 ml of supra pure water and the residue of water was purged out by nitrogen stream.

The organic pollutants adsorbed on XAD-4 resin were diluted by 30+30 ml of acetone and 80 ml of dichloromethane.

The elimintion of the water traces of the organic phase was carried out by running it through a column packed with 10 cm 3 of sicc. Na_2SO_4. The column was washed by 30 ml of dichloromethane.

This solution was concentrated in a normal and a micro Kuderna-Danish apparatus down to approx. 0.5 ml. It was then filled up to 1 ml by dichloromethane and stored in a glass vial with PTFE cap at -6 ^{o}C.

Sample analysis

The GC/MS analyses were completed with the following equipment:

Gaschromatograph (GC):

Type: Hewlett-Packard HP-5710A

Column: SPB-5, 50 m x 0.25 mm I.D.

Injector temp.: 250 °C

Temperature program: 30 C/min. up to 250 °C

Carrier gas: 2 ml/min. He

Mass-spectrometer (MS)

Type: VG-7035

Ionization: EI

Electron energy: 70eV

Ion source temp.: 200 °C

Ion current: 200 A

Scan time: 0.3 s/decade

Total ion chromatograms (TIC) of the above 3 samples can be seen on Figures 1..2..3.

The numbers in circles on the TICs signify the compounds in Table 1, the other numbers are the numbers of scans.

The mass spectra of each compound are available but here they are not shown because of their large amount.

Evaluation

On the basis of TICs and mass spectra we can note the following about pollution in the Maros River:

- In sample 1 compared to the others, there were considerable concentrations of alkanic hydrocarbons which indicate a close pollution source and weak self purification of the water.
- In samples 2 and 3 this kind of pollution was lower. It may be the result of the diluting effects of the effluents of the Maros, the self purification of the water and/or ceasing of pollution sources.
- The presence of 9H-carbazol in each sample indicates the influence of industrial plants being all along the river or the stability of this compound.
- Pesticide residuals can be detected all along the river (e.g. atrazine, terbutrine, etc.). Their concentrations are not so high, they are less than 2 g/l for each, but more than 5 g/l in total.
- The high level of pollution of sample 3 caused by algae and plants did not make it possible to identify the sources of compounds obtained from the TIC (plant, algae origin or industrial, agricultural origin).

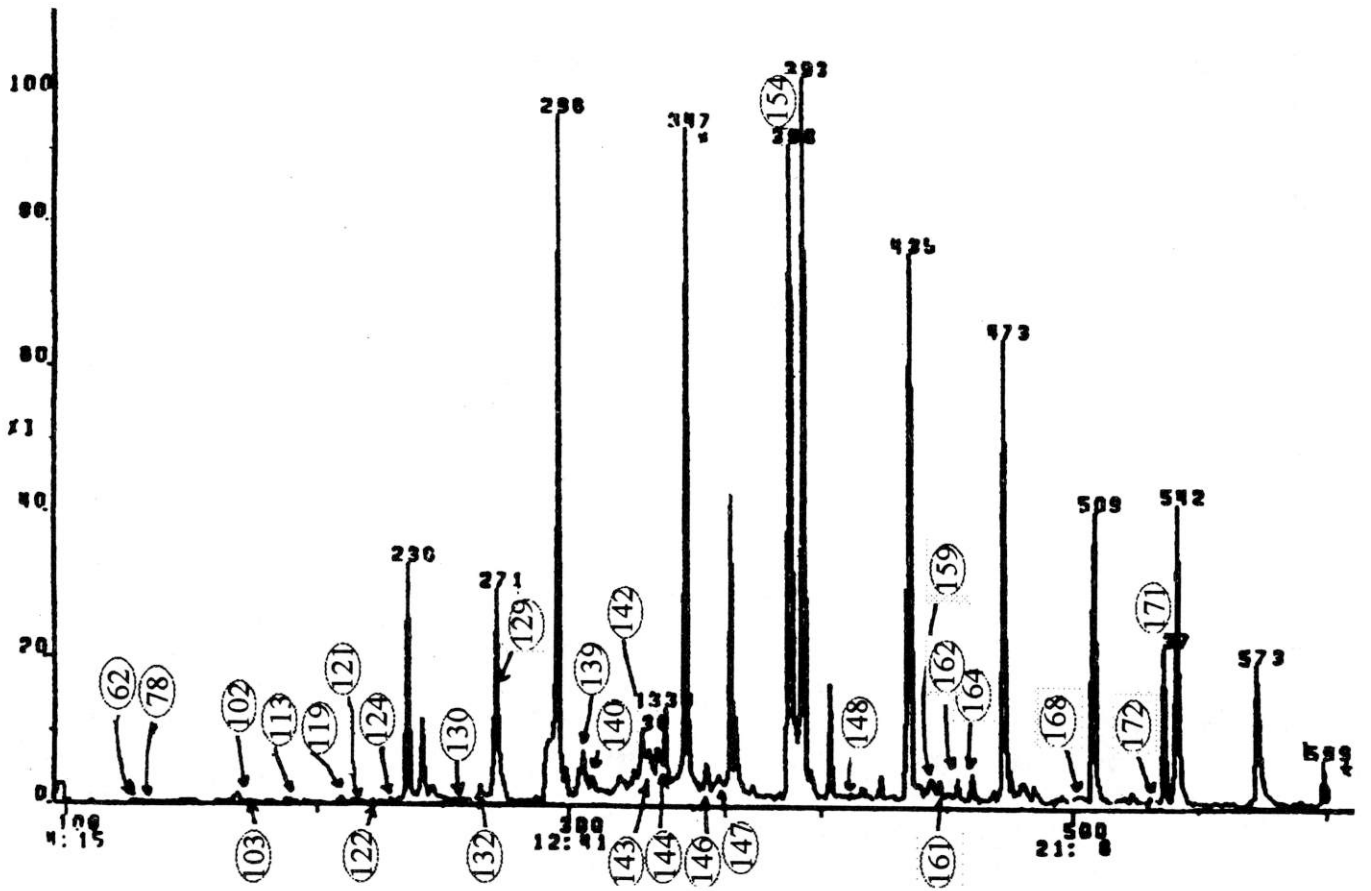

Fig 1. Chromatogram of organic compounds from Toplita region

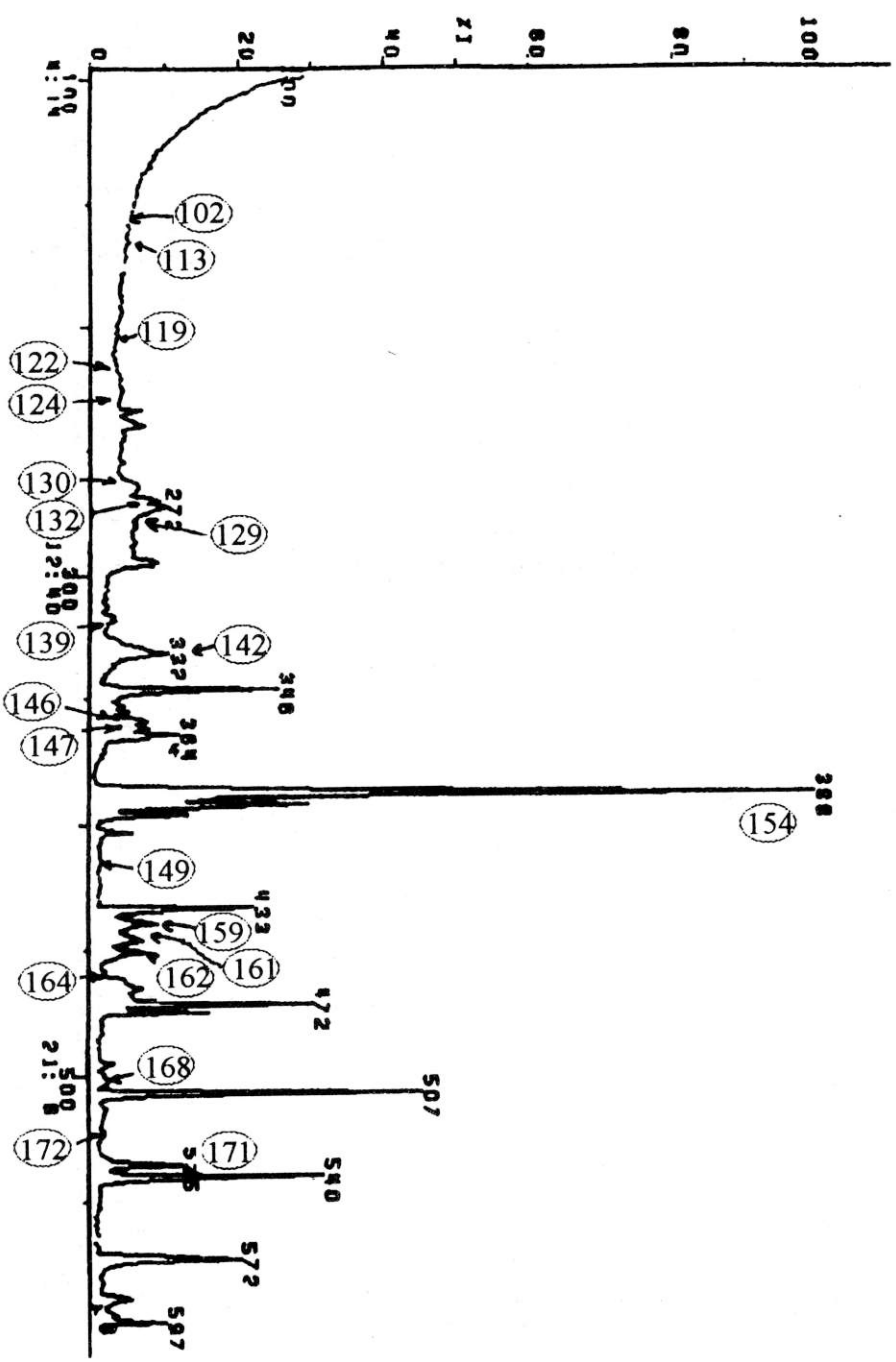

Fig 2. Chromatogram of organic compounds from Sintimbru region

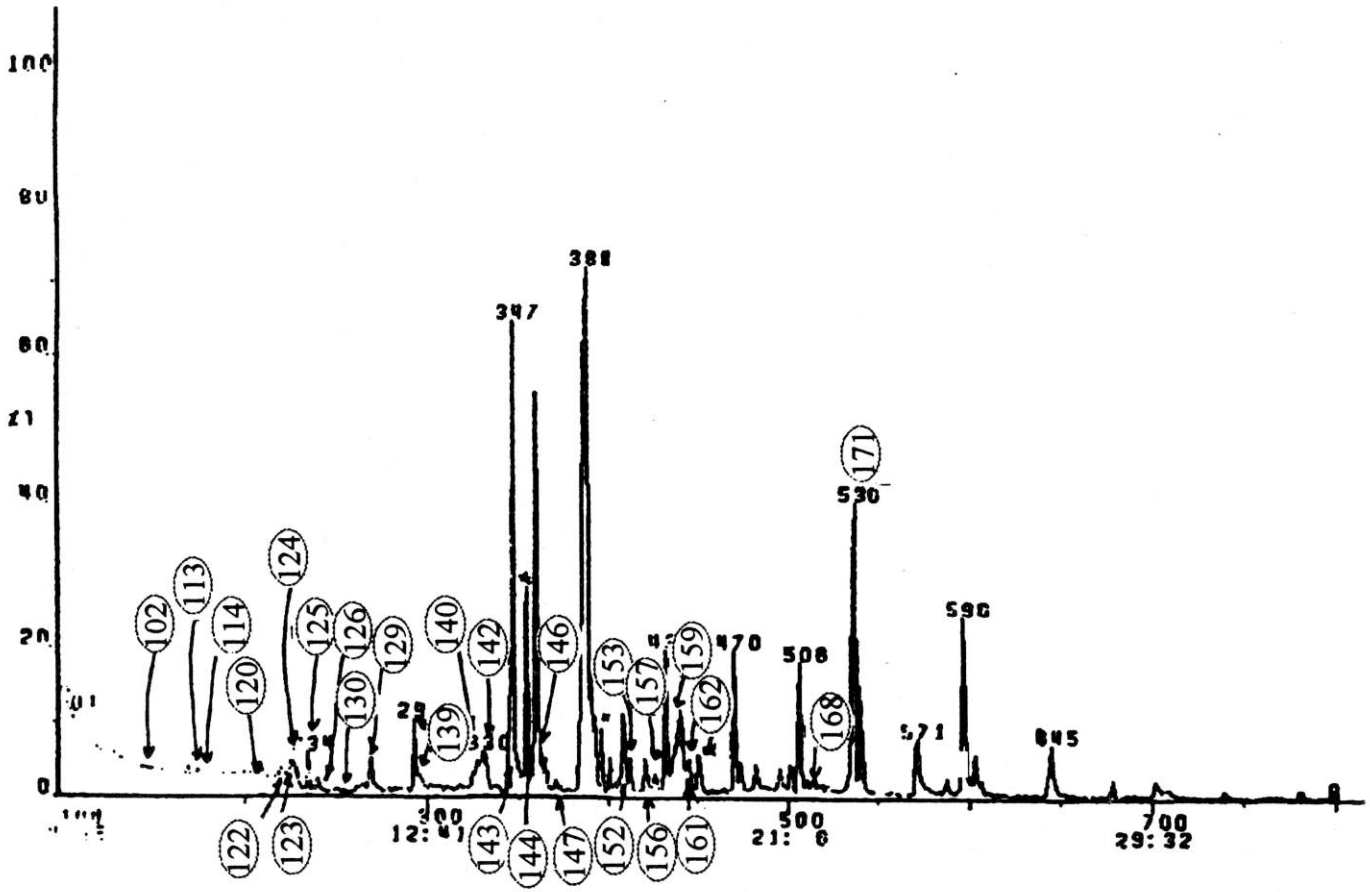

Fig 3. Chromatogram of organic compounds from Makó region

Number of compounds marked on figures

62. o-Cresol
78. 2,4-Dimethylphenol
102. EPTC
103. Biphenyl
113. N-Aca
114. Acenaphtyhlene
119. Anelda
120. 4-Nonylphenol
121. Pyrogallol
122. Propachlor
123. Molinate
124. Dimethyl phthalate
125. Diphenylmethane
126. Acenaphthene
129. Diethyl phthalate
130. Fluorene
132. 9-Methylfluorene
139. 2,6-Di-tertbutyl-4-methylphenol
140. 2.6-Di-tertbutyl-4-ethylphenol
142. Phenanthrene
143. 2,6-Di-tertbutyl-4-methoxyphenol
144. Bisphenol A
146. 2,6-Di-tert-butylmethylphenol
147. Xanthone
148. C18 alkane
149. Ametryn
152. Benzoic acid
153. Anthraquinone
154. Dibutyl phtalate
156. Methylphenathrene
157. 3,6-Dimethylphenathrene
159. Atrazine
161. Tetrabutrine
162. Dimethylphenathrene
164. Pyrene
171. Di(2-etylhexyl.)phtalate
172. Terpenes

Summary

Having finished the first general purpose investigations concerning the organic micropollutants in the Maros River we can state that:

- The occasional samples are useful for only general purpose. For estimating the pollution and its characteristics and self purification efficiency of the river it is necessary to do regular sampling and to know the nature of the polluting sources.

- In order to choose the appropriate methods for the sample preparation and GC analysis, it is essential to know the sampling sites, the expectable kinds of pollutants and the other chemical and biological characteristics of the water.

- The above results describe only a given state of the river at these sites. The applied analysis method does not deal with the volatile materials and those that are adsorbed on the suspending particles eliminated by centrifuging.

-These investigations are useful to plan further studies, to make the polluting sources better known and they indicate that we need much more data to describe the pollution of the 749-km-long River Maros.

Literature

Burchill. P., A.A. Herod. K.M. March. C.A. Pirt. E. Pritchard: Water Res. 17. 1981. (1983).

Colby, B.N.: Evanation of Stable Labeled Compounds as Internal Standards for Quantitative GC/MS Determinations, EPA- 600/2-83-127 (1983).

Crompton . T.R.: Determination of Organic Substances in Water (vol. 1.-2.).John Wiley and Sous; New York, 1985.

Driscoll . J.N., M. Duffy, S. Pappas, M. Webb: J. Chrom. Sci.; 25 369 (1987).

Eight Peak Index of Mass Spectra.Mass Spectrometry Data Center, Aldermaston, U.K.
Heller, S.R., G.W.A. Milne: EPA/NIH Mass Spectral Data Base vol. 1.-8., U.S. Department of Commerce, Washington D.C. 1978-1983.
Hites, R.A.: Handbook of Mass Spectra of Environmental Contaminants. CRC Press, Boca Raton, Florida, 1985.
Keith, L.K.: Advances in the Identification and Analysis of Organic Pollutants in Water (vol. 1.-2.). Ann Arbor Sci. Publ. Inc. Ann Arbor, Michigan 48106, 1981.
Minear, R.A., L.H. Keith: Water Analysis (vol. I.-III.). Academic Press, Inc. New York, 1984.
USEPA: Guidelines of Pollutants under the Clean Water Act: Method 604; USEPA; Fed. Reg; 49 (209) 1984.
WHO: International Standards for Drinking Water, WHO, Geneva, 1971.

Anna Ferge, László Sellei, County Waterworks and Sewage Co., H 5000 Szolnok, Hungary