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## POLYCYCLIC ARENES IN THE BALTIC WATERS

*(Presented by M. Gubergrits)*

Polycyclic arenes belong to the most dangerous representatives of chemical pollutants, a part of them being carcinogenic and another carcinostatic. In comparison with other compounds of acute toxicity, such as herbicides, carcinogens are more harmful since their solutions, already in extremely low concentrations may cause cancer in long or repeated contact with a living organism. Moreover, polycyclic arenes are chemically very stable and decompose relatively slowly under the influence of various factors favouring selfpurification (UV-radiation, atmospheric or solved oxygen, microorganisms). The amount of polycyclic arenes in the biosphere has been determined by the concentration of a typical carcinogen, benzo(a)pyrene (BP). In the USSR, maximum permissible concentration of BP in drinking water is  $5.0 \text{ ng l}^{-1}$  [1]. As several other polycyclic arenes, besides BP, are of carcinogenic or carcinogenic-promoting activity, i. e., of a capacity, in admixture with a carcinogenic substance, for considerably promoting cancer [2, 3], the aim of this investigation was to determine quantitatively the polycyclic arenes concentration in some most polluted points of the Baltic. Up to the present, no literature data are available, although the occurrence of BP in the shelf sea of Estonia [4] and open sea of the Baltic has been studied before [5].

In this work, the data obtained on board the research-ship «Ayu Dag» in the summer of 1980 (June—July) are presented about sea water samples collected in the open sea of the Baltic.

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### Methods

A 4.0 l sea water sample was collected with a batometer (General Oceanics Inc., USA), polycyclic arenes being twice extracted with *n*-hexane (each 100 ml) by mechanical stirring. The residue of extract was carried on a thin-layer aluminium oxide plate, and polycyclic arenes were separated by benzene : acetone (9:1), washed out with a 1:1 mixture of benzene : acetone and evaporated dry. To the solid residue, 2.0 ml of methanol was added, 1.5 ml of it being used for high-pressure liquid chromatographic (HPLC) analysis.

HPLC analysis of polynuclear arenes — a Perkin-Elmer series 3B liquid chromatograph fitted with a 2.6 mm (inside diameter)  $\times$  2.5 cm ODS-HC Sil-x-1 column was used for analysis. The column was eluated at room temperature with a concave gradient 0.2 of 90% methanol in water to 99% methanol with a sweep time of 15 min and isocratically 10 min, a solvent flow rate of 1.0 ml/min.

Positions of elution of each polynuclear arene were monitored by UV absorption at 254 nm and by Perkin-Elmer model 1000 spectrofluorimeter, excitation at 315 nm and emission at 401 nm. Substances were quantitatively determined by standard solutions. The total error of the data does not exceed 10%.







### Results and discussion

The data on the polycyclic arenes content in three most polluted points of the Baltic are given in Tables 1—3. The concentration of polycyclic arenes is highest in the southern part of the Baltic, before the Danish Straits, in the south-east of the Åland Islands (Station LL-12 according to the Helsinki Convention of 1974) and in the region near the southern tip of Öland Island. In all these points the BP concentration exceeds the maximum permissible concentration 2—3 times. Analogical results were obtained at our expedition in 1978, when the BP content in the surface water layer exceeded the maximum permissible concentration 2 times.

Acenaphthene makes up 99.6—99.9% of polycyclic arenes, its concentration being 0.2—0.3 mg l<sup>-1</sup> in the south-east of the Danish Straits and 0.05 mg l<sup>-1</sup> in the central part of the Baltic. The concentration of 4- and

Table 1

Polycyclic arenes content near the southern tip of Öland (Station 6, international code BCS 111—10, co-ordinates N—55°33', O—18°24', depth 90 m)

| Arene                               | Structural formula  | Horizon, m | Content                |  |
|-------------------------------------|---|------------|------------------------|--|
|                                     |   |            | ng l <sup>-1</sup>     | % of total of 4- and 5-nuclear compounds |
| Pyrene                              |  | 5          | 178.5                  | 71.1                                     |
|                                     |   | 40         | 114.5                  | 71.0                                     |
|                                     |   | 80         | 90.5                   | 66.0                                     |
| Chrysene                            |  | 5          | 26.2                   | 10.4                                     |
|                                     |   | 40         | 15.7                   | 9.7                                      |
|                                     |   | 80         | 21.9                   | 16.0                                     |
| Benzo(e)pyrene                      |  | 5          | 35.7                   | 14.2                                     |
|                                     |   | 40         | 20.4                   | 12.6                                     |
|                                     |   | 80         | 17.6                   | 12.8                                     |
| Benzo(k)fluoranthene                |  | 5          | 0.4                    | 0.15                                     |
|                                     |   | 40         | 0.7                    | 0.43                                     |
|                                     |   | 80         | 0.5                    | 0.36                                     |
| Benzo(a)pyrene                      |  | 5          | 10.1                   | 4.0                                      |
|                                     |   | 40         | 10.0                   | 6.2                                      |
|                                     |   | 80         | 6.6                    | 4.8                                      |
| Total of 4- and 5-nuclear compounds |   | 5          | 250.9                  |  |
|                                     |   | 40         | 161.3                  |  |
|                                     |   | 80         | 137.1                  |  |
| Acenaphthene                        |  | 5          | 66.7 × 10 <sup>3</sup> | 99.6                                     |
|                                     |   | 40         | 50.0 × 10 <sup>3</sup> | 99.7                                     |
|                                     |   | 80         | 46.7 × 10 <sup>3</sup> | 99.7                                     |

5-nuclear arenes is  $10^3$ – $10^4$  times lower and their distribution is the following: pyrene (over 70%), followed by benzo(e)pyrene (10–15%), chrysene (5.2–16%) and BP (3.5–6.4%); the concentration of benzo(k)-fluoranthene is very low (0.1–0.4%). The presence of high amounts of alkanes was also observed in the southern part of the Baltic (Stations 6 and 9), but only in the surface layer.

The analysis of these data may lead to an opinion that as only two compounds of the arenes identified, viz. BP and benzo(k)fluoranthene

Table 2

Polycyclic arenes content near the Danish Straits (Station 9, international code BY-1, co-ordinates N-55°00', O-13°18', depth 46 m)

| Arene                               | Horizon, m | Content            |  |
|-------------------------------------|------------|--------------------|--|
|                                     |            | ng l <sup>-1</sup> | % of total of 4- and 5-nuclear compounds |
| Pyrene                              | 5          | 326.0              | 86.8                                     |
|                                     | 40         | 195.0              | 73.0                                     |
| Chrysene                            | 5          | 11.9               | 3.2                                      |
|                                     | 40         | 14.0               | 5.2                                      |
| Benzo(e)pyrene                      | 5          | 22.1               | 5.9                                      |
|                                     | 40         | 40.5               | 15.2                                     |
| Benzo(k)fluoranthene                | 5          | 0.8                | 0.21                                     |
|                                     | 40         | 0.4                | 0.15                                     |
| Benzo(a)pyrene                      | 5          | 14.7               | 3.9                                      |
|                                     | 40         | 17.1               | 6.4                                      |
| Total of 4- and 5-nuclear compounds | 5          | 375.5              |  |
|                                     | 40         | 267.0              |  |
| Acenaphthene                        | 5          | $300 \times 10^3$  | 99.9                                     |
|                                     | 40         | $160 \times 10^3$  | 99.8                                     |

Table 3

Polycyclic arenes content in the surface layer of the Baltic (5 m) in the south-east of the Åland Islands (Station LL-12, coordinates N-59°29', O-22°54', depth 86 m)

| Arene                            | Content            |                                       |
|----------------------------------|--------------------|---------------------------------------|
|                                  | ng l <sup>-1</sup> | % of total of 4- and 5-nuclear arenes |
| Pyrene                           | 273.3              | 78.5                                  |
| Chrysene                         | 27.3               | 7.8                                   |
| Benzo(e)pyrene                   | 34.4               | 9.9                                   |
| Benzo(k)fluoranthene             | 0.6                | 0.2                                   |
| Benzo(a)pyrene                   | 12.2               | 3.5                                   |
| Total of 4- and 5-nuclear arenes | 347.8              |                                       |
| Acenaphthene                     | $240 \times 10^3$  | 99.8                                  |

Table 4

Distribution of polycyclic arenes (% of surface layer, 5 m) in different horizons of the Baltic (Station 6 — see Table 1)

| Arenes                                       | Carcinogenicity | Horizon |      |
|--|-----------------|---------|------|
|  |                 | 30–40 m | 80 m |
| Acenaphthene                                 | —               | 75.0    | 70.0 |
| Pyrene                                       | +               | 64.1    | 50.7 |
| Chrysene                                     | promotor        | 59.9    | 83.5 |
| Benzo(e)pyrene                               | promotor        | 57.1    | 49.3 |
| Benzo(k)fluoranthene                         | +++             | *       | *    |
| Benzo(a)pyrene                               | +++             | 99.0    | 65.3 |
| Total of 4- and 5-nuclear arenes             |                 | 64.3    | 54.6 |
| Total of 4- and 5-nuclear arenes (station 9) |                 | 71.1    |      |

\* Concentration is very low, see Table 1.

(Table 4), are highly carcinogenic, the presence of high concentrations of other 3-, 4- and 5-nuclear arenes represents no danger. But literature data available prove that the methyl, metoxy, etc., derivatives of some weakly carcinogenic substances, such as pyrene and chrysene are much more dangerous [6]. It is also known that a number of compounds which themselves cause no cancer in experimental animals, promote the effect of other strongly carcinogenic compounds (see above). Such data exist, for example, on pyrene [7] and benzo(e)pyrene [6].

The distribution of polycyclic arenes in different horizons of the Baltic (Table 4) corresponds to a natural source of pollution — various types of liquid fuels. Thus it was observed that at a depth of 30—40 m the concentration of most compounds under study decreased by 29—36% and at that of 80 m by 45%. The data presented correlate well with those obtained at our earlier expeditions in the most polluted points: the BP concentration was observed to lessen by 67—79% at a depth of 30—40 m [5].

These data allow no conclusion to be made concerning the mutual distribution of polycyclic arenes in different points of the Baltic nor do they indicate the peculiarity of the sources of pollution, although the relative content of some arenes varies (Tables 1—3).

The problem requires further investigation. In conclusion we point out once more that the data presented on the polycyclic arenes content are characteristic of only some most polluted points of the Baltic.

### Conclusions

1. The concentration of carcinogenic benzo(a)pyrene in the most polluted points of the Baltic exceeds maximum permissible concentration 2—3 times.
2. The overall content of polycyclic arenes was quantitatively determined for the first time (0.2—0.3 mg/l<sup>-1</sup>), and their mutual distribution in three points of the Baltic established: acenaphthene makes up 99.6—99.9%, the concentration of 4- and 5-nuclear arenes is 10<sup>3</sup>—10<sup>4</sup> times lower, pyrene makes up 10, benzo(e)pyrene 10—15, chrysene 5—10 and benzo(a)pyrene 3.5—6.4%.
3. The concentration of polycyclic arenes is highest in the surface layer, diminishing by 29—36% at a depth of 30—40 m and by 45% at 80 m.
4. A frequent occurrence of arenes-promoters, being inactive alone, but dangerous in admixture with other compounds, is a serious source for carcinogenic pollution.

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### POLÜTSÜKLILISED AREENID LÄÄNEMERE VEES

On esitatud Läänemere avaosas kolme kõige enam saastatud punkti (Taani väinade, Ölandi ja Ahvenamaa saarte läheduses) polütsükliliste areenide sisaldus. Määramiseks kasutati esmakordselt kõrgsurve-vedelik-kromatograafiat. Summaarsest hulgast ( $0,2-0,3 \text{ mg l}^{-1}$ ) moodustas 99,6—99,9% atseenaften. Nelja- ja viietuumalisi areene oli 3—4 suurusjärku vähem ja nad jaotusid omavahel järgmiselt: püreeni üle 70%, benso(e)püreeni 10—15%, krüseeni 5—10%, benso(a)püreeni 3,5—6,4%. Seejuures ületas benso(a)püreeni kontsentratsioon kehtestatud piirnormi 2—3 korda. Pinnakihis oli polütsükliliste areenide kontsentratsioon kõige kõrgem, 30—40 m sügavusel ulatus see 29—36%-ni ja 80 m sügavusel 45%-ni. Kokantserogeense toimega püreeni, krüseeni ja benso(e)püreeni tunduv esinemine vees kõrvuti kantserogeense benso(a)püreeniga suurendab Läänemere kantserogeense saastatuse ohtlikku mõju.

Уве КИРСО, Эха УРБАС, К. КУИВ

### ПОЛИЦИКЛИЧЕСКИЕ АРЕНЫ В ВОДЕ БАЛТИЙСКОГО МОРЯ

При помощи жидкостной хроматографии под высоким давлением впервые количественно определено содержание полициклических аренов в трех наиболее загрязненных пунктах открытой части Балтийского моря (близ Датских проливов, острова Эланд и Аландских островов). Из их суммарного количества ( $0,2-0,3 \text{ мг/л}^{-1}$ ) 99,6—99,9% составил аценафтен, содержание четырех- и пятиядерных аренов на 3—4 порядка ниже со следующим распределением (%): более 70 пирена, 10—15 бенз(е)пирена, 5—10 хризена и 3,5—6,4 бенз(а)пирена. Содержание полициклических аренов максимално в поверхностном слое воды и снижается на 29—36% при глубине 30—40 м и на 45% при глубине 80 м. Наличие других полициклических аренов наряду с канцерогенным бенз(а)пиреном повышает канцерогенную опасность из-за возможного коканцерогенного действия пирена, хризена, бенз(е)пирена.