

INVESTIGATION OF THE ORGANIC POLLUTANTS
IN THE ATMOSPHERE OF RUSSE IN 1991

The present independent investigation of the atmosphere of the town of Russe was performed on the initiative of the independent association "Ecoglasnost - Russe" by a team of volunteers of the association, who secured the instrumentation, the sample collection and normal working conditions.

The analyses were carried out by a team of experts - volunteers by using the instrumentation base of the Institute of Organic Chemistry with a Centre of Phytochemistry at the Bulgarian Academy of Sciences.

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In order to solve the problems associated with the analysis of airborne organic pollution we made use of the world's experience in similar investigations, as reported in the publications of NIOSH and EPA, as well as of the special scientific literature./I-20/.

Sampling

The lack of preliminary information on the composition of the organic pollutants necessitated their adsorption from the air by active carbon, Tenax 60-80 mesh (Mackerey-Nagel) or their collection in organic solvents. The volume of the air samples and the wind direction were accounted for during the sampling procedure. The organic pollutants were concentrated prior to their chromatographic analysis by thermal desorption or extraction with organic solvents.

Instrumental methods

a) Gas chromatography. The components were separated by capillary column, 30 or 15 m/0,25um with a 0,5 um thickness of the SE-54 or OV-1 stationary phases. GC analyses were performed on Perkin Elmer mod. 8700 with parallel connected flame ionisation detector (FID) and electron capture detector (ECD).

b) HPLC was carried out with ISCO chromatograph provided with a Chem Research software or Perkin Elmer mod. 250 instrument with a diode array detector mod. 235. Columns with normal or reversed phases were employed.

c) Mass spectrometry. The substances were identified by a JEOL 20 K gas chromatograph-mass spectrometer equipped with thermodesorber TTD 850 DAI .

d) IR spectroscopy. In order to improve the reliability of the experimental results some of the samples were analysed by a Bruker IR spectrophotometer,

Investigated samples

The air samples were collected from August 1991 to November 1991 at localities determined jointly with the director of the Local Environmental Inspection of Russe early in 1990. Additional sites on the banks of the Danube River from the port to the tennis courts (Fig.1) were co-ordinated with the Meteorological Service of Russe. The collection of the samples was carried out by the laboratory personnel of the Local Environmental Inspection and volunteers from the independent association "Ecoglasnost - Russe". The latter took up the mobile sites and the night shifts. More than 600 air samples were collected from July 25 to November 25.

Chromatographic and mass-spectral analyses of the organic pollutants

In order to guarantee high accuracy and reliability of the investigation the compounds with similar physical and chemical properties were separated with the aid of capillary chromatographic methods (Figs. 2-13). The reproducibility was achieved by a five-fold analysis of the sample. The relative error with respect to retention times was lower than 5% and up to 8% with respect to surface areas. A considerable number of the compounds extracted from the adsorbents were identified by the combined gas chromatography-mass spectroscopy method (GC-MS). Not all the compounds could be identified by this method, since the concentration of the larger part of them was below the detectable minimum of the mass spectrometer. Besides this, the available mass spectra data file did not contain all the necessary spectra. The identification of such compounds was made by the retention time of previously identified components. The use of

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a scanning UV-detector in the liquid-liquid chromatographic analysis made it possible to identify some organic compounds by comparing their spectra with those of known compounds.

(Table 1). IR spectroscopy was employed as a complementary tool together with the identification methods in order to corroborate the functional groups of some of the components, such as chloro- derivatives, chlorohydrins, epoxy compounds, etc. (fig. 4).

The total amount of the compounds in the investigated samples was determined by the integrated surface area of the peaks, related to the surface area of the C₁₆ peak, injected in a definite amount (absolute calibration method). The contents of some of the identified compounds, samples of which could be supplied, were determined by the external standard method. Some chloro- derivatives, such as chloropropane, perchloro-ethylene, hexachloroethane, monochlorohydrin were determined semiquantitatively by this method since the analysis was carried out by an electron-trapping detector. With this detector the reaction coefficients, even with compounds of one and the same class, are quite different, e.g. chloropropane, perchloro-ethylene, hexachloroethane.

The analysis of the GC-MS data revealed that the qualitative composition of the samples collected at the sites of the Local Environmental Inspection from August 3 to August 16, 1991 is comparable with the background of organic pollutants determined in Russe in 1990 (21): hydrocarbons (normal and branched C₉-C₂₃, alicyclic) dibutyl- and dioctyl phthalates, tertiary butyl, methylphenols, esters of organic acids.

At the site "House of Culture", as well as at the mobile sites along the bank of the Danube River, the samples collected

between 3 and 6 o'clock in the morning contained chloroaliphatic compounds (Fig. 5). Mono- and dichloropropanes and propenes, perchloroethylenes, monochlorohydrin, and dichlorohydrin were identified during the transborder atmospheric pollution of Russe on August 26 and 27, 1991 (Fig. 6). In comparison to 1990 some chloro-organic substances appeared, not characteristic for the industries in Russe, which were proved by the investigation performed in 1987/88 by the Institute of Organic Chemistry with Centre of Phytochemistry of the Bulgarian Academy of Sciences. Sources of these chloro-organic pollutants, appearing locally and in general in the atmosphere of Russe, could be the installations for the production of allyl chloride and the remaining intermediates in the production of epichlorohydrin and epoxy resins. The analyses of samples, collected during the failure of the Chemical Plants at Giurgiu on October 16, 1991, revealed the same composition as that of the samples collected during the atmospheric pollution of Russe on August 26, 1991 (Fig. 7). The presence of chloro-organic compounds in the atmosphere of the town is a frequently observed event and confirms our supposition that there are serious technical and technological problems in the epichlorohydrin installations in Giurgiu, which cannot be solved and eliminated.

After August 19, 1991 the collection of organic pollutants was enriched by new compounds such as benzthiazol, benzthiol, mercaptobenzthiazole, tri- and tetrachloro compounds, aniline, 1,1-dimethylaniline, phenylnaphtylamin etc. (Figs. 8-13). These substances were identified during the atmospheric pollution on August 26 and September 2, 1990. as

accompanying the vulkacit production in the Chemical Plants of Giurgiu. The compounds identified during the atmospheric pollution of Russe in September (September 1, 4, 23, 25, 27, 30) are products from the synthesis of mercaptobenzthiazole or products from the incineration of the waste resins from the vulkacit installation in the Chemical Plants of Giurgiu. Their composition was confirmed by the pyrolytical gas chromatographic -mass spectrometric analyses of waste resins from vulkacit production (Fig. 12). The presence of benzthiazole was proved also by the analysis of the waste resin performed in Belgium (Appendix 1). The atmospheric pollution in September this year, after the officially declared suspension of the production at the Second Production Platform of the Giurgiu Plants can be assigned to the uncontrolled incineration of the waste resin from the production of vulkacit and other chemicals, carried out by an inappropriate method. The variations in the qualitative and quantitative composition of the organic pollutants in the air samples also demonstrates that they are byproducts or originate from wastes. For example, the incineration of vulkacit waste resin is accompanied by an increased evolution of alkylsulphides, di- and trisulphides, carbon disulphide, and at higher temperature, of polysulphides, thiazole, benzthiazole derivatives and other substances (24). It is noteworthy that no destruction of benzthiazole is observed during pyrolysis up to 980°C (Fig. 42). In the case of incomplete burning at lower temperature a dense and stable bluish smoke is evolved, which upon atmospheric transfer forms a layer of smog over parts or even the whole town of Russe.

CONCLUSIONS

1. The present investigations confirmed and enriched our results obtained in 1990 from air samples of the same region. The organic pollutants in the atmosphere of Russe are: hydrocarbons (saturated, normal and branched, unsaturated, alicyclic, aromatic), tertiary butyl.methyl phenols, butyl- and octylphthalates, esters of organic acids, chloroaliphatic compounds (mono- and dichloropropanes and propenes, chloroaliphatic compounds) monochlorohydrins of glycerol, epichlorohydrin, benzthiazole and its derivatives, mercaptobenzthiazole, phenylnaphtylamin etc.

2. The organic compounds found in the atmosphere of Russe during periods of transborder transfer are of variable qualitative and quantitative composition, but the chlorine and sulphur containing compounds are prevailing. These are by- or waste products of organic chemical industrial synthesis, which, according to us, are not characteristic for the production activities in Russe. The sources of the chlorine and sulphur heterocyclic compounds such as: mono- and dichloropropanes and propenes, perchloroethylene, epichlorohydrin, mercaptobenzthiazole and its derivatives are the facilities for the production of epichlorohydrin and vulkacit, situated on the second platform of the Chemical Plants in Giurgiu.

3. The amounts of the untraditional organic pollutants in the atmosphere of Russe at the mobile sites along the Danube river varied from 0.1 to 10 mg/m³ for the period from August 26th to October 20th, 1991 during transborder pollution.

4. The reiteration of the production failures admitted by the Rumanian authorities on August 26th and October 16th, 1991 clearly shows that the installations in the Giurgiu Plant have

serious technical and technological problems, which cannot be radically solved. The Giurgiu Plants operate with high corrosion processes, which require qualified and permanent maintenance with expensive materials, spare parts and aggregates. Hence, after 4-8 years of exploitation the high cost of maintenance will render the installations unprofitable but they will have to be run until their final expiration. Then a real tragedy will occur for the residents in the region, which eventually might lead to an international conflict.

5. The so called "smog" appearing over the town of Russe is assigned to transborder transfer of organic compounds (as those in the above-described case with the waste products of vulkacit). The proximity of the Plants for organic synthesis, the open landscape and the prevailing north-east and north-west weak winds from spring through autumn facilitate a fast transborder transfer, this reducing the probability of photochemical processes in the atmosphere, and, if the transfer occurs in the night, this probability is negligible.

The permanent atmospheric pollutions in Russe are very dangerous because of the air draughts and the specific architecture of the town. The narrow streets and the closed courtyards retain the polluted air and actually "there is no air to breath" for many hours. At the same time the air in a neighbouring region may be pure.

6. The variety of organic atmospheric pollutants present a serious toxilological problem. The synergetic effect of this mixture of pollutants has a deliterious consequences on the human organism, taking into account the record of allergic, respiratory, skin and cancer deseases inflicted on the residents of Russe.

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