

## COMMUNICATION

ZOFIA IGNASIAK, SŁAWOMIR BIŁOZOR\*

## ELIMINATION OF CARCINOGENIC COMPOUNDS IN CONVENTIONAL WATER TREATMENT PROCESSES

In recent years the interest in the organic-type water micropollutants, capable of producing harmful effects in human organism has increased considerably. This refers to polycyclic aromatic hydrocarbons (PAH) which are particularly dangerous because of their carcinogenic effects.

The mechanism of PAH formation is based on pyrolysis and biochemical synthesis. Due to the above processes carcinogenic hydrocarbons are widespread in man's environment.

The possibility of PAH synthesis by plants and bacteria is suggested by the presence of these compounds in samples of plants and soil taken from different depths [1]. According to BLUMER [6] PAH can be either produced by organisms living in soil or they are there due to the conversion of organic mass present in soil into peat and lignites. It has been also stated that bacteria, and among others *E. coli*, can synthesize benzo (a) pyrene (BaP) during their growth on solid medium [13], and that the PAH concentration levels of 100  $\mu\text{g}$ /per 1 kg of dry weight found in plankton, are also the result of the synthesis.

Numerous scientists have stated a constant level of benzo (a) pyrene in plants, at the levels of 10–20  $\mu\text{g}/\text{kg}$  of dry weight. GRAF and NOWAK [7] have observed that the growth of higher and lower plants was stimulated by cyclic hydrocarbons, and that the highest stimulation of growth was due to the most carcinogenic BaP. According to these authors cyclic hydrocarbons may be classified along with natural substances which define biological functions of plants. Despite regular fertilization with benzo (a) pyrene its contents in plants and fruits did not increase. It has been stated, moreover, that PAH are not cumulated in plants.

From the presented data it follows that there exists a natural level of PAH in soil and plants and that man was always exposed to the effects of these compounds.

An increased content of PAH in a natural environment is due to the development of many branches of industry, of chemical industry (production of plastics and dyes), and coke industry, in particular, as well as due to the development of internal combustion transportation. From the work of BORNEFF [3] it follows that the PAH content in water ranges within:

10–50  $\mu\text{g}/\text{m}^3$  in underground water,

50–250  $\mu\text{g}/\text{m}^3$  in surface water slightly polluted,

to 1000  $\mu\text{g}/\text{m}^3$  in surface water heavily polluted.

In wastewaters the concentration of PAH may exceed 100 000  $\mu\text{g}/\text{m}^3$ . Thus the presence of PAH in surface water may be an indicator of water pollution. PAH concentrations occurring most frequently in aquatic habitats are given in table 1 after HARRISON et al. [9].

\* Department of Water Treatment, the Poznań Section of the Institute of Environment Protection Management.

Table 1

## Polynuclear aromatic hydrocarbons (PAH) occurring in waters

Terminology IUPAC <sup>1</sup>	Previous terminology <sup>2</sup>	Gram-molecular weight	Carcinogenic activity	Term Abbreviation
Anthracene	Anthracene	178		An
Benzo(a)anthracene	1,2-Benzoanthracene	228	+	B(a)A
Benzo(b)fluoranthene*	3,4-Benzofluoranthene	252	++	B(b)F
Benzo(j)fluoranthene	10,11-Benzofluoranthene	252	++	B(j)F
Benzo(k)fluoranthene*	11,12-Benzofluoranthene	252	—	B(k)F
Benzo(a)pyrene*	3,4-Benzopyrene	252	+++	B(a)P
Benzo(e)pyrene	1,2-Benzopyrene	252	+	B(e)P
Benzo(ghi)perylene*	1,12-Benzoperylene	276	—	BghiP
Chrysene	Chrysene	228	+	Ch
Fluoranthene*	Fluoranthene	202	—	Fl
Indeno(1,2,3-cd) pyrene	2,3-o-phenylopyrene	276	+	IP
Phenanthrene	Phenanthrene	178		Ph
Perylene	Perylene	252	—	Per
Pyrene	Pyrene	202	—	Pyr

1 IUPAC — 1957 J. Am. Chem. Soc. 82, 5545-5584 (1960).

2 Terminology before 1957.

3 Carcinogenic activity on mouse skin.

+++ active compound.

++ moderately active.

— feebly active.

— non-active compound.

\*PAH included in WHO standards.

In 1970 World Health Organization — considering ever increasing contents of PAH in surface water and their noxious effects on human organisms — established the standard for PAH concentration in water. The total admissible concentrations for six combined polyaromatic hydrocarbons in drinking water, presented in table 1 amount to 200  $\mu\text{g}/\text{m}^3$ .

In the practice of water treatment it has been stated that during sedimentation the elimination of PAH content ranges within 20–80% [15]. The coagulation applied in laboratory conditions yielded PAH removal of PAH amounting to 90%. A high per cent of the removal of these compounds from water by means of coagulation and sedimentation is due to the fact that PAH present in water are mostly absorbed on the suspension, their solubility in water being very low.

It appeared that much more effective method of PAH removal from water, particularly in reference to benzo (a) pyrene, is the absorption on activated carbon bed [4]. The effects of oxydants applied in technology of water treatment i.e. of chlorine, chlorine dioxide and ozone have been investigated by several scientists. ILLNITSKII et al. have found that of all the PAH, benzo (a) pyrene is the most resistant to ozone, and shows the lowest resistance to chlorine. Benzo(a)pyrene, if adsorbed on soil, was degraded to only 60% at a 2.5 min contact with ozone [9].

BORNEFF [5] subjected aqueous solution of benzo(a)pyrene to air enriched with ozone, and found a 99% elimination of BaP at contact times amounting to 30 minutes.

While analysing the products formed during oxidation of PAH it has been stated that both chlorination and ozonation processes did not result in the formation of carcinogenic compounds [14].

The presence of carcinogenic compounds in water of the river Wisła at the Bielany water intake and their elimination in the process of water treatment were studied by the authors while conducting model

tests on this water supply system in the years 1975, 1976. The purpose of this research was to establish the technology of water treatment for the projected modernization of the Bielany water supply system [10]. The tests were conducted on pilot station, where modelling included the following processes: preliminary chlorination in a contact chamber, coagulation encompassing rapid mixing, flocculation and sedimentation in a vertical flow settling tank, rapid filtration, sorption on activated carbon in powder or granular forms, and ozonization.

For the chlorination process the solution of sodium hypochlorite was used — the doses ranged from 3 to 25 mg of Cl/dm<sup>3</sup>, with contact times up to 10 min. Coagulation of admixtures and water pollutants was conducted with aluminium sulphate, using cationic, anionic and nonionic flocculants. Besides Polish flocculants: Gigtar-5, Rokrysol WF-1, WF-2 WF-3 and WF-5 foreign flocculants produced by Allied Colloids, under trade names: Magnafloc LT-20, LT-22, LT-24, LT-25 and LT-26, and activated silicon dioxide were also used. Optimal doses, determined by jar test method for the coagulant and flocculants amounted to 12–37 mg/dm<sup>3</sup> and 0.1–0.5 mg/dm<sup>3</sup>, respectively.

Filtration was conducted on sand and anthracite-sand beds 100 cm deep, using velocities of 10 and 15 m/h.

Powdered activated carbon CARBOPOL Z-4 in form of water suspension was batched to a rapid mixer in the process of coagulation of admixtures and water pollutants.

For granular activated carbon beds CARBOPOL Z-4  $\varnothing$  1–3 mm was used. For comparative reasons Dutch PKST carbon produced by NORIT, having the same grain size was used. The depth of beds amounted to 150 cm, and filtration velocity 20–30 m/h. Ozonization was conducted by means of a LABO-70 ozonizator produced by TRAILGAZ; the concentration of ozone amounted to 20 g of O<sub>3</sub>/m<sup>3</sup> of air water was ozonized to obtain 0.2 and 0.4 mg of O<sub>3</sub>/dm<sup>3</sup> with contact times amounting to 4 and 8 min, respectively.

In water samples the presence of the following six PAH has been identified [8]:

1. Benzo(a)pyrene — B(a)P;
2. Fluoranthene — Fl;
3. Benzo(k)fluoranthene — B(k)F;
4. Benzo(p)fluoranthene — B(p)F;
5. Benzo(ghi)perylene — BghiP;
6. Indeno(1, 2, 3-cd) pyrene — IP.

For the quantitative analysis three of the polyaromatic hydrocarbons studied were selected: benzo(a)pyrene because of its highest carcinogenic activity, fluoranthene which appears in much higher concentrations than other PAH, and benzo(ghi)perylene. The obtained results are presented in tables 2 and 3.

In the course of investigations conducted high concentrations of PAH have been found in Wisla river water. Low concentrations were stated only at high water levels in the river. In all samples of water fluoranthene prevailed.

Preliminary chlorination and coagulation resulted in a distinct elimination of PAH ranging within 20–73%, of the raw river water contents. The amounts found in treated water exceeded, however, two times the admissible drinking water standards.

Addition of powdered activated carbon during coagulation did not improve the effects of PAH removal. This may be due to the too small doses of powdered (25 mg/dm<sup>3</sup>) carbon or to its poor quality.

In the process of water ozonization a considerable drop in PAH contents has been observed. Elimination of these compounds with respect to raw water ranged within 58–89%. Treated water contained 46–127  $\mu$ g/dm<sup>3</sup>.

An additional filtration through carbon bed after ozonization did not improve the elimination of PAH. Imported carbon proved to have better sorptive properties and was less polluted with cyclic hydrocarbons.

In summary the investigations confirm the literature reports about the effectiveness of coagulation, filtration and ozonization in the removal of carcinogenic compounds present in water. The investigations have not confirmed high effectiveness of activated carbons in both powdered and granular form, in elimination of polyaromatic hydrocarbons from water.

Table 2

Contents of carcinogenic compounds in water from the Vistula

Time of water sampling	PAH content in g/dm <sup>3</sup>			Sum of PAH μg/m <sup>3</sup>
	B(a)P	Fl	BghiP	
October 1974	33	732	95	860
April 1975	36	118	100	254
July 1975	9	63	61	133
October 1975	24	210	68	302
January 1976	48	535	189	772

Table 3

Contents of carcinogenic compounds in water after technological operations

Kind of technological operation	Time of experiments	B(a)P		Fl		BghiP		Sum of PAH	
		μg/m <sup>3</sup>	% of elim.	μg/m <sup>3</sup>	% of elim.	μg/m <sup>3</sup>	% of elim.	μg/m <sup>3</sup>	% of elim.
Preliminary chlorination	April 1975	26	28	44	63	34	66	104	59
Coagulation	July 1975	6	33	68	0	28	54	102	23
Filtration	October 1975	13	54	165	21	64	6	242	20
	January 1976	15	69	130	76	61	68	206	73
Preliminary chlorination	April 1975	26	28	42	64	30	70	98	61
Coagulation	October 1975	21	23	150	29	21	69	192	36
Powdery carbon filtration									
Preliminary chlorination	July 1975	3	67	20	68	23	62	46	65
Coagulation	October 1975	8	67	100	52	19	72	127	58
Filtration, ozonization	January 1976	9	81	45	92	30	84	84	89
Preliminary chlorination	July 1975	2	78	31	51	18	70	51	62
Coagulation	October 1975	4	83	125	41	31	54	160	47
Filtration	October 1975*	3	87	109	48	31	54	143	53
Ozonitation	January 1976	10	79	100	82	32	83	142	82
Activated carbon filtration	January 1976*	3	94	45	92	9	95	57	93

\*Granulated coal produced by NORIT.

## REFERENCES

- [1] BORNEFF J., SELENKA F., KNUTE H., MAXIMAS A., Arch. Hyg. Bakt. **152**, 279 (1968).
- [2] BORNEFF J., FISCHER R., Arch. Hyg. Bakt. **145**, 334 (1961).
- [3] BORNEFF J., KNUTE H., Arch. Hyg. Bakt. **148**, 585 (1964).
- [4] BORNEFF J., FISCHER R., Arch. Hyg. Bakt. **146**, 1 (1962).
- [5] BORNEFF J., Gas. Wass. **110**, 29 (1969).
- [6] BLUMER N., Science (New York) **134**, 474 (1961).
- [7] GRAF W., NOWAK W., Arch. Hyg. Bakt. **153**, 390 (1969).
- [8] GROCHMALICKA J., *Oznaczanie wielopierścieniowych węglowodorów aromatycznych w wodzie wodociągowej „Bielany” w Krakowie*, Zakład Chemii Nieorganicznej i Analitycznej Instytutu Chemii i Analityki Akademii Medycznej w Poznaniu, 1976.
- [9] HARRISON R. M., PERRY R., WELLINGS R. A., Wat. Res. **9**, 331 (1974).
- [10] IGNASIAK Z., BIŁOZOR S., *Badania technologiczne nad ustaleniem optymalnego procesu uzdatniania wody na stacji wodociągowej „Bielany” w Krakowie*, IKŚ Poznań, 1976.
- [11] ILLNITSKII A. P., KHESINA A. Y., CHERKINSKII S. N., SHABAD L. M., Hyg. Sanit. **33**, 323 (1968).
- [12] International Standards for Drinking Water, World Health Organization, Genewa 1970.
- [13] KNORR M., SCHONK D., Arch. Hyg. Bakt. **152**, 282 (1968).
- [14] MÜLLER E., REICHERT J. K., Arch. Hyg. Bakt. **153**, 26 (1969).
- [15] SAMOILOVICH L. N., REDKIN Y. R., Hyg. Sanit. **33**, 165 (1968).
- [16] WYNTER E. L., HOFFMANN D., Cancer **15**, 103 (1962).