CHLORINATED POLYCYCLIC AROMATIC HYDROCARBONS IN THE WASTE WATER OF PULP AND PAPER MILLS

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Introduction

One of the important sources of environmental pollution is pulp and paper mills discharges especially when chlorine bleaching is used. These emissions contain a plenty low and high molecular weight chlorinated compounds including high toxic PCDDs and PCDFs. Analysis of pulp and paper mill waste water showed that some of them contain other kind of potentially hazard chlorinated compounds – polychlorinated PAH. It is known that some chlorinated PAH such as chlorinated pyrene and perylene render toxic and mutagenic action[1].

Material and Methods

Waste water samples of some paper mills in the Siberia were analysed by full scan GC-MS. Extracts were been prepared for dioxin analysis i.e. in preference planar molecules, including PCDD/PCDF and PAH, were concentrated in the final extracts using the procedure described elsewere[2]. Ion trap mass spectrometric detector Finnigan MAGNUM coupled with gas chromatograph Varian 3400 was used for this study. The gas chromatograph was equipped with silica capillary column 25 m x 0.25 mm Quadrex 400-1HT-25-0.1F. The follows temperature program was used: 120°C(1)-20°C/min-220°C-5°C/min-280°C, injector and interface temperature 260°C, carrier gas He flow rate 1 ml/min. Splitless injection was used with purge delay time 0,25 min. Full scan mass spectra were acquired in the range 150-550 using electron impact ionisation at 70 eV.

Identification of components was carried out on the base of the molecular mass, ion isotope clusters, fragmentation routs and retention times. Concentrations were estimated by internal standard method, using the isotope labeled dioxin standards and D_{10}-antracene.

Results and Discussion

In the waste water samples a number of unsubstituted and alkyl substituted PAH (phenanthrenes, dihydrophenantrenes, chrizenes, pyrenes, benzopyrenes, etc.) were found (Table). Also their thiophenic analogs were observed. Predomination of alkyl, especially polymethyl, substituted compounds and structure similarity of PAH and polycyclic thiophenic compounds point to oil residues origin of these compounds.

PAH concentration in waste water samples was from 80 ppt for allkylphenantrenes and alkyldibenzothiophenes to low ppt for benzopyrenes and naphtobenzothiophene.

In some waste water samples chlorinated PAH were found: phenanthrene, methyl and dimethylphenantrenes, pyrenes, methyl and dimethylpyrenes etc. Concentration of these compounds was from sub-ppt to 20 ppt. Chlorinated sulphur compounds were not detected.
Thereby PAH and them sulphur containing analogues are usual contaminants in pulp and paper mill waste water. However, chlorinated PAH are present not at all waste water samples. Besides the structure of chlorinated PAH is very similar to that of unchlorinated PAH which are petroleum origin. Like enough that the origin of chlorinated PAH is combustion of chlorine containing wastes.
Chlorinated PAH were found out previously in water after chlorination, in gas emissions urban air and in exhaust gases of automobiles that is in processes exeptly the first related to fuel combustion processes[3]. Therefore chlorinated PAH in paper mill waste water apparently are connected not with pulp bleaching process but with combustion of oil fuel.

Acknowledgements
This work was supported by INTAS (Project 1990-96).

References

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Table

PAH and chlorinated PAH in waste water from pulp mills, ng/l
1 - Bratsk paper mill; 2 **-** Baykal paper mill; **3 -** AO "Chimprom", Usolye-Sibirskoye;
4 - AO "Sayanskchimprom", Sayansk.

Component	m/z	RT	1	2	3	4
Fluorene	166	201	72.8	-	80.9	36.0
Methylfluorenes	180	259	13.0	13.3	57.6	8.4
Dimethylfluorenes	194	300	18.6	1371.2	210.0	36.4
Trimethylfluorenes	208	335	-	806.5	-	20.4
Acenaphtene	168	270	0.03	-	-	-
Methylacenaptenes	182	262	2.2	-	2.5	-
Dimethylacenaphtenes	196	308	12.7	-	38.8	11.5
Trimethylacenaphtenes	210	375	2.0	111.4	22.5	15.0
Phenantrene/Antracene	178	340	82.3	2108.3	264.6	44.8
Methylphenantreness	191,192	411	41.2	1922.6	146.2	49.4

Methylantracenes	191,192	421	34.6	1714.6	130.9	41.8
Ethylantracene/phenantrene	191,206	452	-	176.8	-	-
Dimethylphenantrenes	205,206	460-540	22.6	1013.8	94.6	36.9
Trimethylphenantrenes	220	587	6.5	151.0	37.2	20.4
Tetramethylphenantrenes	234	650	0.8	12.0	6.6	3.5
1-Me-7-i-Pr-phenantrene	234	647	1.4	154.4	28.1	13.4
Fluorantene	202	509	6.3	185.5	23.5	9.3
Pyrene	202	544	1.6	63.8	16.2	5.4
Methylpyrene	215,216	600-627	1.0	12.0	2.3	1.3
Triphenylene	230	584	0.6	6.5	2.0	5.1
Benzoacenaphtene	226	525	4.1	2.9	-	-
Methylcyclopentanephenantrene	218	530-580	-	78.9	11.1	1.4
Dimethylcyclopentanephenantrene	232	664	-	5.7	4.1	-
Dibenzochinoline	227	570	-		-	1.6
Tetraceene	228	798	-	1.5	-	-
Benzoantracene	228	864	-	2.9	-	0.2
Chrizene	228	872	-	9.9	-	0.9
Methylchrizene	241,242	1023	-	5.3	-	1.1
Benzofluorantene	252	1345	-	-	-	0.1
Dibenzotiophene	184	324	5.4	5.0	16.7	2.2
Methyldibenzotiophenes	197,198	384	23.1	515.0	78.0	12.0
Ethyldibenzotiophenes	197,212	439	1.3	-	-	1.2
Dimethyldibenzotiophenes	211,212	412	33.6	1011.7	53.4	77.1
Trimethyldibenzotiophenes	226	480-600	24.9	263.9	12.6	6.7
Tetramethyldibenzotiophenes	240	620	2.8	-	3.0	2.9
Pentamethyldibenzotiophenes	254	660-715	-	-	-	2.2
Naphtobenzothiophene	234	530	-	4.9	-	-
Chporophenantrene	212	462	15.0	-	7.5	-
Methylchlorophenantrenes	226	549	32.7	-	22.1	43.2
Dimethylchlorophenantrenes	240	570-700	15.7	3.4	4.0	15.8
Trimethylchlorophenantrenes	254	700-820	10.6	-	0.4	3.1
Tetramethylchlorophenantrenes	268	849	9.0	-	-	-
Dichlorophenantrene	246	600-650	1.6	-	4.1	4.4
Dichloromethylphenantrenes	260	739	4.6	3.1	1.2	8.5
Dichlorodimethylphenantrenes	274	850-1000	10.4	-	-	19.0
Dichlorotrimethylphenantrenes	288	980-1180	10.5		-	3.0
Dichlorotetramethylphenantrenes	302	1094	4.2	-	-	-
Trichlorophenantrene	280	839	0.5	-	-	-

Chlorotrimethylfluorene	242	536	-	49.9	22.8	7.8
Chloropyrene	236-238	685	2.7	-	0.8	0.5
Dichloropyrene	270-276	840-1110	30.4	-	-	1.0
Trichloropyrene	304-310		-	-	-	0.6
Tetrachloropyrene	338		-	-	-	0.2
Chloromethylpyrene	250	651	-	-	-	0.3
Chlorochrizene	262	1137	-	-	-	0.2
Trichlorobenzoacenaphtene	272	661	-	-	-	0.7
Chloronaphtobenzothiophene	268-270	780-820	0.2	-	-	-
Chlorodibenzo-p-dioxin	218	333	1.2	-	-	-
Dichlorodibenzo-p-dioxin	252	443	5.5	131.4	19.1	9.4
Trichlorodibenzo-p-dioxin	286	558	0.1	-	0.3	0.7

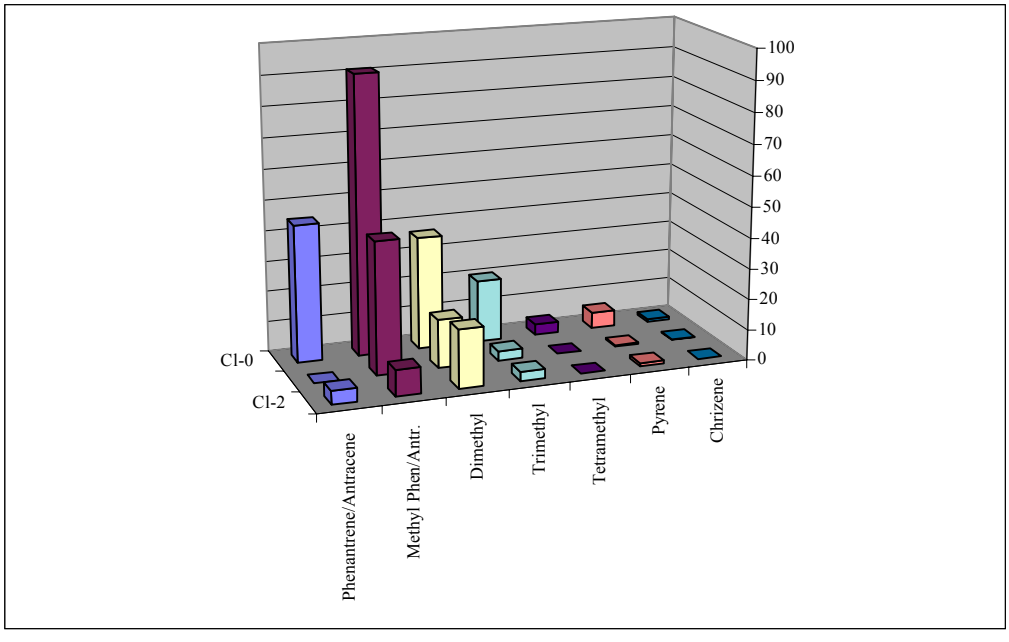

Fig.2. PAH and chlorinated PAH in Sayanskchimprom paper mill waste water (ng/l)