WATER COLUMN PROFILING OF PERSISTENT ORGANIC POLLUTANTS AND PESTICIDES IN FRONT OF THE THREE GORGES DAM DURING IMPOUNDMENT IN AUTUMN 2012

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Introduction

The construction and the closure of the Three Gorges Dam in China led to the creation of a reservoir with a surface area of 1084 km². The large size and water capacity of the reservoir cause the monitoring of pollutants in general to be a demanding task. Sampling techniques as well as sampling locations have to be closely related to the questions which are going to be answered. In case of persistent organic pollutants (POP) like polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP), there is only limited data available concerning the Three Gorges Reservoir (TGR)[1,2]. Nevertheless, first results indicate that the large water body causes high dilution despite of substantial potential freights of POPs making sample enrichment mandatory to adequately estimate these freights.

There are different techniques in determining concentrations of POPs in water. One common approach is the deployment of passive sampling devices which are then exposed for a defined period to the medium which is going to be sampled[1]. Thesamplersimitate the exposition of animals in water which leads to them being also referred to as virtual organisms (VOs). Passive sampling, however, sometimes is not applicable due to limitation of time or concentration of target compounds.

Active water sampling may be an alternative for analytical questions that cannot be answered by means of passive sampling devices. In analogy to solid phase extraction known as a common cleanup step, cartridges packed with suitable sorbent material can be loaded with water sample directly at the sampling location. This approach offers the possibility of collecting large sample volumes leading to high enrichment factors for the detection of trace compounds.

The work presented is based on a sampling campaign that took place in September 2012 at the TGR. The sampling site was located close to the Three Gorges Dam in the middle of Yangtze River. Water samples of about 400 L each were taken in 11, 31 and 61 meters depth by means of active water sampling. Sample extraction and cleanup for OCP, PCB and PAH was accomplished according to our already existing laboratory workflow. For subsequent measurement and quantification, gas chromatography coupled with a high resolution mass spectrometer was used.

Materials and methods

All Solvents as well as sodium sulfate and silica gel used during sample cleanup were purchased from LGC Promochem (Wesel, Germany). EcoChrom Alumina B was purchased from MP Biomedicals (Eschwege, Germany). Supelpak-2 XAD-2 resin was purchased from Sigma-Aldrich (Steinheim, Germany).

For sampling purposes, self-packed cylindrical glass sampling cartridges with a dimension of approximately 22 x 4.5 cm (lengh x diameter) were used. The XAD-resin was trapped within the cartridges with a glass frit at one side and heated glass wool at the other side. During sampling, a filter cartridge, tight packed with heated glass wool was mounted in front of every sampling cartridge. Two identically prepared XAD and filter cartridges were regarded as field blanks. The water sample was sucked through the cartridges which were at the same time covered with a self-made stainless steel cover and submerged in water down to the desired water depth. Water was pumped by a battery driven peristaltic pump purchased from Verder (Haan, Germany) at a flow rate of about 3 L/min. Consequently,drawing enough volume for one sample took about 2 h 15 min. Prior extraction, the cartridges have been stored at 4 °C. Before sample extraction, a standard mixture with ^{13}C-marked standard

substances was added onto the cartridges. Extraction of XAD and filter cartridges was carried out with a soxhlet apparatus during 24 hours with a mixture of Hexane:Acetone 3:1. The content of the XAD cartridges was split by half resulting in one master and one backup part of the sorption media.

The sample cleanup, instrumental analysis as well as quantification were described elsewhere in detail[3]. Nevertheless a brief description shall be given here. The soxhlet extract was concentrated by rotavap, then eluted from a silica gel and alumina b column with a mixture of n-hexane:dichloromethan 1:1. After another concentration step with the rotary evaporator, the sample was transferred to a C-18 SPE-cartridge and eluted with acetonitrile. The eluate was evaporated at 40 °C under a gentle nitrogen stream and finally transferred to a sample vial and adjusted to a total volume of 20 µL.

The measurement was performed on a Agilent GC 5890 series II (Agilent Technologies, Palo Alto, USA) coupled to a high-resolution mass spetrometerFinnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany). Chromatographic separation was achieved by splitless injection (cold injection system CIS4, Gerstel GmbH, Mülheim, Germany) of 1 µL on a RestekStx-ClPesticides2 column with a column length of 30 m, ID 0.25 mm and 0.2 µm film thickness (Restek GmbH, Sulzbach, Germany).

Results and discussion

The separate analysis of master and backup parts of the sampling cartridges was carried out in order to state whether sampling was quantitative. The summed up concentrations of OCP, PCB and PAH in each part of the
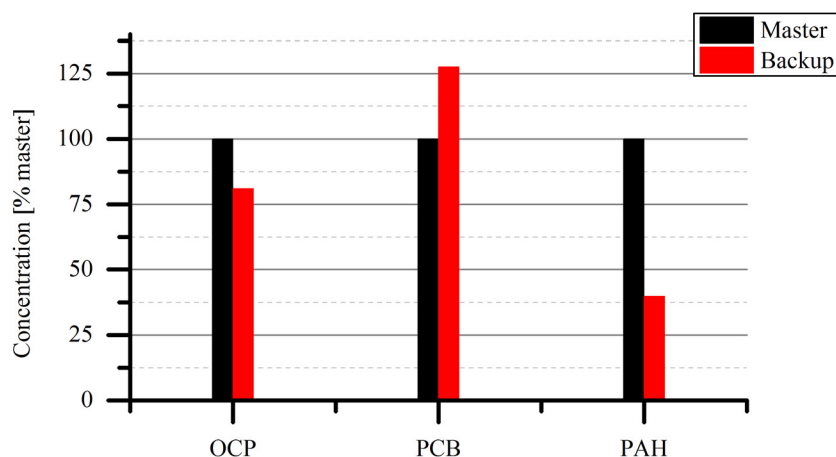

Fig. 1: Total amount of OCP, PCB and PAH of 11 m normalized to the master part of the sampling cartridge

cartridge are presented in figure 1 for the measurement in 11 m water depth which is representative in terms of distribution for the other depths. The values are normalized to the amount measured in the master part. At least for PAH and OCP, the concentration was higher in the master part of the cartridge. The PCBs, however, can be found in a larger amount in the backup part than in the master part. The figure shows that for all three investigated groups of analytes significant breakthrough within the cartridge is observed. Consequently, the sampling results cannot be regarded as quantitative.

In general, determined concentrations of single OCP, PCB and PAH ranged from 0-100, 0-2, and 0-2500 pg/L, respectively, which reflects high dilution of these compounds in the large water body.

With respect to the breakthrough in sampling cartridges, the determined data could be used to profile the single compounds in the different water depths. Table 1 lists the concentration deviation for each compound in 31 and 61 m depth relative to concentrations measured in 11 m water depth. Despite some exceptional high relative differences for single substances, OCP and PCB varied less than 50 % with increasing water depth. For PCB, the results were more inconsistent than for OCP which might originate from their low absolute concentration. As far as the measurements were representative for the TGR at sampling time, concentration of indicator PCB tended to be slightly higher in deep water layers whereas the one of OCP tended to be lower.

The largest relative differences were observed for PAH. These accumulated to higher concentrations in the filter cartridges than in the cartridges packed with XAD. Especially the three-ring homologues seemed to be more

present in 61 mwater depth. Nevertheless the data does not support the thesis of increasing concentration with increasing depth because values measured in 31 m depth are comparable to the ones determined in 11 m depth.

Table 1: Relative concentrations of OCP, PCB and PAHin 31 and 61 m water depth referred to 11 m; '--' stands for reference value being '0'

Compound	XAD-Cartridges		Glass Wool Cartridges	
	Dev. 31 to 11 m [%]	Dev. 61 to 11 m [%]	Dev. 31 to 11 m [%]	Dev. 61 to 11 m [%]
OCP				
alpha-Hexachlorocyclohexane	-17.9	-28.5	-18.3	-39.2
beta-Hexachlorocyclohexane	-18.2	-24.5	-22.0	-45.6
gamma-Hexachlorocyclohexane	-16.4	-10.0	-21.7	-15.2
delta-Hexachlorocyclohexane	-25.0	-28.2	-54.6	-100.0
epsilon-Hexachlorocyclohexane	-13.6	35.7	-100.0	-100.0
Pentachlorobenzene	-23.7	-1.0	-16.8	-23.4
Hexachlorobenzene	-3.1	-4.8	-17.2	-39.7
Pentachloroanisole	-7.0	-4.9	-6.9	-6.6
Octachlorostyrene	-8.7	-13.8	13.4	0.5
4,4'-Dichlorodiphenyltrichloroethane	-42.5	2.7	-33.0	-66.1
2,4'-Dichlorodiphenyltrichloroethane	-35.0	-36.1	-36.1	-44.2
4,4'-Dichlorodiphenyldichloroethane	-34.7	-35.3	-32.4	-27.6
2,4'-Dichlorodiphenyldichloroethane	-37.0	-31.2	-27.3	-43.2
4,4'-Dichlorodiphenyldichloroethene	-39.2	-38.8	-27.6	-41.3
2,4'-Dichlorodiphenyldichloroethene	-52.6	-25.9	-26.8	-38.6
trans-Chlordane	-61.8	-15.7	0.0	0.0
cis-Chlordane	3.5	-100.0	0.0	0.0
oxy-Chlordane	9.0	0.0	0.0	0.0
Heptachlor	0.0	0.0	0.0	0.0
cis-Heptachloroepoxide	-21.4	6.8	-11.3	-100.0
trans-Heptachloroepoxide	-62.1	-100.0	0.0	0.0
Aldrin	--	--	30.9	1749.0
Dieldrin	-27.5	96.9	--	--
Endrin	-18.4	-100.0	0.0	0.0
Endosulfan-I	-60.7	-100.0	0.0	0.0
Endosulfan-II	14.7	-100.0	0.0	0.0
Endosulfan-sulfate	-24.7	-23.4	-17.2	-100.1
Methoxychlor	-48.9	295.0	2.4	676.0
Mirex	-100.0	0.0	--	--
PCB				
PCB #28	-12.9	153.2	35.8	-50.9
PCB #52	-11.3	167.9	-1.6	-51.1
PCB #101	-26.7	124.5	16.3	-35.1
PCB #138	-25.2	236.4	34.6	63.3
PCB #153	-30.9	65.5	43.6	-17.7
PCB #180	-31.8	53.8	74.3	35.0
PCB #77	4.3	154.4	-6.7	-26.4
PCB #81	-50.2	-100.0	--	--
PCB #126	0.0	0.0	--	--
PCB #169	0.0	0.0	--	--

Compound	XAD-Cartridges		Glass Wool Cartridges	
	Dev. 31 to 11 m [%]	Dev. 61 to 11 m [%]	Dev. 31 to 11 m [%]	Dev. 61 to 11 m [%]
PCB #105	-13.9	57.8	22.0	-29.2
PCB #114	0.0	-100.0	--	--
PCB #118	-28.9	78.7	34.0	-26.5
PCB #123	0.0	-100.0	-100.0	-100.0
PCB #156	-33.0	24.8	69.0	-100.0
PCB #157	25.4	0.0	--	--
PCB #167	-66.7	86.5	-34.9	-43.3
PCB #189	0.0	0.0	--	--
PAH				
Naphthalene	--	--	-2.3	1059.1
Acenaphthylene	-8.2	317.1	-8.7	433.9
Acenaphthene	9.2	65.0	-16.3	27.0
Fluorene	0.1	395.2	-19.3	344.0
Phenanthrene	-15.2	195.7	-24.4	81.9
Anthracene	-24.2	310.3	-17.0	22.4
Fluoranthene	-19.0	46.6	-15.5	-10.3
Pyrene	-51.3	-41.1	-17.2	-12.8
Benz(a)anthracene	-48.3	67.4	-7.0	-10.8
Chrysene	--	--	-17.7	-19.5
Benzo(b)fluoranthene	-58.1	83.3	-20.6	-34.3
Benzo(k)fluoranthene	-39.9	140.6	5.0	-12.4
Benzo(a)pyrene	-50.6	129.2	-11.4	-23.0
Indeno(1,2,3-c,d)pyrene	-54.3	333.3	-6.8	-18.7
Benzo(g,h,i)perylene	-100.0	175.0	-14.2	-27.6
Dibenz(a,h)anthracene	-67.1	298.9	-3.0	-23.4

Higher PAH occurrence in the filter cartridges of the 61 m sample might be explained by increased sedimentation induced by the Three Gorges Dam. In contrast, this observation could not be confirmed for larger PAH with the values from the filter cartridges.

All in all, the sampling campaign did not reveal tremendous differences in PCB, OCP and PAH concentration among the three different water depths. Nevertheless further investigation with improved sampling setup might reveal absolute POP concentrations for the TGR.

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