QA/QC – MEASURES FOR CONTINOUS MONITORING OF POPs IN BIOTA SAMPLES COLLECTED IN THE FRAME OF THE GERMAN ENVIRONMENTAL SPECIMEN BANK

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Introduction

Persistent organic pollutants (POPs) are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife [1] . Thus, the continuous monitoring of POPs like chlorinated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in biota specimen is an important task to obtain reliable data of environmental state. The German Environmental Specimen Bank (ESB) collects, processes, and stores selected specimen of plant and animal origin mainly to generate a stock of material for retrospective monitoring. Prior to long-term storing specimen are routinely analysed for a fixed set of chlorinated hydrocarbons, PAHs, and inorganic substances[2]. To verify the accuracy and performance of the conducted POP measurement a number of quality assurance (QA) and quality control (QC) procedures are to do.

The aim of this study is to give an overview about the QA- and QC-procedures in the framework of continuous analytical investigations.

Materials and methods

Analysis techniques

- Internal quality assurance

To guarantee the high performance of the QA standards gas chromatography/ mass spectrometry (GC/MS) is applied. The application of mass spectrometry allows the selective verification of the analyte of interest. The probability of false positive results within the acquired data is irreducible. In the case of chlorinated hydrocarbons the exercise of high resolution mass spectrometry for ultra trace analysis is advantageous.

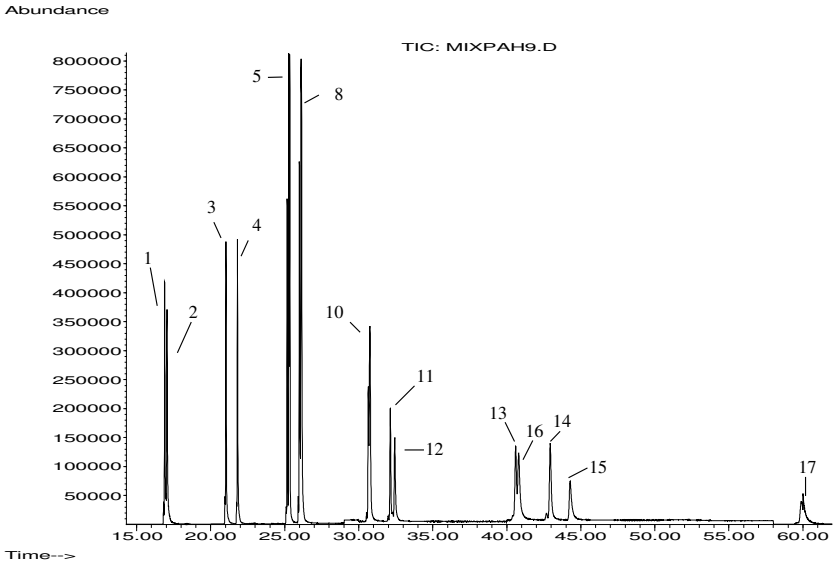
Investigated Substances	Mass Spectrometer	Type
Chlorinated Hydrocarbons	Thermo Finnigan MAT 95 XP and/or VG Autospec	High Resolution (double focussing)
Polycyclic Aromatic Hydrocarbons	Agilent 5973	Low Resolution (quadropole)

Table 1: Used mass spectrometers

The identification of the specific analyte occurs by means of different substance parameters:

- Retention time of the analyte (scheme 1)
- Detection of two substance specific mass traces (scheme 1)
- Control of the isotope ratio or in case of PAHs the fragment ion ratio
- Control of the retention time ratio of the analyte and the isotope labelled standard substance (Table 2 and 3)

1 phenanthrene
2 anthracene
3 fluoranthene
4 pyrene
5 benzo(b)naphtho[2,1d]thiophene
6 benzo(c)phenanthrene
7 benzo(a)anthracene
8 chrysene-triphenylene
9 benzo(ghi)fluoranthene
10 benzo[b+j+k]fluoranthene
11 benzo(e)pyrene
12 benzo(a)pyrene
13 indeno[1,2,3cd]pyrene
14 benzo(ghi)perylene
15 anthanthrene
16 dibenz[a,h]anthracene
17 coronene



Scheme 1: Chromatogram of investigated PAHs and exemplarily the two mass traces (quantifier m/z 188 and qualifier m/z 187) of phenanthrene and anthracene (recorded in single ion monitoring (SIM) modus)

Standard Substances	Quantifier m/z
phenanthrene d_{10}	188
anthracene d_{10}	188
fluoranthene d_{10}	212
pyrene d_{10}	212
benz[a]anthracene d_{12}	240
chrysene d_{12}	240
triphenylene d_{12}	240
benzo(b)naphto[2,1-d]thiophene d_{10}	244
benzo[b]fluoranthene d_{12}	264
benzo(a)pyrene d_{12}	264
dibenz[a,h]antracene d_{14}	292
indeno[1,2,3-cd]pyrene d_{12}	288
benzo[ghi]perylene d_{12}	288
coronene d_{12}	312

Table 2: Deuterium labelled standard PAHs

Standard chlorinated pesticides	Quantifier m/z
β-HCH $^{13}C_6$	294
γ-HCH $^{13}C_6$	294
p,p´-DDT $^{13}C_{12}$	364
p,p´-DDE $^{13}C_{12}$	328
dieldrin $^{13}C_{12}$	390
pentachlorobenzene $^{13}C_6$	254
hexachlorobenzene $^{13}C_6$	288
2,4,4´-trichlorobiphenyle (PCB-28) $^{13}C_{12}$	268
2,2´,5,5´-tetrachlorobiphenyle (PCB-52) $^{13}C_{12}$	302
2,2´,4,5,5´-pentachlorobiphenyle (PCB-101) $^{13}C_{12}$	336
2,3´,4,4´,5-pentachlorobiphenyle (PCB-118) $^{13}C_{12}$	336
2,2´,3,4,4´,5´-hexachlorobiphenyle (PCB-138) $^{13}C_{12}$	370
2,2´,4,4´,5,5´-hexachlorobiphenyle (PCB-153) $^{13}C_{12}$	370
2,2´,3,4,4´,5,5´-heptachlorobiphenyle (PCB-180) $^{13}C_{12}$	402

Table 3: ^{13}C-labelled standard chlorinated pesticides

- Calibration

To examine the mass signals for the quantification a multipoint calibration is necessary. In ideal case the calibration is straight proportional within a wide concentration range. The ratio of the concentrations of the native standard to the labelled standard versus the ratio of areas is plotted (Fig. 1).

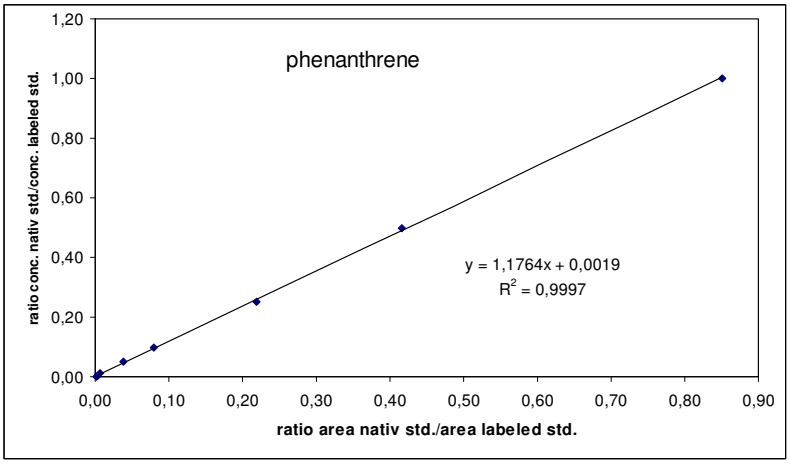


Figure 1: Calibration plot exemplarily for the analysis of phenanthrene

Results and discussion:

Internal Quality Assurance
- Analysis of QA samples

To control the purity of absorber materials, solvents, etc., a laboratory blank is performed with each batch (normally 12) of samples. Additional a quality control pool of known composition and concentration is investigated. Both the laboratory blanks and QC-pools are observed over a wide time range using mean control cards (Figure 2). The mean control card indicates the deviation of a given concentration from the mean. The lower confidence limit (defined as +/- 2 x variance) act as caution limit for attentive observation of the next data. The exceed or the achievement of the upper confidence limit (defined as +/- 3 x variance) results in an intervention and subsequent intensive check of the measurement process.

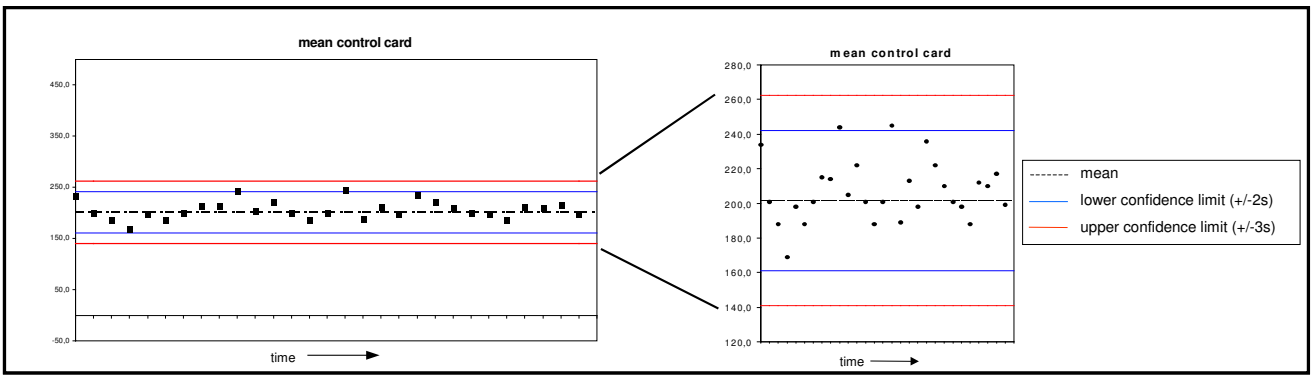


Figure 2: Mean control card for the mean of an analyte of a QC-pool

analyte	mean data [ng/g FS]	standard deviation [ng/g FS]	rel. standard deviation [%]
phenanthrene	194	5,0	2,6
anthracene	3,0	0,21	7,1
fluoranthene	90	3,3	3,6
pyrene	56	2,0	3,5
benzo[*b*]naphtho[2,1]thiophene	5,8	0,19	3,3
benzo[*c*]phenanthrene	4,6	0,17	3,8
benzo[*a*]anthracene	3,9	0,15	3,9
chrysene-tripenylene	48	1,5	3,1
benzo[*ghi*]fluoranthene	5,7	0,58	10
benzo[*b+j+k*]fluoranthene	13	0,47	3,5
benzo[*e*]pyrene	2,6	0,27	10
benzo[*a*]pyrene	1,8	0,089	4,9
indeno[1,2,3-*cd*]pyrene	2,4	0,14	5,8
benzo[*ghi*]perylene	2,7	0,12	4,7
anthanthrene	0,33	0,038	12
dibenz[*ah*]anthracene	0,73	0,053	7,2
coronene	1,3	0,083	6,3

Table 4: Mean data, standard deviation and rel. standard deviation of a QC-pool (set of measurement data, n=10)

- Duplicate Analyses

Due to the performance of the 4 –6 individual analysis of each sample additional duplicate analysis were not part of the QC/QA program.

- Reference Material

To ensure the accuracy of the obtained results ESB reference material was analyzed with each batch of samples. For herbal samples pine shoots of known composition was used as reference material. Either bream muscle tissue or common mussel material of known composition was used as reference material for samples of animal origin.

External Quality Assurance

- Participation on interlaboratory tests

Eurofins Ergo and Eurofins GfA participated on a number interlaboratory tests (IT) in the last years (Table 5). Apart from the annual QUASIMEME IT the Ergo laboratory controls the correctness of the acquired analyse data by participance on several other ITs.

Matrix	Analytes	Year	Organized by
Muscles, fish	Chlorinated hydrocarbons, fat content	2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009	QUASIMEME
Muscles	polycyclic aromatic hydrocarbons	2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009	QUASIMEME
Human blood	PCBs, HCB, DDE	2003, 2004, 2005	Public Health Department of Baden-Württemberg, Germany
Sludge	PCBs	2003, 2004, 2005, 2006, 2007, 2008, 2009	Environmental Department Hamburg, Germany
Cheese, salmon, turkey, etc., human milk	PCDDs/PCDFs, PCBs	2003, 2004, 2005, 2006, 2007, 2008, 2009	Norwegian Institute of Public Health
Various animal food tissues	PBDEs	2006, 2007, 2008, 2009	Norwegian Institute of Public Health

Table 5: Assortment of participations on Interlaboratory Tests in last few years

Acknowledgements:

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References:

1. Stockholm Convention on Persistent Organic Pollutants
2. German Environmental Specimen Bank: www.umweltprobenbank.de