Application of QUECHERS Extraction Coupled With GC/MS for Detection of Polycyclic Aromatic Hydrocarbons and Organochloride Pesticides in Lake Water

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Abstract

The extensive development of industries gives birth to many chemicals which brings contaminations towards environment. The present study is to apply QUECHERS extraction coupled with GC/MS for detection of polycyclic aromatic hydrocarbons (PAHs) and organochloride pesticides (OCPs) in Lake Nokou é of Benin Republic. The method was first benchmarked with standard PAHs and OCPs, and limit of detection (2-194 ppb) and limit of quantification (8-645 ppb) were obtained with recovery rate of 91-110%. The method was then applied to the detection of PAHs and OCPs in the lake water, no benzo[a]pyrene, chrysene or pyrene was detected. The main origin of PAH compounds in Nokou é Lagoon are material combustion and fuels for Polycyclic Aromatic hydrocarbons and due to remoteness pollution for organochorid pesticides compounds.

Keywords: development, analytical method, research, PAHs, OCPs, QUECHERS GC/MS

1. Introduction

Due to diversity of pollutants released and the associated risks, analytic methods to assess the actual extent of damage are still a challenge for the analyst despite the existence of panoply of techniques. To limit exposures to very toxic organic extraction solvents and to optimize the analytical times, multi-residue pretreatment techniques have been developed and are now widely used in research of organic pollutants (Cort &-Aguado et al., 2008; Perret et al., 2004 & Bogiallia et al., 2004). These techniques include assisted microwave, pressurized fluid (ASE), critical CO₂, acetonitrile extractions such as the developed and improved QUECHERS method (Anastassiades et al., 2003, Lehotay et al., 2005 & Kmell ár). et al., 2010). The last method is less expensive, very reliable, effective, fast, reproducible and less toxic. This analytical approach is accompanied by the production of very powerful chromatographs equipped with high-performance sensors such as GC-MS, GC-MS / MS, LC-MS, LC-MS / MS able to separate and detect individual molecules of organic pollutants in a complex mixture resulting from a pretreatment of any environmental matrix (Chamkasem et al., 2013 & Salem et al., 2016). The choice of natural water samples for this method is based on the waters of Lake Nokou é a lake belonging to one of the most important hydrographic complexes in West Africa. This ecosystem, under a strong demographic pressure because of its location in urban areas whose consequences of mismanagement of municipal wastes, are characterized by garbage dump along its banks. It is also the receptacle of wastewater and wastes from the city of Cotonou, lacustrine villages of the town-hall of Sô-Ava, the town of Abomey-Calavi on the one hand and surface water such as the Ou én é River draining runoff that has leached cropland in large part of Benin Republic. Thus, these waters carry residues of agricultural inputs. Studies have revealed that the Cotonou Channel and Nokou é Lake ecosystems are heavily polluted by organic material of all kinds, including PAHs, PCBs and pesticides (Soclo et al., 2008, Yehouenou et al., 2006a & b). According to the results of these authors, the concentration levels in PAH of the channel vary between 70 and 722ng / g of dry sediments and in OCPs of a few ppb in water, sediments and living organisms. Thus, the environmental matrices of such an environment seem appropriate for the simultaneous research and monitoring of PAHs, OCPs and their derivatives by the multiresidue extraction method QUECHERS and gas chromatography coupled to mass spectrometry in an efficient manner. The objective of the study is to develop and adapt these analytical techniques to the evaluation and monitoring of contamination levels of organic pollutants in the lake.

2. Material and Methods

2.1 Stus

The surface water samples were collected in Nokou é lake, whose geographical coordinates are: 6 $^\circ$ 25 '60 "N and 2 $^\circ$ 27'0" E and 42 meters altitude. It covers an area of 339 ha.



Coordinat	es of the samp	ling points
Site names	X	Y

MLA1	2° 23' 52.0"	6°27'33.9"
MLA2	2° 24' 20.0''	6° 26' 29.1"
MLA3	2° 25' 03.1"	6° 24' 26.5"



The three sampling points are presented on the map of the figure with geographic coordinates (MLA1, MLA2, MLA3). The development, validation of analysis methode and analysis of water samples were carried out at the UFR of Sciences and Techniques of the University Center of Anglet / Universit éde Pau et des Pays de l'Adour / France.

2.2 Sampling Campaign

Before the sampling campaign the glassware was previously depended on washing with soapy water, decontaminated with the sulfochromic mixture, cleaned with bidistilled water and acetonitrile before being packed in aluminum foil. Sampling consisted of water sample extraction from 2-liter amber glass bottles following a transect (Berryman et al., 2004a, Loyo-Rosales et al., 2007, Soclo et al., 2008, Gbaguidi et al., 2014, Bennie et al., 1997, Cortes-Aguado et al., 2008 & Gasperi et al., 2009). Before sampling, the bottles are cleaned three times with the sample of water to be taken. In order to stabilize the samples and avoid microbial degradation during transport, they undergo an addition of sulfuric acid (up to pH = 2). The samples are hermetically sealed by interposing foil between the inside of the lid and the sample. They are then labeled according to the date and place of sampling. The storage and transport of the samples to the laboratories were done in coolers equipped with cold accumulators to keep them at 40 $\% \pm 5 \%$. The campaign was carried out during the period of the small rainy season in southern Benin where the waters of the Ou én é River drain from the north the pollutants mainly of agricultural origin in Lake Nokou é

2.3 Validation of the Analytical Method

2.3.1 Reagents

- certified solution of pesticide molecules "Stock TCL Pesticide Mix 2000 ppm in Hexane / Toluene", including: Aldrin, alpha-BHC, beta-BHC, delta-BHC, diene, alpha-endosulfan, beta-endosulfan, sulfate-endosulfan, endrin, endrin-aldehyde, endrin-ketone, gama-BHC, heptachlor, heptachlor-epoxideisomer B, methoxychlor, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT;

- internal standard (EI) of pesticide: atrazine d5;

- certified solution of PAH molecules "Stock EPA 610 PAH 100-2000 ppm in methanol" comprising 16 PAH molecules such as: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranrhene, benzo (k) fluoranrhene, benzo (a) pyrene, indeno [1,2,3-cd] pyrene, benzo [g, h, i] perylene, dibenzo [a, h] anthracene. For dilutions of PAH solutions, the concentration of Acenaphthene

was used as a reference. The concentrations of the other PAH molecules were then deduced by calculation compared to their actual concentrations in the concentrated standards;

Six internal standards of PAHs namely: naphthalene-d8, acenaphthene-d10, pyrene-d10, benzo (a) pyrene-d12 and benzo [g, h, i] perylene-d12.

- analytical grade solvents such as acetonitrile, acetic acid, sulfuric acid, acetone and hexane.

All these molecules were purchased from Sigma-Aldrich in France.

2.3.2 Equipment

We use for this work:

- a gas chromatograph (GC) of the Agilent 7890A type
- a mass spectrometer (SM) with an electron impact ionisation source;
- a precision analytical balance of KERN type;
- QUECHERS Agilent Part No: 5982-5121 kits obtained from Agilent Technologies (Massy, France);
- a muffle oven.

2.3.3 Analytical Conditions

The GC-MS used is equipped with an Agilent DB5-MS UI column. The carrier gas is high purity helium (99.9995%) purchased from Air Liquide (France). The flow rate of the carrier gas is 1 mL.min-1. The temperatures of the injector, the ionization source and the quadrupole are 280 °C., 230 °C. and 150 °C respectively. The pulsed mode (splitless) was adopted for the injection of the purified extracts and the injected volume is 1µL. The oven temperature programming ramp is: initial temperature of 80 °C for 1 min, then 10 °C / min up to 160 °C and finally 3 °C / min up to 300 °C. The temperature of the interface of the mass spectrum is maintained at 300°C. Ion monitoring mode (SIM) was used for quantitative analysis, while full scan mode was used for qualitative analysis (Ben Salem et al., 2016 & Chamkasem et al., 2013).

2.3.4 Validation Criteria

The validation of the method consisted in evaluating: the retention times, the linearity through the calibration (external and internal), the repeatability and the reproducibility, the limits of detection (LOD) and of quantification (LOQ). To do this, standard certified mixed reference solutions of desired molecules are prepared in the range of 0 - 1000 ppb and injected. Using the chromatograms, the mass spectra m/z are determined as well as the retention times and the corresponding areas. From the different calculated areas and the corresponding concentrations, the external and internal calibration curves are plotted in Excel. The slopes, the coefficients of determination R^2 and the ordinates at the origin of the different calculated.

For repeatability, five (05) repetitions of the range of 0 - 500 ppb were performed in the same day. As for the reproducibility, the injection of the standard solution is made over 5 days for the range 0-500 ppb and the coefficients of variation % CV are calculated in each case. So:

 $%CV = \sigma i/\chi i \times 100$ with σi the standard deviation "SD" and χi the arithmetic mean of the analytical values obtained.

- if CV < 2%, the measurements are very homogeneous and the experiment is repeatable or reproducible;

- if 2% < CV < 30%, the measurements are homogeneous and the repeatability or reproducibility of the experiment is acceptable;

- if CV > 30%, the measurements are heterogeneous so the experiment is non-repeatable or non-reproducible (Gbaguidi et al., 2011, Kouzayha, 2011 & Salem et al., 2016).

The limit of detection (LOD) was determined by considering three times the standard deviation of the background noise after ten injections of the reagent blank. While the limit of quantification (LOQ) was determined by considering ten times the standard deviation of background noise after ten injections of reagent blank. The percentages of recovery of the various desired compounds are calculated using the standard solution of the calibration point 100 ppb according to the formula:

$\% R = \frac{\text{calculated concentration-White concentration}}{\text{theoretical concentration}} X100.$

2.4 Extraction of Natural Water Samples

Before analysis of the water samples by GC / MS, they underwent extraction, concentration and purification steps in

accordance with the QUECHERS methodology. This technique has allowed us to expand the range and number of individual molecules of organic pollutants and related metabolites. For the extraction, 15 mL of each water sample to be extracted were introduced into 50 mL flasks to which 15 mL of acetonitrile + 1 % of HAC (acetic acid) and 100 μ l of a mixed solution were added. 1 ppm internal standard (extraction of IE) containing naphthalene d8, phenanthrene d10, perylene d12, atrazine d5 and stirred for a few seconds on vortex. To this mixture is added 6 g of MgSO₄ + 1.5 NaAC (sodium acetate) and stirred manually for 30 seconds. The flasks are centrifuged at 3000 rpm for 2 min. 8 mL of each supernatant is collected in 15 mL glass test tubes for dry evaporation using the Turbovap LV evaporator under a gentle stream of nitrogen. The dry residue was taken up with 500 μ l of acetonitrile and passed through the purification in order to reach very low detection limits.

3. Results and Discussion

3.1 Determination of Retention Times and Analyte Weights

The retention times t_R , the weights M/Z of the analytes and the internal standards used are recorded in Table 1.

Table 1. Retention times t_R and weights of analytes PAHs and pesticides

PARAMETERS	t_{R} (min)	M/Z quantifier	M/Z qualifier
	PAHs		
NAMES OF COMPOUNDS			
Acenaphtene	9.020	153	154
Ac maphyl me	8 830	152	153
Anthracene	11 230	178	179
Benzo [a] Anthracene	17 670	226	228
Benzo [b] fluoranthene	20.710	252	253
Benzo [k] Eluoranthene	20.780	252	253
Benzo [g h i] pervlene	23,890	276	233
Benzo [a] pyrene	23.000	252	253
Chrysene	17 658	232	233
Dibenzo [a, b] anth	23.480	220	220
Fluoranthene	13 820	202	203
Fluorene	9.610	166	165
Indeno [1 2 3-cd] pyrene	23 420	276	277
Naphthalana	7 230	128	120
Dhananthrana	1.230	128	129
Durana	14 360	202	203
1 yrene	INTEDNAL STANDADDS (203
Nanhthalene d8	$\frac{11112}{7210}$	136	137
A consplitatene do	2.210	150	162
Durana d10	14 220	212	211
Banzo [a] pyrana d12	21 300	212	211
Denzo [a] pytene u12 Demulana d12	21.590	264	203
Penzo [g, h, i] normalono d12	21.570	204	200
Benzo [g, n, i] perviene u12	PESTICIDES	288	209
Aldrin	12 010	263	265
Alpha BHC	10.410	183	203
RHC Beta	10.410	185	219
Dalta PHC	0.150	181	219
Dialdrin	15 000	262	215
Alpha Endosulfan	14.460	203	203
Apria Endosultan	14.400	105	241
Endosulfan Sulfate	16.580	287	241
Endosuntan Suntate	15.470	265	272
Endrin Aldebude	15.470	205	247
EndrinKatona	17,580	545 67	217
Gamma BHC	17.380	181	210
Uantachlor	12 220	100	219
Heptachloropoxido	12.230	252	212
Mathoweahlor	17,000	222	222
	17.300	227	165
4,4 -DDD 4 4' DDE	13.040	233	103
4,4 -DDE 4 4' DDT	14.940	240 225	24ð 165
4,4 -DD1	10.03U INTEDNAL STANDADD OF D	255 ESTICIDES	103
Atrazine d5	10 680	2015	220
	10.000	205	220

The retention times determined were used to associate with each molecule sought the corresponding EI. Thus, it is noted that the first molecule to be released is Naphthalene d8 whose retention time t_R is 7.21 min. It is taken as internal standard for Naphthalene ($t_R = 7.23$ min). Acenaphthylene ($t_R = 8.83$ min), Acenaphthene ($t_R = 9.020$ min), Fluorene ($t_R = 9.61$ min) and Anthracene ($t_R = 11.23$ min) have for internal standard the Acenaphthene d10 with a retention time of 8.980 min. Benzo [g, h, i] perylene d12 was removed at $t_R = 23.85$ min. It is taken as the internal standard of Benzo [g, h, i] perylene d12 was removed at $t_R = 23.85$ min. It is taken as the internal standard of Benzo [g, h, i] perylene. Atrazine d5 taken as internal standard of the pesticides was released at 10.68 min. Pyrene d10, $t_R = 14.32$ min was used as internal standard of the phenanthrene molecules ($t_R = 11.15$), fluoranthene ($t_R = 13.82$ min), pyrene ($t_R = 14.36$ min), of Benzo (a) Anthracene ($t_R = 17.67$ min) and Chrysene ($t_R = 17.66$ min). On the other hand, Benzo [a] pyrene d12, $t_R = 21.39$ min was used as internal standard of Benzo (b) Fluoranthene ($t_R = 20.71$ min), Benzo (k) Fluoranthene ($t_R = 20.78$ min), and Benzo (a) Pyrene ($t_R = 21.43$ min). Finally, P12, $t_R = 21.57$ min, was used as an internal standard for diBenzo [a, h] Anthracene ($t_R = 23.48$ min) and Indeno [1,2,3-cd] pyrene ($t_R = 23.42$ min). Our choices are consistent with those of Salem et al. (2016) and Miossec et al., (2018) who worked with the same analytical material as us.

3.2 External and Internal Calibration

The slopes, the coefficients of determination R^2 and the ordinates at the origin of the calibration curve differences are recorded in Table 2. The coefficients of determination obtained for the external calibration vary from 0.90 to 1 whatever the molecule considered. At the level of the PAHs sought, these coefficients vary from 0.97 to 1. For the OCPs, $0.90 \le R^2 \le 1$. For the internal calibration the coefficients of determination vary from 0.99 to 1 for PAHs and from 0.91 to 1 for OCPs. Whatever the external or internal calibration, the values of the coefficient of determination R^2 obtained demonstrate that the method has good linearity in the chosen calibration range. In the following, the central (average) and dispersion characteristics of the chromatogram areas obtained during the repeatability and reproducibility tests are calculated and are recorded in Tables 3 and 4.

Table 2. Slopes, coefficients of determination R^2 and ordered at the origin of the different calibration curves (external and internal calibration)

NAMES OF COMPOLINDS	Cal	ibration ex	terne		Calibration interne			
NAMES OF COMPOUNDS –	Pente	\mathbf{R}^2	ord origine	Pente	\mathbf{R}^2	ord origine		
Acenaphtene	26025.931	1	-320.999	0.338	0.99	0.155		
Ac énaphyl ène	40507.622	0.99	-1623.79	0.525	1	0.379		
Anthracene	77660.874	0.97	-536.587	1.012	0.99	-0.03		
Benzo [a] Anthracene	33608.963	1	-180.003	0.138	0.99	-0		
Benzo [b] fluoranthene	209462.53	0.99	-536.24	1.115	1	0.033		
Benzo [k] Fluoranthene	69303.2	0.99	-310.791	0.368	1	0.024		
Benzo [g, h, i] perylene	84760.274	1	-552.223	0.547	1	-0.01		
Benzo [a] pyrene	101138.28	0.99	-242.498	0.538	1	0.015		
Chrysene	112098.39	0.99	-461.582	0.457	0.99	0.007		
Dibenzo [a, h] anth	16102.971	1	-139.912	0.105	1	-0.01		
Fluoranthene	132819.95	0.99	-996.356	0.539	1	0.02		
Fluorene	34541.411	1	-155.078	0.45	0.99	0.027		
Indeno [1,2,3-cd] pyrene	66142.127	0.98	-463.81	0.292	1	-0.02		
Naphthalene	33028.887	0.99	-1140.17	0.428	1	0.074		
Phenanthrene	73744.429	1	-61.104	0.299	0.99	0.019		
Pyrene	139799.61	0.99	-560.202	0.568	1	0.01		
Aldrin	23448.552	1	-558.931	1.485	1	-0.18		
Alpha BHC	28744.851	0.99	-370.248	1.797	1	0.174		
Bhc beta	29619.104	0.99	-778.547	1.867	1	-0.27		
Delta BHC	8513.85	1	-66.186	0.532	0.99	0.103		
Dieldrin	13525.044	1	-366.082	0.858	1	-0.14		
Alpha endosulfan	9595.239	0.97	-427.169	0.611	0.98	-0.29		
Beta endosulfan	12136.322	0.99	-283.795	0.764	1	-0.07		
Endosulfan sulfate	11721.694	0.99	-332.445	0.744	1	-0.15		
Endrin	7733.677	0.95	-403.269	0.493	0.97	-0.3		
Endrinaldehyde	17354.726	0.98	-698.855	1.106	1	-0.44		
Endrinketone	24964.515	0.99	-263.432	1.559	1	0.206		
Gamma BHC	29158.232	0.98	-712.455	1.828	0.99	-0.16		
Heptachlor	25465.511	0.97	-1175.05	1.625	0.99	-0.82		
Heptachlorepoxide	34749.513	0.99	-979.587	2.197	1	-0.41		
Methoxychlor	179834.01	0.97	-8429.74	11.476	0.98	-5.95		
4,4'-DDD	142215.76	0.99	-2935.9	8.944	1	-0.41		
4,4'-DDE	7522.537	0.90	-485.508	0.48	0.91	-0.38		
4,4'-DDT	105413.21	0.97	-4875.54	6.728	0.99	-3.37		

PAHs: Policycliques Aromatic Hydrocarbons; OCPs: Organochlorine Pesticides.

3.3 Repeatability

In the repeatability tests (Table 3) we noticed that at 10 ppb, 58.54 % of the tests have undetermined % CV (ND) compared to 32.5 % whose % CV have values between 7 and 30 %, have. At the 50 ppb concentration level, 70% of the tests have acceptable repeatability ($5 \le \%$ CV ≤ 30). On the other hand 80 % of the tests have a % CV between 0.35 and 30 at the concentration of 100 ppb. More than 92% of the tests have a % CV between 4 and 30 at the concentration of 500 ppb. According to Salem et al., (2016), these high proportions of ND in low concentration levels under the limit of detection (Miossec et al., 2018). If this hypothesis is true in their case, in our tests the evaporation did not concern that the molecules of low molecular weight. It has affected all molecular weight ranges. To overcome this difficulty, the natural samples to be analyzed are concentrated more than 30 times to get out of the background noise.

Table 3. Repeatability test results

mpana	10 ppb			50 ppb			_	100 ppb			50	500 ppb		
TESTS	Mean	SD	%CV		Mean	SD	%CV		Mean	SD	%CV	Mean	SD	%CV
						PAH	s							
Names of Compounds														
acenaphtene	2141.8	619	29		7824.8	477	6		18343.4	1824	9.94	87866.4	10688	12
Ac énaphyl ène	ND	ND	ND		649.25	185	29		1552.6	220	14.17	6884.8	1415	21
anthracene	ND	ND	ND		160.33	92	57		494.25	143	28.97	3813.8	453	12
Benzo [a] Anthracene	230.0	33	14		4188.8	1072	26		6577.25	2132	32.41	39537.4	3839	10
Benzo [b] fluoranthene	ND	ND	ND		4409.33	789	18		8194	347	4.24	38568.4	3862	10
Benzo [k] Fluoranthene	ND	ND	ND		1927	226	12		3761.4	363	9.66	18833	1721	9
Benzo [g, h, i] perylene	364.0	121	33		1134.6	164	14		2454.2	517	21.05	11225.2	682	6
Benzo [a] pyrene	ND	ND	ND		1289	147	11		2320.4	263	11.34	12411.8	1743	14
Chrysene	ND	ND	ND		634.67	427	67		2181.33	465	21.31	11408.4	1272	11
Dibenzo [a, h] anth	397.33	121	30		2436.2	381	16		5756.4	900	15.64	27364.2	3398	12
Fluoranthene	ND	ND	ND		683.2	137	20		1631	210	12.88	7949	1305	16
Fluorene	ND	ND	ND		710	158	22		2103.5	442	21.02	10757	2395	22
Indeno [1,2,3-cd] pyrene	1055.7	264	25		3699.8	597	16		7704.2	913	11.85	33456.4	4715	14
Naphthalene	ND	ND	ND		882.2	292	33		1754.8	232	13.24	8837.8	1978	22
Phenanthrene	253.3	81	32		1347	256	19		2881	492	17.09	14483.6	1837	13
				IN	TERNAL	L STAND	ARDS C)F PAH	ls					
Naphthalene d8	6950.4	963	14		6739.8	858	13		7449	1452	19.49	7371.6	930	13
Acenaphthene d10	ND	ND	ND		552.5	138	25		606.5	2	0.35	668	136	20
Pyrene d10	20776.6	3434	17		22444.4	3718	17		22592.2	4499	19.91	21604.8	3881	18
Benzo [a] pyrene d12	9111.2	603	7		8988.75	840	9		8342	239	2.86	9422.4	410	4
Perylene d12	8085.5	735	9		8353.67	645	8		8423.25	373	4.42	8182.6	863	11
Benzo [g, h, i] perylene	7809.75	750	10		7550.67	364	5		7768.5	673	8.66	8142.2	802	10
d12						PESTIC	DES							
Aldrin	ND	ND	ND		686.67	237	35		1784.5	518	29.04	11339.8	2300	20
Alpha BHC	ND	ND	ND		1272.8	291	23		3101.5	201	6.49	13112.4	4081	31
BHC Beta	114.0	21	19		986.4	195	20		2566.2	818	31.87	12382.4	3127	25
Delta BHC	ND	ND	ND		786.5	368	47		2093	1038	49 59	5078 66667	3348	66
Dieldrin	ND	ND	ND		297.5	18	6		1061.67	30	2.83	6573	377	6
Alpha Endosulfan	ND	ND	ND		ND	ND	ND	ND	ND	ND	ND	3860 33333	305	8
Beta Endosulfan	ND	ND	ND		346 33	146	42	112	1051.5	189	17.94	5365.2	442	8
Endosulfan Sulfate	23.6	53	-		398.67	143	36		758 75	203	26.72	5444.8	893	16
Endrin	ND	ND	ND	ND	ND	ND	ND		283	130	45.83	2610	688	26
EndrinAldehyde	ND	ND	ND	ND	236.5	175	74		834	366	43.89	7035.6	816	12
EndrinKetone	340.0	191	56	ЦЪ	1410 25	205	15		2694	248	9.20	11384	997	9
gamma BHC	117.5	9	8		594.33	117	20		2024	618	27.49	11626.2	2207	19
hentachlor	ND	ND	ND		247 67	57	20		1114 33	534	47.91	9652.5	2823	29
HentachlorEnovide	ND	ND	ND		1166	340	29		2302.5	694	30.15	15016.2	2025	14
Methoxychlor	ND	ND	ND		2050.67	256	12		5193 75	1126	21.68	62609.2	9638	15
4 4'-DDD	961.8	274	20		5940.25	360	6		11816 5	1061	8 98	64102.8	5202	8
4 4'-DDF	201.0 ND	274 ND	2.9 ND		ND	ND	ND		117 5	21	17 45	3086.5	728	24
4,4 -DDE 4.4' DDT					1200	255	20		3115 75	566	16.41	JU60.J	120	10
-,,-,-,-,-,-,-,-,-,-,-,-,-,-,-,-,-,-,-	ND	ND	ND	INTE	RNAL ST	235 FANDAR	D OF PI	ESTICI	DES	500	10.41	40500.4	4020	12
Atrazine d5	509.33	99	19		1352.5	451	33		1630.4	183	11.23	1728.6	715	41
% Repeatability		32.5				70.0				80.0		9	92.5	

ND = Not detected, SD = Standard Deviation, %CV = coefficient of variation

3.4 Reproducibility

Analysis of the reproducibility data in Table 4 shows that the percentages of validated reproducibility tests vary from 67.7 to 97.5 %. The low percentages are found at the concentration of 10 ppb. Overall, the reproducibility percentages of the assays are acceptable and are considered satisfactory for validating the method and for use in real-world analyzes.

Table 4. Reproducibility test results

MAIS: OF SCV Mon SD	TESTS		10 ppb			50 ppb 100 ppb 500 ppb			100 ppb				
NATE Participation 74 8.47 6.71 3.59.1 1.63.9 3.51 6.61.5 7.81.20 0.05 28919.9 1.50.9 0.001 Acampleine Animance 0.12 3.53 6.47.5 1.60 9.002 1.33 1.61.5 7.81.20 0.05 28919.9 1.50.9 0.010 Animance 0.12 3.02 1.32.0 1.61.0 2.17 1.50 0.66.6 7.00 0.13 0.50.8 7.01 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.001	112515	Mean	SD	%CV	Mean	SD	%CV	Mean	SD	%CV	Mean	SD	%CV
Accouply income 722 48.47 67.14 729.14 11.53 3.531 60.512 4.13.4 0.005 28918.92 91.73 0.005 Acchaply income 21.54 87.30 64.6572 96.06 1.444 155.72 51.86 0.334 6885.48 1.110 0.005 Barco [p. 23.4 3.962 123.823 161.416 25.71 1.560 496.844 4.845 0.975 3813.08 1.724 0.005 Barco [p. 1] 7.3 3.962 1.382.5 0.455 658.65 7.403 0.113 3957.68 2.209 0.007 Piscon [p. 77.35 1.585 5.744 19.225 0.435 0.242 0.230 1882.8 92.815 1.143 3877.08 1.204 0.323 1.204 0.331 1.204.9 0.331 1.233 0.333 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 0.335 <t< td=""><td>NAMES COMPOUNDS</td><td>OF</td><td></td><td></td><td></td><td></td><td></td><td>PAHs</td><td></td><td></td><td></td><td></td><td></td></t<>	NAMES COMPOUNDS	OF						PAHs					
Ac dampace 214.84 53.86 24.76 796.436 99.02 1.33 12037.8 738.120 94.9085 8799.7.6 95.912 0.008 Antracce 20.74 1.8165 8.7.9 666.37 96.61 1.560 466.844 4.845 0.975 3813.08 1.724 0.007 Benzo [b] 234.26 27.87 11.892 4196.78 19.225 0.458 6568.6 7.403 0.113 3953.64 2.900 0.007 Benzo [b] 7.92 4.912 6.304 4413.55 27.74 0.516 8182.8 9.285 1.134 38570.90 5.111 0.013 Benzo [b], 11 2.236 1.838 0.744 1.124.08 3.068 0.319 2.448.8 9.664 0.341 1.124.03 3.368 0.330 Decoratione 2 2.549 1.274.77 1.401.66 3.775.31 2.410.020 3.775.104 2.431 3.40 0.431 1.242.3 3.775.104 1.420.40 3.375.30	Acenaphtene	722	48.477	6.714	3295.104	116.339	3.531	6615.2	4.324	0.065	29819.92	11.573	0.039
Andmesse 20.74 1.8105 8.730 646.572 9.661 1.494 155.372 5.186 0.334 6885.48 1.114 0.000 Andmances 3.23 3.962 123.823 161.416 2.971 5.564 6.968.44 4.848 0.975 3815.08 1.204 0.000 Flowrandbare 2.94.26 27.877 11.892 4.996.78 12.227 0.518 8182.8 92.815 1.134 3857.08 5.111 0.010 Flowrandbare 7.92 4.912 6.304 4.135.5 2.2774 0.516 8182.8 92.81 1.314 3857.08 1.2042 0.303 Group len 2 2.589 17.477 11.4747 11.4747 1.314 0.040 2.337.8 5.643 0.234 2.338 1.343 9.345 0.232 0.338 Flowrandbar 32.090 8.735 2.227 2.434.24 4.625 0.199 7.714.8 4.909 0.714 3.445.9 0.345 0.2277	Ac énaphyl ène	2154.84	53.364	2.476	7864.936	89.092	1.133	15037.8	7381.269	49.085	87893.76	59.412	0.068
Bento [a] Authraces 3.2 3.962 12.823 161.416 2.517 1.500 496.844 4.845 0.975 381.308 1.724 0.045 Benzo [b] Fouranthee 234.26 27.857 11.92 4196.78 19.225 0.458 6568.6 7.403 0.113 3953.684 2.900 0.007 Benzo [k], h.1] Control S.511 0.303 2.277 0.516 8182.8 92.815 1.134 3857.096 5.111 0.013 Benzo [k], h.1] C.544 1.274 1.032.7 5.933 0.308 3.763 1.2.042 0.303 1.124.008 33.682 0.306 Diversite 2 2.494 1.274 1.035.6 2.231 0.231 1.234 0.331 Diversite 302.004 1.210 6.35.52 2.000 0.423 2.178 0.303 1.143.05 9.323 0.311 Diversite 302.04 4.910 0.313 2.714 4.0133 1.724 0.414 0.313 <	Anthracene	20.74	1.8105	8.730	646.572	9.661	1.494	1553.72	5.186	0.334	6885.48	1.411	0.020
Justingsere 5.2 35.0 123.43 101.410 1.231 1.200 490.844 4.935 0.915 351.308 1.124 0.007 Berto [k] 7192 4.912 6.304 4413.55 22.774 0.516 8182.8 92.815 1.134 38570.96 5.111 0.013 Berto [k] 17.92 4.912 6.304 4413.55 22.774 0.516 8182.8 92.815 1.134 38570.96 5.111 0.013 Berto [k] 174 113.4766 3.018 0.313 2.448.8 9.654 0.334 112.425 39.779 0.330 Dibeazo [k] and 2.63 1.237.51 1403.66 27.381 19.406 23.171 0.338 12.425 0.338 114.248 0.308 114.230 0.338 14.32.44 0.021 Dibeazo [k] and 2.63 5.618 12.721 1.007 2.000 3.717 0.3381 22.810 0.122 Discos [k] and 1.33.33 0.74 1.	Benzo [a]	2.2	2.062	102.902	161.416	2 5 1 7	1.500	106.914	4.045	0.075	2012.00	1 724	0.045
Betwo [b] Pluconalhem 234.26 27.857 11.892 4196.78 19.225 0.458 656.66 7.403 0.113 3935.84 2.900 0.007 Betwo [b] Pluconalhem 77.92 4.912 6.304 4413.55 22.774 0.516 818.28 92.815 1.134 38570.96 5.111 0.013 Betwo [a] Nyme 25.818 16.812 4.747 1134.706 5.018 0.219 2.448.8 9.054 0.334 112.400.8 33.682 0.300 Dibaxo [a, h] anth 2.6 3.435 132.120 6.5552 2.000 0.423 2185 8.889 0.388 114.430.36 39.235 0.343 Dibaxo [a, h] anth 2.6 3.650 4.570 2.212 1.532 1.630.2 3.271 0.201 7346.8 9.928 5.18 309.996 9.11 0.446 71.718 4.059 0.571 3.444.9 0.121 Pymane 166.67 9.936 5.18 309.996 9.11 0.446 71	Anthracene	5.2	3.962	123.823	101.410	2.517	1.560	496.844	4.845	0.975	3813.08	1.724	0.045
Berton k] Fluxoanthene 77.92 4.912 6.304 4413.55 22.774 0.516 8182.8 92.815 1.134 3857096 5.111 0.013 Berton [g.h. ii] Fervylene 27.36 1.585 5.794 19272 5.933 0.308 3763 12.042 0.320 1883.66 12.602 0.607 Berton [a] pyrene 2.549 12.7475 140.66 272.381 19.406 273.78 5.630 0.243 1143.25 33.682 0.303 Dibeton [a, h] anh 2.6 3.455 152.120 655.952 2.600 0.423 2165 8.889 0.398 1143.04 63.332 Fluxoranthene 392.064 4.911 1.333 707.4 7.127 1.007 2100 9.165 0.436 1076.8 9.880 0.283 0.212 Pyrene 2.5.306 5.784 2.234 0.486 1.046 17.47 1.313 1.796 883.8 1.1.498 0.130 Pyrene 10.067 5.784 <td>Benzo [b] Fluoranthene</td> <td>234.26</td> <td>27.857</td> <td>11.892</td> <td>4196.78</td> <td>19.225</td> <td>0.458</td> <td>6568.6</td> <td>7.403</td> <td>0.113</td> <td>39536.84</td> <td>2.930</td> <td>0.007</td>	Benzo [b] Fluoranthene	234.26	27.857	11.892	4196.78	19.225	0.458	6568.6	7.403	0.113	39536.84	2.930	0.007
Benzo [s. h. i] perylene 27.36 1.585 5.794 1927.2 5.933 0.308 3763 12.042 0.303 1888.66 12.602 0.067 Benzo [a] pyrene 354.18 16.12 4.747 1134.796 3.618 0.319 2448.8 9.654 0.304 11240.08 33.682 0.300 Diberoo [a, h] anth 2.6 3.277.775 1403.6 272.318 1404.05 23.273 0.331 12425 3.038 11440.36 32.323 0.333 Fluoranthene 392.09 8.750 2.277 24.424 4.650 1907 0.318 2736.10 144.934 0.052 Fluoranthene 36.666 4.911 13.383 707.4 7.127 1.007 2100 9.165 0.435 1070.8 44.035 0.518 3.080 11.22 3.247.4 13.131 1706 844.38 11.449 0.130 Pyrme 252.306 5.784 2.293 1401 674.55 147.47 1.060 147.44	Benzo [k] Fluoranthene	77.92	4.912	6.304	4413.55	22.774	0.516	8182.8	92.815	1.134	38570.96	5.111	0.013
Benzo [a] pyrene 35.1 8 0.51.9 244.8 2 9.65.4 0.394 0.1240.08 3.36.2 0.300 3.52.8 0.395 0.320 Diberzo [a, h] anth 2.6 3.453 132.120 633.952 2.690 0.423 2.185 8.689 0.398 1140.36 392.32 0.330 Diberzo [a, h] anth 2.6 3.450 2.277 2.442 4.620 0.90 576.34 2.1973 0.381 12425 0.082 Fluorente 57.714 2.631 4.560 685.84 12.224 1.782 16302 3.271 0.201 7946.8 9.080 0.122 Aphthalom 1066.76 9.996 5.118 3.609 771.18 4.4099 0.571 3.472.48 11.498 0.109 Pyrene 252.306 5.784 2.293 1346 3.808 0.283 2.874.6 17.473 0.608 672.6 18.399 2.733 Pyrene 252.306 47.01 1.122 553.05 4.075 0.815 594.6 2.8645	Benzo [g, h, i] Perylene	27.36	1.585	5.794	1927.2	5.933	0.308	3763	12.042	0.320	18836.6	12.602	0.067
Chrysene 2 2.549 127.475 1403.6 272.381 19.406 221.78 5.630 0.243 124.25 39.779 0.320 Dibenzo [k] Junth 2.6 3.435 52.922 2.043.4 4.625 0.190 57.34 21.973 0.381 27361.04 14.294 0.052 Indeno [1,2,3-C4] 7.714 2.631 4.560 685.84 12.224 1.782 16.02 3.2171 0.201 794.68 9.680 0.222 Naphthalane 1066.78 59.936 5.618 3699.96 9.111 0.246 7721.8 4.4059 0.571 33472.48 31.544 0.030 Pyrne 2.25.06 5.784 2.293 1.865 3.080 0.283 2.874.6 1.747.3 0.608 14.471.4 1.1710 0.119 Naphthalene d8 6965.858 49.045 0.704 6741.8 4.705 0.851 594.6 2.2463 3.9808 672.2 8.1379 2.237 0.550 Pyrene	Benzo [a] pyrene	354.18	16.812	4.747	1134.796	3.618	0.319	2448.8	9.654	0.394	11240.08	33.682	0.300
Dibenzola [h] amh 2.6 3.435 132.120 635.952 2.690 0.423 2185 8.689 0.398 11430.36 39.235 0.434 Eluoranhe 37.714 2.631 4.560 6485.84 12.224 1.782 1630.2 3.217 0.201 7946.8 0.608 0.122 Pyrene 36.696 4.911 13.383 707.4 7.127 1.007 2.100 9.465 0.436 0.176.8 2.283 0.212 Naphtalene 46.3 4.872 10.524 885.8 9.445 1.066 1744 31.31 1.796 8843.8 11.498 0.130 Pyrnen 252.306 5.784 2.293 134 3.061 13.353 0.763 2.174 3.031 1.796 8843.8 11.498 0.130 Accmaphthene 46.5 0.754 2.273 134 3.031 1.760 873.23 55.35 94.6 2.2454 3.088 672.2 1.375.05 2.309 2.3731	Chrysene	2	2.549	127.475	1403.6	272.381	19.406	2317.8	5.630	0.243	12425	39.779	0.320
Fluoranthene 392.904 8,750 2.227 2434.24 4.625 0.190 5763.4 21.973 0.381 27361.04 14.249 0.052 Indeno [1,2,3-Cd] 36.696 4.911 13.383 707.4 7.127 1.007 2100 9.165 0.436 10760.8 22.830 0.212 Naphthalene 1066.78 59.936 5.618 3699.96 9.111 0.246 7721.8 44.059 0.571 33472.48 31.544 0.094 Pyrnee 2.253.06 5.784 2.293 1344 3.080 0.283 2874.6 1.7473 0.088 14471.4 1.170 0.119 Naphthalene d8 6965.858 49.044 6941.8 4.705 0.851 594.6 22.645 3.808 672.6 18.379 2.733 Pyrnee d10 1709.086 8390.01 1.224 53.555 0.619 8338.2 2.6167 0.314 943.08 4.672 0.059 Pyrnee d12 910.2.06 83.977	Dibenzo [a, h] anth	2.6	3.435	132.120	635.952	2.690	0.423	2185	8.689	0.398	11430.36	39.235	0.343
Hurone 57.71 2.631 4.50 6854 12224 1.782 1630.2 3.271 0.201 7946.8 9.680 0.122 Pyrene 106cn [1,2,3-Cd] 36.696 4.911 13.383 707.4 7.127 1.007 2100 9.165 0.436 10760.8 22.830 0.212 Maphthalene 106c.78 5.934 2.293 111 0.246 7721.8 44.059 0.571 3347.48 31.313 1.796 8843.8 11.498 0.130 Pyrene 252.306 5.784 2.293 1346 0.808 0.283 2874.6 1.7473 0.608 7365.12 2.9062 0.530 Accampthmene d10 151.552 1.701 1.102 553.05 4.705 0.851 594.6 22.615 0.314 942.308 4.672 0.500 Pergene d12 9102.291 1.390 851.372 22.474 0.290 7844 216.69 2.62 8.32 0.531 Perglene d12 <	Fluoranthene	392.904	8.750	2.227	2434.24	4.625	0.190	5763.4	21.973	0.381	27361.04	14.294	0.052
Indeen (12,2-4,3] Pyrene 36.696 4.911 13.383 707.4 7.127 1.007 2100 9.165 0.436 10760.8 22.830 0.212 Naphthalene 1066.78 59.936 5.618 3699.96 9.111 0.246 1771.8 44.059 0.71 33472.48 31.544 0.030 Pyrene 252.306 5.784 2.293 1346 3.808 0.283 2874.6 17.473 0.668 14471.4 17.170 0.119 Pyrene d10 151.552 1.701 1.122 553.05 4.705 0.851 594.6 22.645 3.808 672.6 18.379 273.3 Pyrene d10 1709.08 8390.00 49.091 22435.378 42.803 0.019 591.4 9.503.19 158.167 0.314 942.308 4.672 0.050 Berzo [g h, i] 7992.92 12.415 1.572 7663.754 21.947 0.269 7844 21.666 2.762 8129 8.588 0.675 <td< td=""><td>Fluorene</td><td>57.714</td><td>2.631</td><td>4.560</td><td>685.84</td><td>12.224</td><td>1.782</td><td>1630.2</td><td>3.271</td><td>0.201</td><td>7946.8</td><td>9.680</td><td>0.122</td></td<>	Fluorene	57.714	2.631	4.560	685.84	12.224	1.782	1630.2	3.271	0.201	7946.8	9.680	0.122
Naphthalene 1066,78 59.936 5.618 3699.96 9.111 0.246 7721.8 44.059 0.571 33472.48 31.544 0.030 Pyrene 252.306 5.784 2.033 1846 3.080 0.283 2874.6 17.473 0.608 14471.4 17.170 0.119 Naphthalene d8 6965.858 49.045 0.704 6741.8 4.817 0.071 7455.4 2.8763 0.386 7365.12 39.062 0.530 Accamphthene d10 171090.86 830.001 42.031 0.191 5921.4 9863.132 2.6167 0.314 9423.08 4.672 0.050 Berzo [a] pyrene d12 9012.206 95.297 1.057 8973.2 25.585 0.619 8338.2 2.6167 0.314 9423.08 4.672 0.055 Berzo [a] pyrene d12 9012.206 95.297 1.057 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Perylene d12	Indeno [1,2,3-Cd] Pyrene	36.696	4.911	13.383	707.4	7.127	1.007	2100	9.165	0.436	10760.8	22.830	0.212
Phenambrene 46.3 4.872 10.524 885.8 9.445 1.066 1744 31.313 1.796 8843.8 11.498 0.130 Pyrene 252.306 5.784 2.293 1346 3.808 0.283 2874.6 17.473 0.608 14471.4 17.170 0.119 Naphthalene d8 6965.858 49.045 0.701 614.8 48.17 0.011 7455.4 28.763 0.386 765.61.2 39.062 0.530 Accamphthene d10 151.552 1.701 1.122 553.05 0.619 8338.2 26.167 0.314 492.30 4.672.6 18.379 2.733 Pyrene d12 90.206 95.271 1.057 897.32 25.58 0.619 8338.2 26.167 0.314 492.30 4.672 0.050 Perylene d12 8038.76 105.21 1.309 8361.372 22.474 0.290 7844 216.669 2.762 812.9 7.563 Perylene d12 80.38 68.0	Naphthalene	1066.78	59.936	5.618	3699.96	9.111	0.246	7721.8	44.059	0.571	33472.48	31.544	0.094
Pyrene 252.306 5.7.84 2.293 1346 3.808 0.283 2874.6 17.473 0.008 14471.4 17.170 0.119 INTERNAL STANDARDS OF PAIL Naphnhalene d8 6965.858 49.045 0.704 6741.8 4.817 0.017 7455.4 28.763 0.386 7365.12 39.062 0.530 Acenaphthene d10 151.552 1.701 1.122 553.05 4.705 0.851 594.6 22.645 3.808 672.6 18.379 2.733 Pyrene d10 17090.86 839.0001 49.091 22455.378 42.803 0.191 59211.4 90653.195 158.167 21718.6 175.005 0.805 Benzo [g, h, i] 7892.992 124.115 1.572 756.3754 21.947 0.290 7844 216.69 2.762 8129 38.588 0.475 Perylene d12 702.9 13143 1.171 3.735 1271.2 6.906 0.543 3107.56 22.641 0.762 812	Phenanthrene	46.3	4.872	10.524	885.8	9.445	1.066	1744	31.313	1.796	8843.8	11.498	0.130
Intervent structure of Parts Intervent structure of Parts Naphthele dl 665.858 4.9.045 0.701 7455.4 28.763 0.386 7365.12 3.9.062 0.530 Accenaphthene dl0 151.552 1.701 1.122 553.85 0.619 533.82 22.647 0.314 9423.08 672.6 18.379 2.050 Perylene dl2 9012.206 95.297 1.057 8973.2 25.585 0.619 8338.2 2.6.167 0.314 9423.08 4.672 0.050 Perylene dl2 9012.206 95.297 10.571 8973.2 2.5.585 0.619 8338.2 2.6.167 0.314 9423.08 4.672 0.050 Perylene dl2 9012.206 95.297 12.4115 1.572 7563.754 2.1947 0.290 7844 216.669 2.762 820.92 5.3.71 0.655 Benzo [g. h. i] 781 1.3.12 6.808 1.26.77<	Pyrene	252.306	5.784	2.293	1346	3.808	0.283	28/4.6	17.473	0.608	14471.4	17.170	0.119
Arapinatene us 090.363 49.043 0.044 0441.8 4.817 0.01 143.34 20.03 0.580 1305.12 530.02 0.330 0.280 1305.12 530.02 0.330 0.280 1305.12 530.02 0.330 0.280 1305.12 1300 0.321 0.535.8 142.03 0.191 592.14 93653.195 158.167 21718.6 175.005 0.805 Benzo [a] pyrene d12 9012.206 95.271 1.309 8361.372 22.474 0.269 6896.4 3141.184 49.507 8206.92 53.711 0.055 Benzo [a] pyrene d12 902.992 124.115 1.572 7563.754 21.947 0.290 7844 216.69 2.762 8129 38.88 0.475 Bertylene d12 5.788 48.233 0.21.947 0.290 7844 216.69 2.762 8129 38.858 0.475 Bertylene d12 5.788 48.233 0.21.6477 1.864 1843 100.628 5.460 11381.2	Nonhtholono d9	6065 959	40.045	0.704	6741.9	4 917	INTERNAL 0.071	51ANDARD5 (JF PAHS	0.286	7265 12	20.062	0.520
Acctanguinter uto 111252 1.701 1.122 1.503 4.703 0.501 39-40 2.2033 0.503 1.513 2.153 Pyrene d10 17000.66 8350.01 49.091 22435.78 42.803 0.191 59211.4 93653.195 158.167 21718.6 175.00 0.806 Benzo [g. h. i] 8038.76 105.221 1.309 8361.372 22.474 0.696 6896.4 3414.184 49.507 8206.92 53.771 0.655 Benzo [g. h. i] 7892.992 124.15 1.572 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Perylene d12 7892.992 124.15 1.572 7563.754 21.947 0.290 7844 216.69 2.762 8129 38.588 0.475 Beta end 110.2 7.629 6923 9853.2 3.670 0.372 2250.2 32.438 1.272 12409 9.438 0.066 11.841 5.711 1.914 1074.774 82.856 7.709 6599.6 57.134 0.866 0.	A concept there d10	151 552	49.043	0.704	552.05	4.817	0.071	7455.4 504.6	28.705	2 808	672.6	18 270	0.550
Tyrice (10) Tyrice (11) Tyrice (12)	Acenapititiene d10 Pyrene d10	17090.86	8300.001	1.122	22/35 378	4.703	0.851	59211.4	03653 105	5.606 158 167	21718.6	18.379	2.755
Derived in private int Mail and the private int Perylene d12 7892.992 124.115 1.572 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Perylene d12 Perslene d12 Aldrin 12 5.788 48.233 680.2 12.677 1.864 1843 100.628 5.460 11381.2 89.452 0.786 Alpha BHC 31.344 1.171 3.735 1271.2 6.906 0.543 3107.56 22.651 0.729 13116.2 8.843 0.067 Bhc beta 110.2 7.629 6.923 985.32 3.670 0.372 2550.2 32.438 1.277 10.35 1012 0.596 57.114 0.699 659.13 0.867.6 0.012 0.578 3467.6 0.595 0.012 0.565 0.012 0.578 3467.6 0.574 0.659 6.57.134	Benzo [a] pyrene d12	9012 206	95 207	1.057	8073 2	42.00J	0.171	8338.2	26 167	0.314	9423.08	1 672	0.050
Benzo (g. h. il) 7892.992 124.115 1.572 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Perylene d12 Perylene d12 7892.992 124.115 1.572 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Hdrin 12 5.788 48.233 680.2 12.677 1.864 1843 100.628 5.460 11381.2 89.452 0.786 Aldrin 110.2 7.629 6.923 985.32 3.670 0.372 2550.2 32.438 1.272 12409 54.337 0.438 Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 11.747 75.21 5078.93467 0.595 0.012 Delta BHC 3.8 1.923 68.698 298.298 5.711 1.914 1074.774 82.856 7.709 6599.6 57.134 0.866 Alpha endosulfan 12 5.788 48.233 82.52 <td>Pervlene d12</td> <td>8038 76</td> <td>105 221</td> <td>1 309</td> <td>8361 372</td> <td>22 474</td> <td>0.019</td> <td>6896.4</td> <td>3414 184</td> <td>49 507</td> <td>8206.92</td> <td>53 771</td> <td>0.655</td>	Pervlene d12	8038 76	105 221	1 309	8361 372	22 474	0.019	6896.4	3414 184	49 507	8206.92	53 771	0.655
Perylene d12 7892.992 124.115 1.572 7563.754 21.947 0.290 7844 216.669 2.762 8129 38.588 0.475 Aldrin 12 5.788 48.233 680.2 12.677 1.864 1843 100.628 5.460 11381.2 89.452 0.786 Alpha BHC 31.344 1.171 3.735 1271.2 6.906 0.543 3107.56 22.651 0.729 13116.2 8.843 0.067 Bhc beta 110.2 7.629 6.923 985.32 3.670 0.372 2550.2 32.438 1.272 12.409 54.397 0.438 Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 117.847 5.721 5078.93467 0.595 0.012 Dieldrin 2.8 3.781 111.222 348.2 7.497 2.153 1068.2 32.011 3.00 5367.6 2.1748 0.400 Endosulfan 3.4 3.781	Benzo [g, h, i]												
Aldrin 12 5.788 48.233 680.2 12.677 1.864 1843 100.628 5.460 11381.2 89.452 0.786 Alpha BHC 31.344 1.171 3.735 1271.2 6.906 0.543 3107.56 22.651 0.729 13116.2 8.843 0.067 Bhc beta 110.2 7.629 6.923 985.32 3.670 0.372 2550.2 32.438 1.272 12409 54.397 0.438 Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 117.847 5.721 5078.93467 0.595 0.515 Alpha endosulfan 12 5.788 48.233 2 2.549 1.275 13.2 4.970 37.651 3867.6 20.744 0.536 Beta endosulfan 3.4 3.781 111.222 348.2 7.477 2.153 1068.2 32.011 3.00 5367.6 21.478 0.400 Endrinaldehyde 12 5.788 48.233 825.2 14.601 1.769 834 0 0 704	Perylene d12	7892.992	124.115	1.572	7563.754	21.947	0.290	7844 PESTICIDES	216.669	2.762	8129	38.588	0.475
Alpha BHC 31.344 1.171 3.735 1271.2 6.906 0.543 3107.56 22.651 0.729 13116.2 8.843 0.067 Bhc beta 110.2 7.629 6.923 985.32 3.670 0.372 2550.2 32.438 1.272 12409 54.397 0.438 Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 117.847 5.721 5078.93467 0.595 0.124 Dieldrin 2.8 1.923 68.698 298.298 5.711 1.914 1074.774 82.856 7.709 6599.6 5.71.34 0.866 Alpha endosulfan 12 5.788 48.233 2 2.549 1.275 13.2 4.970 37.651 3867.6 20.744 0.536 Beta endosulfan 3.4 3.781 111.222 348.2 7.497 2.153 1068.2 32.011 3.00 5367.6 21.478 0.400 Endrinulfan 4 3.391 84.79 112.4 5.413 4.816 273.4 23.818 8.712	Aldrin	12	5.788	48.233	680.2	12.677	1.864	1843	100.628	5.460	11381.2	89.452	0.786
Bite beta 110.2 7.629 6.923 985.32 3.670 0.372 2.550.2 32.438 1.272 12409 54.397 0.438 Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 117.847 5.721 5078.93467 0.595 0.012 Dieldrin 2.8 1.923 68.698 298.298 5.711 1.914 1074.774 82.856 7.709 659.6 57.134 0.6866 Alpha endosulfan 1.2 5.788 48.233 2 2.549 1.275 13.2 4.970 37.651 3867.6 20.744 0.536 Beta endosulfan 3.4 3.781 111.22 348.2 7.497 2.153 1068.2 32.011 3.00 5367.6 21.474 0.609 Endosulfan sulfate 22.98 1.988 8.651 397.178 12.036 3.030 752.6 10.164 1.350 5445.2 8.585 0.158 Endrin 4 3.391 84.779 112.4 5.413 4.816 273.4 23.818 8.712 26	Alpha BHC	31.344	1.171	3.735	1271.2	6.906	0.543	3107.56	22.651	0.729	13116.2	8.843	0.067
Delta BHC 3.8 3.564 93.782 776.6 10.899 1.403 2060 117.847 5.721 5078.93467 0.595 0.012 Dieldrin 2.8 1.923 68.698 298.298 5.711 1.914 1074.774 82.856 7.709 6599.6 57.134 0.866 Alpha endosulfan 12 5.788 48.233 2 2.549 1.275 13.2 4.970 37.651 3867.6 20.744 0.536 Beta endosulfan 3.4 3.781 111.222 348.2 7.497 2.153 1068.2 32.011 3.00 5367.6 21.478 0.400 Endosulfan sulfate 22.98 1.988 8.651 397.178 12.036 3.030 752.6 10.164 1.350 5445.2 8.855 0.158 Endrinaldehyde 12 5.788 48.233 825.2 14.601 1.769 834 0 0 7047.4 30.171 0.428 Endrinketone 2.8 2.049 73.192 1423.2 43.234 3.038 2677.4 46.377 1.732<	Bhc beta	110.2	7.629	6.923	985.32	3.670	0.372	2550.2	32.438	1.272	12409	54.397	0.438
Dieldrin2.81.92368.698298.2985.7111.9141074.77482.8567.709659.657.1340.866Alpha endosulfan125.78848.23322.5491.27513.24.97037.6513867.620.7440.536Beta endosulfan3.43.781111.222348.27.4972.1531068.232.0113.005367.621.4780.400Endosulfan sulfate22.981.9888.651397.17812.0363.030752.610.1641.350545.28.5850.158Endrin43.39184.779112.45.4134.816273.423.8188.7122617.416.940.649Endrinaldehyde125.78848.233825.214.6011.769834007047.430.1710.428Endrinketone2.82.04973.1921423.243.2343.0382677.446.3771.73211376.884.2210.740Gamma BHC115.73.4933.019596.68.6491.450224511.1800.49811709.8167.5121.430Heptachlore21.58179.057244.86.4572.6381106.215.2541.3799641.431.6040.282Methoxychlor155.4722.7941.7972037.827.3441.3425133144.4772.81551346.825179.69249.0384,4'-DDE14.8	Delta BHC	3.8	3.564	93.782	776.6	10.899	1.403	2060	117.847	5.721	5078.93467	0.595	0.012
Alpha endosulfan125.78848.23322.5491.27513.24.97037.6513867.620.7440.536Beta endosulfan3.43.781111.222348.27.4972.1531068.232.0113.005367.621.4780.400Endosulfan sulfate22.981.9888.651397.17812.0363.030752.610.1641.3505445.28.5850.158Endrin43.39184.779112.45.4134.816273.423.8188.7122617.416.9940.649Endrinketone2.82.04973.1921423.243.2343.0382677.446.3771.73211376.884.2210.740Gamma BHC115.73.4933.019596.68.6491.450224511.1800.49811709.8167.5121.430Heptachlor21.58179.057244.86.4572.6381106.215.2541.3799641.431.6040.282Methoxychlor155.4722.7941.7972037.82.73441.3425133144.4772.81551346.825179.69249.0384,4'-DDE14.85.54137.43770.82.7753.919117.324.3143.6773095.271.7332.318Aldrin112.665.394.738129.41.9290.9193400.2227.9126.7034656.86.3400.016Heptachlor2.541	Dieldrin	2.8	1.923	68.698	298.298	5.711	1.914	1074.774	82.856	7.709	6599.6	57.134	0.866
Beta endosulfan 3.4 3.781 111.222 348.2 7.497 2.153 1068.2 32.011 3.00 5367.6 21.478 0.400 Endosulfan sulfate 22.98 1.988 8.651 397.178 12.036 3.030 752.6 10.164 1.350 5445.2 8.585 0.158 Endrin 4 3.391 84.779 112.4 5.413 4.816 273.4 23.818 8.712 2617.4 40.094 Endrinaldehyde 12 5.788 48.233 82.52 14.601 1.769 834 0 0 7047.4 30.171 0.428 Endrinketone 2.8 2.049 73.192 1423.2 43.234 3.038 2677.4 46.377 1.732 11376.8 84.221 0.740 Gamma BHC 115.7 3.493 3.019 596.6 8.649 1.450 2245 11.180 0.498 11709.8 167.512 1.430 Heptachlor 2 1.581 79.057 244.8 6.457 2.638 1106.2 15.254 1.379 9641.4	Alpha endosulfan	12	5.788	48.233	2	2.549	1.275	13.2	4.970	37.651	3867.6	20.744	0.536
Endosulfan sulfate 22.98 1.988 8.651 397.178 12.036 3.030 752.6 10.164 1.350 5445.2 8.585 0.158 Endrin 4 3.391 84.779 112.4 5.413 4.816 273.4 23.818 8.712 2617.4 16.994 0.649 Endrinaldehyde 12 5.788 48.233 825.2 14.601 1.769 834 0 0 7047.4 16.994 0.428 Endrinketone 2.8 2.049 73.192 142.2 43.234 3.038 2677.4 46.377 1.732 11376.8 84.2.21 0.740 Gamma BHC 115.7 3.493 3.019 596.6 8.649 1.450 2245 11.180 0.498 11709.8 167.512 1.430 Heptachlor 2 1.581 79.057 244.8 6.457 2.638 1106.2 15.54 1.379 9641.4 31.604 0.328 Heptachlorepoxide 78.554 1.224 1.578 1136.4 42.253 3.647 2300.6 7.537 0.328	Beta endosulfan	3.4	3.781	111.222	348.2	7.497	2.153	1068.2	32.011	3.00	5367.6	21.478	0.400
Endrin43.39184.779112.45.4134.816273.423.8188.7122617.416.9940.649Endrinaldehyde125.78848.233825.214.6011.769834007047.430.1710.428Endrinketone2.82.04973.1921423.243.2343.0382677.446.3771.73211376.884.2210.740Gamma BHC115.73.4933.019596.68.6491.450224511.1800.49811709.8167.5121.430Heptachlor21.58179.057244.86.4572.6381106.215.2541.3799641.431.0640.328Heptachlorepoxide78.5541.2241.5581158.642.2533.6472300.67.5370.3281502213.0380.087Methoxychlor155.4722.7941.7972037.827.3441.3425133144.4772.81551346.825179.69249.0384,4'-DDD950.62234.1863.59648752389.81749.02211704.4464.6963.9706408088.0310.1374,4'-DDE14.85.54137.43770.82.7753.919117.324.3143.6773095.271.7332.318Aldrin112.685.394.738119.920.9193400.2227.9126.0340565.86.3400.016INTERNAL STANDARD F PESTUEDES <td>Endosulfan sulfate</td> <td>22.98</td> <td>1.988</td> <td>8.651</td> <td>397.178</td> <td>12.036</td> <td>3.030</td> <td>752.6</td> <td>10.164</td> <td>1.350</td> <td>5445.2</td> <td>8.585</td> <td>0.158</td>	Endosulfan sulfate	22.98	1.988	8.651	397.178	12.036	3.030	752.6	10.164	1.350	5445.2	8.585	0.158
Endrinaldehyde125.78848.233825.214.6011.7698340007047.430.1710.428Endrinketone2.82.04973.1921423.243.2343.0382677.446.3771.73211376.884.2210.740Gamma BHC115.73.4933.019596.68.6491.450224511.1800.49811709.8167.5121.430Heptachlor21.58179.057244.86.4572.6381106.215.2541.3799641.431.6040.328Heptachlorepoxide78.5541.2241.5581158.642.2533.6472300.67.5370.3281502213.3880.087Methoxychlor155.4722.7941.7972037.827.3441.3425133144.4772.81551346.825179.69249.0384.4'-DDD950.62234.1863.59648752389.81749.02211704.4464.6963.9706408088.0310.1374.4'-DDE14.85.54137.43770.82.7753.919117.324.3143.6773095.271.7332.318Aldrin112.6865.394.738119290.9193400.2227.9126.70340565.86.3400.016 VITEHTAL STANDARD OF PESTICIDESVITEHTAL STANDARD OF PESTICIDES99.6 1.9540.3831351.26.7600.5001	Endrin	4	3.391	84.779	112.4	5.413	4.816	273.4	23.818	8.712	2617.4	16.994	0.649
Endrinketone 2.8 2.049 73.192 1423.2 43.234 3.038 2677.4 46.377 1.732 11376.8 84.221 0.740 Gamma BHC 115.7 3.493 3.019 596.6 8.649 1.450 2245 11.180 0.498 11709.8 167.512 1.430 Heptachlor 2 1.581 79.057 244.8 6.457 2.638 1106.2 15.254 1.379 9641.4 31.604 0.328 Heptachlorepoxide 78.554 1.224 1.558 1158.6 42.253 3.647 2300.6 7.537 0.328 15022 13.308 0.087 Methoxychlor 155.472 2.794 1.797 2037.8 27.344 1.342 5133 144.477 2.815 51346.8 25179.692 49.038 4,4'-DDD 950.622 34.186 3.596 4875 2.389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4'-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.31	Endrinaldehyde	12	5.788	48.233	825.2	14.601	1.769	834	0	0	7047.4	30.171	0.428
Gamma BHC 115.7 3.493 3.019 596.6 8.649 1.450 2245 11.180 0.498 11709.8 167.512 1.430 Heptachlor 2 1.581 79.057 244.8 6.457 2.638 1106.2 15.254 1.379 9641.4 31.604 0.288 Heptachlorepxide 78.554 1.224 1.558 1158.6 42.253 3.647 2300.6 7.537 0.328 15022 13.038 0.087 Methoxychlor 155.472 2.794 1.797 2037.8 27.344 1.342 5133 144.477 2.815 5134.68 25179.692 49.038 4,4'-DDD 950.622 34.186 3.596 4875 2389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4'-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.39 4.738 1298.4 11.929 0.919 3400.2 277.91	Endrinketone	2.8	2.049	73.192	1423.2	43.234	3.038	2677.4	46.377	1.732	11376.8	84.221	0.740
Heptachlor 2 1.581 79.057 244.8 6.457 2.638 1106.2 15.24 1.379 9641.4 31.604 0.328 Heptachlorepoxide 78.554 1.224 1.558 1158.6 42.253 3.647 230.6 7.537 0.328 15022 13.038 0.087 Methoxychlor 155.472 2.794 1.797 2037.8 27.444 1.342 5133 144.477 2.815 5134.68 251.969 49.038 4,4'-DDD 950.622 34.186 3.596 4875 2389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4'-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.909.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12	Gamma BHC	115.7	3.493	3.019	596.6	8.649	1.450	2245	11.180	0.498	11709.8	167.512	1.430
Heptachlorepoxide 78.554 1.224 1.558 1158.6 42.253 3.647 2300.6 7.537 0.328 15022 13.038 0.087 Methoxychlor 155.472 2.794 1.797 2037.8 27.344 1.342 5133 144.477 2.815 51346.8 25179.692 49.038 4,4'-DDD 950.622 34.186 3.596 4875 2389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4'-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.339 4.738 1298.4 11.929 0.919 3400.2 227.912 6.703 40565.8 6.340 0.016 INTERNAL STANDARD OF PESTICIDES Atrazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 % Reproducibility 67.5 97.5 92.5 92.5	Heptachlor	2	1.581	79.057	244.8	6.457	2.638	1106.2	15.254	1.379	9641.4	31.604	0.328
Methoxychlor 155.472 2.794 1.797 2037.8 27.344 1.342 5133 144.477 2.815 51346.8 25179.692 49.038 4,4'-DDD 950.622 34.186 3.596 4875 2389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4'-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.339 4.738 1298.4 11.929 0.919 3400.2 227.912 6.703 40565.8 6.340 0.016 Harazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 % Reproducibility 67.5 97.5 92.5 97.5 92.5 97.5	Heptachlorepoxide	78.554	1.224	1.558	1158.6	42.253	3.647	2300.6	7.537	0.328	15022	13.038	0.087
4.4-DD 950.622 34.186 3.596 4875 2389.817 49.022 11704.4 464.696 3.970 64080 88.031 0.137 4,4-DDE 14.8 5.541 37.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.339 4.738 1298.4 11.929 0.919 3400.2 227.912 6.703 40565.8 6.340 0.016 INTERNAL STANDARD OF PESTICIDES Atrazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 97.5 92.5 97.5	Methoxychlor	155.472	2.794	1.797	2037.8	27.344	1.342	5133	144.477	2.815	51346.8	25179.692	49.038
4.4-DDE 14.8 5.241 57.437 70.8 2.775 3.919 117.32 4.314 3.677 3095.2 71.733 2.318 Aldrin 112.686 5.339 4.738 1298.4 11.929 0.919 3400.2 227.912 6.703 40565.8 6.340 0.016 INTERNAL STANDARD OF PESTICIDES Atrazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 % Reproducibility 67.5 97.5 92.5 97.5	4,4'-DDD	950.622	34.186	3.596	4875	2389.817	49.022	11704.4	464.696	3.970	64080	88.031	0.137
Aidrin 112.686 5.539 4./38 1298.4 11.929 0.919 3400.2 22/.912 6./05 40565.8 6.340 0.016 INTERNAL STANDARD OF PESTICIDES Atrazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 % Reproducibility 67.5 97.5 92.5 97.5 97.5	4,4'-DDE	14.8	5.541	37.437	70.8	2.775	3.919	117.32	4.314	3.677	3095.2	71.733	2.318
Atrazine d5 509.616 1.954 0.383 1351.2 6.760 0.500 1636.6 12.361 0.755 1728.2 7.6941 0.445 % Reproducibility 67.5 97.5 92.5 97.5	Aldrin	112.686 5.339 4.738 1298.4 11.929 0.919 3400.2 227.912 6.703 40565.8 6.340 0.016 INTERNAL STANDARD OF PESTICIDES											
% Reproducibility 67.5 97.5 92.5 97.5	Atrazine d5	509.616	1.954	0.383	1351.2	6.760	0.500	1636.6	12.361	0.755	1728.2	7.6941	0.445
	% Reproducibility		67.5			97.5			92.5			97.5	

ND = Not Detected, SD = Standard Deviation, CV = Coefficient of Variation, LOD= Limits of Detection, LOQ= Quantification

Table 5 shows the values of the detection and quantification limits and the percentages of recovery

NAMES OF COMPOUND	Detection Limits (LOD)	Quantization Limits (LOQ)	Recovery Percentage
	«μg/g »	$\ll \mu g/g \gg$	(% R)
Acenaphtene	0.037	0.123	99
Ac énaphyl ène	0.120	0.401	100
Anthracene	0.021	0.069	99
Benzo [a] Anthracene	0.016	0.053	98
Benzo [b] fluoranthene	0.012	0.039	110
Benzo [k] Fluoranthene	0.013	0.045	100
Benzo [g, h, i] perylene	0.019	0.065	99
Benzo [a] pyrene	0.017	0.058	110
Chrysene	0.012	0.041	99
Dibenzo [a, h] anth	0.026	0.087	108
Fluoranthene	0.022	0.075	108
Fluorene	0.013	0.045	99
Indeno [1,2,3-Cd] Pyrene	0.021	0.070	107
Naphthalene	0.104	0.345	109
Phenanthrene	0.002	0.008	98
Pyrene	0.012	0.040	100
Aldrin	0.071	0.238	100
Alpha BHC	0.039	0.129	109
BHC Beta	0.079	0.263	100
Delta BHC	0.023	0.078	107
Dieldrin	0.081	0.271	108
Alpha Endosulfan	0.133	0.445	98
Beta Endosulfan	0.070	0.234	100
Endosulfan Sulfate	0.085	0.284	100
Endrin	0.156	0.521	97
EndrinAldehyde	0.121	0.403	106
EndrinKetone	0.034	0.115	100
Gamma BHC	0.073	0.244	99
Heptachlor	0.138	0.461	98
HeptachlorEpoxide	0.086	0.282	100
Methoxychlor	0.141	0.468	98
4,4'-DDD	0.062	0.206	100
4,4'-DDE	0.194	0.645	91
4,4'-DDT	0.139	0.462	99

An analysis of the data shows that LODs range from $0.002 \mu g / g$ to $0.194 \mu g / g$. LOQs range from 0.008 to $0.645 \mu g / g$. The lowest LOD is obtained for phenanthrene while the highest value is found in 4,4'-DDE. The percentages of recovery vary between 91 and 110 for respectively 4,4'-DDE and Benzo [a] pyrene. Salem et al., (2016) under conditions similar to ours for a multiresidue assay of 16 PAHs, 12 PCBs and 9 OCPs in the sediments, obtained R² coefficient of determination greater than 0.95 for all the compounds analyzed. The quantification limits (LOQ) found by these authors vary between 0.02 and 9.64 ppb. These differences would be related to the state of the columns and detectors used. The column in our tests is relatively old which would be the cause of the limits of detection and quantification too high. Despite these high limits of detection and quantification the method has good linearity, good repeatability and reproducibility for concentrations greater than 10 ppb and can therefore validly be used in real-world for investigations. As such, the internal calibration has been used.

3.5 Application of the Method to the Analysis of Lake Nokou é Water Samples

The application of the validated method allowed us to search and to dose these two (02) families of contaminants sought in the waters of Lake Nokou é The analysis results are shown in Table 6.

Acenaphtene 2.492 2.894 2.503 Ac ánaphyl àe ND 1.679 0.294 Anthracene 0.046 0.115 0.131 Benzo [a] Anthracene 219.31 0.009 0.017 Benzo [b] fluoranthene 0.0066 ND ND Benzo [g, h, i] perylene 0.0086 ND ND Benzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorantene 10.0225 5.796 10.51 Pluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.441 0.037 Naphthalene 10.225 5.796 10.516 Pyrene ND ND ND Aldrin 0.119 0.119 0.129 Aldrin 0.119 0.119 0.119 BHC	Names of compounds	[MLA1] in ppb	[MLA2] in ppb	[MLA3] in ppb
Ac fashyl ène ND 1.679 0.294 Anthracene 0.046 0.115 0.131 Benzo [a] Anthracene 219.31 0.009 0.017 Benzo [k] Fluoranthene 0.0086 ND ND Benzo [s], hij perylene 0.0086 ND ND Benzo [a, hij perylene 0.008 0.0188 0.025 Benzo [a, hij perylene ND ND ND Chrysene ND ND ND Dibenzo [a, hij anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND Dieldrin	Acenaphtene	2.492	2.894	2.503
Anthracene 0.046 0.115 0.131 Benzo [a] Anthracene 219.31 0.009 0.017 Benzo [b] fluoranthene 0.0001 ND ND Benzo [k] Fluoranthene 0.086 ND ND Benzo [g, h, i] perylene 0.008 0.0188 0.025 Benzo [a, h] aprene ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluoranthene 0.037 0.641 0.037 Naphthalene 10.225 5.796 10.516 Pheranthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.493 Dieldrin 2.026 0.206 0.206 BHC Beta 0.939 0.399 0.399 Dieldrin	Ac énaphyl ène	ND	1.679	0.294
Benzo [a] Anthracene 219.31 0.009 0.017 Benzo [b] fluoranthene 0.0001 ND ND Benzo [g, h, i] perylene 0.008 0.0188 0.025 Benzo [a] pyrene ND ND ND Chrysene ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Pluorente 0.6677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.149 Dieldrin 12.269 0.167 0.17 Alpha BHC 109.280 ND ND Dieldrin 2.267 0.339 0.49 Beta Endosulfan 0.09	Anthracene	0.046	0.115	0.131
Benzo [b] fluoranthene 0.0001 ND ND Benzo [k] Fluoranthene 0.0086 ND ND Benzo [a, h] prylene 0.008 0.0188 0.025 Benzo [a, h] prylene ND ND ND Chrysene ND ND ND Dibenzo [a, h] anth 0.0668 0.159 0.173 Fluoranthene 1207.332 ND ND Fluoranthene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.637 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phrene ND ND ND Aldrin 0.119 0.119 0.120 Algha BHC 10.209 ND ND BHC Beta 11.371 0.157 0.149 Dieldrin 12.269 0.167 0.17 Algha Endosulfan 37.976 0.493 0.493 Beta Endosulfan 0.093 0.119 0.111 EndrinKetone	Benzo [a] Anthracene	219.31	0.009	0.017
Benzo [k] Fluoranthene 0.086 ND ND Benzo [g, h, i] perylene 0.008 0.0188 0.025 Benzo [a] pyrene ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluoranthene 0.6677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC 10.209 ND ND Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.19 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin/Aldehyde	Benzo [b] fluoranthene	0.0001	ND	ND
Benzo [g, h, i] perylene 0.008 0.0188 0.025 Benzo [a] pyrene ND ND ND Chrysene ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Aldrin 0.119 0.15 0.149 BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 ND ND Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin/Alehyde 0.399	Benzo [k] Fluoranthene	0.086	ND	ND
Benzo [a] pyrene ND ND ND Chrysene ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 ND ND Dieldrin 12.269 0.167 0.17 Beta Endosulfan 0.093 0.119 0.111 Endosulfan 0.399 0.399 0.399 Beta Indosulfan Sulfate 0.206 0.206 0.206 Endrin/Aldehyde 0.399 <td< td=""><td>Benzo [g, h, i] perylene</td><td>0.008</td><td>0.0188</td><td>0.025</td></td<>	Benzo [g, h, i] perylene	0.008	0.0188	0.025
ND ND ND ND Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 ND ND Didtrin 12.269 0.167 0.17 Alpha Endosulfan 0.093 0.119 0.111 Endosulfan 0.379 0.399 0.399 Beta Endosulfan 0.0206 0.206 0.206 Endrin Aldehyde 0.399 0.399 0.399 Endrini Ketone 45.784 ND </td <td>Benzo [a] pyrene</td> <td>ND</td> <td>ND</td> <td>ND</td>	Benzo [a] pyrene	ND	ND	ND
Dibenzo [a, h] anth 0.068 0.159 0.173 Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.449 Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin 20.137 0.615 0.606 Endrin 0.399 0.399 0.399 Endrin 0.2033 0.518 0.521 0.518 Gamma BHC	Chrysene	ND	ND	ND
Fluoranthene 1207.332 ND ND Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.449 Delta BHC 109.280 ND ND Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 0.093 0.119 0.111 Endosulfan 0.093 0.119 0.111 Endosulfan 0.093 0.119 0.111 Endosulfan 0.206 0.206 0.206 Endrin/Aldehyde 0.399 0.399 0.399 Endrin/Aldehyde 0.399 0.399 0.399 Endrin/Aldehyde 0.518	Dibenzo [a, h] anth	0.068	0.159	0.173
Fluorene 0.677 0.865 1.23 Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 ND ND Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin Asulfate 0.399 0.399 0.399 Endrin Asulfate 0.399 0.399 0.399 Endrin Ketone 45.784 ND ND Gamma BHC 13.291 0.099 0.094 Heptachlor 42.940 0.533 0.518 Heptachlor 0.518	Fluoranthene	1207.332	ND	ND
Indeno [1,2,3-cd] pyrene 0.037 0.041 0.037 Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 PyreneNDNDNDAldrin 0.119 0.119 0.120 Alpha BHC 10.209 NDNDBHC Beta 11.371 0.15 0.149 Delta BHC 109.280 NDNDDieldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.119 0.111 Endosulfan 0.093 0.167 0.615 Beta Endosulfan 0.206 0.206 0.206 Endrin 20.137 0.615 0.606 EndrinAldehyde 0.399 0.399 0.399 Gamma BHC 13.291 0.099 0.094 Heptachlor 42.940 0.533 0.518 HeptachlorEpoxide 0.184 0.184 0.184 Methoxychlor 0.518 0.521 0.518 4,4'-DDD 4.209 0.0463 0.046 4,4'-DDE 19.324 0.809 0.813 4,4'-DDT 38.829 0.522 0.554	Fluorene	0.677	0.865	1.23
Naphthalene 10.225 5.796 10.516 Phenanthrene 2.073 0.821 1.309 PyreneNDNDNDAldrin 0.119 0.119 0.120 Alpha BHC 10.209 NDNDBHC Beta 11.371 0.15 0.149 Delta BHC 109.280 NDNDDicldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.119 0.111 Endosulfan 0.206 0.206 0.206 Endrin 20.137 0.615 0.606 Endrin 20.137 0.615 0.606 EndrinAldehyde 0.399 0.399 0.399 EndrinKetone 45.784 NDNDGamma BHC 13.291 0.099 0.094 HeptachlorEpoxide 0.184 0.184 0.184 Methoxychlor 4.209 0.0463 0.0463 4,4'-DDD 4.209 0.0463 0.0463 4,4'-DDE 19.324 0.809 0.813 4,4'-DDT 38.829 0.522 0.554	Indeno [1,2,3-cd] pyrene	0.037	0.041	0.037
Phenanthrene 2.073 0.821 1.309 Pyrene ND ND ND Aldrin 0.119 0.119 0.120 Alpha BHC 10.209 ND ND BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 ND ND Dieldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin/Idehyde 0.399 0.399 0.399 0.399 Endrin/Idehyde 0.399 0.399 0.399 0.399 Endrin/Idehyde 0.399 0.399 0.094 184 0.184 Gamma BHC 13.291 0.099 0.094 184 0.184 0.184 Methoxychlor 0.518 0.521 0.518 0.518 0.521 0.5184 4.4'-DDD 4.209 0.04	Naphthalene	10.225	5.796	10.516
PyreneNDNDNDAldrin0.1190.1190.120Alpha BHC10.209NDNDBHC Beta11.3710.150.149Delta BHC109.280NDNDDieldrin12.2690.1670.17Alpha Endosulfan37.9760.4930.49Beta Endosulfan0.0930.1190.111Endosulfan0.2060.2060.206Endrin20.1370.6150.606EndrinAldehyde0.3990.3990.399EndrinKetone45.784NDNDGamma BHC13.2910.0990.094HeptachlorEpoxide0.5180.5210.5184.4'-DDD4.2090.04630.0464.4'-DDE19.3240.8090.8134.4'-DDT38.8290.5220.554	Phenanthrene	2.073	0.821	1.309
Aldrin0.1190.1190.120Alpha BHC10.209NDNDBHC Beta11.3710.150.149Delta BHC109.280NDNDDieldrin12.2690.1670.17Alpha Endosulfan37.9760.4930.49Beta Endosulfan0.0930.1190.111Endosulfan0.0930.190.111Endosulfan Sulfate0.2060.2060.206Endrin20.1370.6150.606EndrinAldehyde0.3990.3990.399EndrinKetone45.784NDNDGamma BHC13.2910.0990.094Heptachlor0.5180.5210.518HeptachlorEpoxide0.5180.5210.5184,4'-DDE42.090.04630.04634,4'-DDT38.8290.5220.554	Pyrene	ND	ND	ND
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Aldrin	0.119	0.119	0.120
BHC Beta 11.371 0.15 0.149 Delta BHC 109.280 NDNDDieldrin 12.269 0.167 0.17 Alpha Endosulfan 37.976 0.493 0.49 Beta Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin 20.137 0.615 0.606 EndrinAldehyde 0.399 0.399 0.399 EndrinKetone 45.784 NDNDGamma BHC 13.291 0.099 0.094 Heptachlor 42.940 0.533 0.518 HeptachlorEpoxide 0.184 0.184 0.184 Methoxychlor 0.518 0.521 0.518 4,4'-DDE 19.324 0.809 0.813 4,4'-DDT 38.829 0.522 0.554	Alpha BHC	10.209	ND	ND
Delta BHC109.280NDNDDieldrin12.2690.1670.17Alpha Endosulfan37.9760.4930.49Beta Endosulfan0.0930.1190.111Endosulfan Sulfate0.2060.2060.206Endrin20.1370.6150.606EndrinAldehyde0.3990.3990.399EndrinKetone45.784NDNDGamma BHC13.2910.0990.094Heptachlor42.9400.5330.518HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDT38.8290.5220.554	BHC Beta	11.371	0.15	0.149
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Delta BHC	109.280	ND	ND
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Dieldrin	12.269	0.167	0.17
Beta Endosulfan 0.093 0.119 0.111 Endosulfan Sulfate 0.206 0.206 0.206 Endrin 20.137 0.615 0.606 EndrinAldehyde 0.399 0.399 0.399 EndrinKetone 45.784 NDNDGamma BHC 13.291 0.099 0.094 Heptachlor 42.940 0.533 0.518 HeptachlorEpoxide 0.184 0.184 0.184 Methoxychlor 0.518 0.521 0.5189 4,4'-DDD 4.209 0.0463 0.046 4,4'-DDE 19.324 0.809 0.813 4,4'-DDT 38.829 0.522 0.554	Alpha Endosulfan	37.976	0.493	0.49
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Beta Endosulfan	0.093	0.119	0.111
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Endosulfan Sulfate	0.206	0.206	0.206
EndrinAldehyde0.3990.3990.399EndrinKetone45.784NDNDGamma BHC13.2910.0990.094Heptachlor42.9400.5330.518HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	Endrin	20.137	0.615	0.606
EndrinKetone45.784NDNDGamma BHC13.2910.0990.094Heptachlor42.9400.5330.518HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	EndrinAldehyde	0.399	0.399	0.399
Gamma BHC13.2910.0990.094Heptachlor42.9400.5330.518HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	EndrinKetone	45.784	ND	ND
Heptachlor42.9400.5330.518HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	Gamma BHC	13.291	0.099	0.094
HeptachlorEpoxide0.1840.1840.184Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	Heptachlor	42.940	0.533	0.518
Methoxychlor0.5180.5210.51894,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	HeptachlorEpoxide	0.184	0.184	0.184
4,4'-DDD4.2090.04630.0464,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	Methoxychlor	0.518	0.521	0.5189
4,4'-DDE19.3240.8090.8134,4'-DDT38.8290.5220.554	4,4'-DDD	4.209	0.0463	0.046
4,4'-DDT 38.829 0.522 0.554	4,4'-DDE	19.324	0.809	0.813
	4,4'-DDT	38.829	0.522	0.554

Table 6. Lake Nokou éwater analysis results

ND: Not Dected

From the analysis of the data in Table 5, we note at the level of PAHs that, out of 16 molecules sought in the lake, three (03) were not detected. Nine (09) out of sixteen PAH molecules were detected at all sites. Contamination levels vary from not determined to 1207.33 ppb on the MLA1 site.

At the level of the OCPs, if on the MLA1 site all the eighteen (18) searched molecules are found, at the MLA sites 2 and 3, three (03) molecules were not detected. These are Delta BHC, EndrineKetone and Alpha BHC. So a total of 15 molecules out of 18 OCPs were detected and quantified at all sites. That is a percentage of 83% of OCPs. The origin of PAH compounds in Nokou éLagoon are material combustion and fuels for polycyclic aromatic hydrocarbons and due to remoteness pollution for organochloride pesticide compounds (Soclo, 2008; Yehouenou, 2006a & b).

4. Conclusion

Whatever the external or internal calibration, the values of the coefficient of determination R^2 obtained are between 0.98 and 1. These values demonstrate that the method has good linearity in the chosen calibration range. For the repeatability the validation percentages vary from 32.5 to 92 %. The low percentages are the repeatability tests for the 10 ppb concentration. This state of affairs would be related to a loss of analyte during the dry extracts. Overall, the reproducibility percentages of the assays are acceptable and are considered satisfactory for validating the method and for use in real-world analyses. For all the molecules sought, the percentage of recovery varies between 91 and 110 % corresponding respectively to Benzo [b] fluoranthene and Benzo [a] pyrene.

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