# Assessment of Environmental Toxic Trace Metals and Pesticides Contents in Selected Fish Species from Guiers Lake by using XRF and GC/ECD Techniques

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Received 14 Oct. 2014;	Revised 20 Dec. 2014;	Accepted 21 Dec. 2014

**ABSTRACT:**The most used QuEChERS and gas chromatography methods were performed, to evaluate the presence of organochlorines, organophosphate, polychlorinated biphenyl and chlorobenzenes in water and in fish. According to the standard ISO IEC 17025, a recovery rate obtained ranged from 70 to 120% assessing the reliability of analysis results. The exceed rate in fish of Malathion is 22.2, and 5.2 ppm in sampling site XGL411 and XGL416 respectively, Endrin is 4 ppm in XGL415, Trifluralin and Parathion is 1.6, 1.4, 1.8 and 4.2 ppm in XGL413, XGL414, XGL415 and XGL417 respectively and Pyrimiphos-Methyl is 1ppm in XGL417. In water, the exceed rate of Trifluralin is 6.5ppb in XGL411 and Parathion and Pyrimiphos methyl is 1.1, 1.8, 1, 1, 1.5 ppb in XGL412, XGL413, XGL414, XGL415 and XGL420 respectively. The purpose of this work is to assess a chemical analysis related to screening pesticides and potentially toxic metal in water and fish samples taken from Guiers Lake. The estimating level of contamination in fish muscles has been performed using X-ray fluorescence technique and the level of Cadmium have to be monitored due to the potential effects on the fish themselves and the organism that consume them.

Key words: Pesticides, Toxic metal, Fish, Guiers Lake, Risk assessment, XRF, QuEChERS

# INTRODUCTION

The growth of industries in developing and developed countries has a big part in the contamination of the fresh waters (Yao *et al.*, 2014, Zhang *et al.*, 2007). The Guiers Lake (GL) is the principal source of fresh water in Senegal. Its distribution is done by the Water Company (SDE) of Senegal. The lake is located in a high agricultural activity area where fertilizers and pesticides are still being used with significant implications to the quality of the environment. The industrial, the household rubbish and the practice of agro chemistry in cultivated field are the main factors of water surfaces contamination (Kennicutt *et al.*, 1994).

During the last invasion of the grasshoppers (Oedaleus senegalensis) in Senegal (Rachadi 1986, Diop 1987), a big campaign against the locusts has been organised throughout the country particularly in the north part of Senegal. It consisted of using, under pulverised form, organochlorines in the agricultural areas to protect the crops and harvest.

After many years, some chemical strategies to fight against the locust on environment were still in use to better perform the ecotoxicological effect of locusts' treatment upon the aquatic fauna such as the fish and their wildlife.

The fight against organochlorine insecticides has been developed throughout the world. This development is at a certain extent supported by frequent and important anthropogenic activities (Alcock *et al.*, 1999). The use of non conventional chemical methods does not affect the crops as a treatment decreased satisfactorily with time (Zick and Cillia 2007, Rick and Nicole 2008, Ruth *et al.*, 2011).

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The overuse of pesticides costs a lot economically and can increase the pollution of the environment with no real profitability. These problems can occur in the developing countries where the fight against insecticides can result into enormous harvest losses destined to local and national consumption or to exportation. There are several measurements that have been taken to implement a management system of crops and plants enemies which are not only based on regular pesticides applications but on paramount toxic items resulting from companies waste located in the GL zone. However the need of using pesticides in the developing countries to improve their agricultural production must be taken into account. In the late 1980s, it was predicted that the total consumption of pesticides will reach 11 billion with 10 % annual inflation rate, according to UNIDO, New York 1985 (Tanabe et al., 1994).

Taking the hazardous effect of pesticides into account, the use of pesticides can vary from one country to another according to the objectives and the national needs. It is also utmost worthwhile to consider the needs in pesticides of the harvest to be exported which will be subjected to the rules and regulations of the importer country. Thus, appropriate pesticides used correctly on due time can be of much importance to agriculture particularly in countries where the climate favours the rapid development of the enemies of crops and plants (UNIDO 1989). Also the runoff effluents from agricultural, the use of fertilizers, herbicides, pesticides and solid wastes disposal can cause severe contamination in Guiers Lake. The QuEChERS (acronym quick, easy, cheap, effective, rugged and safe) (Gilbert et al., 2009) like method of chromatography in gaseous phase coupled with several detectors such as electron captured detection (ECD) (Abhilah and Singh 2008), or diode array (Tuzimski 2011) for the detection of pesticide residues in this type of matrix have been used to determine the presence of organochlorines, organophosphate, polychlorinated biphenyl and chlorobenzenes in water and fish.

The purpose of this work is to carry out a chemical analysis related to the screening of pesticides (CILSS 2012, PPDB 2013) and metal waste potentially toxic in water and fish samples taken from Guiers Lake, particularly in "Taouey", the lakeside depression part of "Ferlo" region from agricultural and industrial activities (Akan *et al.*, 2009). While estimating the level of contamination, the metal concentration (Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Rb, Sr and Cd) level has been evaluated by the x-ray fluorescence technique applied to fish muscles. This study is an asset considering the reliable information that is achieved with this detection system.

In this study eleven (11) water samples, nine (09) taken from Guiers Lake, two (02) from the depression part of "Ferlo" and thirty (30) samples of fish from GL were prepared for analysis.

# **MATERIAL & METHODS**

The GL is located in the northern region of Senegal named St Louis. St-Louis is a region between the latitude of 15°40 and 16°25 North and longitudes of 15°25 and 16° West (Table 2), the lake drains an area of approximately 300 km<sup>2</sup> for a bulk of 600 million of m<sup>3</sup>. The GL can be characterized by the intense anthropogenic activities (Fig. 1). The lake has been polluted by untreated urban wastewaters, as well as by the runoffs from farms and agricultural land, and discharge originating from industrial sources as the Senegalese Sugar Company (SSC). The waste contains organic pollutants, pesticides and toxic metals, etc., which may be harmful to humans and animals.

The traces of pesticides are recovered by washing the wall of the flask using hexane or ethyl acetate and then analyzed by gas chromatography coupled with the mass spectrophotometer (GC/MS).

For the matrix fish, the versatile method for the determination of residues of pesticides by GC/MS with extraction/partition with acetonitrile and cleaning by a dispersive solid-phase extraction (dSPE) procedure (Supelco 1998), standard NF-IN 15662, January 2009, commonly called the QuEChERS Method has been used. The QuEChERS method has been performed for the extraction of a large variety of medicinal plants, and it is the ongoing preferred option for the determination of pesticides in plantsbased products. This extraction procedure was originally developed by (Anastassiades et al., in 2003) for the analysis of pesticides in vegetables and fruits. The homogenized grinded sample is collected and then frozen through acetonitrile in a cartridge of centrifugation. After the addition of magnesium sulphate, sodium chloride and salts of citrate buffers, the mixture is vigorously maintain to a shaking time of 1 min, put to rest, and then centrifuged to separate the phases. An aliquot of the organic phase is cleaned by a dSPE, using adsorbents in bulk and magnesium sulphate to remove traces of residual water. After cleaning process using amino adsorbents, the extract is acidified by addition of a small amount of formic acid, in order to improve the storage stability of pesticides susceptible to databases. The final extract is used directly for the analysis of determination by GC/MS. Acetonitrile is highly compatible with GC/ MS applications with less matrix effects. The monitoring of the quality of the analysis is carried

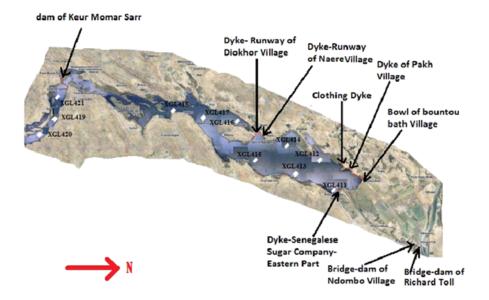


Fig. 1. Location Map for the Guiers Lake study

out using PCB internal standard which is added to the test sample after the initial addition of acetonitrile.

This determination allows assessing the recovery rate of the method (Table 4.1).

		<b>U I</b>		-	-		
Targeted	Family	Biologic	SPC	Behavior i	n aquatic a	rea	
Molecular	Pesticide	Activities	Authorization	Solubility (mg/l)	Stability DT50 at pH 7	Toxicity CL50 fish	PBA
Aldrin	OC <sup>2</sup>	Insecticide	NO	0,027		4,6	Н
Bifenthrin	PY <sup>3</sup>	Insecticide	YES	0,001	Stable	0,26	Н
Chlorothalonil	isophta lonitrile	Fongicide	NO	0,81	Stable	38	1
Chlorpyriphos	$OP^4$	Insecticide	YES	1,05	25,5	1,3	Н
Cypermethrin	PY	Insecticide	YES	0,009	178	2,8	Н
DDT	OC	Insecticide	NO	0,006		7	Н
Deltamethrin	PY	Insecticide	YES	0,0002	Stable	0,26	Н
Dicofol	OC	A carici de	NO	0,8	3,3	510	Н
Dieldrin	OC	Insecticide	NO	0,14		1,2	Н
Dimethoate	OP	Insecticide	NO	39800	68	30200	1
Endosulfan	OC	Insecticide	NO	0,32	20	2	Н
Endrin	OC	Insecticide	NO	0,24		0,73	Н
Fenitrothion	OP	Insecticide	YES	19	183	1300	1
Heptachlor	OC	Insecticide	NO	0,06	1	7	Н
L-Cyhalothrin	PY	Insecticide	YES	0,005	Stable	0,21	Н
Lindane	OC	Insecticide	NO	8,52	752	2,9	Н
Malathion	OP	Insecticide	YES	148	6, 2	18	1
Me-Parathion	OP	Insecticide	NO	55	21	2700	1
Pyrimiphos- Methyl	OP	Insecticide	YES	11	117	404	1
Oxadiazon	oxadiazole	Herbicide	YES	0,57	31	1200	m
Propanil	ani li des	Herbicide	YES	95	365	5400	1
Trifluralin	Toluidines	Herbicide	NO	0,221	Stable	88	Н

Table 1. List of target pesticide residues and their properties

1 PBA Potential Level of Bioaccumulation Pesticide (l:low m:moderated H:High)

2 5OC: Organochlorin Group

3 P6Y: pyrethroids synthesis Group

4 OP: Organophosphorus Group

Fish Label	Fish Specimen	A verage Weight	Nimber of Fish	GPS Position	Nearest Station with
Laber	rish specifici	of Fish	01 11511		Anthropologic Activities
XGL411	Tilapia	600 g	5		Before the effluent station point
				16°27′50.48″N, 15°41′34.55″	of sugar Senegalese Company (SSC) " <b>Richard Toll''</b>
XGL412			0		
	No fish	0g		16°20'49.41 "N, 15°47'11.10 "W	Effluent Station point X6 of sugar Senegalese Company (SSC)
XGL413		1000	6		
	Characin (Alestes- dentex)	1000g		16°22'7.50"N, 15°46'40.11 "W	Arrival of " <b>Taouey</b> " river to Guiers Lake at 2000 m from the East South part to the central si
XGL414	Oreochromus niloticus		1		point At 1000m from the Central Site
	and Synodontis clarias	1000g		16°19'49.41 "N, 15°50'12.65 "W	point to the Northern part
XGL415	Characin (Alestes	600g	2	16°14'29.34"N,	" <b>Saninthe</b> " Monitoring Station- reference point of sampling
	dentex)			15°48'7.94"W	1 1 0
XGL416		600g	3		At 250 m from the Central Site
	Tilapia			16°14'43.24"N, 15°51'20.94"W	point to the Northern part
XGL417	Hogfish (Lachnolaimus	400g	3		Station Water Company of Senegal " <b>Ngnith</b> " at 1800 m
	maximus)			16°11'8.09"N, 15°54'7.21"W	from the Central Site point to th Southern part
XGL418	Chrysichtinigrodigius	2Kg	2	16° 9'37.17"N, 15° 53'8.35"W	At 1400 m from the Central Site point to the Western part
XGL419		800g	3	15 55 6.55 W	Site point before the working
	Tilapia			15°56'7.32"N, 15°56'42.51 "W	station of "Gueoul"
XGL420	Siluridae	1 Kg	2	1 5° 55' 1 3.97 "N, 1 5° 55' 21.14 "W	Depression part of " <b>Ferlo</b> ", at 3000m from the working statio point " <b>Gueoul</b> "
XGL421	Tilapia	1.2Kg	3	1 <i>5 55</i> 21.14 W	Station Water Company of Senegal "Keur Momar Sarr"
	1			15°57'9.35"N, 15°58'4.51"W	2km from the central site point the Northern part

# Table 2. GPS-positions for the studied areas according to Google earth map

In Table 1 the list is drawn from the pesticides with exceeding content of the Maximum Residue Level (MRL) on the pilot project Global Environmental Facilities (UNDP 2010), the housewife's shopping basket and the study on the content of pesticides in waters in the area of the "Niayes" extends from Dakar to the river mouth of Senegal. This part foreshore stretches over a length of 180 km, and its width varies from 5 to 30 km inside the land.

As pointed out in the principles of the methods of analysis, each sample was analyzed with the addition of a well-known quantity from the internal standard polychlorobiphenyl 128 or 2,4,4'-Trichlorobiphenyl (PCB). The latter follows the same conditions for extraction, purification, storage prior to analysis and chromatographic detection as the targeted pesticide in the sample. The determination of the recovery rate of the PCB standard method is an asset for a better sensitivity of pesticide residues for the quality and the performance of the analytical methods used. In addition, this internal standard, in the software GC-MS, is used to correct the inter element effects and to ensure the reliability of the concentration values.

According to the standard ISO CEI 17025, a recovery rate obtained ranging from 70 to 120% was

found to assess the reliability of the calibration (Table 3.1 and 4.1). The blank sample was carried out for each subsample (water and fish) to assess that experimental setup and solvent are free of targeted pesticides. The absence of background peaks, above a signal-to-noise ratio at the retention time of each pesticide, showed that no interferences occurred.

The limit of detection (LOD) was evaluated by multiplying the average value of the noise sampled at the retention time of each pesticide and the limit of quantification (LOQ) was ten times the average value of the noise in this same region of interest.

For the analysis of toxic metals the standard IAEA407 fish muscle has been used to evaluate the performance of the x-ray spectrometer.

Bivariate correlation using Spearman rho was performed to examine with statistical difference (P < 0.05) relationship of elements among the sampling site point; in order to find out the link between potential source of contamination and anthropogenic activities.

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The rates found can be doubly attributed to the stability of the product and its affinity for the living organism's i.e. high potential bioaccumulation for trifluralin. Malathion is a second POP present in 3 samples ranging from 0.26 to 1.11 mg a.s. /kg. The main sources of this molecule found in fish samples are difficult to assess due to the fact that it has not been found in water samples and has also itself a low potential bioaccumulation. The mobility of fish can, also, conceal the real origin contamination. T h e following elements of interest, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Rb, Sr, and Cd, which are present in fish tissues, were mainly identified by their strong concentrations. Some elements were not possible to be detected due to their low detection limit in sample muscles or to the presence of the well-known mutual spectral interference effects of X-ray peaks intensity. The sensitivity curves were determined for both X-ray K and L series of the XRF spectrometer and were fitted using logarithmic model (Fig. 2) by applying a polynomial type function taking a weight of fit into account.

Table 3. Concentration	01	pesticide	residues	ın	water 1	n	ррв	

Sample			1	GLA1 2	XGL41 3 0.18	XGL4 4 0.1	1 XGL41 5 0.1	<b>XGL41</b> 6 <0.1	XGL4 17 <0.1	XGL4 18 <0.1	XGL4 19 <0.1	XGL4 20 0.15	• XGL4 21 <0.1
Me-Parathior Methyl Trifluralin	1+Pyrimiph	.OS-		.0.1	<0.13	< 0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.13	<0.1
Sample	XGL411	XGL412					ecovery l XGL416	Rate % XGL417	XGL41	8 XGL	419 X(	H420	XGL421
Added Amount (µg) Amount	0.498	0.498	0.498	0.4	98	0.498	0.498	0.498	0.498	0.49	98 0	.498	0.498
Found (µg) Recovery	0.581	0.589	0.596	0.5	80	0.576	0.583	0.421	0.598	0.52	23 0	.516	0.5186
Rate (%)	116.666	118.373	119.701	116.	486 1	15.703	117.14859	84.598	120.08	0 105.	140 10	3.614	104.136

Table 4. Concentration of pesticides residues in fish (ppm)

Pesticides Name	XGL4 11	XGL 413	XGL 414	XGL 415	XGL 416	XGL 417	XGL 418	XGL 419	XGL 420	X GL 421
Endrin	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0,01
Malathion	1.11	< 0.05	0.54	< 0.05	0.26	< 0.05	< 0.05	<0.05	< 0.05	< 0.05
Me-Parathion	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.05	< 0.01	< 0.05	< 0.05	< 0.05
+Pyrimiphos-Methyl										
Trifluralin	< 0.05	0.08	0.07	0.09	< 0.05	0.21	< 0.05	< 0.05	< 0.05	< 0.05

#### Table 4.1. Fish Recovery Rate %

	XGL411	XGL413	XGL4							
Samples			14	15	16	17	18	19	20	21
Added Amount (µg)	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995	0.0995
Amount found (µg)	0.0803	0.0789	0.0922	0.0766	0.0881	0.0734	0.0846	0.0935	0.0939	0.0702
Recovery Rate (%)	80.3	78.9	92.2	76.6	88.5	73.8	85.0	93.9	94.4	70.6

	Molecule	Sampling Sites	Result s	LOQ	Exceed Rate		Molecule	sampling sites	Results	LOQ	Exceed Rate
	Malathion	XGL411	1,11	0,05	22,2						
		XGL416	0,26	0,05	5,2		Trifluralin	XGL411	0,65	0,1	6,5
	Endrin	XGL415	0,04	0,01	4		Parathion and	XGL412	0,11	0,1	1,1
	Trifluralin	XGL413	0,08	0,05	1,6	~	Pyrimiphos	XGL413	0,18	0,1	1,8
FISH		XGL414	0,07	0,05	1,4	WATER	methyl	XGL414	0,1	0,1	1
		XGL415	0,09	0,05	1,8			XGL415	0,1	0,1	1
		XGL417	0,21	0,05	4,2			XGL420	0,15	0,1	1,5
	Parathion and	XGL417	0,05	0,05	1						
	Pyrimiphos methyl										

Table 5. Concentration of pesticides in fish (ppm) and in Water (ppb) in exceed rate

The obtained concentrations in fish muscle were converted in dry weight by taking into account the samples moisture content. The moisture content was evaluated to be about 80%. Before this procedure, the fat content in muscle was performed consequently by using nitric acid attack and mineralization under oven; the results of the replicate measurements and the standard deviation are summarized in Table 6. Analysis of fish muscle is very worthwhile in order to understand diseases and bioaccumulation based on metal contamination in fish species. However, the variability of elements in fish is facing a challenge whether the presence of some individual or group of element could be correlated to the absence or the presence of another. For each element, correlations between fish muscles were investigated. Cu and Mn, S, Cl, K, Ca, Fe, Zn, Pd were positively correlated (p < 0.05) but negatively correlated with Mo, P and K (p < 0.01). There is no correlation with Cu, Fe and Cd. Fig. 3 shows the correlation between elements using

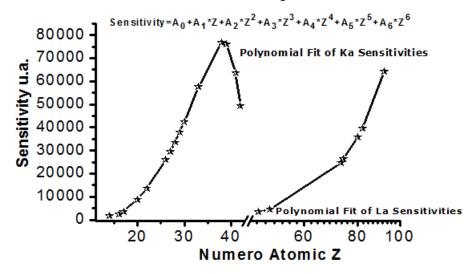


Fig. 2. Sensitivity Portable X-ray fluorescence spectrometer for X-ray K and L series

							1		
			Mean ± SD (range	e) inorganic elemen	Mean $\pm$ SD (range) inorganic element concentration (mgkgin dry weight)	/kgin dry weight)			
XGL411	XGL413	XGL414	XGL415	XGL416	XGL417	XGL418	XGL419	XGL420	XGL421
$13,39\pm 612.59$	55026,27±637.63	54369,98±556.88	54543,45±622.4	55208,49±645.86	54571,62±632.18	62198,27±809.16	$53841, 38\pm658.75$	$54092,37\pm$	54166,63±645.12
								647.05	
$10,04 \pm 417.94$	$16856, 38\pm 415.74$	12639,16±355.71	18950,34±430.54	$10120,15\pm 369.99$	21 120,51 ±446	19355,25±447.88	13 262,5 ±415.67	23110,82±469.94	12239,01 ±397.4
$21,71\pm 313.71$	26179,07±365.84	21237,22±318.15	24592,29±354.28	19216,01±338.78	$21202,99\pm 331.9$	26266,04±375.29	26991,11398.79	27653,67±377.9	24648,86±378.04
13,87±20.59	$1522,45\pm 26.56$	$1103,74\pm 21.98$	908,52±21.3	$1181,68\pm\!25.36$	1961,4±29.59	789,91±20.83	2050,87±32.75	1507,87 ±26.68	$1386,86\pm27.18$
14,94±269.99	41387,77±301.34	37371,17±278.66	40744,88±306.29	$32315,13\pm279.4$	36690,62±272.65	41067,73±302.38	$41328,83\pm\!310.5$	$46638, 3 \pm 324.52$	38520,26±313.73
85,72±174.57	16899,11±144.34	9166,71±106.62	18805,85±156.31	10724,85±119.89	39827,81±228.58	23702,69±74.06	$2021,92\pm 81.27$	20837,07±165.56	<b>5</b> 937,81 ±102.85
3,66±17.12	447,27 ±17.46	465,27±17.11	446,51±17.36	457,62±17.43	419,65±17.16	448,46±19.06	452,25±17.06	479,98±19.5	674,85±25.98
$6,85 \pm 22.14$	ND	131,78±18.63	95,85±18.74	91,97±18.79	ND	1298,2±40.11	ΟN	57,02±17.9	213,59±23.18
14,46±6.24	35,88 ±6.63	16,25±5.75	44,61±6.99	41, 19±6.82	14,82±6.01	22,51±6.61	62, 1±7.36	16,01±6.19	49,25±7.38
31,47±5.53	119,95 ±6.42	68,73±5.01	117,51±6.4	64,37±5.3	$62,23\pm 5.03$	78,05±5.74	$107,06\pm 6.29$	127,04±6.59	88,91±6.11
94,64±1.19	$20,98 \pm 1.14$	$14,23\pm 1$	23,71±1.18	$13,89\pm 1.01$	21,15±1.14	18,1±1.12	14,9±1.02	25,77±1.23	14,69±1.04
$46,88 \pm 1.4$	$44,57 \pm 1.39$	$27,88\pm1.1$	34,4±1.26	21,8±1.06	124,16±2.21	67,43±1.73	$7,9\pm 1$	$51,33\pm1.49$	12,8±1
$12,98 \pm 1.3$	$13, 17 \pm 1.3$	13,53±1.2	14,28±1.28	15,83±1.27	7,67±1.39	22,4±1.49	16,48±1.25	12,85±1.31	16,92±1.31
$6,87\pm1.34$	$17,09 \pm 1.36$	$16,03\pm1.3$	17,33±1.37	17,75 ±1.37	$15, 56 \pm 1.34$	16,56 ±1.41	$17,5 \pm 1.38$	16,67 ±.37	17,94±1.43
$8,15\pm1.18$	$17, 99 \pm 1.2$	$17, 72 \pm 1.14$	18,63±1.21	$19,5\pm 1.22$	$16 \pm 1.17$	$17,89 \pm 1.24$	$19,6 \pm 1.23$	$18,02 \pm 1.21$	$20,11\pm1.27$
$4,16 \pm 1.72$	$4,05\pm1.74$	<b>4</b> ,66 ±1.64	$4,62\pm\!1.75$	$5,18\pm 1.77$	$4\pm1.74$	$4,46\pm1.84$	<b>4</b> ,8 ±1.76	$4,88 \pm 1.76$	5,17±1.82
$2,87\pm3.74$	$11,39 \pm 3.77$	11,77 ±3.52	12,85±3.78	$13,4\pm 3.79$	$11, 31 \pm 3.77$	$10,97 \pm 3.96$	14,67 ±3.81	$11, 36 \pm 3.77$	$13,15\pm 3.9$

Table 6. Inorganic element accumulated into the muscle tissue of fish from Guiers Lake (ppm).

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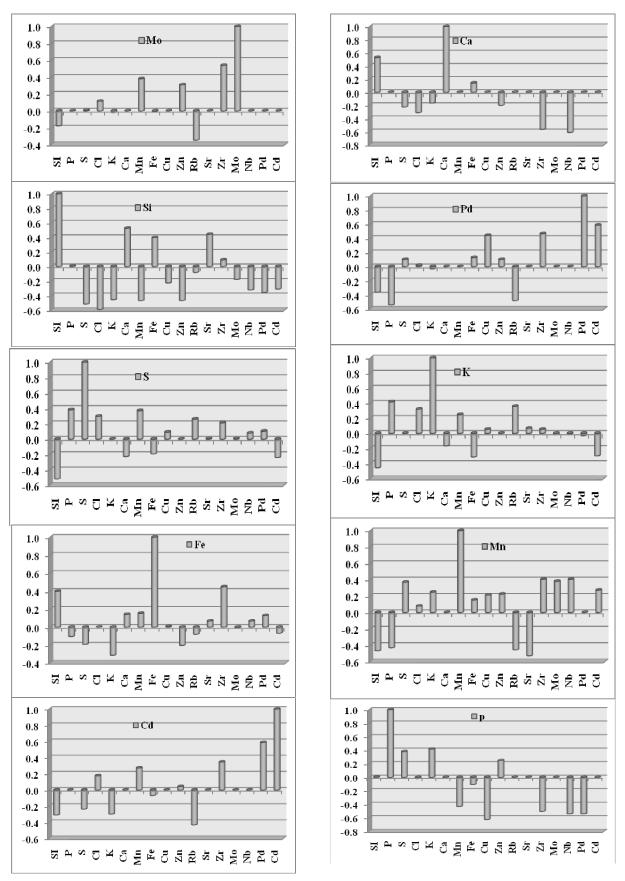


Fig. 3. Spearman test correlation of metals level between fish samples

Spearman rho coefficient.Copper combined with other contaminants such as Zn can produce an additive toxic effect on fish (Herbert and Vandyke 1964, Rompala *et al.*, 1984). In the sampling point XLG420 two young fish were found and it's the area where there is strong correlation between Zn/Cu. The same behaviour between Zn/Cd in the depression of "Ferlo" assesses the industrial waste effluent.

In the sampling point XGL418, copper concentration was found to be ranging from 16.01-62.1mg/kg. The effects of high concentration of copper in fish are not well established; however, there is an evidence that high concentrations of copper in fish can yield to contamination (Woodward *et al.*, 1994). The level of zinc is ranging from 62.23-127.04 mg/kg and the high concentration is located in the sampling point XGL420 where the lower part of GL is located.

This point should be the more interesting part of the lake and will reflect the consequence of the runoff from the Lake gathering all sediments and algae in this area. Zinc concentrations indicate the increase of industrial activities in the boundaries area of the lake as Zn is known to be an indicator for urban development (Förstner and Littman 1979). Cadmium was estimated ranging from 10.97-14.67 mg/kg and the higher mean concentration was found in sampling point XGL419. The presence of phosphorus and sulphur are significantly higher ranging from 1012.15-23110.82mg/kg and 19216.01-27653.67 mg/kg, respectively and the higher mean concentration was observed in XGL420 site. The mean concentration of iron was found to be ranging from 57.02-1298.2 mg/kg. Iron is expected due to the physiological role played, in blood synthesis (Yamazaki et al., 1996). The manganese concentration is ranging from 419.65 to 674.85 mg/ kg. The higher level of Mn is in XGL421 site point. These values reported are significantly elevated in Tilapia, assuming atmospheric fallout as probable apportionment source (Ghazaly 1992). There few studies on the dietary and the adverse effects associated with particular tissue levels on the organism themselves. Burger et al. has shown the essential trace elements and the toxicity of manganese (Burger and Gochfeld 1995). Calcium and Potassium are essential to cellular metabolism and generally found in high concentrations in biologic tissues, since these elements are very common and usually appear in higher concentrations, it is difficult to ascribe them to a specific source. The significant higher concentration of calcium and potassium is ranging from 39827.81 to 2021.92 mg/kg and 46638.3-32315.13mg/kg, respectively. The more polluted site points in calcium and potassium were located in XGL417 and XGL419 respectively. It is

found that metal contamination affects liver more than muscle fish tissues (Esquinoza *et al.*, 2010). This phenomenon has to be investigated and need active experiments involving fish metabolic activities.

### CONCLUSIONS

We note fortunately the absence of the targeted pesticides in most of water samples located in XGL418 site point in the heart part of the lake and in XGL419 site point located in the structure of "Gueoul" from which the channel of the "Cayor" is supplied. The study recommends a periodic monitoring for endrin and trifluralin. The prime is a Persistent Organic Pollutant heavily regulated by the Stockholm Convention. The latter, the trifluralin, is an herbicide which is very stable in water with a high potential to bioaccumulate in biological tissues of organisms and biomagnify throughout the food web. It was pointed out the no longer relationship between toxic trace metals and pesticides presence in site points regarding the source of contamination coming from anthropogenic activities. Senegal is member of several organizations, gathering several countries, working for the regulation of the use of POPs, metal contaminants in environmental monitoring in west of Africa. Pesticide information on this board range of POPs and Herbicides in water and fish is most of the time not available to the farmers and/or to the public. The toxicokinetics and the ecodynamics have to be taken, during the period of spraying pesticides over the crops, into consideration. The water has to be under monitoring due to the beverage of four millions consumers through the Water Company (SDE) of Senegal.

### ACKNOWLEDGEMENTS

We are grateful to the association of peasants "Association des Maraîchères de la zone des Niayes" in the Guiers Lake for their assistance and their guidance to carry out the sampling in the Lake. We also acknowledge the FAO Senegal for their help and their support to this work. The authors thank the International Atomic Energy Agency for their support to this work by providing instrument and all the facilities to carry out this work.

### REFERENCES

Amath, D.M. (2013). Study on the development of a strategy for the implementation of the post-registration of pesticides in member states of the permanent interstate committee for drought control in the Sahel (CILSS). Post registration surveillance activities in Senegal. 19 pp.

Alcock, R.E., Jones, K.C., McLachlan, M.S. and Johnston, A.E. (1999). Response to comment on Evidence for the presence of PCDD/Fs in the environment prior to 1900 and further studies on their temporal trends. Environmental Science and Technology, **33**, 206-207. Akan, J. C., Abdulrahman, F. I., Sodipo, O. A. and Akandu, P.I. (2009). Bioaccumulation of some heavy metals of six freshwater fish caught from Lake Chad in Doron Buhari, Maiduguri, Borno State, Nigeria. Journal of Applied Science in environmental Sanitation, **4(2)**, 103-114.

Abhilash, P. C. and Singh, N. (2008). Multiple residue extraction for organochlorine pesticides in Medicinal Plants. Bull. of Environ. Contam. and Toxico., **81(6)**, 604-607.

Anastassiades, M., Lehotay, S.J., Stajnbaher, D., Schenck, F.J. (2003). Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid Phase Extraction" for the determination of pesticide residues in produce. J. AOAC Int., **86**, 412-431.

Burger, J. and Gochfeld, M. (1995). Growth and behavioral effects of early postnatal chromium and manganese exposure in herring gull (Larus argentatus) chicks. Pharmacol. Biochem. Behav., **5**, 607-612.

Burger, J. and Gochfeld, M. (2005). Heavy metals in commercial fish in New Jersey. Environmental Research. <u>http://dx.doi.org/10.1016/j.envres.2005.02.001, 37–41.</u>

Diop, T. (1987). Contribution to the study of the dynamics of populations in Locust Valley Senegal. Thesis Univ. Paris VI, in French.

Espinoza, Q. F. R., Modenes, A. N., Palacio, S. M., Szymanski, N., Welter, R. A. and Rizzutto, M.A. (2010). Evaluation of trace element level in muscles, liver and gonad of fish species from Sao Francisco River of the Parana Brazilian State by using SR-TXRF techniques, **68**, 2202-2207.

Förstner, U. and Littman, G. T. W. (1979). Metal pollution in the aquatic environment, Berlin: Springer-Verlag, 2nd edition. French and European Standards, International Standard Organization ISO 6468 Water quality. (1997). Determination of certain organochlorin insecticides polychlorinated biphenyls and chlorobenzenes. Method by gas chromatography after liquid-liquid extraction.

Ghazaly, K.S., (1992). A comparative study of trace element accumulation in tissues of the teleost Tilapia zilii from contaminated and clean areas. Bull. Nat. Inst. Ocean Fish, ARE. 18.

Gilbert, L,B., Garcia, R.,J.F. and Molina, D.A. (2009). Sample pre-treatment and determination of pesticide residues in fatty vegetable matrices; a review. Talanta., **79**, 109 -128.

Herbert, D. M. and Vandyke, J. M. (1964). The toxicity to fish of mixtures of poisons. Annals in Applied Biology, **53**, 415-421.

IASC statements lute against Drought in the Sahel-Sahelian Pesticides Committee. (2012). Application for approval of pesticides. Ouagadougou, Burkina Faso.

Kennicutt, M.C., Wade, T.L., Presley, B.J., Requejo, A.G., Brooks, J.M. and Denoux, G.J. (1994). Sediment Contamination in Casco Bay, Marine: Inventories, sources, and potential for biological impact. Environmental Science and Technology, **28**, 1-15.

PPDB the Footprint Pesticide Properties Database. (2013). Database collated by the University of Hertfordshire as part

of the EU-funded FOOTPRINT project (FP6-SSP022704): http://www.eufootprint.org/ppdb.html.

Rachadi, T. (1986). Point de la situation acridienne à la fin de la saison des pluies, Bilan de la lutte antiacridienne. Mission Transsaharienne II. Fondation de France, CIRAD, PRIFAS. P. 244. 119 pp.

Rick, A. R. and Nicole, D. (2008). An unforeseen chain of events: lethal effects of pesticides on frogs at sublethal concentrations. Ecological Applications, **18**, 1728–1742.

Rompala, J. M., Rutosky, F. W., Putnam, D. J. (1984). Concentrations of environmental contaminants from selected waters in Pennsylvania. 102 pp.

Ruth, M. L., Liliana, B. M., Veronica, E. K. and Monica, C. S. (2011). Pesticide distribution in an agricultural environment in Argentina. Journal of Envi. Sc. and Healthy, PartB. **46**, 662-670.

Sigma-Aldrich Co. (1998). Guide to solid phase extraction. Supelco, Bulletin 910.

Tanabe, S., Itawa, H. and Tatsukawa, R. (1994). Global contamination of persistent organochlorines and their ecotoxicological impact on marine mammals. Sci. Total Environ., **40**, 163 - 177.

Tuzimski, T. (2011). Determination of analytes in medical herbs extracts by SPE coupled with two-dimensional planar chromatography in combination with diode array scanning densitometry and HPLC-diode array detector. J. Sep. Sci., **34**, 27–36.

UNDP project (2010). National Ecovillages Agency and Government of Senegal N<sup>0</sup>4313. Participatory Conservation of Biodiversity and Low Carbon Development of Pilot Ecovillages Adjacent to Protected Areas in Senegal. 1-15.

United Nations Industrial Development Organization. (1989). Formulation of Pesticides In Developing Countries, New York. Woodward, D.F., Brumbaugh, W. G. A., Deloney, J., Little, E. E. and Smith, C. E. (1994). Effect of contaminant metals on fish in the Clark Fork River in Montana. Transactions of the American Fisheries Society. **123**, 51-62.

Yamazaki, M., Tanizaki, Y. and Shimokawa, T. (1996). Silver and other trace elements in a freshwater fish, Carasius auratus langsdorfii, from the Asakawa River in Tokyo, Japan, Environ. Pollut., **94**, 83–90.

Yao, T., He, C., Zhang, P., Gao, H. and Zhou, C. (2013). Distribution and sources of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in surface waters of Jinzhou Bay in China. Procidia Environmental Sciences, **18**, 317-322.

Zhang, Z., He, L., Li, J. and Wu, Z. (2007). Analysis of Heavy Metals of Muscle and Intestine Tissue in Fish in Banan Section of Chongqing from Three Gorges Reservoir, China. Polish J. of environ. Stud., **16**, 949-958.

Ziv, A. and Cilia, L. F. (2007). Accelerated biodegradation of pesticides: An overview of the phenomenon, its basis and possible solutions; and a discussion on the tropical dimension. Crop Protection Journal, **26**, 1733-1746.