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Assessment of contamination by organochlorine pesticides in the Loukkos area (Morocco)

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Abstract: This work is to assess the degree of contamination by organochlorine pesticides (OCP) in Loukkos area in the northwest of Morocco: 12 organochlorine pesticides including aldrin, DDT and its isomers (DDD and DDE), dieldrin, endrin, α endosulfan, heptachlor, heptachlor epoxide, hexachlorobenzene (HCB), α HCH and γ HCH were monitored. Results of this study showed a significant contamination by organochlorine pesticides in the drained Loukkos area. Heptachlor detected in seven monitoring stations (P1, P2, P3, P4, P5, AM.O.L, and AV.O.L) was the most dominant with concentrations ranging from 0.053 to 0.371 µg/L exceeding the limit recommended by WHO and EU standard (0.03 µg/L). DDT was detected only in one station among the seven stations sampled, his concentration in P4 was (0.268 µg/L) exceeding the limit recommended by EU standard (0.1 µg/L), while its metabolite DDE (pp') was detected on traces in P2 (0.016 µg/L), his presence could reflect previous use of DDT in the area. Lindane (γ HCH) was detected at traces in stations P1 (0.051 µg/L) and P2 (0,084 µg/L). Similarly dieldrin was detected in P2 at 0.067 µg/L. Since OCP were banned in 1984, contamination of the water in the region would be linked directly to the intensive use of the past before the ban in 1984, to the illegal use of some old stocks of these compounds or to eventual and also to ease the transition in sandy soils in the region.

Key Words: Organochlorine pesticides, Loukkos area, Morocco

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Introduction

In Morocco, ground and surface water constitute an important hydraulic asset of the country (ONEM, 2001, El Morhit *et al*., 2013). Throughout the Moroccan territory 32 deep aquifers and 48 surface aquifers and other ongoing exploration (basin Essaouira, Ouarzazate, Errachidia, Guercif, Guelmim and Sahara) are listed (Bouhmadi, 1992; Agoussine, 1993).

Drained Loukkos area is formed by the Loukkos River and its tributaries: Drader, Soueir, Skhar & Smid El Ma. Ground waters are composed of 3 exploitable aquifers: Drader-Soueir-Skhar, R'Mel and basin of the lower Loukkos. Aquifer of R'Mel represents the main drinking water source in the north-west of Morocco for urban areas Larache and Ksar El Kebir, rural and agricultural areas (Web 1; El Kelouti, 2004; HCP, 2008).

Loukkos area is exposed to high anthropogenic influences associated with farming that enhance the vulnerability of groundwater of R'mel and Ouled Ougbane zone. This vulnerability is mainly associated with the permeability of the sandy soil of R'mel area and the recharge from surface water, the misuse of pesticides including some (OCP). Actually despite their ban in 1984, some of OCP are still used for hygienic and health purposes (DDT, HCH) (MARA, 1984).

Organochlorine pesticides were widely used in the period 1960-1984 to control various disease vectors and crop protection. The amount used was estimated to exceed 10000 metric tons per year (ODI, 1984).

A recent survey in Loukkos area reported a stock of about 300 kg of DDT and 1200 kg HCH in the town of Larache and showed that about 80 active ingredients belonging to 10 chemical families were recorded, their repartition was as follows: 64% of fungicides, 14% of herbicides, 19% of insecticides and 3% of acaricides (El Bakouri, 2006; MADRM; 2005, Idrissi *ei al.*, 2005; PNUD, 2005; Chouibani and Jaafari, 2009). On another hand frequent irrigation and agricultural practices contribute to the extent of pesticide pollution (MAVA, 1994). Various studies have been dedicated to the contamination of the area by OCP (Ben Driss 2009; Benbakhta *et al*., 2006; Belamie *et al*., 1988; El Bakouri, 2006). The present work aims to assess the level and the origin of contamination by OCP in water resources in Loukkos area. Monitoring of organochlorine pesticides (OCP) was conducted in seven representative stations in the area Loukkos. This study is very important, motivated by the socio-economic burden to the ecosystem area Loukkos.

Materials and methods

Study Area

Loukkos area is located to the north-west of Morocco on the Atlantic coast between Tangiers and the region of Gharb in the middle of the Rabat-Tangiers axis (Fig. 1).

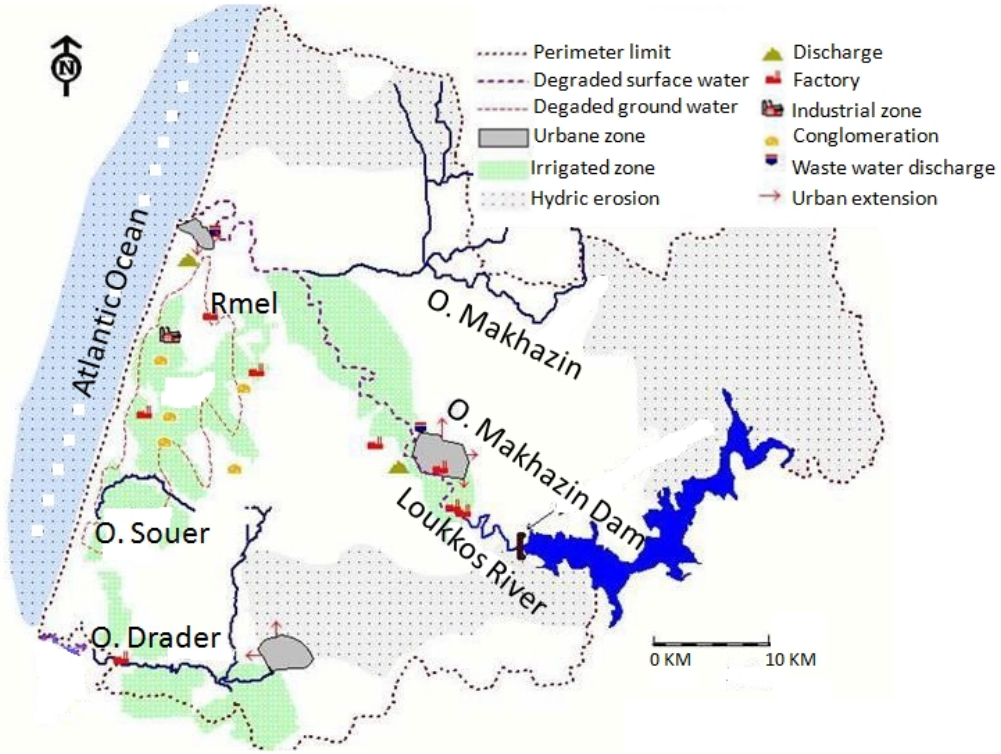

Fig. 1: Location map of the various components of the environment perimeter Loukkos (source ORMVAL).

It covers an area of about 2560 km², agricultural area of about 1473 km² (ORMVA, 2003). The area is known for its intensive farming activity mainly in the sub-areas of Laouamra, Zouada, Souaken where groundwater R'mel and Ouled Ougbane are vulnerableto pollution with pesticides and waste water. The soils of the studied area are dominated by:

-Alluvial clay soils more or less heavy in the valley.

-Sandy soils, with low retention properties (R'Mel and Drader).

-The black soil and clay loam soils hills.

Reports from agricultural authority Loukkos zone were indicated that both nitrate and pesticides or other pollutants are easily leachable in these soils (Debbarh, 2002).

Average monthly temperatures range

between 11 ºC and 25 ºC, with a minimum in January and a maximum in August (ORMVAL, 2004). The average annual rainfall is about 700 mm, concentrated between October 15 and April 15. The potential evaporation is high ranging from 1200 mm to 1900 mm/year that reaches 60-70% during the dry season (May to September) (El Bakouri, 2006).

Selection of stations

Seven stations (P1, P2, P3, P4, P5, AM.O.L and AV.OL) were selected for this study (Fig. 2):

-P1: Well located in Lahlalfa Douar, near Oued El Makhazine dam.

-P2: Well located in Ryayna Douar between the Ksar El Kbir city and Souken area.

-P3: Well located in the center of the area Souaken (irrigated agriculture).

-P4: Well located in the center Kariat Mouraa Rmel domain Laouamra (irrigated agriculture).

-P5: Point of the AEP (point of the network of drinking water) in the administration of the guard dam on the Loukkos River.

-AM.O.L: located at the outlet of the dam Oued El Makhazine (sample taken at the foot of the dam on the upstream of Loukkos River).

-AV.O.L: located downstream of the Loukkos River (before guard dam on Loukkos River).

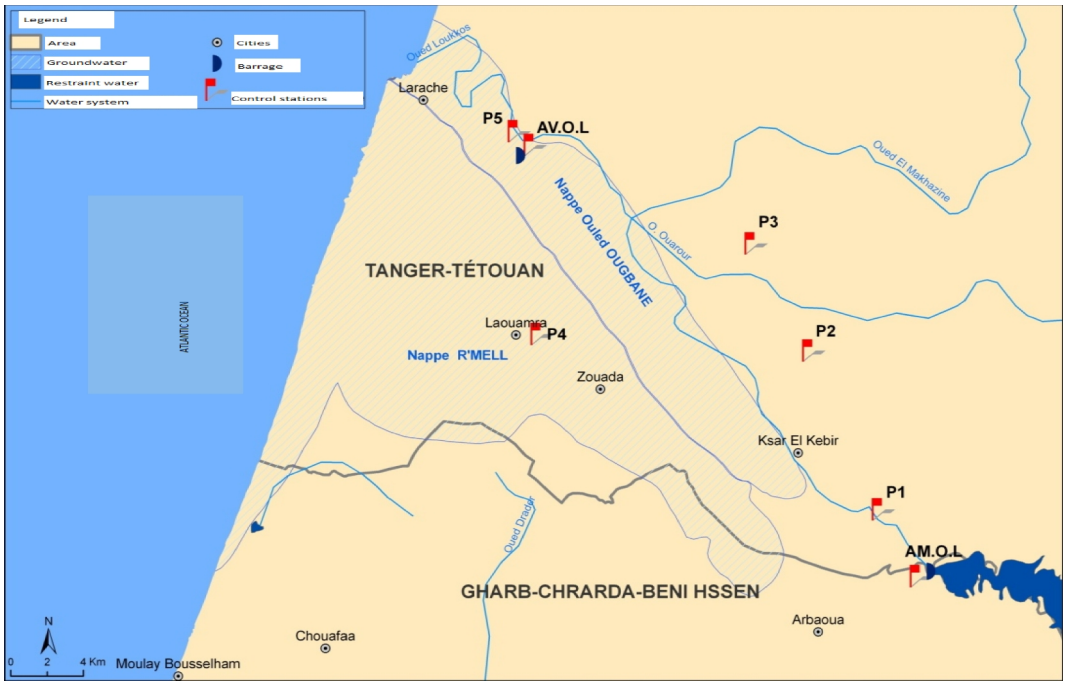

Fig. 2: Delineation of the study area and station sampling.

The stations were selected on the basis of their proximity of to the source of water and to populated areas.

Sampling

Water sampling was conducted according to the International and European standards ISO5667-11 and ISO5667-3.

Sampling of water took place during four sampling campaigns: February (winter), May (spring), August (summer) and November (autumn) 2008. Sampling strategy adopted tended to ensure spatial coverage of the entire area.

Water samples were collected in previously cleaned and sterilized brown glass bottles (1L) and stored in the refrigerator (4 °C) until analysis.

Pesticides and standard solutions

Twelve organochlorine pesticides chosen for this study were: aldrin, DDT and its isomers (DDD and DDE), dieldrin, endrin, α endosulfane, heptachlor, heptachlor epoxide, hexachlor-obenzene (HCB), αHCH, γHCH (lindane).

Standard solutions were provided by Promochem and were of purity ranging from 96 to 99.8%. Standard solutions were prepared by diluting the stock solution, using the n-hexane "Pestipur." Standard solutions were stored in the freezer. Blanks were prepared in ultrapure water were analyzed in the same condition than water samples.

Testing procedures

Analysis of organochlorine pesticides in water was performed by Analysis Methods according to the EN ISO 6468.

Samples of water (1L) were extracted in decantation flask (2L). 1L was extracted twice with 50 mL of n-hexane (pestipur). Extracts were combined, dried on anhydrous Na_2SO_4 and concentrated using a rotary evaporator (<40 °C). Samples were cleaned up on florisil and subsequently concentrated by Danish Kuderna to 8 mL, under a stream of N_2 or He to 1 mL. Analysis was performed using a gas chromatograph apparatus (Varian CP3380), equipped with an ECD (^{63}Ni) detector and a non-polar capillary column CP-Sil 8CB 30m×0.25mm×0.25µm (5%diphenyl-95% dimethylpolisiloxane). The injection was carried out in split less mode with a volume of 1 µl. The conditions of temperature were scheduled as follows:

-Detector at 300 °C

-Injector at 280 °C

-Column: 70 °C to 140 °C at 20 °C/min to 260 °C at 5 °C/min

Identification of the different compounds was achieved on the basis of their retention time (RT) and the quantification was made by comparing the relative peak area with the respective area in standard solution. External quantification was performed by injecting a mixture of standard compounds after two

Tab. 1: Mean levels of organochlorine pesticides detected at seven stations.

Stations	Organochlorine Pesticides detected	M±σ (µg/L) (Min-Max)	WHO Guideline values (µg/L)	EU Values (µg/L)
P1	Lindane	0.051±0.011 (0.041-0.068)	0.1	0.1
	Heptachlor	0.166±0.008 (0.156-0.176)	0.03	0.03
	∑ POC	0.217	0.5	0.5
P2	lindane	0.084±0.001 (0.082-0.086)	0.1	0.1
	heptachlor	0.147±0.005 (0.139-0.149)	0.03	0.03
	DDE (pp')	0.016± 0.0002 (0.015 - 0.016)	0.1	0.1
	Dieldrine	0.066±0.001 (0.065-0.068)	0.03	0.03
	∑ POC	0.313	0.5	0.5
P3	heptachlor	0.053±0.002 (0.050-0.055)	0.03	0.03
P4	DDT	0.268±0.001 (0.267-0.270)	-	0.1
	heptachlore	0.371±0.002 (0.369-0.375)	0.03	0.03
	∑ POC	0.639	0.5	0.5
P5	Heptachlor	0.052±0.005 (0.045-0.056)	0.03	0.03
AM.O.L	heptachlor	0.2±0.008 (0.19-0.21)	0.03	0.03
AV.O.L	heptachlor	0.36± 0.009 (0.35-0.37)	0.03	0.03

M: mean, σ: standard deviation, (Min-Max): (Minimum-Maximum); ∑ POC: total organochlorine pesticides

injections of sample extracts.

Results and discussion

Mean values of organochlorine pesticides measured in waters of the seven stations are presented in (Tab. 1). It appears that most of stations are contaminated at different levels depending on the compound. Among the detected compounds, heptachlor was most commonly found and has higher levels

compared with other compounds (Tab. 1).

Contamination of groundwater of aquifers

(R'mel and Ouled Ougbane) Analysis showed the presence of OCP in the waters of five stations at detectable levels that vary among compounds (Tab. 1).

Among the detected compounds, heptachlor is the most commonly found in the stations P1, P2, P3, P4 and P5 (Fig. 3) and has higher levels compared with other compounds.

Water contamination by heptachlor of these stations could represent a real risk for the health of the population. The other compounds were not detected in most sampling points or were generally in trace amounts (Tab. 1). Their low contamination may be due to their low frequent use itself due to their non availability in the market but could be provided illegally. On another hand these compounds were banned in Morocco since 1984. However some old stocks of these compounds in the region of Loukkos could be behind their availability to some usages (Idrissi *et al*., 2005; PNUD, 2005).

The presence of DDT in groundwater in samples from R'mel station P4 (0.268 µg/L) could be attributed to recent applications in the vicinity of the station. The presence of DDE major metabolite of DDT was detected at trace level (0.016 µg/L) in samples from the station P2 (Fig. 4) is bellow the limit set by the standard EU and WHO (0.1 µg/L) (Web 2).This result demonstrates the low ratio of DDE compared to DDT, which involves the recent use of DDT in the vicinity of the station P2. Levels of lindane detected in stations P1 (0.051 µg/L) and P2 (0.084 µg/L) respectively (Fig. 3) were less than the limit standard EU and the WHO (0.1 µg/L) while the level of dieldrin detected in station P2 (0.066 µg/L) exceeding the limit standard EU and WHO (0.03µg/L) (Fig. 4). Spatial analysis of the levels of OCP showed that the highest level was recorded in station P4, whereas in the other stations this level remained low to detectable (Fig. 3). Levels of OCP reported in this study could be considered as potential risk for consumers as it was reported by other authors (Boutin, 1987).

Urgent actions are necessary to overcome potential negative health impact on the population (Sauvergain, 1981; McKenzie *et al*., 1994; Gustafson, 1993; Jury *et al*., 1978).

Contamination of surface waters

Monitoring of heptachlor in waters of (AM.O.L and AV.O.L) stations in Loukkos River (Tab. 1) showed the levels of 0.20 µg/L and 0.36 µg/L at up and downstream respectively, exceeding the limit standards WHO, EU (0.03 µg/L) and Moroccan standard for the quality of surface waters (0.1 µg/L) (NMBO, 2002).

Spatial analysis of heptachlor in the Loukkos River shows that AV.O.L station presented the highest level of contamination, while the low levels were recorded at the station AM.O.L (Fig. 3). Close focus on the variation of the level of

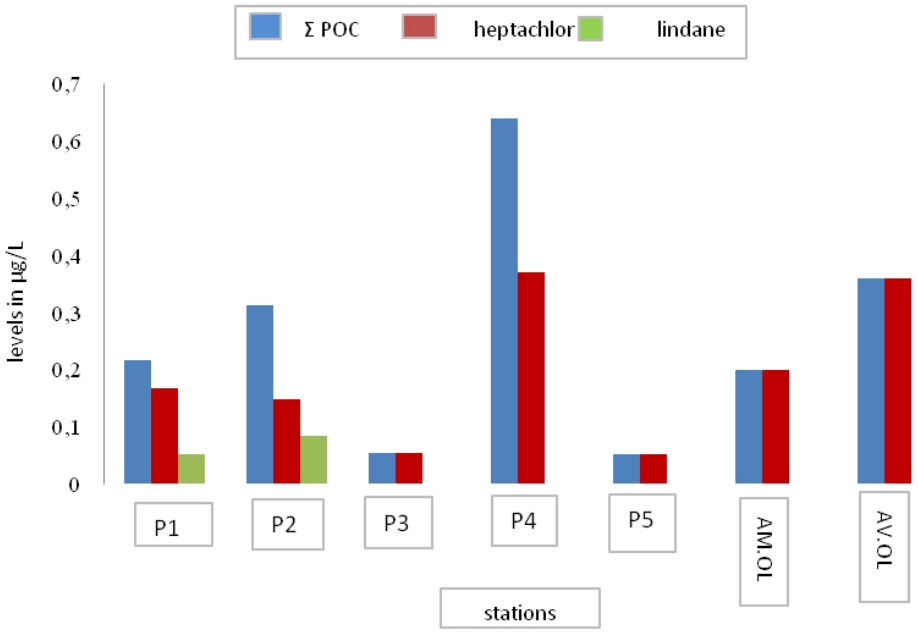

Fig. 3: Spatial variation of levels of Σ POC, heptachlor and lindane in the 7 stations.

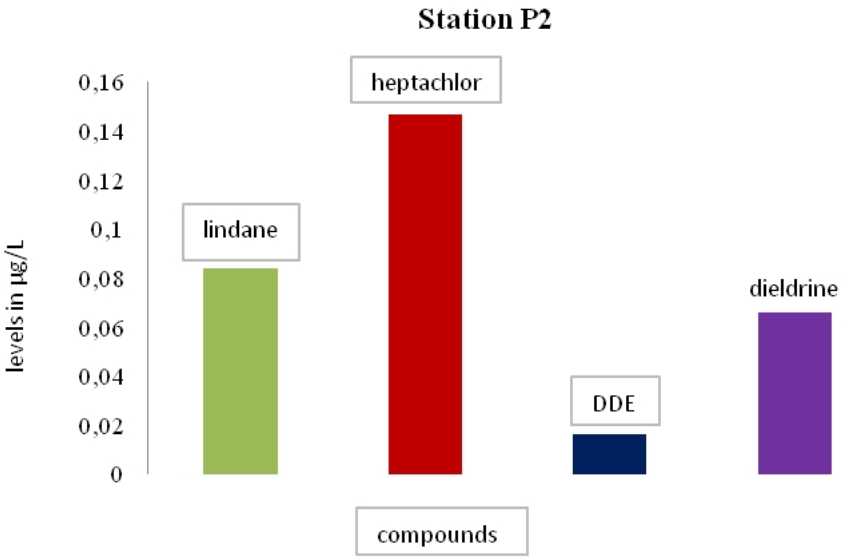

Fig. 4: Concentrations of the compounds in the P2 station.

contamination showed a net increase from upstream to downstream of the Loukkos River being almost twice fold at down than upstream, this fact could be attributed to the position of AV.O.L station at downstream of the river where convert its tributaries loaded with pollutants including heptachlor.

Comparison of mean levels of DDT and heptachlor with other parts of the world

The comparison of the levels of heptachlor and DDT with other parts of the world (Tab. 2) shows that the level of contamination of this study is generally lower. Our results for heptachlor (0.158 µg/L) are comparable to water wells in Togo Adéta (0.33 µg/L), whereas they are much lower compared to Senegal (3.43 µg/L Niayces level, Dakar). By cons, for surface water our results for the Loukkos River (0.28 µg/L) are comparable to those of Togo (Anié River (0.24 µg/L), Mono River (0.11 µg/L). The concentration 0.268 µg/L of DDT detected in the water-R'mel Laaoumra-Morocco is generally lower compared to the waters of Senegal (9.72 µg/L) and Tanzania (9 µg/L) whereas our result is higher than that of water Togo (0.03 µg/L).

Tab. 2: Comparison of mean levels of heptachlor and DDT detected in samples with those identified in other studies.

Countries	Water	Heptachlor (µg/L)	DDT (µg/L)	Ref.
Senegal Niayces, Dakar	Well water	3.43	9.72	1
Togo Adéta	Well water at Adéta	0.33	0.03	2
Tanzania	Well water		9	3
Morocco Loukkos	Well water	0.158	0.268	4
Togo Anié River	Surface water	0.24	-	2
Togo Mono River	Surface water	0.11	-	2
Morocco Loukkos River	Surface water	0.28	-	4

Ref. : (1) Cissé *et al*. (2003); (2) Mawussi (2008); (3) Kishimba *et al*. (2004); (4) Present study

Conclusion

The study results showed the presence of these pesticides at varying degrees. Heptachlor was the most dominant with concentrations ranging from 0.053 to 0.371 µg/L exceeding the limit set by International standard (0.03 µg/L). DDT is present less frequently because it

is detected only in one station among the seven sampled (0.268 µg/L), his metabolite DDE was found in trace amounts.

On the basis of the values recorded, the situation of the level of contamination would not be alarming in comparison with other countries. However to ensure appropriate protection of health and the environment, it is necessary to implement coherent set of measures of education, training and monitoring of organochlorine pesticides banned by the Stockholm Convention.

References

- ✓ Agoussine M. (1993) Contribution à l'étude hydrogéologique de la plaine de Guelmim (Anti-Atlas occidental marocain). Modélisation et gestion des ressources en eau souterraines. Thèse 3eme cycle, université Cadi Ayyad, Marrakech.
- ✓ Bouhmadi B. (1992) Étude hydrogéologique de l'aquifère du bassin du bas Loukkos (Ksar El Kebir, Maroc). Thèse de 3ème cycle. Université Addelmalek Essaadi, Tetouan.
- ✓ Ben Driss N. (2009) Evaluación y cartografía de vulnerabilidad a la contaminación en el acuífero de "R'Mel" (Larache, Marruecos) y contribución a la realización del mapa de riesgo Tesis inédita de la Universidad Complutense de Madrid, Facultad de Ciencias Geológicas, Departamento de Geodinámica, leída el 8 de julio de 2009.
- ✓ Benbakhta B., Fekhaoui M., El Abidi A., Idrissi L., and Lecorre P. (2007) Résidus de pesticides organochlorés chez les bivalves et les poissons de la lagune de Moulay Bousselham (Maroc), Afrique Science, 3(1): 146-168.
- ✓ Belamie R., Coller M., Giroud S. (1988) Les pesticides en agriculture : quantités utilisés et contamination des milieux aquatiques. Oceanis; 14: 681-90.
- ✓ Boutin C. (1987) L'eau des nappes phréatiques superficielles, une richesse naturelle vitale mais vulnérable. L'exemple des Zones rurales du Maroc, Sci. Eau., 6 (3): 357-365.
- ✓ Chouibani M. and Jaafari A. (2009) Inventaire des pesticides obsolètes au Maroc (PASP. Maroc). Direction de la Sécurité Sanitaire des Produits Alimentaires, Colloque International sur la gestion du risque 09-11 novembre 2009.
- ✓ Cissé I, Tandia A.A., Fall S.T., Diop E-HS. (2003) Usage incontrôlé des pesticides en agriculture périurbaine : cas zone des Niayes au Sénégal. Cahiers d'études et de recherches francophones Agricultures 12: 181-186.
- ✓ Debbarh A. (2002) Irrigation et environnement au Maroc : Situation actuelle et perspectives, Pollution du milieu (eaux et sols), P: 5, Actes de l'atelier du PCSI, Montpellier, France, 28-29.
- ✓ El Bakouri H. (2006) Développement de nouvelles techniques de détermination des pesticides et contribution à la réduction de leur impact sur les eaux par utilisation des substances organiques naturelles (S.O.N). Thèse doctorale. Univ., Abdelmalek Essadi. Fac. Des Sc. et Technique Tanger. 212: 44-47.
- ✓ El Morhit M., Fekhaoui M., Serghini A., El Blidi S., El Abidi A. and Yahyaoui A. (2013) Typology of water quality in the Loukkos river estuary (Morocco), Larhyss Journal, 12: 7-24.
- ✓ El Kelouti M. (2004) Office Régionale de Mise en Valeur Agricole du Loukkos- Ksar El kébir, Maroc. Actes du séminaire, Modernisation de la gestion de l'irrigation dans le périmètre du Loukkos (Maroc), P:2, Rabat : 19-23 avril 2004, Projet INCO-WADEMED.
- ✓ Gustafson D.I. (1993) Pesticides in Drinking Water. New York: van Nostrand Reinhold.
- ✓ Idrissi M., Ameziane S., Benyahia S. and Bencheikh R.S. (2005) Analyse de la situation des pesticides obsolètes au Maroc, PASP-PAN-AFRICA, Déclaration de Bamako 12 juillet 2005, Atelier Régional Afrique francophone, Rapport n°1 /PASP/ juillet 2005.
- ✓ Jury W.A., Focht D.D. and Farmer W.J. (1978) Evaluation of pesticide groundwater pollution from standard indices of soil-chemical adsorption and

biodegradation. J. Environ. Qual., 16: 422-428.

- ✓ Kishimba M.A., Henry L., Mwevura H., Mmochi A.J., Mihale M. and Hellar H. (2004) The status of pesticide pollution in Tanzania, Talanta, 8(64): 48-53.
- ✓ MADR (2005). Ministère de l'agriculture et du développement rural du Maroc, 2005. Programme africain relatif au stock des pesticides obsolètes, Caire, Atelier régional du 21 au 24 février 2005.
- ✓ MARA (1984) Arrêté du ministère d'Agriculture et de réforme Agraire relatif à l'interdiction des pesticides organochlorés, N°466.
- ✓ MAVA (1994) Ministère de l'Agriculture et de mise en Valeur Agricole (MAVA); Office de mise en valeur agricole du Loukkos. Études d'évaluation environnementale du périmètre du Loukkos. Phase I, description de l'environnement et phase II, identification et évaluation des effets sur l'environnement. Maroc: Groupement CID/NEDECO/Maroc. Développement.
- ✓ Mawussi G. (2008) Bilan environnemental de l'utilisation de pesticides organochlorés dans les cultures de coton, café et cacao au Togo et recherche d'alternatives par l'évaluation d'un insecticide d'extraits de plantes locales contre le scolyte du café (*Hypothenemus hampei* Ferrari). Thèse de doctorat de l'université de Toulouse.
- ✓ McKenzie S.F., Tiller D., Allen D. (1994) Organochlorine pesticide residues in water and sediments from the Ovens and Kings rivers, North-East Victoria, Australia. Arch Env Contam Toxicol., 26: 483-90.
- ✓ NMBO (2002) Norme Marocaine BO : N°5062 (5.-12-2002), Arrêté n°1275-01(17-10-2002) définissant la grille de qualité des eaux de surface.
- ✓ ODI (1984) L'industrie des pesticides au Maroc: Situation actuelle et perspective d'avenir. Colloque de l'ANAPAV sur les pesticides agricole, Rabat.
- ✓ ONEM (2001) Ministère de l'Aménagement du Territoire, de l'Eau et de l'Environnement, «Rapport sur l'Etat de l'Environnement du Maroc (REEM)» Département de l'Environnement, Observatoire National de l'Environnement du Maroc (ONEM), Octobre, Ed, 2, 296.
- ✓ ORMVA (2003) du Loukkos, situation géographique, projet d'économie d'eau. Revue H.T.E.N°126- juin 2003.
- ✓ ORMVAL (2004) Office Régional de Mise en Valeur Agricole du Loukkos (ORMVAL), Bulletin de l'ORMVAL, Altopress, Tanger, 2004.
- ✓ PNUD (2005) Département de l'Environnement et PNUD, Inventaire national des POP au Maroc, Rapport de synthèse, Juillet 2005, résultats de l'inventaire des POP, 5-9.
- ✓ Sauvergain P. (1981) Les micropolluants organiques dans les eaux superficielles continentales. Rapport n° 2. Association française pour l'étude des eaux, 225.
- ✓ Web1: www.water.gov.ma/userfiles/file/2-Loukkos-déf.pdf
- ✓ Web2: www.who.int/water_sanitation_health/d w q/gdwq3rev/fr/index.html