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ORIGINAL ARTICLE

Effect of water treatment process on organochlorine pesticide residue levels in Ahvaz water treatment plant 2

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One of the main hazards of human life and health is the presence of pesticides in the aquatic system is. The Karun River is the surface water source in the preparation of drinking water for the city of Ahvaz city at the Ahvaz Water Treatment Plant. (AWTP No. 2.) This study was done in order to investigate the statue of qualification and the quantification of the contamination of water entering into (AWTP No. 2) by selected organochlorine pesticides [(α, β, γ, δ) HCH, heptachlor, alderin, dielderin, (op', pp') DDT, (α, β) endosulfan and metoxychlor], plus the water treatment effects on these pesticide residues removal. For this purpose, one composite sample from each of the water treatment process steps was taken monthly which was comprised of 20 grab samples in 2008. Water samples were acidified to pH < 2, extracted three times with n-hexane, and concentrated using a rotary vacuum evaporator for Florisil column chromatography cleanup and fractioned by elution with three different solvent mixtures of petroleum and diethyl ether. Finally, the elutes were concentrated to dryness using rotary vacuum evaporator and then the residues were dissolved in hexane and analyzed by GC μECD. All 12 investigated organochlorine pesticides were detected. Results of this study indicated that concentration of investigated pesticides decreased (according to the kind of pesticide) by 20% to 80% and the mean of total concentration was reduced by 49% during water treatment process steps. There was a significant positive correlation (r=97.75%) between variation in the concentration of poisons and the total organic matter ($KMnO_4$ value)
Key words: organochlorine; pesticide; organic matter; Ahvaz; water treatment plant

Introduction

Over the past fifty years, pesticides have been an integral part of the world of agriculture. In the United States alone, production of pesticides reaches hundreds of millions in kilograms. Extensive use of pesticides in the areas of agriculture and public health in developing countries has resulted in environmental pollution. Studies of the creatures in the wild have clearly revealed that these pesticides have caused extensive contamination of the fish and bird species.
With an abundance of healthy fruit and vegetables made available at low prices, no one entertains the doubts about the performance of pesticides in order to protect agricultural products. However, there is no such thing as "safe pesticide". Due to the non-alarming nature of such pesticides as the carcinogenicity potential of delayed poisoning of the nerves and fertility, experts and political leaders have shifted focus on pesticides to be the biggest concern of World Health Organization.
Out of all the pesticides, chlorinated pesticides receive the most attention due to their lipophyllic nature, low biological decomposition, capability of biological concentration and introduction into the food chain. The key route of man's contact with these pesticides is water and food. Nowadays, WHO and FAO's main target is to pay attention to the traces of these poisons in water, food, and environment, especifically, the risks due to long-term contact even with small amounts of poisons and consequently their chronic poisoning. Of the total 1795.34 Million cubic meters of located polluting wastewater produced and dumped yearly into the Karoun River, 1452.62 million cubic meters (81% of the total) is dumped into the upstream water hole of the treatment plants in Ahvaz. Of this quantity, 1412.75 million cubic meters (79% of the total) produced yearly is

agricultural waste. Due to the heavy quantity of agricultural wastewater dumped into the Karoun River and the research findings indicating the poisons in the river, the study of the performance of treatment processes in reducing chlorinated organic poisons has become the target of this research.

Material and Methods

All glassware used in this analysis were carefully washed with soapy water, rinsed with distilled water ethanol, acetone and pesticide grade n- hexane respectively. All the solvents used (n-hexane, petroleum ether. diethyl ether, acetone) were pesticide residue analysis grade purchased from Merck Com. The Organochlorine pesticides standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and the working solutions were prepared in hexane at 1 μg ml^{-1}. The sorbent material used, which was activated after drying at 150 C for 12 h before use, was Florisil 60–100 mesh obtained from Sigma–Aldrich.

Collection sample

In order to investigate the statue of qualification and quantification of the contamination in three point (entering waters into (AWTP)No.2—after clarification & treated water) by selected organochlorine pesticides [(α, β, γ, δ)HCH, heptachlor, alderin, dielderin, (op’, pp’) DDT, (α, β) endosulfan and metoxychlor], 15 to 20 litter grab water samples were collected monthly at different hours during the day. After combining the 15-20 samples and preparing a mix, sample “in situ” water was acidified by sulfuric acid to pH 2 to eliminate biological activity in water. Then, 2.5 litters were filled into an amber bottle and then transported to laboratory for subsequent extraction and analysis.

Liquid-liquid extraction

250 ml of water was extracted three times with 20ml *n-hexane*. The extract was combined and concentrated using a rotary vacuum evaporator to 10 ml.

Purification:

Extracts were purified by passing them through a glass column (20 cm, 0.8 mm id) packed with Florisil (10 cm) and Na2SO4 (2 cm), which was then eluted with ether: hexane solution: 200 ml at 6:94 v/v, followed by 15:85 v/v and 50:50 v/v. Thereafter, elutes were evaporated to dryness using a rotary vacuum and the residues were dissolved in 10ml hexane for gas chromatography analysis.

The spiked matrix samples were analyzed as part of QA/QC. For this purpose adequate amount of the analysts of interest were spiked into the sample. Also, another aliquot of the samples was analyzed without spiking.

Apparatus

Analyses were done using an Agilent 6890N (HP) with a micro-cell electron capture detector (μ-ECD). A DB-5 column 30 mm ×0.25mm i.d containing 5% phenyl-methylpolysiloxane with a phase thickness of 0.25μm was used. The temperature program used for the analysis was: 210C to 275 C (13min) at 4C min^{-1}. The injector and detector were set to 300°C and 320°C in the split less mode. Nitrogen was used as the carrier at 0.7 ml min^{-1} and the make-up gas at 35 ml min⁻1. Identification of peaks was based on the comparison of the retention times of compounds in the standard solutions. Quantification of the analyzed compounds was performed using the internal standard method. The concentration of pesticide residues in water ranged from 84% to 98% compared to the mean concentration of chlorinated organic poisons throughout the treatment process.

Results and Discussion

Comparison of the mean concentration for 12 chlorinated organic pesticides under this study has been drawn using ANOVA for T-Independent sample test and the results obtained have been included in Graphs 1-4 and Table 1.

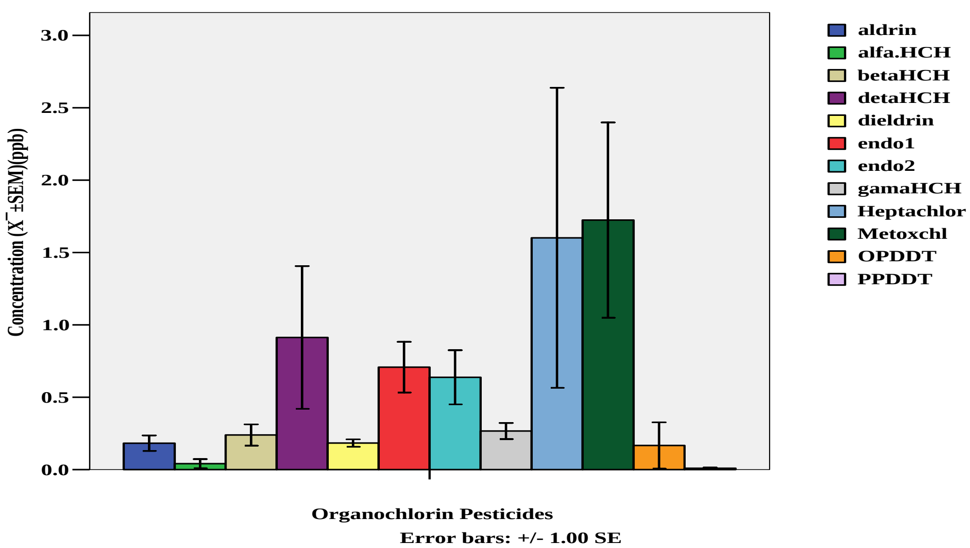

Fig. 1. Average concentration of 12 organochlorine pesticides in raw water samples of Ahvaz water treatment plant 2

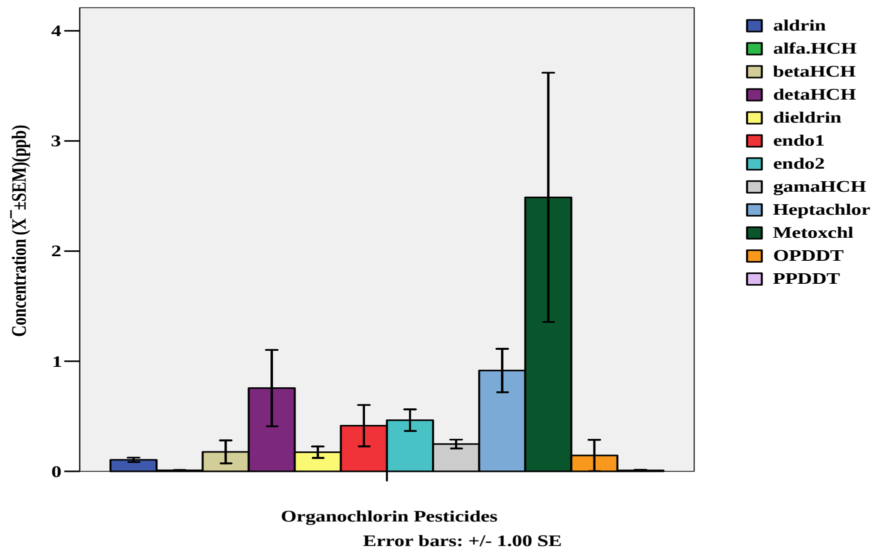

Fig. 2. Average concentration of 12 organochlorine pesticides in clarified water samples of Ahvaz water treatment plant 2

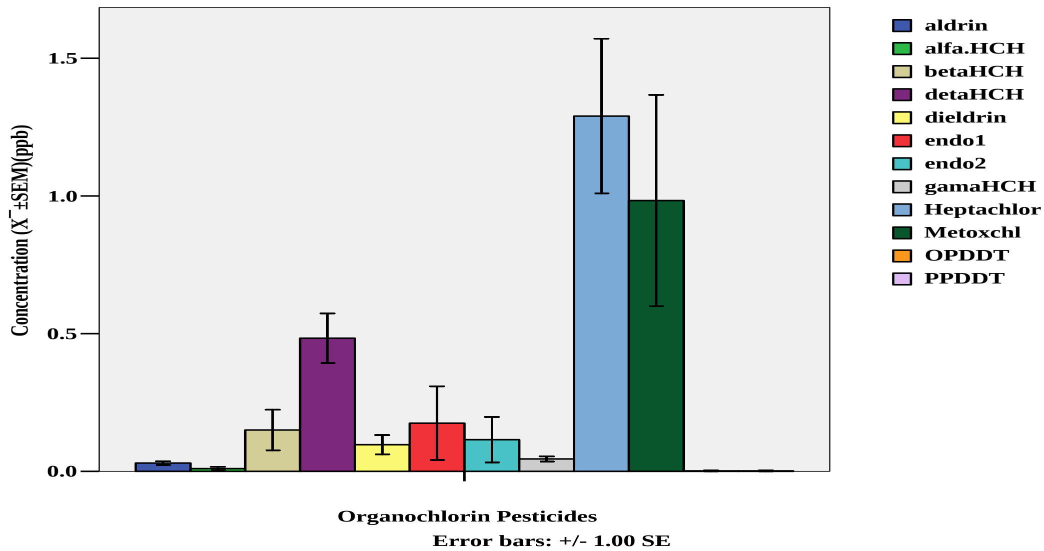

Fig. 3. Average concentration of 12 organochlorine pesticides in filtered water samples of Ahvaz water treatment plant 2

Table. 1. Average concentration and reduction percentage of organochlorine pesticides in different stage of treatment process.

Pesticides	RAW WATER	clarified		Treated		
	Mean (PPb)	Mean (PPb)	% removal	Mean (PPb)	% removal	% total removal
Aldrin	0.1823	0.1042	42.8212	0.0300	71.2216	83.5449
α – HCH	0.0409	0.0093	77.2981	0.0100	-7.5826	75.5767
β – HCH	0.2388	0.1765	26.0564	0.1500	15.0336	37.1728
δ – HCH	0.9126	0.7561	17.1467	0.4833	36.0777	47.0383
Dieldrin	0.1833	0.1737	5.2197	0.0967	44.3618	47.2660
α – Endosulf	0.7075	0.4146	41.4043	0.1750	57.7893	75.2664
β –Endosulf	0.6376	0.4644	27.1736	0.1150	75.2349	81.9645
γ – HCH	0.2663	0.2476	7.0460	0.0450	81.8240	83.1047
Heptachlor	1.6012	0.9155	42.8248	1.2900	-40.9044	19.4377
Metoxychlor	1.7238	2.4877	-44.3118	0.9833	60.4723	42.9568
Total Aldrin[1]	0.3656	0.2780	23.9692	0.1267	54.4342	65.3560
Total HCH [2]	1.4586	1.1895	18.4491	0.6883	42.1345	52.8102
Total ORG [3]	6.6701	5.9027	11.5057	3.3817	42.7098	49.3014

[1] aldrin +dieldrin, [2] α + β + γ + δ HCH Total, [3] Organochlorin Pesticides

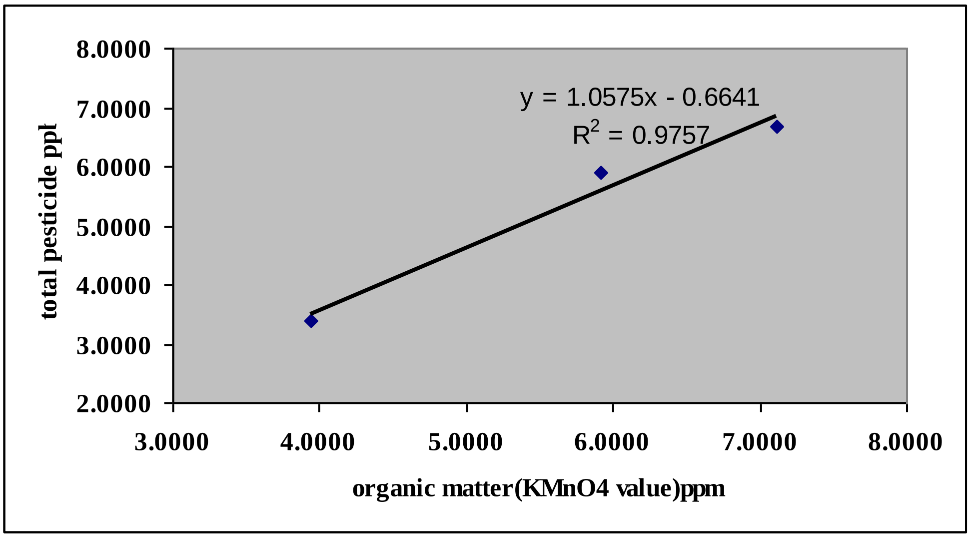

Fig. 4. Correlation between variation in concentration of poisons and total organic matter (KMnO4 value).

Conclusion

The results of the study indicate traces of chlorinated organic poisons in the raw water of Treatment Plant # 02, Ahvaz and their considerable decrease throughout the process (Graphs 1-3). Table 01 indicates that reduction changes throughout the treatment process and also with the type of poison. During α-HCH coagulation and settlement, γ –HCH filtration and, on balance, throughout the entire treatment process, α-HCH, γ –HCH, Aldrin and Endosulfan indicated the greatest rate of reduction. A correlation coefficient of 97.75 % for reduction of organic materials (KMNO4 value) and reduction of poisons (Graph # 04) indicate the significance of the test for determining the value of organic materials based on the KMNO4 value in the study of the performance of the treatment process in the reduction of organic contaminants. The most significant result that can be derived from the 50 % reduction in the total poison concentration (Table # 01) is the importance of the common treatment processes (coagulation, settlement and filtration) in reducing the chemical contaminants. Hence, by optimization of such processes as coagulation, settlement and filtration, it is possible to not only reduce physical contaminants (turbidity), but also to improve the chemical desirability of water. With respect to the difficulties, that using such modern technologies as ozonation and reverse osmosis create in developing countries increased efficiency in the common treatment processes can pose as a higher priority. Researchers propose that in the future we study the efficiency of such techniques as Enhanced Coagulation in the reduction of contaminants.

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