

Organochlorine and organophosphoric insecticides, herbicides and heavy metals residue in industrial wastewaters in Cyprus

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Abstract

Most industries in Cyprus possess permits either for disposal at central wastewater treatment plants (the treated effluent of which is reused or disposed into the sea), or discharge on soil, or reuse either for irrigation or groundwater recharge or discharge into the sea. A preliminary investigation undertaken by the University of Cyprus in regards to dangerous substances was the first step towards establishing a new licensing and monitoring system. Liquid–liquid extraction was used for the extraction of the selected pesticides from wastewaters. Gas chromatography with two different detection methods (ECD and FTD) was applied for the determination of 17 pesticides (12 organochlorine insecticides, 3 organophosphoric insecticides and 2 herbicides). In addition ICP and a mercury evaporation unit were used to determine the concentrations of heavy metals in the samples. The results revealed the presence of several priority substances in wastewaters, in most cases at concentrations well below the regulatory limits. Non-compliance was observed for a limited number of metals. Sixteen out of 17 organic substances that were monitored for 1-year period time were traced in different wastewater streams. What was found out is that there is a need to expand the analytical determinations and the monitoring to more wastewater streams and more priority substances, in order to safeguard the water resources in Cyprus.

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1. Introduction

The water shortage problem in Cyprus was identified and dealt in time. The slogan, ‘*Not a Drop of Water to the Sea*’, determines the water policy of the Government. The demand for water is expected to increase in the forthcoming years, while at the same time the capabilities for developing new water resources will be lessened. Therefore, in order to satisfy the increasing water demand and to eliminate the dependency of the towns and tourist centers on rainfall, the Government has turned its attention to other non-conventional sources such as the use of reclaimed water for irrigation, groundwater recharge, the desalting of brackish water, the shifting of agriculture into less water-demanding crops, the introduction of new effective

management procedures through the establishment of a Water Entity, the efficient use of available water including the better use of pricing and water conservation measures and the preservation of the water quality. Taking this into consideration and in the framework of the implementation of Directives 76/464/EEC and 80/68/EEC related to industrial emissions of dangerous substances in water bodies in Cyprus, a study commissioned and prepared for the Ministry of Agriculture, Natural Resources and Environment was undertaken by the Laboratory of Environmental Engineering of the University of Cyprus in collaboration with the State General Laboratory. The aim of the work was to identify industrial units that could potentially constitute pollution sources for water bodies either through direct discharge or through indirect discharge via the central wastewater treatment plants where they discharge their wastewater for treatment.

The present work focused on a number of pesticides and heavy metals. Pesticide residues in surface waters have been a concern since the 1940s [1,2]. Monitoring studies in Euro-

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pean countries have shown widespread detection of pesticides in ground and surface water [3–6] despite the fact that some of them have been banned or severely restricted in the EU as a consequence of the application of Directive 79/117/EEC [7], Council Regulation 805/2004/EC [8] and Directive 91/414/EEC [9]. Directive 79/117/EEC can be regarded as the predecessor of Directive 91/414/EEC and concerns the prohibition of active substances that, even if applied in an appropriate manner, could give rise to harmful effects. Council Regulation 850/2004/EC deals with the persistent organic pollutants (POPs) and implements the Stockholm Convention in EU. All the substances that have been banned in Cyprus are provided elsewhere [10].

Various water-monitoring surveys in the EU and USA have proved the presence of herbicides [11], some of their metabolites [12], and to a lesser extent insecticides [13] in surface and ground water. Organochlorine pesticides (OCPs) are of great concern as they are known for high toxicity [14], persistence in the environment, [15] and bioaccumulation in the food chain [16]. Organophosphorus pesticides (OPPs) are being used to replace OCPs in many countries nowadays because they can degrade more easily in the environment. However, they can be still traced in surface waters [17]. Conventional water treatment practices do not remove soluble pesticides that may then affect drinking water quality [18]. The presence of pesticides in the aquatic system as a result of their common use, persistence in the environment and toxicity, is one of the main hazards to life and health not only to humans but also to animals and plants [19–22]. Since many pesticides are partially water soluble, they may leach into surface and groundwater at greater than ppb levels.

Heavy metals may also be found in the sludge and in the water phase of wastewaters. The input of these heavy metals is usually from local industries and household laundries when referring to urban wastewaters. Their toxic effects are widely known [23–26].

In 1976, the EU Council of Ministers adopted the Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the community (Discharge of Dangerous Substances Directive 76/464/EEC [27]). This paper provides an overview of the methodology followed and the results obtained through an initial study [10] the aim of which was to investigate the potential pollution sources in relation to a number of such substances in Cyprus.

2. Materials and methods

2.1. Identification of industries/processes which could potentially have dangerous substances in their wastewaters

For the selection of the industries and processes which could potentially have dangerous substances in their wastewaters, information was collected and screened, based on the following:

- Selection of industries that are relevant to the industries and processes listed in Appendix II of the Questionnaire on Directive 76/464/EEC;
- Historical analyses and previous studies with findings relevant to the identification of dangerous substances, carried out by various governmental departments [28,29];

- Analysis of material safety data sheets (MSDS) and other information included in the applications of the industries submitted within the process of obtaining a water discharge permit from the Environment Service;
- International references – literature review.

Following the screening method as described above, Table 1 was developed. The existing management of treated wastewater in the industrial units examined is as follows. E1, E2, PH, F, IC, T2, and PS1–3 dispose their wastewaters at centralized wastewater treatment plants. AC1 and AC2 store their solvents, while their wastewater effluents are disposed on soil (AC1) or at central wastewater treatment plant (AC2). CM disposes its wastewaters in tailing ponds and dumps. EGS1–3 disposes their cooling waters into the sea while their treated wastewaters on soil. D and VO have a permit for groundwater disposal, ORP for storage-evaporation, FM for soil disposal and T1 for soil disposal-irrigation. The effluents from WP1 are disposed on soil or are reused for irrigation. WP2 stores the effluents in ponds-lagoons. The effluents from WP3–4 are either disposed on soil, or reused for irrigation or are disposed into the sea. WP5 has a permit for soil disposal, reuse for irrigation, and groundwater recharge. The effluents from WP6 are disposed on soil. It is noted that all permits are currently under review by the competent authorities. Maximum concentrations for a number of parameters are included in the permits according to the specific methods of disposal. However, it is important to note that further investigations are required in order for the permits to include terms related to dangerous substances.

2.2. Selection of industrial streams to be studied

Due to limitations in regards to the resources available a selection of 16 industrial units was made from which samples were collected seasonally for a period of 1 year. Spot check sampling (grab samples) was performed. Here it is worth noting, that an extensive monitoring program for emerging/priority substances is under development. This is also in compliance with the Water Framework Directive 2000/60/EEC [30], incorporating into a National Plan all other relevant EU-legislation. Within the context of Article 8 of the Water Framework Directive the monitoring program will integrate the provisions of Directives 76/464/EEC [27] and 80/68/EEC [31] within the monitoring of surface water status, groundwater status and protected areas. The compounds studied during this investigation belong to different chemical categories. Therefore, development and application of different methodologies was required for their determination. Moreover, optimization and evaluation of the methods was a critical issue, in order to achieve high sensitivity and low detection limits for the substances of interest, as their potential presence in water (since wastewaters are discharged among others in water bodies) may result in adverse effects on water quality and human health even at trace concentrations. The classification of the substances studied into different chemical categories is presented in Table 2.

Table 1
Information on the management of wastewater for selected industrial units, which could potentially have dangerous substances in their wastewaters

Industrial sectors and/or processes	Industry ID	Potential pollutants in wastewaters	Industrial sectors and/or processes	Industry ID	Potential pollutants in wastewaters
Electroplating	E1	Phenols (chlorophenols exist in List I), Cd, Cr, Cu, Hg, Ni, Pb, Sn, Zn, aldrin, nitrogen, phosphorous, chlorides, cyanides, flurides	Central WTP	WP3	List I substances, Cd, Cu, Pb, Zn, trichloroethylene
Electroplating	E2	Cr, Ni, Pb, Zn	Central WTP	WP4	List I substances, Cd, Cu, Pb, Zn
Pharmaceutical industry	PH	List I substances, As, Cd, Hg	Central WTP	WP5	List I substances, Cd, Cu, Pb, Zn
Manufacturing of agricultural chemicals (pesticides, algaecides, fertilizers, parasiticides, etc.)	AC1	Organophosphoric, endosulfan, dichlorvos, azinphos-ethyl, malathion, xylene, simazine, naphalene, dimethoate	Central industrial WTP	WP6	Phenols (chlorophenols exist in List I), Cd, Cu, Cr, Hg, Ni, Pb, Zn, aldrin, nitrogen, phosphorous), chlorides, cyanides, flurides
Manufacturing of agricultural chemicals (pesticides, algaecides, fertilizers, parasiticides, etc.)	AC2	Organophosphoric, dichlorvos, endosulfan, malathion, simazine, xylene, aldrin, Cd, Cr, Cu, Ni, Pb, Zn, DDT, dieldrin, endrin, hexachlorobenzene, Hg, azinphos-ethyl, azinphos-methyl, dichlorvos, endosulfan, fenthion, parathion, simazine, atrazin, heptachlor, linuron, methamidophos	Electricity generation station	EGS1, EGS2, EGS3	List I substances, B, Cd, Cu, Cr, Ni, Mo, Zn, Pb, V, Zn
Ferrous metal foundry	F	Cd, Cr, Cu, Hg, Ni, Pb, Zn, trichloroethylene	Tannery	T1	As, B, Cd, Co, Cr, Cu, Hg, Zn
Cooper mine - electrolysis	CM	List I substances	Tannery	T2	List I substances
Iron casting	IC	List I substances	Filter manufacturing and filter maintenance	FM	List I substances, Cd, Cu, Cr, Hg, Ni, Pb, Zn
Manufacturing of paints and solvents	PS1, PS2, PS3	List I substances, Cd, Hg	Used oil recycling plant	ORP	Cd, Cu, Cr, Hg, Ni, Pb, Zn
Central WTP industrial and urban	WP1	List I substances, Cd, Cr, Cu, Hg, Ni, Pb, Zn	Delicatessen	D	List I substances, Cd, Cu, Cr, Ni, Pb, Zn
Central WTP and landfill	WP2	List I substances, Cd, Cr, Hg	Manufacturing of vegetable oil	VO	List I substances, Cd, Cu, Cr, Hg, Ni, Pb, Zn

2.3. Sampling techniques

2.3.1. Herbicides and organophosphoric insecticides

The sample for these measurements was collected in 2.5 L glass bottles pre-rinsed with acetone and then with hexane. One

milliliter of HgCl_2 1% was added to the samples for preservation. During transportation the samples were kept at less than 10°C and away from light. The samples were extracted within 7 days. The holding time after extraction was 14–28 days (samples kept in a freezer).

Table 2

Chemical categories of the substances under study

Chemical categories of priority substances

Organochlorine insecticides

Aldrin, DDT^a, *op*-DDD^b, *pp*-DDE^c, dieldrin, endrin, HBZ^d, hexachlorocyclohexane (α -BHC, β -BHC)^e, lindane, heptachlor, heptachlor epoxide

Herbicides (triazines and dinitroaniline)

Simazine, trifluralin

Organophosphoric insecticides

Diazinon, chloropyrifos, dichlorvos

Metals

As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sn, Zn

^a DDT: dichloro diphenyl trichloroethane.

^b DDD: dichloro diphenyl dichloroethane.

^c DDE: dichloro diphenyl dichloroethylene.

^d HBZ: hexachlorobenzene.

^e BHC: hexachlorocyclohexane.

2.3.2. Organochlorine insecticides

The sample was collected in 1000-ml glass bottles pre-rinsed with acetone and then with hexane. One milliliter of HgCl_2 1% was added to the samples for preservation. During transportation the samples were kept at less than 10°C and away from light. Extraction took place preferably immediately after sampling but not later than 7 days of holding time at 8°C . The holding time after extraction was 14 days (samples kept in a freezer).

2.3.3. Metals

Water samples were collected in 1000-ml polyethylene or polypropylene bottles, which had been soaked in HNO_3 10% overnight and washed twice with distilled water. During transportation the samples were kept at less than 10°C .

2.4. Analytical methods

Several methods are required in order to screen organic environmental pollutants, because the polarity and other chem-

ical properties of the components vary considerably. A variety of extraction techniques [32–36] have been employed over the years to determine pesticides and their degradation products, including liquid–liquid extraction (LLE) [37], solid-phase extraction (SPE) [38], solid-phase micro extraction (SPME) [39,40], semi-permeable membrane device (SPMD) [41,42], supercritical fluid extraction [43], and single drop microextraction (SDME) [44] followed by various chromatographic techniques such as gas and liquid chromatography coupled with electron capture detector (ECD) [45], nitrogen-phosphorus (NPD) [46], diode-array [47,48], gas chromatographer (GC) with cold injection [49] detection systems, and ultra performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry [50].

2.4.1. Herbicides and organophosphoric insecticides

The method that was followed is based on the US Environmental Protection Agency (EPA) Method 507 [51]. A liquid–liquid extraction procedure was applied before GC-FTD (Flame Thermionic Detector) analysis. A measured volume (750 ml) of the sample was transferred in a 1-L beaker and acidified with HCl 2 N to pH 2. Then the sample was transferred in a 1-L separatory funnel. One hundred milliliters of CH_2Cl_2 were added and the funnel was shaken well for 2 min with periodic venting to release excess pressure. Then the organic phase was allowed to separate from the water phase for a minimum of 10 min. The organic phase was collected in a spherical flask of 250 ml. The extraction procedure was repeated a second time, combining the extracts in the flask. Five grams of anhydrous Na_2SO_4 were added in the extract in the flask. The flask was shaken and then left to sit for 15 min. The methylene chloride was decanted into another flask of 500 ml. The remaining sodium sulfate was rinsed with two portions of 25 ml CH_2Cl_2 and the rinses were decanted in the flask of 500 ml. The sample was evaporated to 1 ml using rotary evaporator. Five milliliters of *n*-hexane (Lab-Scan) were added and then the extract was again evaporated to 1 ml. This was repeated for second time. The volume was then adjusted to 2 ml with hexane.

For the measurement, a GC Shimadzu 17A equipped with a Flame Thermionic Detector (FTD) was used. For the GC the following program was used: From 60 °C (5 min) to 210 °C (5 min) at 15 °C/min, and to 300 °C (3 min) at 5 °C/min. The injection temperature was 250 °C and the detector temperature was 300 °C. The volume of injection was 4 μl . Other information related to the method includes: splitless mode for 1 min, flow of the helium carrier gas: 8 ml/min. The column used for the chromatographic separation was an SPB-5 (Supelco), fused silica, 30 m \times 0.53 mm ID.

2.4.2. Organochlorine insecticides

The method that was followed is based on EPA Method 508 [52]. A measured volume (600 ml) of the sample was transferred in a 1 L separatory funnel. Five grams of NaCl were added and the funnel was shaken well until NaCl was completely dissolved. Fifty milliliters of CH_2Cl_2 were added and the funnel was shaken vigorously for 2 min with periodic venting to release excess pressure. Then the organic phase was allowed to separate from the

water phase for a minimum of 10 min. The organic phase was then collected and transferred in a spherical flask of 250 ml. The extraction procedure was repeated a second time, combining then the extracts in the flask. Five grams of anhydrous Na_2SO_4 were added in the extract in the flask. The flask was shaken and then was left to sit for 15 min. The methylene chloride was decanted into another flask of 500 ml. The remaining sodium sulfate was rinsed with two portions of 25 ml CH_2Cl_2 and the rinses were decanted in a 500-ml flask. The sample was then evaporated to 1 ml using a rotary evaporator. Ten milliliters of *n*-hexane (Lab-Scan) were added and then the extract was again evaporated to 1 ml. This was repeated for a second time. The volume was then adjusted to 5 ml with hexane. Two milliliters of this sample were diluted to 5 ml with hexane after having added 1 ml of Stock IS.

The instrumentation used consisted of a GC Shimadzu 14A with an auto injector AOC-14 and C-R4AX Chromatopac, supported by an ECD. The column used for the chromatographic separation was an SPB-5 (Supelco), fused silica, 30 m \times 0.53 mm ID. Helium carrier gas flow was established at 30 cm/s linear velocity and the temperature was programmed from 60 °C (5 min) to 200 °C (5 min) at 10 °C/min, then to 250 °C (5 min) at 2 °C/min and finally to 270 °C (24 min) at 3 °C/min. The injector temperature was 250 °C and the detector temperature 300 °C. The injection volume was 4 μl splitless mode with a 3 min delay.

2.4.3. Metals

Metals except Hg were determined with an Inductively Coupled Plasma (ICP Fisons 3410). An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz torch that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and a spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000–8000 K. One hundred milliliters of well-mixed samples were transferred to beakers. Five milliliters of HNO_3 1:1 (v/v) were added in each sample. Watch glasses were used in order to cover the beakers and prevent sample contamination. Then, samples were allowed to reach 80–85 °C using hotplates to a final volume of about 10–20 ml before metal precipitation. The digestion procedure was repeated twice. The beaker walls and the watch glass cover were washed with metal-free water and then the rinse water was filtered. The filtrate was then transferred to a 100-ml volumetric flask (with the addition of ca. 10 ml of water). Spectrosol 1000 mg/l of metals in HNO_3 were used as standard solutions for the determination of the metals. The method followed is Standard Method 3120B [53].

The determination of Hg was achieved using an Atomic Absorption Spectrometer (Shimadzu AA-6501) and a Mercury vaporizer unit (Shimadzu MVU-IA) following the cold-vapor atomic absorption spectrometric method (Standard Method 3112B [54]) (flame continuous $\lambda = 253.7$ nm, lamp current:

Table 3
Average concentrations of herbicides and organophosphoric insecticides in $\mu\text{g/L}$

Parameters/industries	Dichlorvos ($\mu\text{g/L}$)	Trifluralin ($\mu\text{g/L}$)	Simazine ($\mu\text{g/L}$)	Diazinon ($\mu\text{g/L}$)	Chloropyrifos ($\mu\text{g/L}$)
FM	0.66	0.569	0.491	1.194	1.556
AC2	2.38	–	–	0.482	0.862
MDL ^a	0.005	0.005	0.005	0.03	0.03
MQL ^b	0.01	0.01	0.01	0.05	0.05

(–): not examined.

^a Method detection limit.

^b Method quantitation limit.

4 mA, slit: 0.5 nm, mode: non bkgr, signal processing peak height).

2.5. Quality control and quality assurance

The validation of the methods applied was done according to the method of the International Standards Organization: ISO 17025:2000. The quantification limits, precision (reproducibility and repeatability) and accuracy (average recovery and recovery range) for both the instrumental stage and the complete method for each pesticides studied were validated.

According to this, each time a set of 20 of samples was extracted or reagents were changed, a Laboratory Reagent Blank was analyzed, in order to determine interfering peaks and reduce the possibility of contamination.

Blank samples and spike samples of three different concentrations (0.01, 0.05, and 0.1 $\mu\text{g/L}$) were run to check for interference and cross-contamination. The spiking average ranged from 0.003 to 0.012 $\mu\text{g/L}$ with a standard deviation that ranged from 0.001 to 0.004 $\mu\text{g/L}$. The repeatability ranged from 0.002 to 0.011, while the reproducibility ranged from 0.001 to 0.006. Finally the uncertainty ranged from 0.003 to 0.013.

For each substance studied the mean recovery value was set to fall in a range of $\pm 30\%$, while the relative standard deviation

(RSD) was set to be less than 20%. If any of the samples failed these criteria, the procedure was repeated.

A minimum detection limit (MDL) and a minimum quantitation limit (MQL) were determined for each substance. Surrogate recoveries from a sample or method blank were set from 70 to 130%.

3. Results

The values of the seasonal mean concentrations detected in the samples, taken from the industrial units between June 2005 and June 2006, are presented in Tables 3–5 and Figs. 1–4. Table 3 and Fig. 1 show the results for the herbicides and organophosphoric insecticides (dichlorvos, trifluralin, simazine, diazinon and chloropyrifos). These compounds have been investigated in two industrial units only *i.e.* FM and AC2. As expected, the manufacturing industry of agricultural chemicals (AC2) had a greater concentration of organophosphoric pesticides than the filter manufacturing and filter maintenance (FM). The main pollutant in AC2 was dichlorvos, while in FM chloropyrifos.

Table 4 and Fig. 2 show the concentrations of the metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), molybdenum (Mo), lead (Pb), stannum (Sn), and zinc (Zn) in the studied areas. As previously mentioned, due to limited resources and due to the fact that not all

Table 4
Average concentrations of heavy metals

Industry	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Hg ($\mu\text{g/L}$)	Mo (mg/L)	Ni (mg/L)	Pb (mg/L)	Sn (mg/L)	Zn (mg/L)
FM	–	<0.020 ^a	<0.050 ^a	<0.100 ^a	<0.5 ^a	–	<0.100 ^a	<0.150 ^a	–	0.34
VO	–	<0.020	<0.050	<0.100	–	–	<0.100	<0.150	–	0.20
EGS1	–	0.023	<0.050	<0.100	<0.5	1.00	<0.100	0.300	–	<0.02 ^a
ORP	–	<0.020	<0.050	0.3	<0.5	–	<0.100	<0.150	–	0.425
D	–	<0.020	<0.050	<0.100	–	–	<0.100	<0.150	–	0.13
E1	–	<0.020	8.8	<0.100	<0.5	–	2.20	<0.150	0.40	0.30
F	–	<0.020	0.4	1.60	3.1	–	0.50	1.40	–	4.60
AC2	–	<0.020	<0.050	31.6	0.9	–	<0.100	<0.150	–	17.00
PH	<0.150 ^(DL)	<0.020	–	–	<0.5	–	–	–	–	–
PS2	–	<0.020	–	–	<0.5	–	–	–	–	–
WP1	–	<0.020	<0.050	<0.100	<0.5	–	<0.100	<0.150	–	<0.02
WP2	–	<0.020	<0.050	–	<0.5	–	–	–	–	–
WP3	–	<0.020	–	<0.100	–	–	–	<0.150	–	0.1
WP4	–	<0.020	–	<0.100	–	–	–	<0.150	–	<0.02
WP5	–	<0.020	–	<0.100	–	–	–	<0.150	–	0.03
WP6	–	<0.020	0.5	<0.100	<0.5	–	2.30	<0.150	–	0.30

(–): not examined. Digits in bold show the concentrations actually measured during the study.

^a Method detection limit.

Table 5
Average concentrations of organochlorine insecticides

Industrial unit code	Aldrin (µg/L)	HBZ ^a (µg/L)	Lindane (µg/L)	β-BHC ^b (µg/L)	pp-DDE (µg/L)	Heptachlor (µg/L)	α-BHC (µg/L)	Dieldrin (µg/L)	Heptachlor-epoxide (µg/L)	op-DDD (µg/L)	Endrin (µg/L)
FM	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
VO	–	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	–	<0.002
EGS1	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
ORP	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	0.013	<0.001	<0.002	<0.002
D	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
E1	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
F	–	–	–	–	–	–	–	–	–	–	<0.002
AC2	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	–	–	–	<0.002
PH	0.016	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
PS2	<0.001	0.004	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
WP1	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
WP2	<0.001	<0.001	<0.001	<0.002	<0.001	<0.001	0.084	<0.001	<0.001	<0.002	<0.002
WP3	<0.001	<0.001	0.005	<0.002	<0.001	<0.001	<0.001	0.012	<0.001	0.006	<0.002
WP4	<0.001	<0.001	<0.001	0.136	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.002
WP5	0.010	<0.001	<0.001	<0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	0.007
WP6	<0.001	<0.001	0.049	0.325	0.145	0.014	<0.001	<0.001	<0.001	<0.002	<0.002
MDL ^c	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002
MQ ^d	0.002	0.002	0.002	0.004	0.002	0.002	0.002	0.002	0.002	0.004	0.004

(–): not examined. Digits in bold show the concentrations actually measured during the study.

^a Hexachlorobenzene.

^b Hexachlorocyclohexane.

^c Method detection limit.

^d Method quantitation limit.

metals were expected to be found in all industrial units, the analysis was performed selectively. Therefore, Mo was investigated only at EGS1, Sn at E1, and As at PH. Mercury was detected in the wastewaters of two units (F and AC2). Nickel was detected in the samples taken from E1, F, and WP6, copper in the samples taken from ORP, F, and AC2, lead in the samples taken from

EGS1 and F, zinc in the samples taken almost from all units (FM, VO, ORP, D, E1, F, AC2, WP3, WP5 and WP6), chromium in the samples taken from E1 and F, and finally cadmium was detected only in the samples taken from EGS1. Copper had the highest concentrations in wastewaters, followed by zinc. Chromium and then nickel and lead were found in smaller concentrations. Cop-

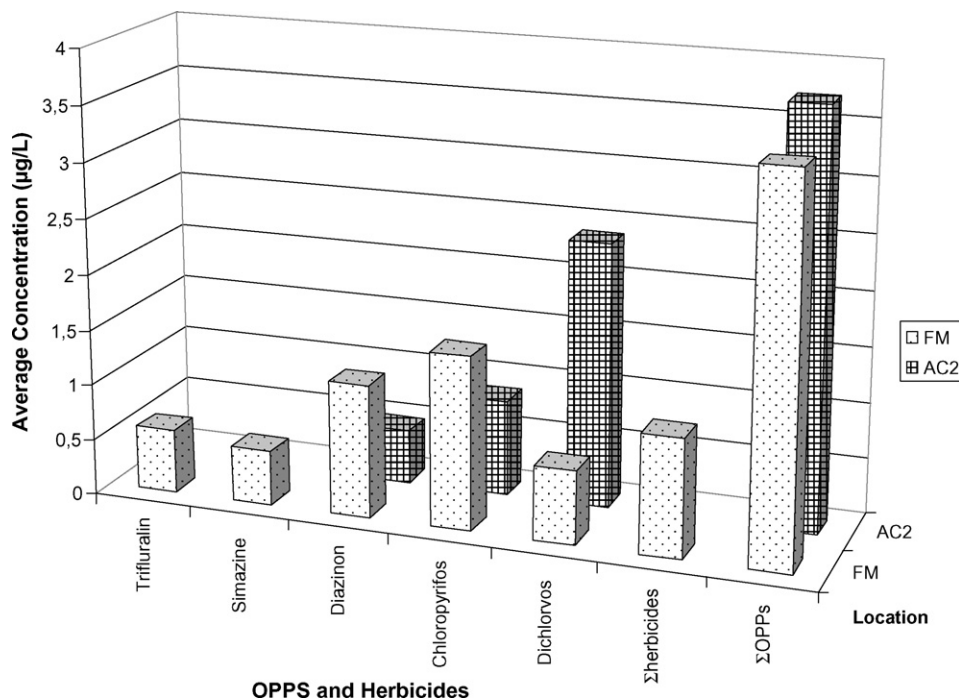


Fig. 1. Average concentrations of organophosphoric pesticides in µg/L from wastewater from filter manufacturing and filtering maintenance (FM) and manufacturing of agricultural chemicals (AC).

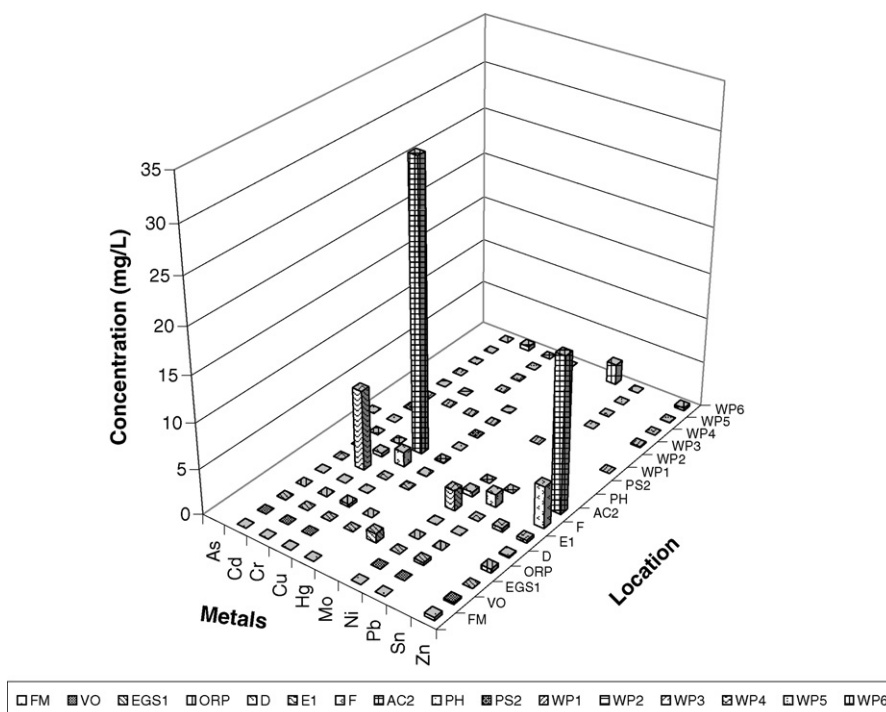


Fig. 2. Average heavy metals concentrations in mg/L.

per was mainly found in the wastewaters of AC2, while zinc not only at the wastewaters of AC2, but also at those of FM, VO, ORP, D, E1, F, WP3, WP5, and WP6.

Table 5 shows the results obtained for the organochlorine insecticides. Except heptachlor epoxide, all other com-

pounds examined were determined in at least one wastewater stream. β -BHC and *pp*-DDE had the highest concentration, and were found mainly in wastewaters of WP6. The rest of OCPs were found in traces in different wastewater streams.

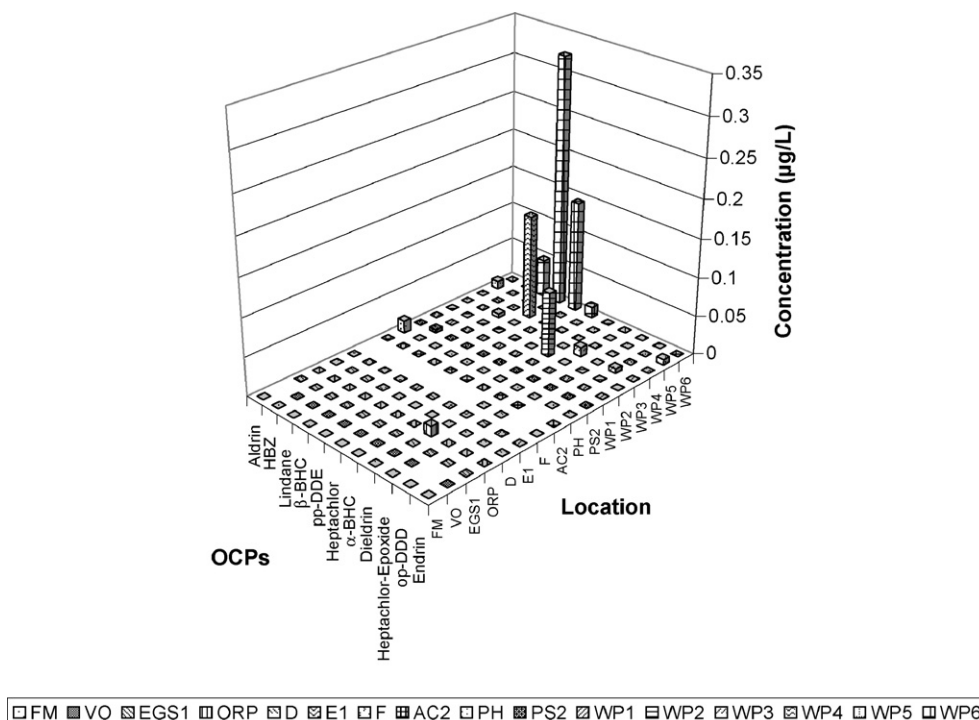


Fig. 3. Average concentrations of organochlorine pesticides in µg/L.

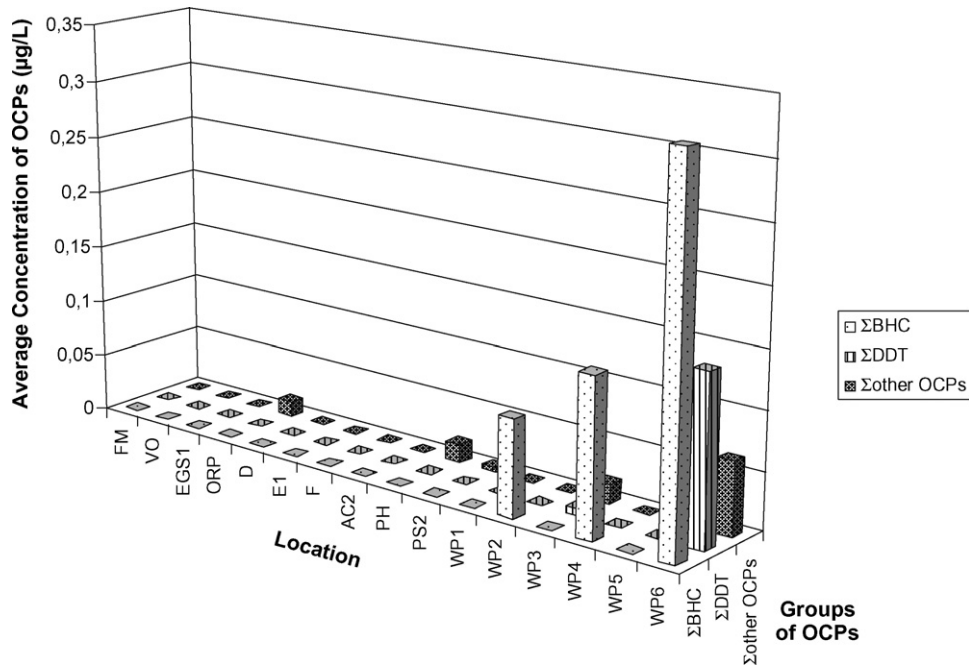


Fig. 4. Composition of OCPs in studied areas. Σ BHC = α -BHC + β -BHC; Σ DDT = *pp*-DDE + *op*-DDD; Σ other OCPs = aldrin + dieldrin + endrin + hexachlorobenzene (HBZ) + lindane + heptachlor + heptachlor epoxide.

4. Discussion

All substances examined are substances that could potentially pose health risks to human and the aquatic environment, due to their physicochemical and toxicological properties. Most of these compounds are monitored at European level through a number of Directives. Member States of the EC are required to eliminate pollution of the surface waters from these substances, some of which have also been characterized as priority substances and included in the new Water Framework Directive 2000/60/EC. The main sources of these substances in surface waters are industrial and agricultural activities. Therefore, this study facilitated the preliminary identification of the pollution sources in regards to these special compounds.

Quality objectives (according to the Ordinance of 8/2001 of the Government of Cyprus) for the maximum concentrations of various pesticides in water are shown in Table 6. The concentrations found were much lower than these objectives. However, it is important to note that these concentrations were found in wastewaters of selected industrial/wastewater treatment plants and the fate and effects of pesticide residues for irrigating purposes with treated wastewater were not studied. Additionally, it must be mentioned that although DDT has been banned for agricultural use in many countries since the 1970s, traces can still be found in wastewaters.

Quality objectives also exist in Cyprus for the wastewater treatment plants (for discharge into the sea and also for irrigation purposes) for Zn (0.1 mg/L), Pb (0.15 mg/L), Cd (0.01 mg/L) and Cu (0.1 mg/L). Moreover, quality objectives (for irrigation purposes) exist in Cyprus for EGS1 in regards to Cd (0.01 mg/L), Cr (0.1 mg/L), Zn (2 mg/L), Pb (0.5 mg/L) and Cu (0.2 mg/L). It can be seen that, in a limited number of cases, non-compliance

with the regulatory limits was observed (e.g. Cd 0.023 mg/L at EGS1, Zn 0.3 mg/L at WP6). In general, the results showed that the samples and the particular industries examined do not have effluents with high concentrations of heavy metals. In addition the results indicate that the effluents of many of the industries

Table 6
Quality objectives for the maximum concentrations of substances in waters (according to the Ordinance of 8/2001 of the Government of Cyprus)

	Substances	Concentration (μ g/L)
1	Carbon tetrachloride (CCl ₄)	12
2	DDT	10 for the isomer <i>pp</i> -DDT 25 for the total DDT
3	Pentachlorophenol (PCP)	2
4	Aldrin ^a Dieldrin ^b Endrin ^c Isodrin ^d	10 10 5 5
5	Hexachlorobenzene	0.03
6	Hexachlorobutadiene	0.1
7	Chloroform	12
8	1,2-Dichloro-ethane	10
9	Trichloroethane	10
10	Tetrachloroethylene	10
11	Trichlorobenzene	0.4

The precision and the accuracy of the reference method of determination must be $\pm 50\%$ at a concentration which represents twice the value of the determination limit.

^a Concentration is for internal littoral water.

^b Concentration is for outfall waters.

^c Concentration is for internal littoral water except from the outfall waters.

^d Concentration is for the sea territorial waters only.

examined do not contain cadmium, chromium, copper, lead, nickel, and zinc.

The physicochemical properties of the pesticides such as degradability, solubility and adsorption could explain further the distribution of organochlorine and organophosphoric insecticides and herbicides. Strongly adsorbed and persistent pesticides (high K_{OC} and high $T_{1/2}$) remain adsorbed on the soil and are able to contaminate surface water easily [55]. Trifluralin for example has been reported to have K_{OC} 7000 g/ml and soil half-life 60 days [56]. The fact that both chloropyrifos and trifluralin have high K_{OC} , their relative high persistence and their abundant production and use can explain their relatively high concentration in wastewaters streams. Although DDT has been banned in Cyprus since late 1970s and despite its strong adsorption to soil [57], it was also found in the treated wastewater of WP3 and WP6.

The substances that were investigated cannot be removed by classical methods during treatment and it is very important to point out an interesting particularity of Cyprus, which is the granting of permits to industries to discharge treated effluent into soil tanks-lagoons or even for irrigation of different types of cultivation. Although this is to some extent justified by the absence of rainfall for more than 8 months per year and although such permits are only granted under certain circumstances and complemented with strict limits, someone could argue that by the land disposal method, the pollutants will eventually reach either the surface or the ground water. In all cases of existing permits, the authorities took under serious consideration the existence of surface or ground water reservoirs in the surroundings and ensured that the distance from the source to any water body could safeguard that no pollutants could practically reach sensitive areas.

However, no studies have been made on the self-destroying mechanisms of many organic substances under local conditions. It will be useful to conduct such studies in the future so that natural attenuation processes are accounted for. In all surveys that were held in Cyprus in various water bodies, the analysis results revealed that there was no detection of any dangerous substances, in concentrations that could pose a threat to public health.

5. Conclusions

This paper demonstrates that organochlorine and organophosphoric insecticides, herbicides, and heavy metals exist in a number of wastewater streams in Cyprus. Twelve OCPs, 3 OPPs, 2 herbicides and 10 heavy metals were monitored from June 2005 to June 2006 in wastewaters released by different industrial sectors.

Herbicides and organophosphoric insecticides have been investigated in two industrial units only (a manufacturing industry of agricultural chemicals, and a filter manufacturing and filter maintenance industry). From these two, the first one had a greater concentration of organophosphoric pesticides with the main pollutant being dichlorvos. The main pollutant in the second industry was found to be chloropyrifos.

Metals were investigated selectively in the various industrial units. Copper had the highest concentrations in wastewaters, followed by zinc. Chromium and then nickel and lead are found in smaller concentrations. In general, the results showed that the samples and the particular industries examined do not have effluents with high concentrations of heavy metals.

Concerning organochlorine insecticides, except heptachlor epoxide all other compounds examined were determined in at least one wastewater stream.

It is worth noting that quality objectives for 'non-conventional' parameters should be integrated in the permits granted by the competent authorities because currently this is not the case for a number of substances like for example pesticides. Moreover, an extension of the number of the industries to be examined, the enlargement of the range of pesticides and the inclusion of the metabolites of the pesticides, and the synergistic effects of these substances on the environment will be considered in future work. Concluding, a better understanding of the pesticide inter-media transfer, ecotoxicity and risk assessment is required for a more in-depth understanding of the potential problems.

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