THE OCCURRENCE OF PRIORITY SUBSTANCES REGULATED BY 76/464/EEC AND 2000/60/EC WFD DIRECTIVES IN THE SURFACE WATERS SUPPLING WATER TREATMENT PLANTS OF ATHENS, GREECE

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ABSTRACT

An investigation into the occurrence of priority substances regulated by 76/464/EEC Directive and 2000/60/EC Water Framework Directive, was conducted for a period of one year in the surface water sources supplying the water treatment plants (WTPs) of Athens and in the raw water of WTPs. Samples from four reservoirs (Mornos, Yliki, Marathon, Evinos) and four water treatment plants of Athens (Galatsi, Menidi, Polydendri, Aspropirgos) were taken seasonally. The substances are divided in eight specific groups, including eight volatile organic compounds (VOCs) (Benzene, 1,2-Dichloroethane, Dichlomethane, Hexachlorobutiadiene, Trichlorobenzene, Naphthalene, Pentachlorobenzene, Trichloromethane), a category of nine compounds including polycyclic aromatic hydrocarbons (PAHs), phenols and diethylhexylphthalate (DEHP, 4-nonylphenol, 4-octyphenol, Anthracene, Fluoranthene, Benzo-a-pyrene, Benzo-b-fluoanthene, Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno (1,2,3-cd)pyrene), four organochlorine insecticides (Alachlor, Endosulfan, Hexachlorobenzene, Hexachlorocycloexane), three organophosphorus insecticides (Chlorfenviphos, Chlorpyrifos, Trifluralin), four herbicides (Atrazine, Diuron, Isoproturon, Simazine) and Pentachlorophenol, six organotins (Tributyltin, Dibutyltin, Monobutyltin, Monophenyltin, Diphenyltin, Triphenyltin) and four metals (mercury, lead, nickel and cadmium). The presence of VOCs has been determined by a modification of purge and trap (PAT) gas chromatography – mass spectrometric method (GC-MS). The determination of PAHs was accomplished using liquid-liquid extraction (LLE) coupled to GC-MS analysis. Solid phase extraction (SPE) procedure and GC with electron capture detector (ECD) and nitrogenous phosphorus detector (NPD) were applied to quantify the organochlorine and organophosphorus insecticides, respectively. High-performance liquid chromatography with diode array detection (HPLC-DAD) was used to screen water samples for herbicides and pentachlorophenol. Organotins were determined by gas chromatography - flame photometric detector (GC-FPD). Finally, the determination of lead, nickel, cadmium was made by electrothermal atomization atomic absorption spectrometry (ETAAS), while cold vapor - AAS (CVAAS) with flow injection analysis (FIAS) was used for the determination of mercury. The results showed that the surface waters of Athens are not burdened with toxic substances identified as EU priority substances. Atrazine, hexachlorocycloexane, endosulfan, trifluralin, anthracene, 4-nonylphenol and some organotin species were observed at very low concentrations occasionally.

Keywords: priority substances, surface waters, water treatment plants

1. Introduction

A number of legislative actions have been enacted from European Union in order to protect the surface waters from toxic pollutants that pose risks to human health and to the aquatic environment. These pollutants belong to a different number of chemical categories, as volatile

organic compounds (VOCs), organochlorine and organophosphorus insecticides, herbicides, organotins and polycyclic aromatic hydrocarbons (PAHs) (Lekkas *et al*., 2000). One significant Directive is 76/464/EEC whose the goal is the elimination and the reduction of water pollution by certain dangerous substances listed in the directive. The substances of List I of the 76/464/EEC Directive pose health risk to humans and to the aquatic environment, as they appear physicochemical and toxicological properties. Some of these compounds have also been characterized as priority substances and included in the Water Framework Directive (WFD) 2000/60. The agricultural and industrial activities are the main sources of these compounds in surface water (Lekkas *et al*., 2003a). The implementation of this directive must be closely co-ordinated with the implementation of the proposed European WFD 2000/60 which commits European Union member states to achieve good qualitative and quantitative status of all water bodies by 2015. The main objective of WFD is the protection and enhancement of surface water and groundwater.

The substances of 76/464/EEC Directive are divided into two lists, List I includes seventeen substances which must be eliminated from the surface water and List II which includes one hundred and fifteen substances that must be investigated in order to be embodied in the List I of the directive (Lekkas *et al*., 2000)

In Greece, determination of the substances. of Lists I and II in surface waters has been performed and reported in previous studies (Lekkas *et al*., 2003a; 2004; Nikolaou *et al*., 2007). This work presents the results of the investigation of priority list of substances regulated by Directive 76/464/EEC and the EC Water Framework Directive 2000/60/ in the surface water sources supplying the water treatment plants (WTPs) of Athens in Greece. The substances are divided in eight specific groups, including eight volatile organic compounds (VOCs), a category of nine compounds including polycyclic aromatic hydrocarbons (PAHs), phenols and Diethylhexylphthalate (DEHP), four organochlorine insecticides, three organophosphorus insecticides, four herbicides and pentachlorophenol, six organotins, and four toxic metals.

The investigation of the presence of these substances was implemented by established a monitoring network throughout the four reservoirs (Mornos, Yliki, Marathon, Evinos) and four water treatment plants (WTPs) of Athens (Galatsi, Menidi, Polydendri, Aspropyrgos) with representative sampling points. Sampling campaigns were executed seasonally for a period of one year (May 2004 – March 2005).

2. Material and methods

2.1. Sampling

Three sampling points were collected in Mornos water body (Input, Giona, Kokkinos), two sampling points in Yliki (Input, Mouriki), one in Marathon (Ventouri) and one in Evinos. Samples were also collected from the raw water entering the four WTPs. Four sampling campaigns were conducted for the inland waters of the Athens area (May 2004, September 2004, January 2005 and March 2005). Sampling was collected in appropriate bottles and were transported at 4 °C to the Water and Air Quality Laboratory (WAQL) of the Aegean University in Mytilene for analysis. The sampling procedure has been described elsewhere (Lekkas *et al*., 2003a; 2004; Nikolaou *et al*., 2007).

2.2. Analytical procedure

These substances belong to different chemical categories and their determination was performed by different analytical methods. The determination of VOCs was carried out by a modification of purge and trap (PAT) gas chromatography – mass spectrometric method (GC-MS). The determination of PAHs, phenols and diethylhexylphthalate (DEHP) was accomplished by liquid-liquid extraction (LLE) GC-MS method. Solid phase extraction (SPE) procedure and GC with electron capture detector (ECD) and nitrogenous phosphorus detector (NPD) were applied to quantify organochlorine and organophosphorus insecticides, respectively. High-performance liquid chromatography associated with diode array detection (HPLC-DAD) was used to screen water samples for herbicides and pentachlorophenol. Organotins were determined by gas chromatography - flame photometric detector (GC-FPD). The determination

of lead, nickel, cadmium was made by electrothermal atomization atomic absorption spectrophotometer (ETAAS), while cold vapor-AAS (CVAAS) with flow injection analysis (FIAS) was used for the determination of mercury. These methods were optimized and validated in order to be routinely used for the determination of different chemical species in surface water samples and selected after experimental modification which resulted in the best analytical performance achievable with the particular instrumentation, expressed by the calculated recoveries and detection limits. The analytical methods applied in this survey have been described elsewhere (Lekkas *et al*., 2003b).

3. Results

Table 1 presents the concentrations ranges for each category of priority substances that detected during this sampling campaign.

Table 1: Concentration ranges of priority substances that investigated in reservoirs waters supplying the WTPs of Athens for a period of one year.

Priority substances	Ranges of concentration (μg/l)
VOCs	nd
PAHs (anthracene)	0.19-0.33
Phenols (4-nonylphenol)	0.08-2.54
Diethylhexylphthalate	nd
Organochlorine insecticides	0.002-0.005
Organophosphorus insecticides (trifluralin)	nd-0.110
Herbicides (atrazine)	0.05-0.025
Pentachlorophenol	nd
Organotins	0.004-0.020
Metals	0.33-14.8

nd: not detectable concentration

3.1. Volatile Organic Compounds (VOCs)

VOCs were not detected in samples analyzed during the present investigation. It is well known that these compounds are released into environment during their production, distribution, storage, handling and use. Their absence from surface waters studied could be attributed to the absence of relative point sources as they can enter surface water supplies from many point and non-point sources (Kostopoulou *et al*., 2000).

3.2. Polycyclic Aromatic Hydrocarbons (PAHs), Phenols and Diethylhexylphthalate (DEHP)

Anthracene was the only PAH detected during last sampling (March 2005) in two sampling points. These concentrations ranged from 0.19 μg/l (raw water of Aspropyrgos WTP) to 0.33 μg/l (Mornos-Giona). The presence of this compound in water intended for purification do not create problems in drinking water, because anthracene is easily adsorbed to suspended particles and sediments (Notar *et al*, 2001). As a result it is expected complete removal during water treatment process, which confirmed during drinking water sample analysis in the WAQL (Kanaki *et al*., 2005)

During the same sampling, 4-nonylphenol was the only one of this compounds category that detected in all sampling points except one (Evinos) in concentration levels that ranged from 0.08 to 2.54 μg/l. These levels are lower than the concentrations reported in the literature. However the presence of this substance in several samples at the last sampling, indicates contamination associated with detergents where nonylphenol ethoxylates used that subsequently are degraded to 4-nonylphenol (Ying *et al*., 2002).

3.3. Organochlorine Insecticides

The organochlorine insecticides were detected at very low concentrations. Endosulfan was detected during the third sampling campaign, in input of Yliki lake (0.003 μg/l), as hexachlorocyclohexane that detected during the same sampling in four sampling points (Yliki Mouriki and WTPs of Menidi, Aspropyrgos and Galatsi) with the concentrations to be ranged from 0.002 to 0.005 μg/l. Alachlor was also detected in Mornos and Polydendri WTP in 0.002 μg/l for each plant. Hexachlorobenzene was not detected during this investigation.

3.4. Organophosphorus Insecticides

The only detectable compound was trifluralin, during the second sampling campaign in the WTP of Aspropirgos at a level of 0.110 μg/l.

3.5. Herbicides and Pentachlorophenol

The herbicide atrazine was detected only in Yliki-Mouriki (0.025 μg/l) and in WTPs of Polydendri (0.05 μg/l), and Galatsi (0.05 μg/l). Atrazine was used at significant quantities in Greece because it is a selective herbicide for growing maize. Also, it is used in different bush and tree crops. According to Solomon *et al*. (1996), atrazine in surface waters photolyzed and hydrolyzed slowly resulting in accumulation in static waters (lakes and reservoirs). In the long term, concentrations of atrazine are heavily depended on phenomena of dilution and hydraulic renewal of water (Solomon *et al*., 1996).

3.6. Organotins

Four organotins were detected only in five cases at very low concentration levels. In particular, tributyltin occurred during the third and fourth sampling in Aspropirgos GTP (0.004 μg/l) and in water of Yliki-Mouriki (0.007 μg/l), respectively. Dibutyltin was observed only in water of Yliki-Mouriki (0.008 μg/l) during the fourth sampling. Diphenyltin and triphenyltin were detrected only during the first sampling in Menidi WTP, at concentrations of 0.005 and 0.020 μg/l, respectively. No detection of monobutyltin and monophenyltin was observed during this investigation.

3.7. Metals

Regarding metals, mercury was not detected in any sampling. Lead was detected only in one sample (Marathon-Ventouri) during the second sampling (2.3 μg/l). Cadmium was present at two sampling points, in Mornos-Giona (2.52 μg/l) during second sampling campaign and in Polydendri WTP in three cases (first sampling-0.90 μg/l, second sampling-0.48 μg/l, fourth sampling-0.33 μg/l). The highest concentrations were observed for nickel that detected in the following sampling points: input of Mornos (fourth sampling-8.6 μg/l), Mornos-Kokkinos (fourth sampling-12.6 μg/l), Evinos (fourth sampling-2.6 μg/l), input of Yliki during all sampling (3,5-6.4 μg/l), Yliki-Mouriki during all sampling at concentrations that ranged from 9.3 to 12.4 μg/l, Marathon-Ventouri (second sampling-5.6 μg/l),in Polydendri WTP during third sampling (8.3 μg/l) and in Galatsi WTP during second sampling at 1.8 μg/l.

4. Conclusions

The occurrence of priority list of substances regulated by 76/464/EEC Directive, as well as by 2000/60/EC Water Framework Directive in the reservoirs supplying the WTPs of Athens was investigated for a period of one year. The results have shown that the overall pollution of surface waters of Athens is very low and does not exceed the limits set by EU in any case. The presence of some compounds, in a limited number of cases, could be attributed to waste disposal, agricultural activities, and to a limited industrial activity in the area nearby the water bodies.

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