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Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance ☆

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Abstract

The fate and the mass balance of persistent organic pollutants (POPs) during the conventional activated sludge treatment process were investigated in the wastewater treatment plant of the city of Thessaloniki, northern Greece. The POPs of interest were 7 polychlorinated biphenyls and 19 organochlorine pesticides. Target compounds were determined at six different points across the treatment system: the influent, the effluent of the primary sedimentation tank, the effluent of the secondary sedimentation tank, the primary sludge, the activated sludge from the recirculation stream, and the digested/dewatered sludge. The distribution of POPs between the dissolved and the adsorbed phases of wastewater and sludge was investigated. A good linear relationship between the distribution coefficients, K_d, and the octanol–water partition coefficients, K_{ow}, of the solutes was observed only in raw wastewater, suggesting that other factors affect the phase distribution of organic compounds in treated wastewater. For all POPs, a significant increase in partitioning with a decreasing solids concentration was observed, revealing an effect from non-settling microparticles remaining in the "dissolved" phase during the separation procedure. A good linear relationship was also revealed between $\log K_d$ and the dissolved organic carbon (DOC) content of wastewater, suggesting that DOC favors the advective transport of POPs in the dissolved phase. Almost all POPs showed good mass balance agreements at both the primary and the secondary treatment. The losses observed for some species could be attributed to biodegradation/biotransformation rather than volatilization. The relative distribution between the treated effluent and the waste sludge streams varied largely among different compounds, with *p-p′*-DDE being highly accumulated in the waste sludge (98%) but almost 60% of α-HCH remaining in the treated effluent.

Keywords: Chlorinated pesticides; PCBs; Phase distribution; Sewage sludge; Wastewater treatment plant

1. Introduction

Persistent organic pollutants (POPs) constitute a class of man-made chemicals with a pronounced persistence against chemical/biological degradation, environmental mobility, a tendency for bioaccumulation in human and animal tissue, and significant impacts on human health and the environment, even at extremely low concentrations. The chemical properties of POPs, such as low water and high fat solubility, stability in the face of degradation processes, and a low vapor pressure, are the hallmarks of their efficacy as pesticides and for their persistence at the environment (Kim and Smith, 2001). Despite their ban in the USA and Europe in the mid-1970s, some of them were still in use into the 21st century in developing countries (Pandit et al., 2001), until the Stockholm Convention for POPs banned the production and use of those chemicals worldwide in 2001.

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In a wastewater treatment plant (WWTP), POPs can originate from urban or agricultural runoff or drainage into the sewerage system, including wet and dry deposition from the atmosphere (Blanchard et al., 2001, 2004), and via industrial discharges. The fate of these xenobiotic organic compounds in WWTPs will be governed by their physico-chemical properties, the quality of the wastewater, and the process design and operating conditions of the treatment system (Byrns, 2001; Petrasek et al., 1983). For several reasons, the conventional activated sludge process is not completely effective for controlling the discharge of toxic compounds (Petrasek et al., 1983). WWTPs are widely recognized as an important source of toxic contaminants in the aquatic environment (Pham and Proulx, 1997); therefore, control of their effluents is essential.

POPs entering the primary treatment stage of a WWTP are likely to be removed primarily by sorption onto suspended solids and subsequent sedimentation and secondarily by volatilization to the atmosphere through diffusional exchange at the air–water interface (Byrns, 2001). Sorption to the sludge has been shown to remove up to 70% of polychlorinated biphenyls (PCBs) (Morris and Lester, 1994), 32% of heptachlor (Hannah et al., 1986), and up to 91% of lindane (Kipopoulou et al., 2004). The existence of miscible organic solvents and fine particles ($<100\,\mu m$) can increase the percentage of hydrophobic chemicals that remain in the effluent of the primary sedimentation tank (Morris and Lester, 1994). Chemicals entering the secondary treatment stage may be removed through sorption to the activated sludge, air stripping due to the forced injection of air, and biotransformation/biodegradation (Byrns, 2001). Sorption on activated sludge has been shown to remove up to 65% of heptachlor (Hannah et al., 1986), up to 18% of lindane (Hannah et al., 1986), and up to 60% of aroclor 1254 (Petrasek et al., 1983). Despite their persistence, possible biodegradation has been suggested for certain POPs, such as lindane (Dorussen and Wassenberg, 1997; Kipopoulou et al., 2004), while biotransformation was noticed for some compounds, such as for aldrin to dieldrin and for DDT to DDE and DDD (Saleh et al., 1980) It has been suggested that in several instances removal by air stripping might be important for some POPs. Thus, heptachlor and aroclor 1254 might be removed up to 50% by volatilization, whereas lindane would hardly be volatilized (Petrasek et al., 1983). Data in the literature show that the removal of POPs during the wastewater treatment process is compound-dependent and plant-specific (Saleh et al., 1980; Pham and Proulx, 1997; Petrasek et al., 1983; Kipopoulou et al., 2004)

The aim of the present study was to thoroughly investigate the fate of a wide range of POPs in the conventional activated sludge treatment process. For this purpose, a WWTP of 750,000 equivalent inhabitants that receives mainly domestic effluents and urban runoff was selected. Twenty-six POPs [7 PCBs and 19 organochlorine (OC) pesticides] were determined in raw sewage as well as at particular points of the wastewater and sludge streams that best characterized the treatment process. The distribution of POPs between the dissolved and the sorbed phases of wastewater and sludge was investigated. The mass balance of each contaminant was calculated for each stage of wastewater and sludge treatment. In addition, their daily discharges from the WWTP via the waste sludge and the treated effluent were estimated.

2. Materials and methods

2.1. Plant description

The WWTP of the city of Thessaloniki serves about 1 million residents by treating daily 120,000–150,000 tons of raw wastewater. About 5–10% of the total flow is contributed by industry. The plant also receives the majority of the local urban runoff, which is composed primarily of atmospheric and traffic-related emission deposition on road surfaces. The treatment process includes screening, grit removal, primary sedimentation without the use of chemical coagulants, conventional activated sludge treatment and effluent disinfection using Cl_2. The treated wastewater is discharged in Thermaikos Gulf via a channel. Sewage sludge is anaerobically digested, thickened, dewatered, and, finally, deposited in a municipal landfill (Manoli and Samara, 1999; Karvelas et al., 2003). The flow chart of the plant is shown in Fig. 1.

2.2. Sampling

Sampling was conducted on 20 different dates distributed among four campaigns during the period of November 2001–January 2003. During each campaign, wastewater and sludge samples were collected over 5 consecutive days, excluding Saturday and Sunday. Twenty-four-hour composite, flow-proportioned samples of wastewater were collected from three different points along the treatment system, namely, the influent of the plant (raw wastewater, RW) and the effluents of the primary and secondary sedimentation tanks (PSE and SSE, respectively). Grab samples of sludge were collected from the primary sedimentation tank (PS) and the recirculation stream (activated sludge, AS) concurrently with wastewater samples. Grab samples of the final sludge (FS) were collected after a period of 21 days, which is the nominal retention time of sludge in the anaerobic digesters. All samples were collected in brown glass vessels with Teflon caps precleaned with acetone and *n*-hexane. Upon receipt in