INVESTIGATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN THE INFLUENT AND EFFLUENTS OF WASTEWATER TREATMENT PLANT IN NAGPUR REGION, MAHARASHTRA, INDIA

Devtade V[1]*, Nandanwar K[2]*, Khan NA[3‡], Gandhi K N[4‡], Kashyap S M[5], Thacker NP[6†]
*project fellows, †chief scientist, ‡scientist
[1-6] CSIR-National Environmental and Engineering Research Institute (NEERI), Nagpur, India

Introduction

Pharmaceutical and personal care products (PPCPs) have been identified in the environment and are considered as potent endocrine disruptors (EDCs) and emerging pollutants[1-4]. Therefore, a variety of PPCPs have been detected widely at **ng/L** concentration level in the effluents of waste water treatment plants (WWTPs) since conventional water-treatment processes do not seem to be sufficient to remove PPCPs from sewage water[5-7]. Information about physico-chemical characteristics such as acidity, lipophilicity, volatility and sorption potential is a useful tool to remove different PPCPs from waste water[8].Mostly PPCPs reach environment by disposal of hazardous wastes from industries, individual households, after showering and bathing[9].According to Daughton's report there may be as many as 6 million PPCP substances commercially available worldwide and that the use of pharmaceutical is increasing 3-4% by weight per annum[10]. In 2012, the Strategic Approach to International Chemicals Management (SAICM), which gathers industry representatives and public organizations in 120 countries, reached an agreement regarding the fact that endocrine disrupting chemicals, classified as emerging contaminants, are a global political issue. It highlights the potential adverse effects of endocrine disruptors on human health and the environment and calls the attention to the need to protect vulnerable humans and ecosystems[11]. In the present work the local sewage treatment plant is selected for investigation. The occurrence of targeted pharmaceuticals and personal care products (PPCPs) in wastewater treatment plants of Nagpur region was studied over monthly basis. Sampling exercises were carried out for a period of six months (Aug2013–Feb2014) from Bhandewadi sewage treatment plant (STP) located in south central Nagpur, Maharashtra, India. Four commonly occurring PPCPs were identified under the class of stimulant, surfactant, steroids and antimicrobial agents. Grab samples were collected from influent and effluents of the STP representing the raw and treated sewage. Analytical method based on common pre-concentration step on SPE is applied followed by derivatization to GC-MS analysis (USEPA-Method 1694). A set of PPCPs have been selected for investigation which include triclosan (antibiotic), 4-nonylphenol (surfactant), 17β-estradiol (hormone) and caffeine (stimulant).The identified PPCPs have been detected at the concentrations of ND- 13.59 µg/L levels in the effluents of waste water treatment plant (WWTP). The conventional water-treatment process is not efficient enough to remove PPCPs from sewage water. This study on the removal of targeted PPCPs by a local sewage treatment plant demonstrated that concentrations of most of the selected compounds cannot be affectively reduced by normal treatment processes. Therefore an increased focus on the potential release of active pharmaceutical and personal care ingredients and from different production regions is utmost important.

Materials and Methods

Chemicals

Reference standards of 6 PPCPs, triclosan (TCS), 4-nonylphenol (NP), 17β-estradiol (ES), caffeine (CF), ibuprofen (IBU) and paraxanthine (PX) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Analytical grade (AR) ethyl acetate, acetonitrile, acetone, hexane, dichloromethane and methanol chemicals (Merck, Darmstadt, Germany) were used throughout the study without any further purification; ultrapure water was produced by a Milli-Q unit (Millipore, USA). Stock solutions of individual compounds were prepared in methanol, and a mixture standard solution was prepared by diluting the stock solutions before each analytical run. Glassware's containing the stock solutions were wrapped with aluminum foil and stored refrigerated at 4^{o}C in the dark. Working solutions of single analytes as well as mixtures of analytes were also stored in a similar way as for the stock solutions.

Sample collection

The occurrence of targeted pharmaceuticals and personal care products (PPCPs) in wastewater treatment plant of Nagpur region was studied over monthly basis. Bhandewadi sewage treatment plant (STP) of 100 MLD capacity in south central Nagpur, India representing moderate to high-income group society selected for sampling. Aeration and sludge treatment were commonly operating processes of treatment plant. 3 L of grab samples were collected from influent and effluents of the STP representing the raw and treated sewage water. Sampling exercises were carried out during Aug2013–Feb2014 period and simultaneously two replicate samples were also collected in prewashed amber-colored glass bottles, kept in cool, transported to the laboratory within one hour of their collection and stored in a refrigerator at 4°C until further analysis.

Sample analysis

USEPA-Method 1694is adopted for this work; samples were filtered through Whatman filter. (GF/F, Whatman). Solid Phase Extraction (Auto Trace 280 SPE instrument by Dionex Corporation Version 1.00 Cartridge Model) equipped with C18 cartridge used for the exaction of waste water samples. Before loading samples, the C18 cartridges were preconditioned with 10 mL Millipore water, 10 mL methanol followed by 6 mL ethyl acetate in series by gravity. All the samples were passed through the SPE cartridge with the aid of a vacuum to control the flow rate at 5-8 mL/min. The cartridge was then washed with 10 mL water and dried under vacuum for about 15 min. The sample was eluted with 10 mL methanol and 6 mL acetonitrile: methanol (1:1) by gravity. Combined sample extracts were evaporated to dryness under gentle nitrogen gas and reconstituted with 1mL acetonitrile, further extract analyzed using GC-MS technique.

GC-MS Detection

An ion trap GC-MS equipped with Electron impact (EI) mode and MS capability was used for analysis of targeted compounds. The ion trap and manifold were kept at 150˚C and 40˚C respectively. The ion trap was connected by a heated (230˚C) transfer line to GC. Separation was carried out using DB-5 capillary column having length 30 m, 0.25mm ID and 0.25 micron film thickness. Column was connected to injector directly into ion source of ion trap mass spectrometer. The injector temperature was set at 270˚C. Oven temperature was programmed from 60˚C, hold for 1 min, heated to 270˚C at rate of 15˚C/ min and hold for 20 min. The EI mode was operated at electron energy of 70eV. The gas flow of 1.0 mL/min has been optimized. The samples (1µl) were injected .The filament of the ion source was switched off during elution of the solvent. The full-scan mass spectra are obtained over a proper *m/z* range. Positive identification of a compound requires elution within the expected retention-time window; in addition, sample spectra and ion-abundance ratios are required to match those of the reference standard compounds.

Results and discussion

A set of PPCPs have been selected for the investigation which include an antibiotic, analgesic, surfactant, a hormone and stimulant. The standardized USEPA method was applied to field samples collected from the identified STP of the Nagpur region. The concentration of triclosan and nonylphenol in both influent and effluents doesn't seem to have significant difference. Generally, the TCS concentration in the surface water is greatly influenced by the input of wastewaters discharged from households, hospitals and industries. Concentration of nonylphenol rose from inlet to outlet due to rapid biodegradation of polyethoxylates to mono and diethoxylates during the wastewater treatment. 17β-estradiol found at highest concentration of all target compounds with its effective removal in all effluents. Caffeine seems to be lower side among all detected micro pollutants. A detail of results are presented in the **Table 1**.

Table 1: Detection range of targeted PPCPs (µg/L) in influent and effluent of Bhandewadi STP in Nagpur region.

Analyte	13-Oct		13-Nov		13-Dec		14-Jan	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Triclosan	ND-5.96	ND	ND-9.33	ND	ND-4.61	ND-0.40	ND-4.28	ND-2.89
17β-estradiol	ND-10.11	ND	ND-13.59	ND	ND	ND	ND-1.4	ND-3.23
4-nonylphenol	ND-5.19	ND	ND-9.72	ND-1.9	ND-10.66	ND	ND-4.32	ND-4.61
Caffeine	ND-2.89	ND	ND-2.02	ND-2.89	ND-1.63	ND	ND-0.47	ND

ND* Not detected i.e., below detection limit

Conclusion

This study on the removal of targeted PPCPs by a local sewage treatment plant demonstrated that concentrations of most of the selected compounds cannot be affectively reduced by normal treatment system. Conventional treatment processes of local treatment plant examined do not seem to be sufficient enough to remove the micro pollutants. Presence of TCS, NP, ES, and CF in the effluents of treatment plant demonstrated the contamination of natural surface water by PPCPs. Future designs of STPs should perhaps focus on the most difficult-to-remove, toxicologically significant compounds so as to maximize the removal of all emerging micro pollutants. The present report will provide vital information on the expected levels of contamination for different PPCPs in surface waters of the region studied.

Acknowledgment

This work was financially supported by the Department of Science and Technology (DST), New Delhi. The authors would like to express their gratitude to Director and all colleagues of Pesticide Residue Laboratory, CSIR-NEERI Nagpur, Maharashtra, India.

References:

1. Daughton C.G., Ternes T.A., Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health Perspect.* (1999) 107: 907–938.
2. Daughton C.G., Jones-Lepp T(Eds.)., Pharmaceuticals and personal care products in the environment; overarching issues and overview, Scientific and Regulatory Issues, *ACS Symposium Series 791, American Chemical Society, Washington*, DC, (2001): 2–38.
3. Veldhoen N., Skirrow R.C., Osachoff H., Wigmore H., Clapson D.J., Gunderson M.P., The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development, *Aquat.Toxicol.* 80 (2006) 217–227 (Erratum in: Aquat. Toxicol. 83 (1) (2007)84).
4. Kummerer K., Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks, Springer, Berlin, Germany, 2008.
5. Yu K, Li Bi, Zhang T., Direct rapid analysis of multiple PPCPs in municipal wastewater using ultrahigh performance liquid chromatography–tandem mass spectrometry without SPE pre-concentration. *Anal. Chim. Acta.* (2012); 738: 59-68.
6. Patrick J. Ferguson, Melody J. Bernot, Jason C. Doll, Thomas E. Lauer. Detection of pharmaceuticals and personal care products (PPCPs) in near-shore habitats of southern Lake Michigan. *Sci Total Environ. (*2013); 458: 187–196.
7. Jaena R, Jeill Oh, Shane A, Snyder, Yeomin Y. Determination of micro pollutants in combined sewer overflows and their removal in a wastewater treatment plant (Seoul, South Korea). *Environ Monit Assess (*2014)
8. Sonia S, Marta C, Francisco O, Juan M. L, How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters?, *Rev Environ Sci Biotechnol.* (2008); 7:125–138.
9. EUROPA., http://ec.europa.eu/environment/water/index_en.html

10. Daughton C., Pollution from combined activities, actions and behaviours of the public: pharmaceuticals and personal care products. SETAC News. (2003); 14(1), 5-15.
11. Strategic Approach to International Chemicals Management., SAICM., (2012) ; <http:// www.saicm.org>