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# Studies on Emerging Contaminants in Water, Soil and Sediment Samples from selected locations of Pune District, Maharashtra, India

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## ABSTRACT

The objective of this study is to evaluate the Emerging Contaminates (ECs), contamination levels, occurrence and fate in the water, soil and sediments samples taken from the different locations of Pune, India. The Study area includes the samples from the upstream regions to the central and further moving on to observe the changes in the downstream regions which is highly polluted. In this study the concentration of detected levels of pesticides (contaminants) were noted to be ranging from ND to 720 µg/l. Mostly, very commonly used pesticides namely HCH, Endosulfan, Parathion-methyl and Chlorpyrifos have been closely studied. This study involves the seasonal variation in the levels of the pollutants specially post monsoon. Mostly Pharmaceuticals, such as Acetaminophen, Levofloxacin, Azithromycin were present in high concentration ranging from 98µg/l, 65 µg/l, 305 µg/l respectively from the water samples collected from the Central Region, where it's thickly populated. In comparison with developed countries like USA, it was observed that these ECs were present in the waste water 50-65% in lesser concentration than in India. This study also includes the determination of heavy metals (Cd, Cr, Cu, Co, Fe, Mn, Mg, Ni, Pd and Zn) in the samples collected so to proceed further with the heavy metal accumulation and speciation studies. All of the mentioned heavy metals appeared to be above the permissible limits ranging from moderately toxic to highly toxic. This study will not only help the local authorities but also give us the understanding of how important it is to study the present condition of our water bodies and to regulate initiatives for monitoring the ECs, so to embrace and enjoy better health, life and sustainability.

**Key words :** *Emerging contaminants, Pesticides, Pharmaceuticals, Heavy metals, Pune district, Maharashtra (India), Wastewater*

## Background

Pune City as well as the adjacent areas are surrounded with different Chemical Industries, Pharmaceutical industries and waste water treatment plants. The Effluent hence generated are discharged at times after treatment and sometimes before treatments in our rivers like Mula, Mutha and Bhima

River. These rivers are being constantly polluted as a result of these. And the current situations is not very pleasant. Every person residing in Pune can see the health of these rivers each day. Silently and steadily these contaminants are becoming a part of our food chain via bioaccumulation and biotransformation and are causing serious health disorders. The emerging contaminants are such hazardous chemi-

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cals that cause dreadful diseases in very small concentrations like nanograms per litre (ng/L) to micrograms per Litre and hence we should think of targeting the study of these contaminants on an urgent basis so that we can have some data and reports. Some pilot studies can be initiated as quickly as possible to look into this problem that has potential of disrupting human health as well as ecosystem to a great extent.

## Introduction

The consumption trend of pesticides in India usually works out to be, 76% of insecticides, 14% of fungicides and 10% of herbicides for commercial crops and cash crops like coffee, cotton, sugarcane, banana, and horticulture practices (WRI, 1998; Yadav *et al.*, 2015). Endosulfan, Hexachlorocyclohexane (HCHs) and DDT are among the most commonly used pesticides in India, out of which, HCH and DDT together contribute to approximately 67% of total pesticide consumption (Kumari *et al.*, 2001). Along these, Phorates, Chlorpyrifos and methyl parathion are also used in huge quantities in the modern agricultural practices. Hence, HCHs, DDTs and Endosulfan are included in the list of priority substances reported in directive 2008/105/EC (European Commission 2008) and their maximum environmental quality standards (EQSs) in inland surface water bodies are 0.2, 0.5 and 2.5 µg/l respectively. (European Commission, 2000).

Organochlorine pesticides were observed in the groundwater in Maharashtra and the groundwater was found to be more polluted than the surface water (Lari *et al.*, 2014).

Concerning the pharmaceutical compounds, it is being noticed that their entry to the wastewater treatment plants (WWTPs) has been likely possible due to the post consumption discharge to the sewer system and consequent passage into the WWTPs. The recent studies outline the fact that, for an individual pharmaceutical, contribution by means of discharge to the aquatic environment could be as high as 90% of the parent compound (Zuccato *et al.*, 2005). In WWTPs, a large variety of pharmaceuticals undergo a series of reactions resulting in a complex mixture of daughter compounds (Bound and Voulvoulis, 2005; Zuccato *et al.*, 2005) that may produce synergetic effects and become more bioactive than the parent compounds. The aim of this study is to assess the availability of Emerging Contaminants

(ECs) in water, sediment and Soil at selected locations of Pune District. This study also addresses to the Pharmaceutical Contaminants in the Waste Water samples from the Central Regions where the main city is located and the population is high. Further, to check the levels of Heavy Metals Contamination in Water, Sediment and Soil Samples.

## Materials and Methods

### Selection of Sampling Sites

In Order to study the contamination of Emerging Contaminants, Pune District area was divided into two parts, West and East. The Major rivers originate from western region, pass through Pune city and merge together in Ujani backwaters. Thus, sampling sites were divided into three – Upstream, Central and Downstream. Upstream is mostly covered with lush green jungles as well as major area is covered with agricultural lands. Moving down to central region, we observe that the Pune City is thickly populated and several pharma industries, Automobile industries, chemical fertilizer industries and several working hubs, STPs and ETPs etc are surrounding the central region of this district. Further moving down to east (downstream), Ujani Backwaters, the recipient of all the wastes and run off, is highly polluted. We collected seven samples, each of surface water, sediment and soil from seven locations of the Pune district both by Grab and Composite sampling technique. Two Waste water samples were also collected from two sewage treatment plants from the central region which is thickly populated.

### Selection of Contaminants to be studied

In this study, the pattern of the pesticide's usage in India specially in Central India was studied and several research reviews along with research papers were examined for the same. It was noted that HCHs, Endosulfan, Chlorpyrifos and Methyl parathion contributed to maximum of the whole share. The pharmaceutical compounds selected for this study comprises of group of medicines like analgesic and anti-inflammatory (acetaminophen), anti-histamine (ranitidine), anti-epileptic (carbamazepine), psychoactive (caffeine), antibiotics (azithromycin, levofloxacin, norfloxacin), β-Blockers (atenolol and metoprolol) and lipid regulator (atorvastatin) which are regular and very common drugs based upon the medicine consumption pat-

tern in India. Most commonly studied heavy metals are Cu, Cr, Cd, Co, Fe, Mg, Mn, Pb, Ni, Zn.

## Methodology

A high precision analytical weighing balance (Model Vibra and 420 ADJ, Adair Dutt, Mumbai, India) was used for weighing the certified reference standards of pesticides and environmental contaminants such as PAH and PCBs (CRS with >99 % purity). A high-speed homogenizer (DIAX-900, Germany), a vortex-mixer (Tarsons, Kolkata), a centrifuge (Kubota Corp., Tokyo, Japan), a low-volume concentrator (TurboVap® LV, Caliper Life Science, USA) and a micro-centrifuge (Microfuge Pico, Kendro, D-93 37520, Osterode, Germany) were used during the sample preparation process. PTFE syringe filters (0.22 µm) were purchased from Pall Life Sciences (Ann Arbor, MI, USA). Certified reference standards of environmental contaminants such as PAH, PCBs, and pesticides with >97% purity were procured by Sigma Aldrich (St. Louis, Missouri, United States and Bengaluru, India) and Chem Service (West Chester, United States). LC-MS grade and analytical Reagent (AR) such as acetonitrile, ethyl acetate, methanol and acetic acid was purchased from Thomas Baker (Chemicals) Pvt. Ltd (Mumbai, India). The HPLC grade pure water was acquired from a water purification system (Sartorius AG, Gottingen, Germany). The dispersive solid phase extraction (d-SPE) sorbents, namely primary secondary amine (PSA) and C<sub>18</sub> florisil and anhydrous magnesium sulphate (MgSO<sub>4</sub>) were purchased from Agilent Technologies (Bengaluru, India).

## Standard solutions

Individual pesticides, its metabolites and environmental contaminants such as PAH and PCBs' stock standard solutions (about 1000 µg/ml) were prepared by dissolving 10 mg of each analyte in 10 mL of LC-MS grade methanol, acetonitrile and ethyl acetate and stored at -20 °C. An intermediate standard mixture (10 µg/mL) and a working standard mixture (1 µg/ml) of pesticides and environmental contaminants such as PAH and PCBs were made in a glass vial by mixing appropriate proportions of the separate stock solutions and stored at -20°C. The calibration standards of 1, 2, 5, 10, 25 and 50 µg/L for UHPLC-MS/MS and 5, 10, 25, 50, 100 and 250 µg/l for GC-MS/MS were made through a series of

dilutions with solvent and control matrix.

## Samples collection

A set of samples for water, sediment and soil were similarly collected from various regions of Pune District, Maharashtra. All samples were labelled and packed in clean plastic bottles, transported on ice to the laboratory and stored at 0°C till further sample processing.

## Sample preparation

### Water and sediment samples

The sample preparation was done according to the QuEChERS method (Anastassiades *et al.*, 2003). A homogenized sample (10 ± 0.1 g) was extracted with acetonitrile (10 ml), after adding anhydrous magnesium sulphate (4 g) and sodium chloride (1 g). Subsequent to the phase separation, the supernatant was subjected to the d-SPE with 25 mg PSA + 150 mg MgSO<sub>4</sub>. For LC-MS/MS, 500 µl the extract was further diluted in 500 µl of methanol-acidified water (1:1). For the GC-MS/MS analysis, the cleaned extract was filtered through 0.2 µm membrane filter. Sample extraction was conducted within two days of collection. For each sample, duplicate samples and quality assurance/quality control (QA/QC) samples were analyzed for targeted pharmaceuticals. Samples were analyzed using high performance liquid chromatography tandem mass spectrometry (LC/MS/MS). The pesticides were examined similarly after extraction using Gas Chromatography Mass Spectrometry (GC/MS). Similarly, the heavy metal analysis was done using AAS (Atomic Absorption Spectrometry).

## Results and Discussion

In this study the concentration of detected levels of pesticides (contaminants) were noted to be ranging from ND to 720 µg/l. Mostly, very commonly used pesticides namely HCH, Endosulfan, Parathion-methyl and Chlorpyrifos have been closely studied. HCHs ranged from 60-275 µg/l, 112-390 µg/l, 130-412 µg/l in water, sediment and soil samples respectively.

Likewise, Endosulfan ranged from 72-660 µg/l, 91-698 µg/l, 110-720 µg/l in Water, Sediment and Soil Samples respectively.

Thereafter, Methyl Parathion was observed ranging from 12-88 µg/l, 21-92 µg/l, 28-102 µg/l in wa-

ter, sediment and soil samples respectively.

Later, Chlorpyrifos was noted within the range of 51-298 µg/l, 77-292 µg/l, 99-322 µg/l.

This study involves the study of the levels of the pollutants specially post monsoon. Mostly Pharmaceuticals, such as Acetaminophen, Levofloxacin, Azithromycin were present in high concentration ranging from 98µg/l, 65 µg/l, 305 µg/l respectively from the water samples collected from the Central Region, where it's thickly populated. In comparison with developed countries like USA, it was observed that these ECs were present in the waste water 50-65% in lesser concentration than in India.

This study also includes the determination of heavy metals (Cd, Cr, Cu, Co, Fe, Mn, Mg, Ni, Pd and Zn) in the samples collected so to proceed further with the heavy metal accumulation and speciation studies.

All of the mentioned heavy metals appeared to be above the permissible limits ranging from moderately toxic to highly toxic. We can observe the levels of pesticides, pharmaceuticals as well as heavy met-

als are quite high as we move from the upstream to the central and further more to the downstream regions. Such environmental contamination can result in harmful effects in three ways (Larsson, 2007). The presence of antibiotics in the wastewater may result in total failure of the wastewater treatment process by interfering the microbial population that helps in degradation of the complex organic matter present in the wastewater. Secondly, it can result in alteration in the microbial ecosystem, resulting into disturbance of the ecological balance. Thirdly, such large group of antibiotics in the environment can result in propagation and development of antibiotic-resistant microorganisms.

All these factors clearly indicate that the detailed and deep study of these contaminants, their sources to the water bodies and their possible serious impacts on the human health and environment must be studied closely. This being a serious matter of concern for Our Nation, India, should be regarded essential and regular monitoring of aquatic sources should be made compulsory. Research centres in

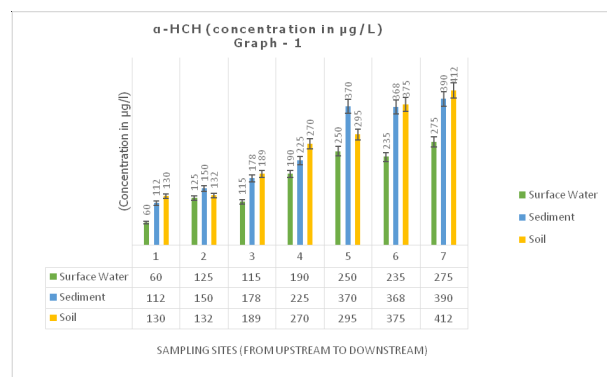


Table 1. Concentration of HCH in Water, Sediment and Soil samples (in µg/l)

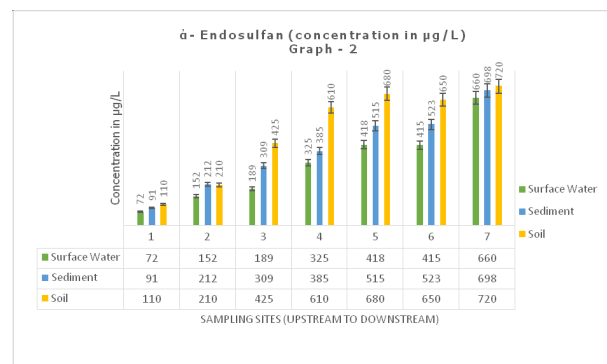


Table 2. Concentration of Endosulfan in Water, Sediment and Soil samples (in µg/l)

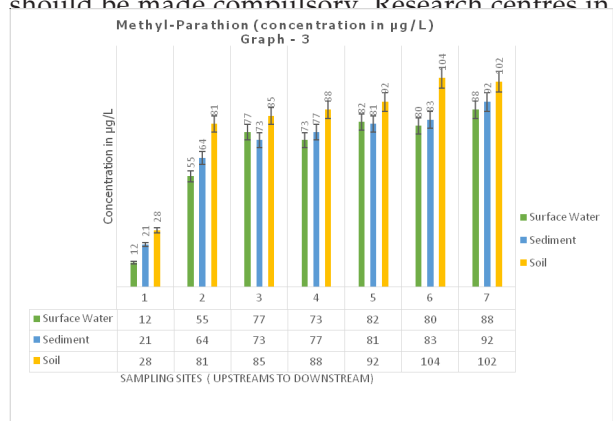


Table 3. Concentration of Methyl-Parathion in Water, Sediment and Soil samples (in µg/l)

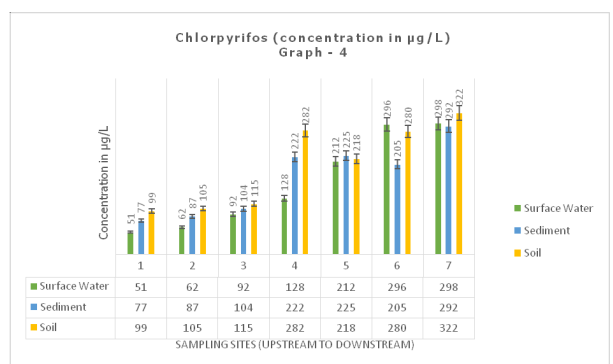
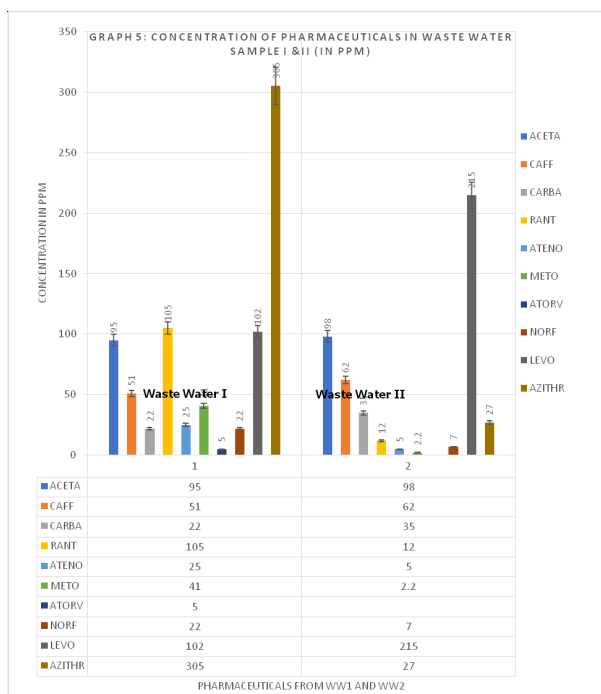
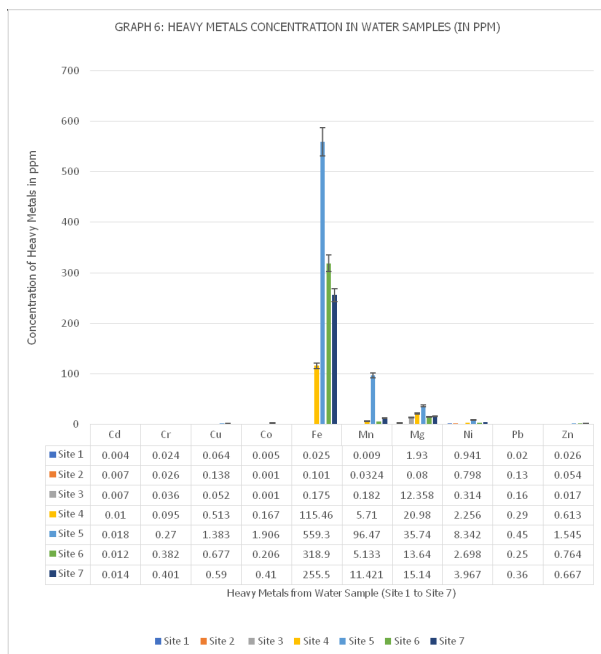


Table 4. Concentration of Chlorpyrifos in Water, Sediment and Soil samples (in µg/l)



**Table 5.** Concentration of Pharmaceuticals in Waste Water Samples I and II (in µg/l)



**Table 6.** Heavy Metal Concentration in Water Samples - Site 1 to Site 7 (in ppm)

India along with cooperation of regulatory bodies such as the CPCB and the National River Conservatory Directorate (NRCD) should increase scope of

their conventional monitoring of such toxic compounds.

### Conclusion

This study indicates the wide range of ECs in Surface Water, Sediment and Soil of Selected Locations of Pune District (Maharashtra, India). Among pesticides, the most commonly used chemicals like HCHs, Endosulfan, Methyl Parathion and Chlorpyrifos have been studied and concluded to be present in almost all the samples in more quantity that the permitted Environmental Quality Standards. Surely, this indicates not only the ill health of the current population but also as a threat to the future generation and as an alarming situation for the entire ecosystem as a whole.

In order to address to this situation, the keen study of ECs should be targeted on an urgent basis so that we can have some data and reports to understand and acknowledge the present situation and come up with regulatory initiatives and resolutions for a better future where human health as well as ecosystem will be safeguarded.

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