©2020. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http:// creativecommons.org/licenses/by-nc-nd/4.0/

2

1 Analysis of emerging contaminants: A case study of the underground and drinking water samples in Chandigarh, India

- Devika Vashisht,^a Amit Kumar,^a Surinder Kumar Mehta,^{a*}Alex Ibhadon^{b*} 3
- ^aDepartment of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, 4 Chandigarh 160 014, India. 5
- 6 ^b Department of Chemical Engineering, Faculty of Science and Engineering, the University of 7 Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom.
- 8 *Corresponding author: a.o.Ibhadon@hull.ac.uk, skmehta@pu.ac.in
- Abstract 9

10 The present report deals with the analysis of emerging contaminants and the quality of 11 drinking and underground water supply in Chandigarh, India. A water sampling monitoring and analysis was conducted by collecting a total of 54 samples of underground & drinking 12 13 water of Chandigarh to analyse the health risk associated with the spread of emerging 14 contaminants in the water sources. The quality of water samples was also assessed by 15 measuring the colour, odour, temperature, pH, electrical conductivity (EC), biological oxygen 16 demand (BOD), dissolved oxygen (DO), total dissolved solids/ salts (TDS) and hardness. For 17 the emerging contaminants (Endosulphan (ES) and Hexachlorohexane the estimation of (HCH)) in the water samples, an extraction procedure was carried out by dispersive liquid-18 19 liquid extraction method followed by analysis using gas chromatography-mass spectrometry 20 (GC-MS). The levels of ES and HCH obtained were compared with the drinking water 21 standards of the Bureau of Indian Standards (IS: 10500). The levels of HCH and ES in all the 22 water samples tested were found to be below the detection limit. It cannot be denied that the 23 industrial discharge and other agencies seems to be complying with the regulations. The Initiatives by the Central and State Govt of India seems to have created sensitivity and 24 25 awareness among the public specifically among the farmers. The limit of detection (LOD) were 1.0×10^{-3} and 2.4×10^{-3} ppm for ES and, HCH respectively. However, some water pollution 26

- 27 indicators such as TDS, EC, DO and total hardness were found to exceed the limits specified
- 28 by the Bureau of Indian Standards (BIS).

29 Keywords:

30 Emerging Contaminants; Chandigarh; Endosulphan; Hexachlorohexane; Underground water

31 List of Abbreviations:

- 32 BIS- Bureau of Indian Standards
- 33 BOD- Biological Oxygen Demand
- 34 DCM- Dichloromethane
- 35 DO- Dissolved Oxygen
- 36 DDT- Dichlorodiphenyltrichloroethane
- 37 EC-Electrical Conductivity
- 38 EDTA-Ethylenediamine tetraacetate
- 39 ES- Endosulphan
- 40 GC-MS- Gas Chromatography-Mass Spectrometry
- 41 HCH- Hexachlorohexane
- 42 IPCC- Intergovernmental Panel on Climate Change
- 43 ICP-MS- Inductively Coupled Mass Spectrometer
- 44 LOD- Limit of Detection
- 45 TDS- Total Dissolved Salts
- 46 QC- Quality Control
- 47 QA- Quality Assurance
- 48
- 49
- ---
- 50
- 51

52

1. Introduction

53 The global population of the world is expected to exceed 9.8 billion by 2050 [1]. The 54 rapid population growth is expected to have associated impacts such as increased demand for 55 food, water and other basic needs. This, in turn, will put more pressure on the agricultural sector 56 for increased production of food creating added stress on resources such as water and fuels etc. 57 [2]. About 70 % of the world's accessible freshwater is used for agriculture [3]. However, the 58 decreasing availability of drinking water makes it a valuable asset which should be used 59 sensibly. Water pollution pressures brought about by activities such as industrial discharge, 60 agricultural run offs, mining, and sewage disposal, have resulted in the contamination of both 61 surface and underground water resources. Conventionally, groundwater was assumed to be the 62 most unspoiled, cleaner and pristine source of water compared to surface water supply. However, in the past decades, the problems of ground water contamination and pollution are 63 64 widespread globally [4] and developing countries are most affected in particular [5]. To 65 overcome this global issue, promising development on waste-water remediation techniques based on different mechanisms such as organic ligand-based metal ion chelation [6], molecular 66 67 organic frameworks (MOFs) [7], nanomaterials [8], transformation of waste to useful materials 68 [9,10] etc. have been made and can be found in the literature.

69 India is one of the affected developing countries with 17% of the world's population 70 and 4% of the world's freshwater resources ranking it among the top ten water-rich countries 71 [11,12]. However, India is the third most polluted nation in the world and is currently 72 designated as water-stressed by the intergovernmental panel on climate change (IPCC) with 73 current utilizable freshwater much lower than international standards. Heavy dependence on 74 groundwater, years of limited rains and disproportionate demand for water due to rapid 75 population increase, urbanization and industrialization have put considerable stress on water 76 management [13,14]. Eighty percent of India's drinking water comes from groundwater, a 77 resource that is depleting and continuously being compromised by large scale discharge of 78 industrial and agricultural effluents, primarily emerging contaminants and toxic metals (Water 79 Aid Assessment, 2017) [15]. Emerging contaminants are naturally occurring or synthetic 80 chemicals which needs to be monitored and regulated in the environment. These contaminants 81 include pharmaceuticals, pesticides, metals, surfactants, industrial effluents, and solvents [16]. 82 Three EU-listed priority 'emerging contaminants' (Dichlorodiphenyltrichloroethane (DDT), 83 Endosulphan (ES) and hexachlorocyclohexane (HCH)), represent more than 67% of the total 84 pesticide used in India and their presence in water is causing the spread of antibiotic 85 ingredients, enabling bacteria to develop immunity to antibiotics, and creating superbugs [17].

Pesticides are the chemicals used directly or as mixtures in some solvents to prevent, fight and kill weeds, pests, fungi, and rodents [18]. The transfer of these harmful chemicals from the site of the application by runoff leads to bioaccumulation in living beings. About 3% of the total consumption of pesticides in the world is in the India. The contamination of surface and groundwater due to excessive use of pesticides is a serious threat to the environment and living beings [12].

92 The use of pesticides is highest in the Indian states of Maharashtra, Uttar Pradesh 93 followed by Haryana and Punjab. In 2016-17, a significantly increased consumption was 94 recorded in Maharashtra and Uttar Pradesh, while it declined in Punjab and Haryana [11]. In a 95 report by Centre for Science and Environment, the packaged bottles of water samples of about 96 17 different brands in the Delhi region were analysed for 12 organochlorines and 8 97 organophosphorus pesticides. Among the organochlorines, 94% of all the samples were 98 detected with γ -isomer of HCH (Lindane). 70.6 % of the samples were found to contain DDT. 99 The reason was found to be the water supply to Delhi which is majorly from the river Yamuna, 100 one amongst the most polluted rivers in India. Industrial and domestic waste from the city gets 101 deposited along the bank which was the major contributor to pollution [19].

102 According to a report by Mittal et al. [20], the advent of the Green Revolution in 1965 103 witnessed a tremendous increase in agricultural productivity. This Green Revolution filled the 104 bread bags with increased production of food and crops such as pulses, wheat, sugarcane, 105 cotton, etc. The revolution was based on the introduction of new and chemical fertilizers, 106 pesticides and high yielding seed varieties. Punjab was the hub of this revolution as it made the 107 farmers of Punjab self-sufficient and removed their dependency over other states. However, 108 due to excessive usage of pesticides, the Malwa region in the state of Punjab has recorded in 109 recent times a large number of cancer and reproductive disorder cases. The environmental, 110 occupational and social factors were found to be responsible for such a high pesticide 111 consumption.

112 The capital city of Punjab and Haryana is Chandigarh which is known for its wellmanaged, planned infrastructure and architecture in addition to its cleanliness, water supply, 113 114 electricity, transport, and sanitation facilities. When the 'City Beautiful' Chandigarh was planned, the availability of e subsoil water was adequate to meet the city's requirements. As 115 116 the population of the city increased, the tube wells dried up and surface water from Bhakra 117 dam main line was deployed to meet the city's water supply requirements. The supply of water 118 to the city of Chandigarh comes from two sources: (i) Surface water from Bhakra Main Canal 119 tapped at Kajauli (27 km from Chandigarh) (ii) Underground water pumped through deep bore 120 tube wells [21]. Despite the progressive developments, there are villages and rural areas 121 surrounding Chandigarh which lie close to the municipal domestic waste dumping ground and 122 industrial site whose activities usually lead to contamination of the water supply. In addition, 123 the nearby areas lying within 14-20 km of Chandigarh are fields where cultivation of various 124 crops is practiced by farmers. According to Mahajan et al. [22] and Puri et al. [23], many cases 125 of gastroenteritis were reported because of the contaminated water supply in January 2017. It 126 was identified in the study that mixing of the drinking water with sewage leakage from pipes

127 was the chief reason for the contamination and disease outbreak. The quality of groundwater 128 in the Chandigarh which is the major source of freshwater is susceptible to deterioration due to 129 primitive dumping practices, agricultural activities and rapid industrialization. The nearby 130 states of Chandigarh, i.e. Haryana, Punjab and Delhi have also reported poor quality of 131 groundwater. A comprehensive analysis of the Chandigarh's underground and drinking water 132 has been performed. The main objectives of the investigation were to assess the quality of water and monitor the levels of ES & HCH in the drinking and underground water samples of 133 134 Chandigarh and nearby region. To our knowledge, no report on the physio-chemical analysis 135 and monitoring of emerging contaminants, ES and HCH in the drinking and groundwater of 136 the Chandigarh has been carried out. However, the reports on examination of physiochemical 137 parameters of the drinking water in the neighbouring cities of Chandigarh are available in 138 literature [24-29]. In this study, an investigation of the levels of emerging contaminants and 139 physiochemical parameters has been carried out and interpreted as pollutant pressures.

140

2. Materials and Methods

141 **2.1. Study area**

142 Chandigarh is located at the foot of the Himalayan range. The city beautiful, 143 Chandigarh is fast emerging as one of the most advanced cities in India. It is spread over 114 144 sq. km, located at Shivalik Foot Hills, surrounded by Patiala ki Rao on the northwest and 145 Sukhna Choe on Northeast. The layout plan of the Chandigarh is as shown in figure 1.





147

Figure 1. Location of the Chandigarh in map of the India

The climate of the Chandigarh is sub-tropical with hot summer and cold winter except during the monsoon when the moist air of oceanic origin reaches the areas. The annual rainfall of the Chandigarh is 1061 mm, which is unevenly distributed over the area in 49 days. The southwest monsoon from the last week of June and withdraws at the end of September and contributes 80% of the annual rainfall.

153 The city has been divided into 6 zones for water supply. Each of these zones is supplied 154 water through independent water works. The Mother water works is Water Works, Sector 39, Chandigarh which receives water from Kajauli and various tube wells. At the water works-39, 155 156 the canal water received is treated at the water treatment plan. The raw water from Kajauli, 157 Punjab is transmitted through the main transmission to the water treatment plant in Sector-39. 158 The water is then treated, disinfected and stored which is further pumped to five different 159 waterworks. These waterworks further pump the water to the Chandigarh's water distribution 160 system [30].

161 **2.2. Sample Collection**

The sample collection was done during the months of February to June 2019. 1L ambercoloured glass bottles with polytetrafluoroethylene lined screw caps were used for sampling. The sample bottles were rinsed with deionized water and sterilized in hot air oven at 170 °C for 1h. Once sterilized, the bottles were allowed to be cooled. A total of 54 samples were collected (Figure 2). The specific sample point for tap and underground water is shown in figure S1. Tables S1 and S2 represent the location of the sample in terms of Longitude and Latitude and allotted sample IDs for tap and groundwater samples, respectively.

169 2

2.2.1. Sampling from a tap

170 To draw a sample from the tap, both the tap and its outlet was cleaned with a clean cloth. The 171 tap was opened until it reached its maximum rate of flow. After, the water flow for 1-2 minutes 172 to clear the service line, tap was closed. After sterilization, the tap was opened again, this time 173 allowing the water to flow for 1-2 minutes at a normal rate. Immediately, the sterilized bottle 174 was held under the water jet and filled up to the shoulder leaving the space in the bottle for shaking to be easier before the analysis. Securely labelled the bottle with, sample location, date, 175 176 time and sample ID. The bottle was placed into transport box and returned to the laboratory 177 within 24 h.





Figure 2. Location of all the sampling points of the study area

180 **2.2.2.** Sampling from hand pumps, tube wells and borewells fitted with a pump:

To collect samples from hand pumps, the pump was operated for at least 20 minutes. Cleaned the mouth of the pump thoroughly and using the same process described for tap, sterilized for a minute with the flame. The pump was operated for further 2 minutes and the sample was taken from the pump.

185 **2.2.3.** Sample transportation:

The water samples were chilled and made sure that the temperature did not cross 10 ^o C. After being transported, the samples were immediately shifted to the refrigerator until the extraction. Water samples were extracted within 24 h of the collection and the extracts were then stored in amber glass vials before the analysis using GC-MS. The EPA recommendations were followed to preserve the samples for various measurements (Table S3)

191

2.3.Reagents and standards

192 The standard reference samples of the pesticide ES and HCH were obtained from Sigma-193 Aldrich and were of high purity grade. The choice of pesticides for the study was based on the 194 statistics of the consumption of pesticides in India. The specifications of the target pesticides 195 are tabulated in Table S4. All the solvents used, including dichloromethane (DCM), hexane, 196 and ethanol were of analytical grade and were procured from Avra synthesis Pvt. Ltd. To carry out calibration studies, solutions of ES and HCH with concentrations 5.0×10^{-2} ppm, 5.0×10^{-3} 197 and 5.0×10^{-4} ppm were prepared by appropriate dilutions of the standard stock solution. 198 199 Aqueous solutions of standards were prepared by spiking a fixed amount of the working 200 standard. The extraction of the standard solutions was carried out using liquid-liquid extraction 201 procedure, analysed using GC-MS and the recovery % was noted.

202 **2.4. Instrumentation**

The analysis was carried out with Thermo Scientific Trace 1300 GC coupled with Thermo TSQ 800 Triple Quadrupole MS. The specifications of the GC-MS instrument used for the studies have been given in Table 1. The temperature was measured using well calibrated digital thermometer. Pico Lab India digital conductivity meter was employed for electrical conductivity meter. The conductivity meter was calibrated using a saturated KCl (0.01M) solution and the temperature was adjusted to 25 °C.

Item	Condition
GC	Make-Thermo Scientific
	Model- Trace 1300GC coupled with Thermo TSQ
	800 Triple Quadrupole MS
Detector	BP 5MS
Column	BP 5MS (30 m \times 0.25 mm \times 0.25 $\mu m)$
Pesticide	Organochlorines
Injection Volume	1.0 µL
Injector Temperature	260 °C
Carrier gas/ flow rate	Helium gas/ 1.2 mL/min
Oven Programming	Initial Temp 100 °C Hold Time: 1.0 min
	Temp1: 280 °C Hold Time: 13.0 min Rate 15
	°C/min
Total run time	26 min

200		
209	able 1. Specifications of GC-MS Instrument employed for the studies	S

210 **2.5. Methods**

211 The on-site analysis of samples was done to note down the colour, odour, pH, and temperature.

212 Rest of the parameters were recorded in the lab.

213 **2.5.1.** Colour and Odour

The colour of the water sample was noted down by direct observation without any filtration or centrifugation. Only simple visual comparison method was used for colour measurements. It is known that most of the organic and inorganic substances exhibit a characteristic odour. So, all the samples were directly observed for the odour.

218 **2.5.2.** Temperature

The behavioural characteristics of the aquatic organisms, solubility of salts, *etc.* are dependent on the temperature. The temperature was noted down with the help of a digital thermometer by immersing it in the water body and allowing sufficient time to get a constant reading.

222 **2.5.3. pH**

The pH of water is an index to signify the basicity/acidity of the water sample. The value of any sample may vary in the laboratory and it may not be the same as on the sample site because of the loss or absorption of any gases, sediments, etc. So, the pH value was taken at the time of sample collection. A 100 mL of sample was taken in a beaker and the pH was noted. Before making another measurement, the electrode was rinsed twice. This procedure was repeated thrice to get reliable value.

229 **2.5.4.** Total Dissolved Salts (TDS)

The presence of carbonates, hydrogen carbonates, chlorides, nitrates, sulphates of calcium,
magnesium, sodium, potassium and organic material contributes to TDS. The higher value of
TDS is indicative of the non-potability of the water for drinking purposes.

233 **2.5.5. Electrical Conductivity (EC)**

The electrical conductivity of the water is representative of the amount of salts present in it. The high value of the electrical conductivity indicates the presence of the high amount of the

dissolved salts in the water sample. It is the measure of the ability of an aqueous solution to
conduct electricity. A 100 mL of the water sample was analysed by immersing the cell into the
sample. The cell was washed thoroughly with distilled before and after the measurement.

239

2.5.6. Biological Oxygen Demand (BOD)

The BOD determines the amount of dissolved oxygen required for the organic break down of the organic material by the aerobic organisms. The water sample to be analysed were made sure to be free from chlorine, pH to be in the range of 6.5-7.5 and to have adequate amount of microbiological population.

244 Specialized barcoded, sequentially numbered, borosilicate glass and chemical resistant 300 mL 245 BOD bottles with no air space were used. One bottle with dilution water as blank was also 246 analysed. The DO was evaluated by using Winkler's procedure (titration method). Each bottle 247 was then kept in dark incubator for 5 days at 20 °C. After 5 days the DO reading was again 248 noted. To measure the BOD value of the water sample collected, the constant temperature was 249 maintained $(20 \pm 1^{\circ}C)$ in the chamber. The dilution water was aerated followed by the addition 250 of potassium phosphate, magnesium sulphate, calcium chloride and ferric chloride per 1 L of 251 dilution water to saturate the water with oxygen. The dilution water was placed in a constant 252 temperature chamber to maintain the temperature of 20 °C until the analysis and sample 253 dilution begun. A similar procedure was followed for the environmental sample. The sample 254 container was then placed in the temperature chamber and aerated for about 15 minutes. 255 Different dilutions of the sample were prepared and analysed. The sealed BOD bottles 256 containing samples were kept in the incubator for about 5 days at $20 \pm 1^{\circ}$ C for 5 days. 3 BOD 257 bottles per sample were used.

258 **2.5.7.** Total Hardness (EDTA Method)

Ca (II) and Mg (II) ions in the water samples sequester upon the addition of disodium ethylene diamine tetraacetate (Na₂EDTA). Eriochrome Black T was used as an indicator to detect the endpoint which showed red colour in the presence of Ca (II) and Mg (II) ions and blue colour when the ions were sequestered.

263

2.5.8. Procedure for Extraction of ES and HCH from water samples

(a) For ES [24]: Water samples collected in pre-cleaned and sterilized 500 mL amber-coloured
bottles were sealed with stopper covered with aluminium foil. The samples were then extracted
using hexane by using a liquid-liquid extraction procedure. A 300 mL water sample was
extracted with about 10% NaCl in a separating funnel thrice with DCM (2×50 mL) and once
with hexane (25 mL), shaking for two minutes and allowing the phase to separate for about 10
minutes. These extracts were dried over sodium sulphate and then in a rotatory evaporator. The
dried extracts were then dissolved in hexane and analysed using GC-MS.

271 (b) For HCH [31]: 500 mL of water sample along with 10% NaCl was taken in separating 272 funnel and shaken well to dissolve. This was followed by the addition of about 35 mL of DCM 273 and shaken well. The funnel was placed on a stand for 10 minutes to separate the organic and 274 aqueous layers. The DCM layer was collected in a conical flask. The partitioning procedure was followed twice using 40 mL of DCM again. A partitioning experiment was also performed 275 276 using 50 mL hexane. The entire organic layer was collected and combined to which 5-10 g of 277 anhydrous sodium sulphate was added. This was then concentrated on the rotatory evaporator 278 to 5 mL. To this extract, 20 mL of hexane was added and again concentrated to 2-3 mL. This 279 concentration process was repeated thrice. The residue was evaporated to dryness. The dried 280 extract was then taken in 1 mL of n-hexane for injection into the GC-MS sampler.

281 Quality Control (QC) and Quality Assurance (QA):

282 Adequate QC and QA procedures in analysis are required to obtain reliable results. For pH 283 measurements, before measuring the samples, the pH meter electrode was calibrated with 284 buffers of pH 4.0, 7.0 and 12.0. Similarly, for EC measurements, only glass beakers were used 285 for taking the samples. Calibration was done with KCl-1.41 µmhos/cm before measuring the samples. To measure TDS, a well calibrated digital TDS meter used. For minimum quality 286 287 control blank reagents, internal standard, and spiked samples were examined. All interferences 288 from glassware and reagents were examined and made sure to be under control by running a 289 blank reagent every time with the sample of interest. For all the samples, the recovery value 290 (Table 2) of all the field replicates was found to fall in the range of $R \pm 30\%$. The minimum 291 detection limit was calculated from the calibration curve using three laboratory field blanks. 292 The internal library search was also validated for spiked samples and the field samples were 293 then analysed using the library search available within the analysis software.

294 To perform the recovery studies, aqueous solutions of a known appropriate amount of standard 295 mixture were prepared, extracted and analysed using GC-MS to validate the extraction 296 procedure. The recovery rates were estimated for three different concentrations. The average 297 recovery and relative standard deviation at three concentrations are shown in table 2. For the 298 method qualification, the specificity of the analytical procedure was checked by analysing a 299 solvent blank and a prepared blank. Calibration curves of each analyte were generated to check 300 the linearity of the peak area versus concentration of HCH and ES. As clear from figure 3 301 excellent linear behaviour was observed for both the cases. Good recoveries were observed by 302 adding a known amount of analyte at different concentrations and respective % of RSD was 303 evaluated (Table 2). All the quality assurance parameters are enlisted in Table S5.



304

305

Figure 3. Calibration curve for (a) HCH and (b) ES

306	Table 2.	The recovery	rates obtained	for spiked	samples
-----	----------	--------------	----------------	------------	---------

Pesticide	Spiked	Measured	recovery %	mean	R. S. D. %
				recovery (%)	
НСН	0.200	0.175	87.5	82.0	5.9
	0.400	0.303	75.0		
	0.500	0.418	83.6		
ES	5.000	4.738	94.7	92.0	7.7
	7.000	6.004	85.7		
	9.000	8.608	95.6		

307

308 **3. Results and Discussion**

The results of various parameters including both on site and in lab analyses for different water samples collected are tabulated in Table 3. The colour and odour were found to be unobjectionable. The assessment of water quality is essential to get valuable information that is useful for the public, policymakers, and decision-makers to ensure public safety and health. The permissible values and the standards of the drinking water are shown in table S7.

314 Table 3. Various parameters of different sample locations

Sample	pН	Temp	TDS	DO	BOD	Total	Permanent	EC	ES	НСН
ID					(×10 ⁻ ³)	Hardness	Hardness			
12 TW	7.56±0.08	28.5	422	6.2	0.4	224	195	955.80±0.43	BDL	BDL
13 TW	7.42±0.20	28.5	289	6.1	0.5	153	129	849.03±0.86	BDL	BDL
5 TW	7.83±0.02	28.5	251	5.8	1.9	133	120	243.86±0.37	BDL	BDL
17 HP	7.40±0.00	28.6	204	5.1	0.2	108	96	827.76±1.68	BDL	BDL
18 TW	8.18±0.07	28.7	252	5.8	1.3	134	128	535.50±0.58	BDL	BDL
16 HP	8.91±0.38	28.5	543	6.3	2.2	340	222	1545.66±3.39	BDL	BDL
11 TW	7.76±0.02	28.7	232	5.6	0.4	123	115	1124.6±3.29	BDL	BDL
9 TW	7.41±0.03	28.6	261	5.8	0.5	138	129	950.33±2.86	BDL	BDL
15 TW	7.83±0.12	27.9	223	6.1	0.3	118	110	703.73±1.91	BDL	BDL
4 TW	7.83±0.08	29.8	556	5.8	0.4	295	278	427.93±5.79	BDL	BDL
14 TW	7.33±0.03	30	484	5.0	0.6	257	249	768.20±1.73	BDL	BDL
1 TW	7.11±0.000	28.4	295	5.8	0.4	156	148	987.30±1.76	BDL	BDL
2 TW	8.12±0.09	28.3	320	6.1	0.2	170	157	508.40±0.54	BDL	BDL
3 TW	7.65±0.02	28.6	274	7.1	0.5	145	138	521.73±3.18	BDL	BDL
10 HP	7.80±0.04	28.9	352	5.8	0.3	187	165	509.70±2.21	BDL	BDL
8 HP	7.13±0.03	27.6	280	6.1	1.3	148	134	1226.1±1.35	BDL	BDL
6 TW	7.47±0.02	30.1	279	6.6	0.6	148	138	972.36±0.53	BDL	BDL

22 TW	7.77±0.01	25.6	365	6.5	0.3	193	179	967.17±9.11	BDL	BDL
21 TW	6.49±1.37	27.8	254	6.2	1.1	135	130	560.77±10.73	BDL	BDL
7 TW	7.37±0.09	24.5	387	6.7	0.8	205	189	560.23±25.15	BDL	BDL
20 TW	7.23±0.07	28.6	467	6.4	0.3	248	243	473.20±16.49	BDL	BDL
19 TW	7.58±0.07	27.4	280	6.3	0.5	148	139	756.60±22.25	BDL	BDL
23 TW	7.72±0.11	28.4	245	6.9	0.6	183	178	366.03±17.21	BDL	BDL
І Тар	7.66±0.04	26.5	259	6.6	0.3	137	129	925.13±8.58	BDL	BDL
24 Tap	7.31±0.19	24.9	264	6.5	0.5	140	131	576.10±4.47	BDL	BDL
22 Tap	7.44±0.17	26.7	492	5.8	1.2	261	254	765.13±31.57	BDL	BDL
25 Tap	7.40±0.20	25.8	267	5.6	1.4	195	187	486.97±5.89	BDL	BDL
12 Tap	7.57±0.12	26.3	487	5.6	1.4	258	253	763.77±30.65	BDL	BDL
15 Tap	7.53±0.08	27.8	412	5.2	1.1	218	210	830.90±7.96	BDL	BDL
19 Tap	7.28±0.13	26.7	379	6.1	0.7	201	197	835.37±10.81	BDL	BDL
28 Tap	7.28±0.10	29.8	273	6.4	0.8	145	137	855.50±11.59	BDL	BDL
17 Tap	7.26±0.04	27.5	376	6.4	1.3	199	187	772.37±15.34	BDL	BDL
11 Tap	7.51±0.11	24.9	287	6.8	0.5	152	145	877.50±14.77	BDL	BDL
23 Tap	7.37±0.03	26.8	297	6.6	1.4	157	151	679.40±3.44	BDL	BDL
30 Tap	7.26±0.01	25.6	201	5.9	1.3	107	101	921.50±2.12	BDL	BDL
14 Tap	6.95±0.14	29.8	189	5.6	1.2	100	95	592.93±2.09	BDL	BDL

16 Tap	7.58±0.03	28.7	398	5.9	1.3	211	117	586.97±3.95	BDL	BDL
8 Тар	7.30±0.07	26.8	289	5.5	1.2	153	145	1135.77±14.17	BDL	BDL
5 Tap	6.92±0.05	27.4	359	5.7	0.9	190	178	487.97±4.14	BDL	BDL
6 Тар	7.37±0.04	24.8	290	6.3	0.7	154	149	568.30±18.60	BDL	BDL
7 Тар	6.85±0.02	26.1	328	6.1	0.9	174	169	636.43±12.01	BDL	BDL
10 Tap	7.75±0.06	25.3	284	6.5	1.1	151	145	434.87±3.75	BDL	BDL
21 Tap	7.64±0.01	25.5	192	6.3	1.3	102	98	460.13±29.86	BDL	BDL
26 Tap	7.65±0.06	24.6	279	6.7	1.6	148	138	730.13±1.67	BDL	BDL
27 Tap	7.60±0.07	27.6	293	5.7	1.4	155	146	742.43±7.18	BDL	BDL
29 Tap	7.35±0.03	28.8	267	5.9	1.5	142	137	844.40±20.58	BDL	BDL
2 Tap	7.74±0.02	25.4	310	6.1	1.3	164	157	733.37±5.05	BDL	BDL
9 Тар	6.95±0.06	26.3	330	6.8	1.4	175	165	956.20±19.45	BDL	BDL
3 Тар	6.42±0.22	26.6	430	6.3	1.2	228	219	1379.27±8.62	BDL	BDL
4 Tap	7.63±0.05	28.4	327	6.8	1.3	173	164	473.90±12.17	BDL	BDL
34 Tap	7.34±0.03	28.3	343	5.6	0.7	182	177	729.37±7.79	BDL	BDL
20 Tap	7.45±0.03	25.4	456	5.8	0.3	242	239	392.50±4.46	BDL	BDL
13 Tap	7.66±0.03	26.4	245	6.3	0.7	130	123	831.73±9.26	BDL	BDL
18 Tap	7.55±0.09	27.8	294	5.2	1.1	156	147	749.60±8.09	BDL	BDL

315 **Temperature**

The temperature of all water samples collected from the tap, tube wells, and hand pumps was found to lie in range 25 to 30 °C. (Figures S2 and S3)

318 **pH**

319 Although the hydrogen ions do not have any adverse effect on the health, it can cause many 320 further effects such as taste, stained laundry, greenish-blue staining of sinks and household 321 items, reduced efficiency of water-based appliances like geysers, heaters, etc. Most of the tap, 322 tube well and hand pump water samples collected for this report were found to be within the 323 acceptable range of 6.5 to 8.5 as per the guidelines by IS:10500 (Figure 4a). 52% of samples were found to have a pH value between 7.5 and 8.5. The pH values of the water samples were 324 325 found to lie between 6.42 and 8.91 with an average value of 7.47±0.38. So, the pH values of 326 all the samples lie between the permissible limits indicating no harmful impact from 327 agricultural and health perspectives. However, the pH values less than 6.5 can affect the aquatic 328 life, formation of necessary vitamins and minerals in humans and more than 8.5 could give 329 salty taste to water in addition to problems such as corrosivity to pipelines, eye irritations and 330 skin problems.





Figure 4. Percentage of the samples having different (a) pH (b) TDS (c) Hardness (d) BOD (e) DO and (f)
EC values

336 **TDS**

337 To parameterize the salinity of the drinking and groundwater samples, TDS measurements 338 were done. The bicarbonate, chloride and sulphate salts of Ca, Mg, K, Na give rise to the TDS. 339 The permissible limit of TDS for drinking water samples is up to 500 mg/L (Table S7). Most 340 of the water samples were observed to have the TDS value below the prescribed limit. TDS of 341 the study area varied between 120 to 556 mg/L with a mean value of 322.44±88.30. Less than 342 5 % of the samples collected were found to have the TDS value above 500 mg/L (Figure 4b). However, the values were not extremely higher than the prescribed limit suggesting suitability 343 344 for drinking. It is advised to boil the water before drinking. Discharge from these dumping sites 345 could be one of the chief reasons for the contamination of water and deviation of the physiochemical parameters beyond the prescribed limits. TDS of the study area varied between 346 347 120 to 556 mg/L with a mean value of 322.44±88.30.

348 **Total Hardness**

Another quality parameter is the hardness of the water. The permissible limit of the hardness 349 350 of water according to guidelines by IS: 10500 is 300 mg/L. The collected water samples from 351 various sites of the study area were found to lie in the range of 100 to 340 mg/L (Figure 4c) 352 with an average of 173.87±49.28. 98% of samples were found to have the hardness values below 300 mg/L which is the prescribed limit by IS: 10500. 33 samples were found to be 353 354 moderately hard and 1 sample (sample point 16HP) was found to fall in very hard category 355 (Table S6). Infact, the local authorities have marked the hand pump (16HP) red. There is a need 356 to stress the proper management of the domestic, industrial and agricultural waste to save the public health. The hardness of the water is due to the dissolved salts of Ca^{2+} and Mg^{2+} which 357 percolates through the earth's crust. Higher content of these salts restricts the use of water for 358 359 domestic, agricultural and industrial purposes.

360 **BOD**

BOD value is a parameter to evaluate the strength of waste in the water samples. The very low values of BOD are indicative of the good condition of the water. All the tap, tube well, and hand pump water samples were found to be within the permissible range (Figure 4d). All the samples were found to have the BOD values between nil to 5.0 which is the prescribed limit by IS: 10500. The higher the BOD value, the more quickly oxygen is depleted and less oxygen is available for the aquatic life which suffocates them and ultimately leads to their death.

367 **DO**

Like BOD, the content of dissolved oxygen displays the organic pollution associated with it. The limit prescribed for DO is 5 mg/L. The water samples of the study area had the DO value in the range of 5 to 7.1 mg/L (Figure 4e). 57% of samples were found to have the DO values greater than 6 which is the prescribed limit by IS: 10500. The DO values indicate the

modification due to aerobic/anaerobic mechanisms. Very low or high DO values can disturb
the aquatic and human life. In addition to this, water with very high DO values facilitates
corrosion of the water pipelines which restricts the smooth supply of water for domestic
purposes.

376 Electrical Conductivity (EC):

The EC parameterizes the extent to which electricity can pass through the water. 61% water samples collected for this report were found to be within the range of 200-800 μ S/cm (Figure 4f). 39% of samples were found to have the EC values above 800 μ S/cm. The EC values were found to fall between 243.86 and 1545.00 μ S/cm. No permissible limits are suggested by WHO (2011) and BIS (2012) for EC. Seepage from the nearby dumping zones could be one of the sources of contamination resulting into higher EC values and consequentially increased salinity and mineral content.

384 ES and HCH levels:

All the 54 water samples were found to have levels of emerging contaminants ES and HCH below the detection limit. The GC-MS spectrogram of the ES and HCH standards are shown in figures 5 (a & b). The spectrogram of sample 17Tap is shown in figure 5c. No peaks corresponding to characteristic retentions time of the target pesticide could be observed in any of the water samples which signified the presence of the target below the detection limit. The levels of ES and HCH being below detection limit indicated that the Initiatives by Central and State Govt. seems to create sensitivity among the public specifically among the farmers.





393 Figure 5. Chromatogram of a standard reference sample of (a) ES, (b) HCH and (c) water sample 17Tap

4. Conclusions

An analysis of 54 samples from drinking and underground water of Chandigarh and nearby region was carried for the presence of emerging contaminants ES, HCH and the assessment of water quality. The results from this study indicated the levels of pesticides ES and HCH, below the limit of detection in drinking and groundwater samples of Chandigarh and nearby regions. Some of the parameters such as colour, odour, temperature, pH and BOD were well within the prescribed limits for all the water samples. However, some of the physio-chemical parameters 401 i.e. TDS, EC, DO and TH which are directly related to water quality, were above the limits 402 specified by the BIS. The leachate from the nearby dumping areas could be responsible for the 403 enrichment of groundwater of Chandigarh with contaminants pushing the parameters beyond 404 the prescribed limits. Based on our findings, the water supplied to Chandigarh is safe for 405 drinking. However, some of the areas surrounding Chandigarh are heavily polluted by 406 domestic, industrial, agricultural and construction waste which is also indicated by the higher 407 physiochemical parameters of the water samples from regions such as the Mullanpur and 408 Dhanas region. As a solution to this, we recommend regular monitoring and assessment of the 409 parameters should be made at the water works. The levels of ES and HCH being below 410 detection limit indicated that the Initiatives by Central and State Govt. seems to create 411 sensitivity among the public specifically among the farmers. The use of Integrated Pest 412 Management (IPM) techniques such as light traps, bonfires, trap crops are being encouraged 413 as opposed to the use of pesticides. The use of bio-pesticides is being promoted by the 414 government at special subsidized and loans for farmers. Training courses in self-protection, use 415 of masks, use of spray pumps and measures for the disposal of pesticide containers are being 416 propagated among the farmers. All these efforts and initiatives by various government agencies 417 seem to be producing results. However, the high levels of some of the physic chemical 418 parameter is a matter of concern and needs to be addressed by the authorities so that they can 419 be regulated and brought down back below the limits specified by BIS. The local water quality 420 regulating authorities have marked water hand pumps with poor water quality in red colours to 421 warn the public of non-suitability of water for drinking. It is important that monitoring and 422 analysis of the water supply to Chandigarh is continuously carried out. It is recommended that 423 the potential of microbial and radiological material can be explored for the treatment of water. 424 We recommend few steps for prevention and solution to water pollution problem i.e. Treatment 425 of domestic sewage water and subsequent utilization of treated sewage water for irrigation of 426 public parks can not only prevent pollution of water bodies but also reduce the demand for 427 fresh water in the irrigation sector and become a useful resource for irrigation. Strict 428 enforcement of the laws should be made to ensure the safe disposal of the effluents from the 429 industries, avoiding the usage of non-biodegradable material like plastic can reduce the 430 pollution. Cleaning of rivers, lakes and other water bodies can also prevent water pollution. 431 The studies done so far are limited to a period of six months only and may vary depending on 432 seasons. The outcomes of this study can help in planning of remedial measures, management 433 and establishment of system for regular assessment of the groundwater quality to save the 434 public health.

435 **5.** Acknowledgments

The authors would like to acknowledge the Global Challenge Research Fund (GCRF)-Internal
Pump Priming fund 2019 by the University of Hull, Hull, the UK for the funding to carry out
the analysis on emerging contaminants. Authors thank Prof S. K. Kansal and Mr S. S. Bhinder
of UICET and SAIF/CIL, Chandigarh for providing environmental lab and instrumentation
facilities.

441 **6. References**

442 [1] World Population Prospects: The 2017 Revision, United Nations Department of Economics
443 and Social Affairs (UNDESA), 2017.

[2] M. F. P. Bierkens, Y. Wada, Non-renewable groundwater use and groundwater depletion a
review, Environ. Res. Lett. 14, 2019, 063002(1)- 063002(43).

446 [3] A snapshot of the world's water quality: towards a global assessment. Nairobi, United

447 Nations Environment Programme (UNEP), 2016.

- [4] The United Nations World Water Development Report 2017, Wastewater: The Untrapped
 Resource, Paris, United Nations Educational Scientific Cultural Organization (UNESCO),
 www.unesco.org/new/en/natural-sciences/environment/water/wwap/wwdr/2017-wastewater-
- 451 the-untapped-resource/.
- 452 [5] M. Kumar, G. Singh, T. Chaminda, P. V. Quan, K. Kuroda, Emerging water quality
 453 problems in Developing countries, Sci. World J. 2014, 1-2.
- 454 [6] D. Vashisht, S. Sharma, R. Kumar, V. Saini, V. Saini, A. Ibhadon, S. C. Sahoo, S. Sharma,
- 455 S. K. Mehta and R. Kataria Dehydroacetic acid derived Schiff base as Selective and Sensitive
- 456 Detection of Cu (II) in Aqueous Media, Microchem. J. 155, 2020, 104705 (1)-1040705(10)
- 457 [7] E. M. Dias, C. Petit, Towards the use of metal–organic frameworks for water reuse: a review
- 458 of the recent advances in the field of organic pollutants removal and degradation and the next
- 459 steps in the field, J. Mater. Chem. A, 3, 2015, 22484-22506.
- 460 [8] D. Vashisht, E. Sharma, M. Kaur, A. Vashisht, S. K. Mehta, K. Singh, Solvothermal
- 461 assisted phosphate functionalized graphitic carbon nitride quantum dots for optical sensing of
- 462 Fe ions and its thermodynamic aspects, Sprectrochim. Acta A 228, 2020, 117773.
- 463 [9] R. K. Liew, C. Chai, P. N. Y. Yek, X. Y. Phang, M. Y. Chong, W. L. Nam, M, H, Su, W.
- H. Lam, N. L, Ma, S. S, Lam Innovative production of highly porous carbon for industrial
 effluent remediation via microwave vacuum pyrolysis plus sodium-potassium hydroxide
 mixture activation, J. Clean. Prod. 208, 2019, 1436-1445.
- 467 [10] P. N. Y. Yek, R. K. Liew, M. S. Osman, C. L. Lee, J. H, Chuah, Y. K. Park, S. S. Lam,
- Microwave steam activation, an innovative pyrolysis approach to convert waste palm shell into
 highly microporous activated carbon, J. Environ. Manage, 236, 2019, 245-233.
- 470 [11] I. C. Yadav, N. L. Devi, J. H. Syed, Z. Cheng, G. Zhang, K. C. Jones, Current status of
- 471 persistent organic pesticides residues in air, water and soil and their possible effect on

- 472 neighbouring countries: A comprehensive review of India, Sci. Total Environ. 511, 2015, 123473 137.
- 474 [12] B. J. Bhadbhade, S. S. Sarnaik, P. P. Kanekar, Bioremediation of an industrial effluent
- 475 containing monocrotophos, Curr. Microbiol, 45, 2002, 346-9.
- 476 [13] S. K. Jain, A. Sharma, R. Kumar, Freshwater and its management in India, Int. J. River
- 477 Basin Management, 2, 2004, 259-270.
- 478 [14] S. Sabater, F. Bregoli, V. Acuna, D. Barcelo, A. Elosegi, A. Ginebreda, R. Marce, I.
- 479 Munoz, L. Sabater-Liesa, V. Ferreira, Effects of human-driven water stress on river
- 480 ecosystems: a meta-analysis, Sci. Rep. 8, 2018, 11462
- 481 [15] S. Nayak, Distributional Inequality and Groundwater Depletion: An analysis across major
- 482 states in India, Ind. Jn. of Agri. Econ. 64, 2009, 90-107.
- 483 [16] P. E. Rosenfeld, L. G. H. Feng, Emerging Contaminants, Risks of Hazardous Wastes,
 484 2011.
- [17] K. M. Gani, A. A. Kazmi, Contamination of Emerging Contaminants in Indian Aquatic
 Sources: First Overview of the situation, J. Hazard. Toxic Radioact. Waste, 21 (2017),
 04016026(1) to 04016026(12).
- 488 [18] J. H. Giliomee, ed., 2009, Pesticides, H. A. Strydom, N. D. King, Environmental
 489 management in South Africa, Second Edition.
- 490 [19] H. B. Mathur, S. Johnson, R. Mishra, A. Kumar, Analysis of Pesticide Residue in Bottled
- 491 Water-Delhi Region, Centre for Science and Environment, 2003, 1-40.
- 492 [20] S. Mittal, G. Kaur, G. S. Vishwakarma, Effects of Environmental Pesticides on the health
- 493 of Rural Communities in the Malwa Region of Punjab, India: A Review, Hum. Eco. Risk
- 494 Assess, 20, 2014, 366-387.

- 495 [21] Municipal Corporation Chandigarh, (2017, October 3), Water Supply, Retrieved from
- 496 <u>http://mcchandigarh.gov.in/?q=water-supply</u>.
- 497 [22] M. Mahajan, Prompt management averted an ongoing waterborne outbreak in the city
- 498 beautiful, Chandigarh: an example to be followed, East J. Med. Sci. 2, 2017, 49-50.
- 499 [23] S. Puri, S. S. Sarpal, A. Kumar, N. K. Goel, An outbreak of vibrio cholera in Vikas Nagar,
- 500 Chandigarh, India. Med. J. DY Patil Univ. 7 (2014), 147-151.
- 501 [24] A. Kaushik, H. R. Sharma, S. Jain, C. P. Kaushik, Pesticide pollution of River Ghaggar in
- 502 Haryana, India, Environ. Monit. Assess. 160, 2010, 61-69.
- 503 [25] C. Rout, A. Sharma, Assessment of drinking water: A case study of Ambala cantonment
- 504 area, Haryana, India. Int. J. Environ. Sci. 2, 2011, 977-987.
- 505 [26] P. Singh, J. P. Saharan, K. Sharma, S. Saharan, Physio-Chemical & EDXRF analysis of
 506 groundwater of Ambala, Haryana, India, Researcher, 2, 2010, 68-75.
- 507 [27] D. P. Gupta, Sunita, J. P. Saharan, Physiochemical analysis of Groundwater of selected
- 508 area of Kaithal City (Haryana) India, Researcher, 2, 2009, 1-5.
- 509 [28] H. S. Hundal, K. Singh, D. Singh, Arsenic content in ground and canal waters of Punjab,
- 510 North-West, India, Environ. Monit. Assess, 154, 2009, 393-400.
- 511 [29] A. Sharma, Physico-chemical analysis of tap water of Chandigarh (UT), India, Int. J. Curr.
- 512 Sci. 14, 2015, 51-54.
- 513 [30] D. Tiwari, A. K. Bhatia, Central Ground Water Board. (2013), Ground Water Information
- 514Booklet,Chandigarh.Retrievedfrom
- 515 <u>http://cgwb.gov.in/District_Profile/Chandigarh/CHANDIGARH.pdf</u>
- 516 [31] V. Dineshkumar, P. Logeswari, A. R. Nisha, P. T. A. Usha, Assessment and evaluation of
- 517 Hexachlorohexane (HCH) and Dichlorodiphenyltrichloroethane (DDT) residues and extent of

- 518 DNA damage in cattle of Kasargod District, Northern Kerala, India, Int. J. Pharm. Sci. Res. 5,
- 519 2014, 4741-4750.