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A Critical Evaluation of Mercury Contamination in Groundwater of Punjab

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Abstract

Groundwater in Punjab State has been over-exploited for irrigation purposes during the last few decades. As a consequence, it has been contaminated with heavy metals including Mercury, which is highly toxic for human health. The permissible limit for Mercury in groundwater is 0.001 mg/L (1ppb). Mercury concentration in groundwater has been estimated using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which is calibrated using a standard protocol. Ferozepur district in Punjab is a "Hot Spot" for Mercury contamination. The range of Mercury contamination varies from 0.001 mg/L to 0.038 mg/L in Punjab groundwaters. It is of geogenic origin but its source needs to be investigated to determine contribution of anthropogenic sources such as fertilizers, pesticides and coal-based thermal plants in Punjab. Tarn Taran district has recorded high values of Mercury in its groundwater after Ferozepur district. Department of Water Supply and Sanitation (DWSS) Reports of Punjab Government have been studied for assessment of health hazards to public. A critical examination of DWSS reports reveals that these are contradictory and confusing for general public. Mitigation measures need to be adopted for removal of Mercury from groundwater sources in Punjab.

Keywords: Groundwater, Mercury, DWSS, Permissible limit, Water Quality Reports

INTRODUCTION

Punjab is a northwestern State in India, bordering Pakistan to the west, and extends from 29°30' to 32°32' North and 73°55' to 76°50' East. It is surrounded by the Indian states of Jammu and Kashmir in the north; the hilly state of Himachal Pradesh in the east; and by the states of Haryana and Rajasthan in the south. It covers a geographical area of 50,362 square kms (Figure 1). During the sixties and the seventies, Punjab was at the forefront of India's green revolution started in Punjab during the nineteen sixties which made Punjab one of India's most prosperous and economically developed states. Agricultural production in Punjab was driven by three factors: the fertile alluvial soils, supply of free electricity to farmers, and use of surface irrigation and groundwater resources. Large tracts of land dedicated to agriculture were being irrigated by canals and deep-bore tubewells. Punjab has overexploited groundwater resources resulting in continuous lowering of groundwater levels, which proved to be a major cause of contamination beyond the permissible limits. Department of Water Supply and Sanitation (DWSS) of Punjab has an efficient network of water supply schemes (Figure 2) based on tubewells, hand pumps and canals.

The underground water reservoirs of Punjab are highly contaminated due to high levels of Uranium (U) and heavy metals. The Tribune (www.tribuneindia.com) has reported concerning high toxicity of U and heavy metals in the waters of Punjab during the last decade. The author has investigated the groundwater contamination in Punjab due to heavy metals (Uranium, Arsenic, Selenium) [1–8] and other contaminants (Fluoride, Nitrate, Sulphate) [9–12] based on data collected by

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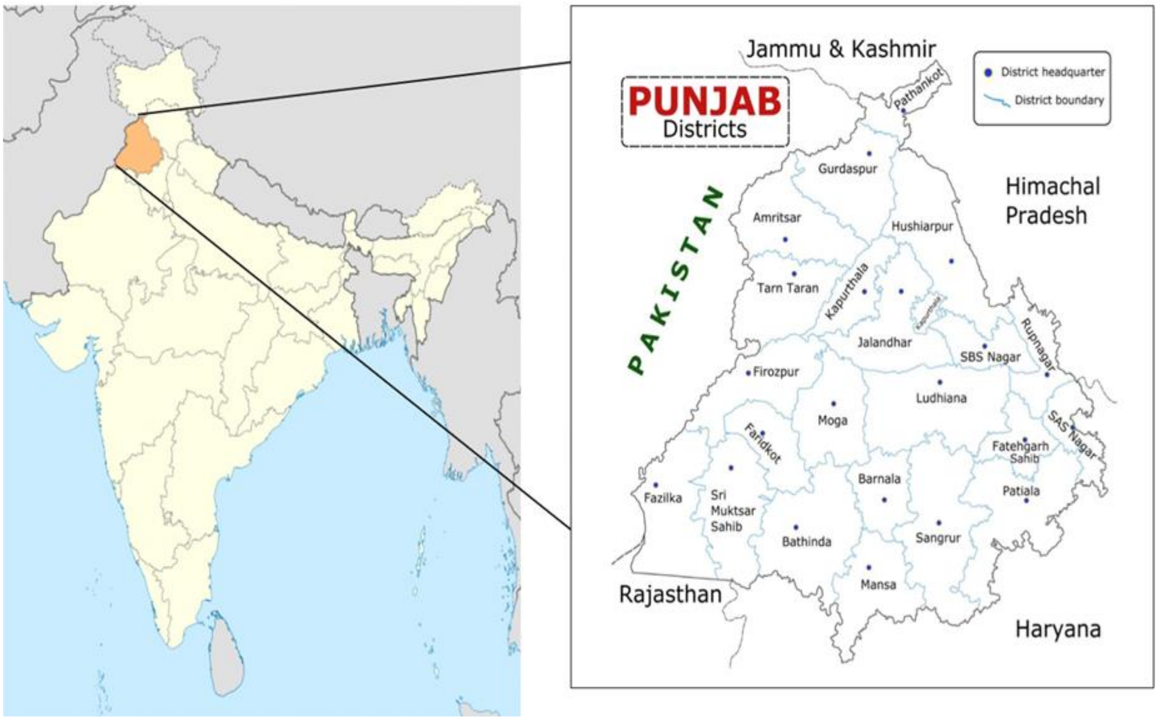

Figure 1. District Map of Punjab, India including districts with Mercury contamination.

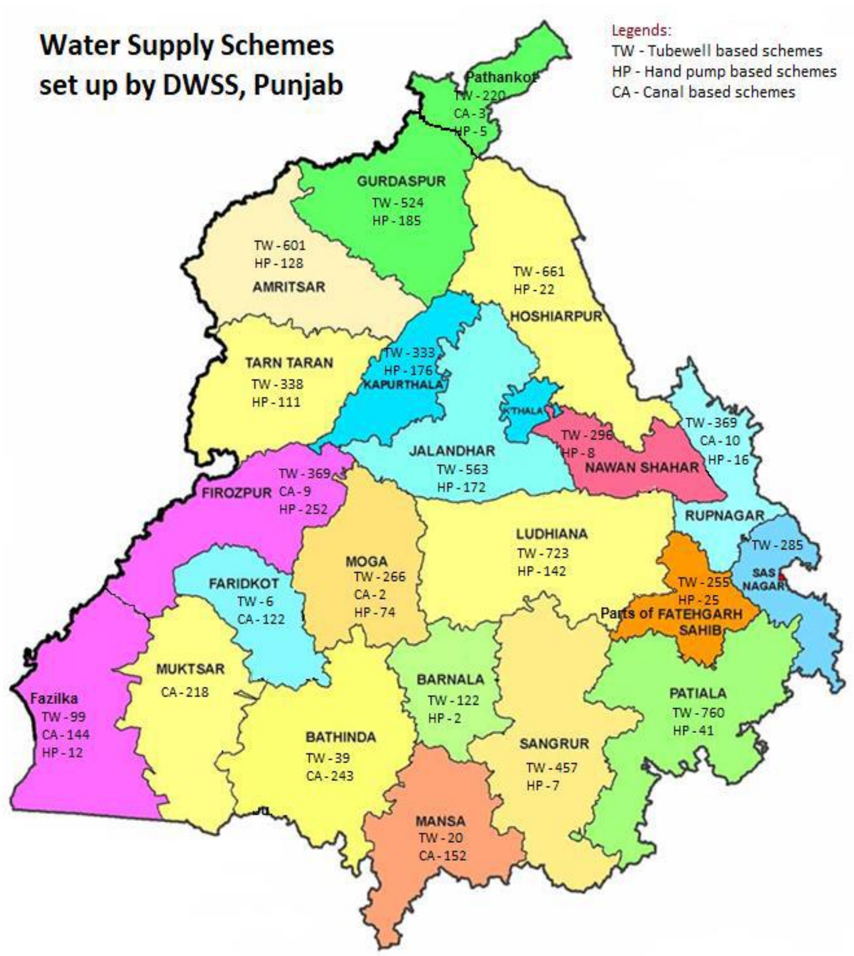

Figure 2. Water supply schemes in operation in Punjab [Ref. 13].

DWSS [13–15]. Groundwater samples were collected by DWSS from more than 50% habitations (villages) of Punjab for analysis using state of art instrumentation including Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ion Chromatography Mass Spectrometry (IC-MS) in its sophisticated laboratory set up in Mohali (Punjab).

Mercury (Hg) has been detected in 110 habitations out of a total of 6831 covered in DWSS survey but the number of quality- affected (QA) habitations having Mercury more than permissible limit is just 41 [14]. Most of the QA affected habitations due to Hg fall in the district of Ferozepur. The highest value of Hg (0.038 ppm) in groundwater is reported in Hero Kalan village of Mansa district. The analysis presented in this paper is also based on DWSS data collected in 3 phases during 2009 to 2016 and compiled in April 2016 under World Bank Funded Project [16]. Most of this data is available on Ministry of Water Resources, Government of India website [17].

Hg abundance in crustal rocks is very low compared with other elements. Groundwater contamination with Hg is found in many countries due to industrial sources. Mercury is considered to be an element that is injurious, even lethal, to living organisms. Its inorganic form is harmful as Hg vapor which can cause damage to respiratory, neural, and renal systems [18, 19]. The toxicity of organic form, methylmercury (CH_3Hg^+; MeHg), is much more than the inorganic form [20]. The incidents of methylmercury attacks on population have been reported in 1956 and 1971 in Minimata, Japan [21] and in rural Iraq [22], respectively, where it was found that the exposure affects the nervous system and can prove fatal. In mercury consumption, India has become a 'world leader' displacing USA. Mercury is used in various applications, for example, in chlor alkali plants, in pesticides, batteries, electrical and electronic gadgets, thermometers, dental amalgam fillings, paints, etc [23].

There are very few reports on study of Mercury contamination of groundwater and environment in India [24, 25]. I could find only one study of "Heavy Metal Pollution in Groundwater of Malwa Region of Punjab" by Sharma and Dutta [26] where Mercury contamination of Punjab groundwaters has been included. In the World Bank Report [16], contamination due to Arsenic and Fluoride is given top priority as these present the most urgent risk to population in Punjab, surpassing the risk of uranium, Considering the high level of toxicity of Hg, it is imperative to undertake such investigation. India is a signatory to the United Nations Minamata Convention of 10th October, 2013 at Kumamoto (Japan), to ban the production, import, export of Hg and its products by 2020 to protect human health and natural environment from the adverse effects of Hg emission [27]. On the contrary, India has enhanced its imports of Mercury many-folds to meet the demands of local industry during the last two decades [23].

SAMPLE COLLECTION AND ANALYSIS

Water samples were collected in 500 ml amber coloured superior quality plastic bottles from the area of study by the field staff of DWSS. The cleaning of bottles was carried out by washing first with soap solution and then with distilled water. Next step was rinsing the bottles with deionised water and drying with a blower. Groundwater from the source was allowed to flow freely for 5–10 minutes before collection in plastic bottles. Samples were subject to filtration using the 0.2-micron filters on the spot. 2 ml of conc. HNO_3 was added to each sample and labelled using scotch tape. Nitric acid solubilization is required before the determination of total recoverable mercury. The preservation and digestion of mercury in acid is used to minimize interferences by poly-atoms.

The mercury analysis of collected water samples has been done using Model 7700 Agilent Series ICP-MS following standard procedure in the Regional Advanced Water Testing Laboratory (RAWTL) in SAS Nagar (Mohali), India. RAWTL is accredited by the National Board for Accreditation of Testing and Calibration Laboratories (NABL). The method measures ions produced by a radiofrequency inductively coupled plasma (ICP). Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by Argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed, and valid corrections applied. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix [12]. Data analysis is done automatically by inbuilt system of ICP-MS. In addition to Hg, data for 40 more trace elements can be retrieved using ICP-MS.

CALIBRATION OF ICPMS

Calibration experiment is necessary for the estimation of concentration of heavy metals, including Mercury, in groundwater using the Agilent 7700 Series ICP-MS, with a detection limit ranging from <100 ppb to <1 ppt. The quantification was performed against the Certified Reference Material (CRM) 2A by Agilent Technologies (Part Number 8500-6940). Six concentration standards were meticulously prepared and introduced into the ICP-MS through an S10 auto-sampler unit. To establish a reliable calibration, a linear curve was constructed, exhibiting a high correlation coefficient ($R2 \geq 0.999$) for all selected metals. Following the calibration, one quality control (QC) check and analysis of two different standards (20 and 50 ppb) were conducted both before and after sample processing. The Relative Standard Deviation (RSD) was determined to be below 4%, aligning with the standards set by the Bureau of Indian Standards (BIS) for measuring drinking water samples.

This comprehensive methodology ensures the accuracy and precision of heavy metal concentration measurements, supported by rigorous calibration procedures and quality control checks in accordance with industry standards.

RESULTS AND DISCUSSION

The executive summary of World Bank Report [16] sums up the aim and objective of the Project as follows: “Punjab State wants to undertake rural drinking water supply on priority basis. Higher incidence of cancer was reported from some regions of Punjab along with reports of exposure of children to heavy metals in Punjab. As a consequence of these reports, the Department of Water Supply and Sanitation (DWSS) of Punjab Government conducted testing of all its water supply sources. The survey conducted by DWSS of the groundwater resources exploded the myth that water is generally of good quality. On the contrary, it was found to be contaminated with various trace elements which included heavy metals (uranium, lead, chromium, cadmium and nickel) and other elements like aluminium, arsenic, selenium, fluoride, and nitrate with concentrations higher than the permissible limits.

Punjab State is committed to supply improved quality water to its inhabitants after an objective study of its groundwater resources. The State allocated $59 million for its component to improve water quality through the World Bank financed Punjab Rural Water and Sanitation Sector Improvement Project (US$ 248 million, approved in 2015)”.

Mercury finds no mention in executive summary. However, there is a passing reference to Mercury on page 16 of Report [16] as follows: “With respect to mercury with acceptable and permissible limit of 1 μg/l, the same pattern emerges as for selenium. In Phase 1 and 2, few wells have been analysed. In Phase 1, 10 % (2 out 19 wells) and in Phase 2, 5 % (3 out of 61) of the analyses surpass the limit. On the other hand, in Phase 3 only 0.1 % of the concentrations are not acceptable (4 out of 3363). The highest observed value was 0.038 mg/l in Hero Kalan of Mansa district, followed by 0.02 mg/l in a well in SAS Nagar”. This report was prepared in June 2015 when all habitations of Punjab were not yet fully covered in this survey.

A CRITICAL EVALUATION OF DWSS REPORTS

The comprehensive report of trace elements contamination of groundwater was prepared by DWSS in April 2016 in which more than 50% habitations were covered in Punjab [16]. Mercury was considered under emergent parameters along with Aluminium, Chromium, Cadmium, Nickel, Lead, Selenium and Uranium. The mandatory parameters list included Arsenic, Fluoride, Nitrate, Iron and TDS (Total

Dissolved Salts). The stress was laid on the evaluation of mandatory parameters in groundwater supply of rural areas of Punjab relegating the emergent parameters to secondary consideration under the World Bank Project.

The World Bank Project Report has listed 110 villages with Mercury contamination of groundwater in the range of 0.001 mg/L (permissible limit) to 0.038 mg/L (Table 1). Ferozepur district turned out to be a "Hot Spot" with 57 villages contaminated with Mercury but all within the permissible limit. Out of 26 districts surveyed, 8 were contaminated with Mercury. The districts showing higher level of Mercury than the permissible limit include: Hoshiarpur (3), Bathinda (2), Ludhiana (6), Roop Nagar (10), SBS Nagar (7), Mansa (4), Moga (3), and Patiala (2). Ferozepur district did not report Mercury higher than the permissible limit. The same was true of Fazilka district. No correlation of Mercury with depth of groundwater sources (tubewells) was established.

In 2018, DWSS published its Annual Water Quality (AWQ) Report [13] showing 2989 QA habitations due to both mandatory and emerging parameters in groundwater of Punjab. This report shows 17 QA habitations due to high concentration levels of Mercury, out of which 2 had been shown treated under short term measures, and remaining 15 to be treated under long term measures of DWSS. List of QA districts includes Jallandhar (7), Ludhiana (2), Fatehgarh Sahib (2), SBS Nagar (2), Roop Nagar (1), and Patiala (1). Surprisingly, this report fails to show any QA habitation in districts of Malwa belt (Ferozepur, Bathinda, Mansa, Moga) as reported in World Bank Report [2016]. This report looks highly controversial and contradictory to World Bank Report. No reasons have been given for this discordance.

In 2021, DWSS presented its AWQ report [14] on 1st April showing 1525 QA habitations (Table 2). The number of QA habitations due to Mercury is 41 (Figure 3) in four districts of Ferozepur (28), Fazilka (9), Gurdaspur (3), and Ludhiana (1). This report does not match with previous reports but shows that groundwater in Malwa districts is contaminated due to Mercury concentration higher than the permissible limit. Mercury contamination is fifth in sequence after Arsenic, Fluoride, Uranium, and Selenium as reported in Water Quality Status of Punjab.

Table 1. Mercury concentration in groundwater of Punjab as reported in DWSS Report [16]

S. N.	Name of district	Name of village	Source of groundwater	Mercury conc.(mg/L)
1	Amritsar	Sialka	Tubewell	0.001
2	Amritsar	Ibban Kalan	Tubewell	0.001
3	Bathinda	Basti Market Committee	Handpump	0.002
4	Bathinda	Jethuke	Handpump	0.002
5	Ferozepur	Khushal Singh Wala	Tubewell	0.001
6	Ferozepur	Bhagwan Pura	Tubewell	0.001
7	Ferozepur	Tega Singh Wala	Tubewell	0.001
8	Ferozepur	Usman Randhawa	Tubewell	0.001
9	Ferozepur	Attari	Tubewell	0.001
10	Ferozepur	Sultan Wala	Tubewell	0.001
11	Ferozepur	Basti Ram Lal	Tubewell	0.001
12	Ferozepur	Basti Bagicha Singh	Tubewell	0.001
13	Ferozepur	Basti Chamre Wali	Tubewell	0.001
14	Ferozepur	Basti Khan Ke	Tubewell	0.001
15	Ferozepur	Basti Jhuge Kahan Singh	Tubewell	0.001
16	Ferozepur	Basti Ram Lal	Tubewell	0.001

17	Ferozepur	Basti Bagicha Singh	Tubewell	0.001
18	Ferozepur	Basti Khan Ke	Tubewell	0.001
19	Ferozepur	Basti Bhane Wali	Tubewell	0.001
20	Ferozepur	Basti Ladhu Wali	Tubewell	0.001
21	Ferozepur	Basti Chamre Wali	Tubewell	0.001
22	Ferozepur	Basti Walia Wali	Tubewell	0.001
23	Ferozepur	Basti Ladhu Wali	Tubewell	0.001
24	Ferozepur	Basti Walia Wali	Tubewell	0.001
25	Ferozepur	Dulchi Ke	Tubewell	0.001
26	Ferozepur	Hamad Wala	Tubewell	0.001
27	Ferozepur	Baggu Wala	Tubewell	0.001
28	Ferozepur	Basti Gainder	Tubewell	0.001
29	Ferozepur	Nizam Wala	Tubewell	0.001
30	Ferozepur	Khan Ke Ahil	Tubewell	0.001
31	Ferozepur	Padhri	Tubewell	0.001
32	Ferozepur	Bhamba Singh Wala	Tubewell	0.001
33	Ferozepur	Palla Megha	Tubewell	0.001
34	Ferozepur	Wan	Tubewell	0.001
35	Ferozepur	Sayian Wala	Tubewell	0.001
36	Ferozepur	Kasu Begu	Tubewell	0.001
37	Ferozepur	Rukna Begu	Tubewell	0.001
38	Ferozepur	Pandori Khatrian	Tubewell	0.001
39	Ferozepur	Wara Mansurwala	Tubewell	0.001
40	Ferozepur	Basti Gajjan Singh	Tubewell	0.001
41	Ferozepur	Satiye Wala	Tubewell	0.001
42	Ferozepur	Satiye Wala	Tubewell	0.001
43	Ferozepur	New Colony (BSF)	Tubewell	0.001
44	Ferozepur	Pioneer Colony	Tubewell	0.001
45	Ferozepur	Alle Wala	Tubewell	0.001
46	Ferozepur	Basti Gajjan Singh	Tubewell	0.001
47	Ferozepur	Pioneer Colony	Tubewell	0.001
48	Ferozepur	Alle Wala	Tubewell	0.001
49	Ferozepur	Sudh Singh Wala	Tubewell	0.001
50	Ferozepur	Kothe Ambar Har	Tubewell	0.001
51	Ferozepur	Ambarher	Tubewell	0.001
52	Ferozepur	Jhatra	Tubewell	0.001
53	Ferozepur	Khosa Dal singh	Tubewell	0.001
54	Ferozepur	Marur	Tubewell	0.001
55	Ferozepur	Gogoani	Tubewell	0.001
56	Ferozepur	Jhita	Tubewell	0.001
57	Ferozepur	Basti Baghe Wala	Handpump	0.001
58	Ferozepur	Bhadru	Tubewell	0.001
59	Ferozepur	Gillan Wala	Tubewell	0.001
60	Ferozepur	Lakha Bubna	Handpump	0.001
61	Hoshiarpur	Chak Kalan	Tubewell	0.001
62	Hoshiarpur	Badial	Tubewell	0.001
63	Hoshiarpur	Chak Sheru	Tubewell	0.001

64	Hoshiarpur	Ravidas Nagar Adamwal	Handpump	0.003
65	Hoshiarpur	Kotla Gaunspur	Handpump	0.003
66	Hoshiarpur	Adamwal	Handpump	0.003
67	Hoshiarpur	Mirpur	Tubewell	0.001
68	Hoshiarpur	Mehadpur	Tubewell	0.001
69	Hoshiarpur	Tanda Churia	Tubewell	0.001
70	Hoshiarpur	Jharing	Tubewell	0.001
71	Kapurthala	Mirpur	Handpump	0.001
72	Kapurthala	Harijan Basti	Tubewell	0.001
73	Ludhiana	Dakha	Tubewell	0.002
74	Ludhiana	Rajgarh	Tubewell	0.004
75	Ludhiana	Rano	Tubewell	0.003
76	Ludhiana	Raul	Tubewell	0.003
77	Ludhiana	Gazipur	Tubewell	0.002
78	Ludhiana	Tanhur	Tubewell	0.002
79	Mansa	Aklian	Tubewell	0.005
80	Mansa	Bir Khurd	Tubewell	0.005
81	Mansa	Hero Kalan	Tubewell	0.038
82	Mansa	Dodra	Tubewell	0.002
83	Moga	Langiana Kalan	Tubewell	0.006
84	Moga	Langiana Khurd	Tubewell	0.006
85	Moga	Abadi of Langiana purana	Tubewell	0.006
86	Moga	Balkhandi	Tubewell	0.009
87	Patiala	Nathu Majra	Tubewell	0.004
88	Patiala	Panjeta	Tubewell	0.002
89	Patiala	Jogewala	Tubewell	0.001
90	Patiala	Ballad Kalan	Tubewell	0.001
91	Ropar	Kalsera	Tubewell	0.011
92	Ropar	Lamlehri	Tubewell	0.004
93	Ropar	Nanowal	Handpump	0.004
94	Ropar	Raipur	Handpump	0.004
95	Ropar	Gujjar Basti Jhinjri	Tubewell	0.004
96	Ropar	Mianpur	Tubewell	0.004
97	Ropar	Rampur	Handpump	0.004
98	Ropar	Bacholi	Handpump	0.004
99	Ropar	Jhajjar	Tubewell	0.004
100	Ropar	Bani	Tubewell	0.004
101	SAS Nagar	Padiala	Tubewell	0.001
102	SBS Nagar	Khabdalpur	Tubewell	0.003
103	SBS Nagar	Phirni Majara	Tubewell	0.003
104	SBS Nagar	Rurki Kalan	Tubewell	0.003
105	SBS Nagar	Ghamour	Tubewell	0.003
106	SBS Nagar	Sajawalpur	Tubewell	0.003
107	SBS Nagar	Bharapur	Tubewell	0.003
108	SBS Nagar	Kathgarh	Tubewell	0.020
109	Tarn Taran	Kot Bhudha	Tubewell	0.001
110	Tarn Taran	Bhahuwal	Tubewell	0.001

Table 2. A comprehensive report of groundwater contaminants in Punjab [Ref. 14].

Name of district	Arsenic	Fluoride	Uranium	Selenium	Mercury	Iron	Nitrate	Mixed parameter (cadmium, Lead, Nickel, Sulphate, etc.	Grand total
Amritsar	332	0	0	0	0	1	0	0	333
Barnala	0	4	10	2	0	0	5	1	22
Bathinda	0	3	1	0	0	0	0	1	5
Faridkot	5	5	0	0	0	0	0	7	18
Fatehgarh Sahib	2	40	3	2	0	1	3	3	54
Fazilka	12	10	29	0	9	4	0	31	95
Ferozepur	46	13	43	0	28	2	14	2	148
Gurdaspur	224	0	0	0	3	0	0	2	229
Hoshiarpur	13	0	8	4	0	0	0	0	25
Jalandhar	1	0	0	15	0	1	2	6	25
Kapurthala	6	0	0	1	0	1	0	1	9
Ludhiana	1	1	4	18	1	1	9	0	35
Mansa	2	0	0	0	0	0	4	0	6
Moga	3	4	42	2	0	2	2	0	55
Patiala	12	185	9	4	0	7	0	19	236
Ropar	30	0	0	9	0	0	10	0	49
Sangrur	1	5	21	4	0	1	3	4	39
SAS Nagar	2	5	0	0	0	0	0	0	7
SBS Nagar	0	1	0	11	0	0	3	0	15
Tarn Taran	111	5	1	2	0	0	1	0	120
Grand Total	803	282	171	74	41	21	56	77	1525

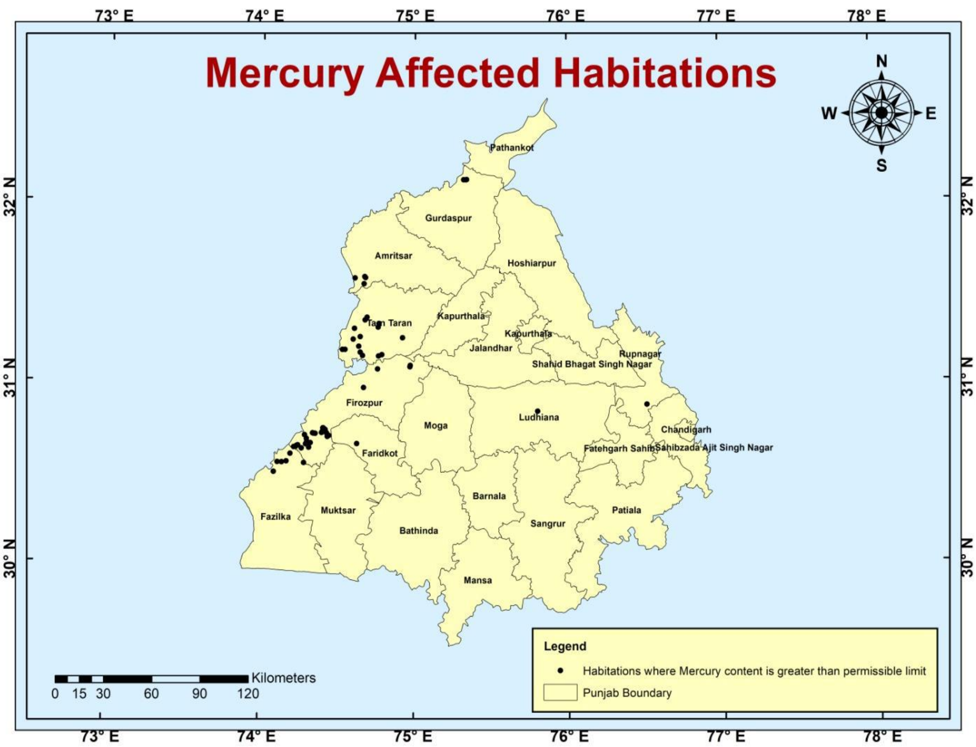

Figure 3. Mercury contaminated habitations in Punjab shown by black dots [Ref. 14].

DWSS annual water quality report for financial year 2021-22 was released on 1st April 2022 [15]. It classifies Mercury among the heavy metals (Iron, Selenium, Cadmium, Nickel, Chromium, Lead etc.) and not as an independent contaminant. The report claims 1381 QA habitations and 144 quality improved habitations over and above the 2021 report. It records: "Hence, out of 1525 quality affected habitations, water quality was found within permissible limits in 144 habitations. Therefore, water quality in 1381 habitations was found to be above permissible limits and hence was found quality affected".

In this report [15], there lies another "Big Surprise". The highly contaminated QA districts due to Mercury include Tarn Taran (11), Ferozepur (4), Fazilka (4), Ropar (1), and Ludhiana (1). Hence, the focus of DWSS report has shifted from Malwa to Majha. Tarn Taran groundwater is contaminated by Uranium, Arsenic, and Mercury; 15 villages have Mercury contamination; 4 in permissible limit and 11 above the limit. In all 21 villages need to be decontaminated in Punjab for Mercury.

It was expected that DWSS report for 2023 will be released in April but our expectations have been belied. The mitigation measures for Arsenic and Uranium have been given top priority but there is no mention of Mercury in these reports. Punjab has implemented RO System as a mitigation measure but it has failed to perform effectively and being discarded. AMRIT technology developed by IIT Madras was employed to remove Arsenic and Iron in some districts of Majha belt [7]. Ultimately, Punjab has opted for use of Canal water for water supplies to residences, which is most economical compared with other mitigation technologies in vogue.

Devi et al. [24] report impact of urbanisation on Mercury levels in Gomti river basin of Lucknow. DWSS reports concern only rural areas of Punjab and no data is collected on Punjab rivers. However, Sharma and Dutta study [27] of heavy metals pollution in groundwater of Malwa region revealed that groundwater samples of all villages investigated in Ferozepur district were found to be contaminated with Mercury, thus making it a "Hot Spot".

CONCLUSIONS

1. Mercury contamination of groundwater in Punjab is of serious concern due to its health hazards.
2. There is a need to investigate contribution of anthropogenic sources including fertilizers, pesticides and thermal plants.
3. Groundwater reports issued by Department of Water Supply and Sanitation (DWSS) of Punjab Government are highly contradictory and confusing for the general public.
4. A high-level committee of experts, including Chemists, Geologists, and Hydrologists must be constituted to advise Punjab Govt. and World Bank of mitigation measures for elimination of Mercury from water resources in Punjab.
5. Industrial release of Mercury as an effluent must be curbed in Punjab.

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