

Heavy Metals Contamination in Groundwaters of Punjab: A Man-made Curse and its Mitigation

Hardev Singh Virk^{1*}

Abstract

The curse of heavy metal contamination in groundwaters of Punjab state is causing health hazards for the population of Punjab. It is not so much a natural disaster as its origin can be traced to a man-made crisis in Punjab. Potentially toxic elements, including high levels of Uranium (U) contamination in the Malwa belt of Punjab, Arsenic contamination in the Majha belt, and Selenium contamination in the Doaba belt of Punjab, have been reported by the author in groundwater of Punjab. Department of Water Supply and Sanitation (DWSS) of Punjab Government has collected and conducted groundwater survey of almost all villages of Punjab state to determine heavy metal contents of groundwater in the underground water table of Punjab. Groundwater quality data pertaining to heavy metals, such as Arsenic, Selenium, Mercury, Iron, and Aluminum, have been also reported. The present study pertains to trace elements, namely heavy metals like Nickel, Cadmium, Chromium, and Lead in groundwater of Punjab state. The present investigations reveal that Nickel and Cadmium are both equally rampant in Punjab with concentration variation from 0.02 mg/l to 0.947 mg/l and 0.003 mg/l to 0.162 mg/l, respectively. Chromium concentration in groundwater shows a variation from 0.053 mg/l to 0.308 mg/l. Almost 80% of villages with high chromium concentration fall within the boundaries of Hoshiarpur district. Lead is highly toxic and its concentration in groundwater above the safe limit has been found in 708 habitations with a variation from 0.010 mg/l to 0.479 mg/l. The origin and occurrence of heavy metals may be traced to overexploitation of groundwater resources in Punjab.

Keywords: Groundwater, heavy metals, contaminants, health hazards, mitigation

INTRODUCTION

Guru Nanak in his composition Japuji, a text in Sri Guru Granth Sahib, wrote more than 500 years about the importance of clean air and water in human life: “*Pawan guru, pani pitta, mata dharat mahat*” (Air is the Guru, Water is the Father, and Earth is the Great Mother of all). It is a sad story that followers of Guru Nanak in Punjab have ignored the implications of his message and overexploited the groundwater resources to such an extent that Punjab is on the brink of a disaster. Heavy metals in groundwaters of Punjab are creating health hazards for the general population. Uranium poisoning in Punjab first made news in March 2009, when a South African Clinical Metal Toxicologist, Carin Smit [1], visiting Faridkot city in Punjab found surprisingly high levels of uranium in 88% of the blood samples collected from amongst mentally retarded children in the Malwa region of Punjab. Uranium (U) distribution in the groundwaters of Punjab and its potential health hazards has been studied in collaboration with Department of Water Supply and Sanitation (DWSS) of Punjab Government, SAS Nagar (Mohali) during the last decade, mostly in the Malwa belt of Punjab [2–10].

*Author for Correspondence

Hardev Singh Virk
E-mail: hardevsingh.virk@gmail.com

¹Professor of Eminence in Physics Department (Honorary) Sri Guru Granth Sahib World University, Fatehgarh Sahib, Punjab, India

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After U investigations in groundwater, the study of other heavy metals, for example, Arsenic, Selenium, Iron, and Mercury [11–16] was undertaken. Arsenic contamination is widespread in the Majha belt of Punjab consisting of districts of Amritsar, Gurdaspur and Tarn Taran [11–13]. Health risk assessment of Arsenic and other potentially toxic elements (PTEs) in groundwater of Majha belt reveal high risk of cancer due to ingestion of groundwater [14]. Selenium contamination occurs in groundwater of Doaba belt consisting of districts of Jalandhar, Kapurthala, and Hoshiarpur [15]. Mercury contamination is widespread in Ferozepur and Tarn Taran districts of Punjab [16].

It will be of interest to readers of Water Pollution and Purification Journal that DWSS has collected data from more than 50% habitations (villages) of Punjab and analysed in its sophisticated laboratory set up in Mohali (Punjab), using state of art instrumentation including ICPMS (Inductively Coupled Plasma Mass Spectrometry) and Ion Chromatography Mass Spectrometry (IC-MS). 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. The heavy metals included in the present study are Nickel, Cadmium, Chromium, and Lead. The samples having contents more than permissible limits set by BIS (India) [17] are included in this study. The annual water quality reports of DWSS and World Bank Project reports have been the basis of present study [18–22]. Most of this data is available on Ministry of Water Resources, Government of India website [23].

LOCATION MAP AND WATER SUPPLY SCHEMES IN PUNJAB

Punjab state extends from the latitudes 29.30° North to 32.32° North and longitudes 73.55° East to 76.50° East. Punjab is bounded on the west by Pakistan, on the north by Jammu and Kashmir, on the northeast by Himachal Pradesh and on the south by Haryana and Rajasthan (Figure 1). Punjab is an agricultural state having most fertile land in the Indian sub-continent. Punjab forms a part of the Indus River basin, one of the most prolific groundwater reservoirs on this planet. However, due to overexploitation of groundwater for extensive farming, the water table has gone down at an alarming rate causing groundwater contamination due to heavy metals. DWSS of Punjab Government has implemented water supply schemes based on tube-wells, hand pumps and canal water for distribution of potable water to rural areas (Figure 2).

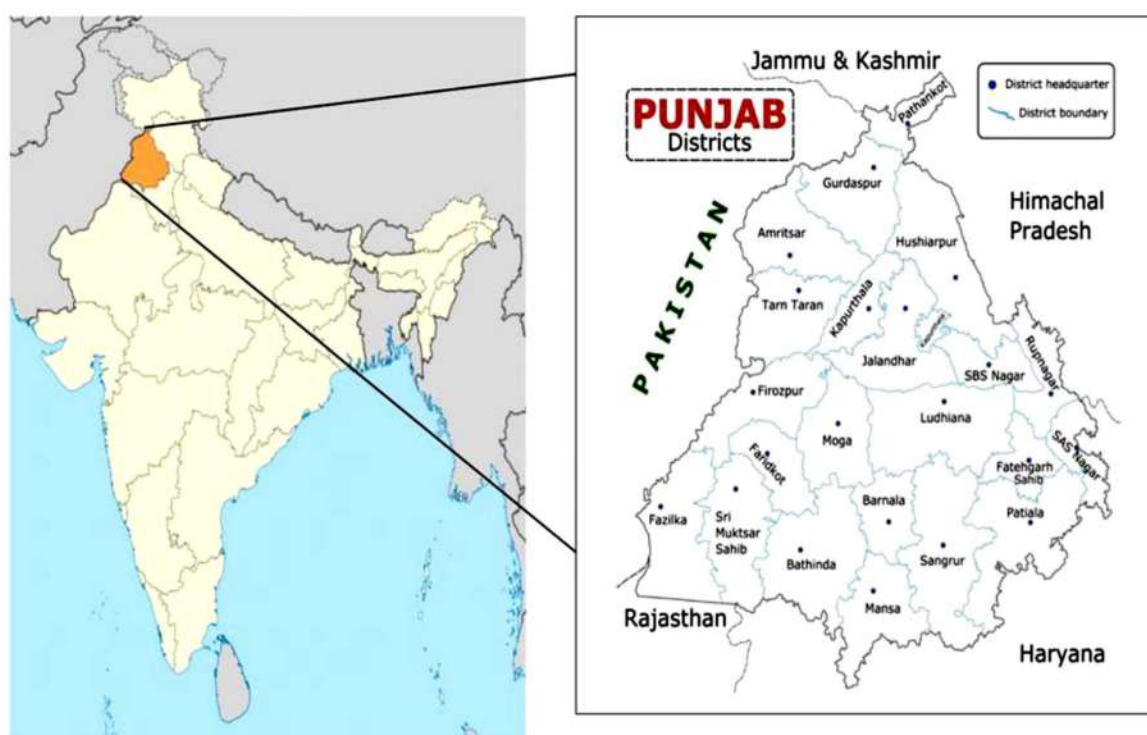


Figure 1. District Map of Punjab, India with Heavy Metal Contamination in Groundwater.

Water Supply Schemes set up by DWSS, Punjab

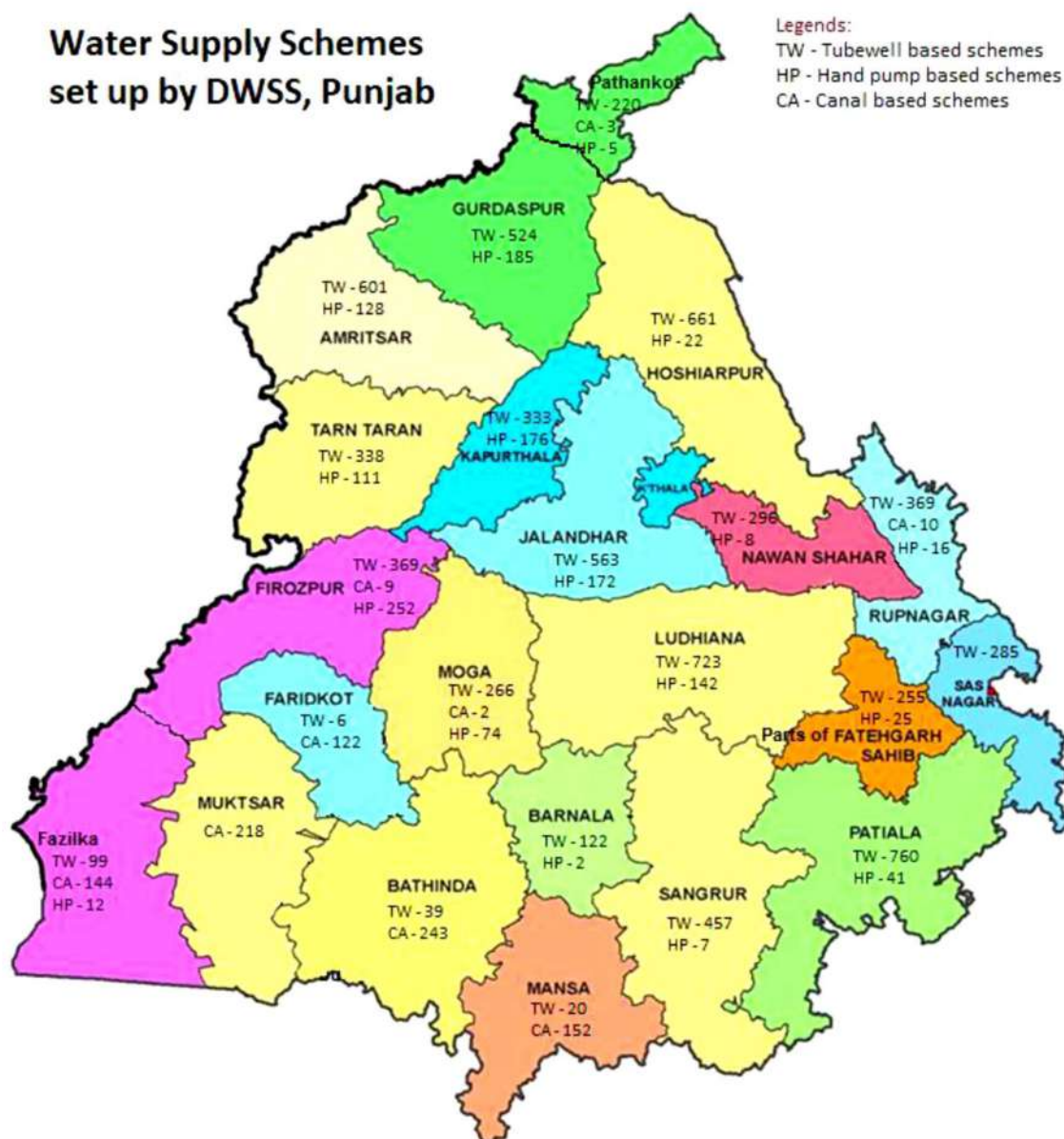


Figure 2. Water supply schemes in operation in Punjab [Ref. 18].

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 metal. The preservation and digestion of heavy metal in acid is used to minimize interferences by poly-atoms.

The heavy metal 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) of DWSS in SAS Nagar (Mohali), India (Appendix I & II). RAWTL is accredited by the National Board for Accreditation of Testing and Calibration Laboratories (NABL). A specimen sample of RAWTL certificate of analysis is shown in Appendix III. This certification is repeated every year by the supplier

of ICPMS. The instrument component details, testing procedures, and standards used are illustrated in Appendix I.

The ICPMS method of multiple-element analysis of heavy metals 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].

ICPMS has a mass spectrometer with inductively coupled plasma (ICP) suitable for multi-element and isotope analysis. The spectrometer is capable of scanning a mass range from 5 m/z (AMU) to 240 m/z (AMU) with a resolution of at least 1 m/z peak width at 5 % of peak height (mr = relative mass of an atom species; z = charge number). The instrument may be fitted with a conventional or extended dynamic range detection system. Most quadrupole ICP-MS, high-resolution ICP-MS and collision cell ICP-MS instrumentation is fit for this purpose. Data analysis is done automatically by inbuilt system of ICP-MS. In addition to U, data for 40 more trace elements can be retrieved using ICP-MS.

Calibration of ICPMS and High Precision Analysis [24]

Calibration experiment is necessary for the estimation of concentration of heavy metals 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) (Appendix III). 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 ($R^2 \geq 0.999$) 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 [17].

A visit to Regional Advanced Water Testing Laboratory (RAWTL) of DWSS at Mohali revealed that facilities exist for high precision analysis using quality control, standard reference materials for calibration and reproducibility of results of analysis. The detection limit of ICPMS for heavy metals Ni, Cd, Cr, and Pb are 5ppb, 1ppb, 5ppb, and 5ppb, respectively. The limits of detection (LoDs) and limits of quantification (LoQs) are defined in terms of σ and S, where σ is the standard deviation of the response and S is the slope of the calibration curve. For each heavy metal, calibration curve was established using standard reference material. The key difference between LoD and LoQ is that LoD is the lowest concentration of analyte in the test sample that is easily distinguished from zero, while LoQ is the lowest concentration of analyte in the control sample that is determined with reasonable repeatability and accuracy. Quantitatively, these limits are defined as follows: Limit of detection, $LoD = 3.3\sigma / S$, and the limit of quantification, $LoQ = 10\sigma / S$. RAWTL technical staff has done this exercise for all heavy metals using calibration curves. The mass to charge ratio used for analysis of heavy metals in this experiment is given in Table 1.

Table 1. Mass/Charge ratio for heavy metals analysis.

Element	Symbol	m	z	m/z
Nickel	Ni	60	+2	60/2
Cadmium	Cd	111	+2	111/2
Chromium	Cr	52	+3	52/3
Lead	Pb	208	+2	208/2

This comprehensive methodology used at RAWTL ensures the accuracy and precision of heavy metal concentration measurements, supported by rigorous calibration procedures and quality control checks in accordance with industry standards. Water samples were collected and analysed from more than 50 % villages of Punjab. Hence, it was not possible to study inter- and intra-day variation of heavy metals in groundwater. It is planned to study heavy metal contents in pre- and post-monsoon samples of groundwater in Punjab.

RESULTS AND DISCUSSION

The present study is first of its kind where heavy metal concentration in groundwater has been investigated for more than 50% habitations/villages of Punjab. However, it lacks some salient features like spatial distribution with respect to time and space, geochemical analysis of heavy metals in groundwater, carcinogenic and non-carcinogenic health hazards of heavy metals due to ingestion of groundwater. The scope of this study is limited to highlight groundwater contamination in Punjab due to Ni, Cd, Cr, and Pb.

There are some rudimentary studies about heavy metal contamination of groundwater in Punjab [25-27]. Partap Singh Bajwa, a Rajya Sabha member, raised a call attention motion in Parliament concerning heavy metal contamination in groundwater of Punjab [28]. Guru Nanak Dev University researchers [29] took the initiative to study heavy metal contents (cadmium, cobalt, chromium, copper, lead and zinc) in Ropar wetland, Punjab, India and its environs. Malwa region of Punjab, known as “*cancer belt*”, of Punjab, has been investigated for heavy metals, arsenic, lead, iron, cobalt, chromium, zinc and mercury, in groundwater [30]. Similar studies have been carried out in Pakistani Punjab in recent years [31].

Nickel and Cadmium Contamination in Punjab

The survey of literature reveals that most of the workers have investigated Uranium and Arsenic in groundwaters of Punjab. Gopal Krishan et al. [32] made a comprehensive survey of trace elements in groundwater of Punjab and reported that Nickel (Ni) and Cadmium (Cd) concentrations are within the acceptable limit (AL). DWSS data reveal that both Ni and Cd concentrations in groundwater of Punjab are beyond the acceptable limit (AL) fixed by BIS India [17] and the World Health Organisation (WHO) [33, 34]. Nickel and Cadmium AL values have been considered to be 0.02 mg/l (ppm) and 0.003 mg/l (ppm), respectively.

According to DWSS report, 183 samples collected from different habitations are evaluated for Ni concentration higher than AL of 0.02 mg/l, out of a total number of 6404 habitations covered in this survey. Patiala district has maximum number of water quality affected (QA) habitations (52) with Ni conc. higher than AL, with Jabo Majra at minimum level of 0.02 mg/l and Dera Rajla at maximum level of 0.106 mg/l. However, the highest conc. of Ni, 0.947 mg/l, has been reported in groundwater sample of village Dhurkot Charat Singh of Moga district. Table 2 represents the list of 50 habitations out of 183 having Ni conc. higher than AL. After Patiala, the QA districts are Ludhiana, Moga, Jalandhar, and Hoshiarpur having 33, 16, 15, and 13 habitations, respectively, with Ni contamination higher than AL. SAS Nagar (Mohali) has only one habitation with QA groundwater.

Nickel is a lustrous white, hard, ferromagnetic metal. It occurs naturally in five isotopic forms: 58 (67.8%), 60 (26.2%), 61 (1.2%), 62 (3.7%), and 64 (1.2%). The primary source of nickel in drinking-water is leaching from metals in contact with drinking-water, such as pipes and fittings. However, nickel may also be present in some groundwaters as a consequence of dissolution from nickel ore-bearing rocks. The source of Ni in groundwater of Punjab is uncertain. It needs to be investigated whether its source is geogenic or anthropogenic?

The health hazards of Ni in groundwater used for public consumption are due to its carcinogenicity. A detailed account is given for acute and long-term exposure to Ni in WHO reports [34, 35]. Human oral exposure to nickel is primarily associated with gastrointestinal and neurological symptoms after acute exposure. A number of studies on the carcinogenicity of nickel compounds in experimental

animals are available [36, 37]. Generally, tumours are induced at the site of administration of the nickel compound. There are only a limited number of studies on carcinogenic effects after oral exposure to nickel compounds in humans.

Table 2. Nickel Contamination in Groundwater of Punjab (AL = 0.02 mg/l).

S.N.	Name of district	Name of Village	Source of Groundwater	Nickel (mg/l)
1	Moga	Dhurkot Charat Singh	Tubewell	0.947
2	Moga	Fateh Pur Karian	Tubewell	0.652
3	Hoshiarpur	Gawal Chak Shangar	Tubewell	0.497
4	Hoshiarpur	Sathwan	Tubewell	0.497
5	Hoshiarpur	Haler	Tubewell	0.458
6	Hoshiarpur	Passi Bet	Tubewell	0.385
7	Hoshiarpur	Galowal	Tubewell	0.385
8	Hoshiarpur	Aki Tunda	Tubewell	0.385
9	Moga	Tuth Garh	Tubewell	0.348
10	Ludhiana	Lalton Kalan	Tubewell	0.330
11	Hoshiarpur	Dalowal	Handpump	0.330
12	Hoshiarpur	Daggan	Handpump	0.330
13	Hoshiarpur	Bhambowal	Tubewell	0.330
14	Moga	Mallian Wala	Tubewell	0.313
15	Hoshiarpur	Patti Kaler	Tubewell	0.305
16	Hoshiarpur	Jiwanwal	Tubewell	0.305
17	Hoshiarpur	Badhan	Tubewell	0.305
18	Hoshiarpur	Dewal	Tubewell	0.305
19	Ludhiana	Alakylui	Tubewell	0.263
20	Ludhiana	Lalton Kalan	Tubewell	0.262
21	Moga	Matwani	Tubewell	0.256
22	Ludhiana	Bir Shanewal	Tubewell	0.250
23	Moga	Ramuwala Nawan	Tubewell	0.245
24	Ludhiana	Gill	Tubewell	0.238
25	Ludhiana	Dhandra	Tubewell	0.231
26	Ludhiana	Marewal	Tubewell	0.221
27	Ferozepur	Basti Jaimal Wali	Tubewell	0.219
28	Ferozepur	Jamail Wala Alias Pirana	Tubewell	0.219
29	Ferozepur	Badhni Jamail Singh	Tubewell	0.219
30	Ludhiana	Panglian	Tubewell	0.205
31	Ludhiana	Phulanwal	Tubewell	0.202
32	Moga	Ramuwala Harchoke	Handpump	0.197
33	Ludhiana	Dewatwal	Handpump	0.193
34	Moga	Basti Sandhuan	Handpump	0.182
35	Moga	Dhurkot Kalan	Tubewell	0.180
36	Ludhiana	Mahmudpura	Tubewell	0.175
37	Moga	Khotte	Tubewell	0.173
38	Moga	Nahal	Tubewell	0.173

39	Ludhiana	Majara	Tubewell	0.172
40	Ludhiana	Bhanohar	Tubewell	0.166
41	Moga	Manawan	Tubewell	0.162
42	Moga	Inder Garh	Tubewell	0.157
43	Moga	Budh Singh Wala	Tubewell	0.155
44	Ludhiana	Meendiar Kala	Tubewell	0.148
45	Ludhiana	Pamali	Tubewell	0.145
46	Moga	Charik	Tubewell	0.144
47	Moga	Kothe Jaitto Ke	Tubewell	0.142
48	Ludhiana	Panglian	Tubewell	0.135
49	Ludhiana	Pawah	Tubewell	0.133
50	Ludhiana		Tubewell	0.130

Cadmium (Cd) contamination of groundwater in Punjab is as rampant as Nickel contamination. DWSS report reveals that 182 habitations have Cd conc. higher than the AL value of 0.003 mg/l. The lowest value of 0.003 mg/l is detected in groundwater of Lalton Kala village of Ludhiana district and highest value of 0.162 mg/l in Kanian Khurd village of Moga district. The maximum number of QA habitations (117) due to Cd contamination in Punjab are found in Patiala district. The next district is Ludhiana with 27 QA habitations. SAS Nagar (Mohali) has no QA habitation.

Cadmium contamination of groundwater in south-western Punjab has been studied by Bangotra et al. [38]. They report that Cd contamination levels are lower than other trace elements: Mn (13.93) > Cu (13.12) > Se (4.14) > As (3.28) > Hg (3.27) > Pb (1.29) > Co (0.20) > Cd (0.10) $\mu\text{g L}^{-1}$. The Cd value is reported to be 30 times lower than AL of 0.003 mg/l or 3 $\mu\text{g/l}$. It almost corresponds to the detection limit of measuring instrument (ICP-MS). The Science Wire [39] report also points to dangerous levels of trace elements, including Cd, in 50% of districts of Punjab but no concentration levels in groundwater are reported. Krishan et al. [32] mention negligent levels of Ni and Cd in groundwater of Punjab. Table 3 lists 50 habitations of Punjab spread over 8 districts having Cd contamination higher than 0.007 mg/l, more than double the AL value.

Like Nickel, source of Cadmium in groundwater of Punjab is not yet fully understood. Science Wire [39] reports that the exact sources of the heavy metals are unclear, but experts suspect geological factors and overuse of fertilisers. Punjab plains are overlain by thick sediments of alluvial deposits due to Indus-river system. Cadmium is an impurity in phosphate fertilizers and gets deposited in the soil and water due to intensive irrigation of crops. Cadmium and its compounds are highly toxic and exposure to this metal is known to cause cancer and targets the body's cardiovascular, renal, gastrointestinal, neurological, reproductive, and respiratory systems [40].

Table 3. Cadmium Contamination in Groundwater of Punjab (AL = 0.003 mg/l).

S.N.	Name of district	Name of Village	Source of Groundwater	Depth (meter)	Cadmium (mg/l)
1	Moga	Kanian Khurd	Handpump	80	0.162
2	Moga	Basti Nanak Pura	Handpump	80	0.050
3	Jalandhar	Bir Bansian	Tubewell	130	0.019
4	Ludhiana	Bains	Tubewell	130	0.016
5	Sangrur	Shergarh	Tubewell	120	0.016
6	Ludhiana	Bains	Tubewell	120	0.016
7	Sangrur	Shergarh	Tubewell	240	0.014
8	Fazilka	Ghubaya	Tubewell	250	0.013

9	Fazilka	Ch. Mouje Wala	Tubewell	250	0.013
10	Fazilka	Lamoher Khurd	Tubewell	250	0.013
11	Sangrur	Shergarh	Tubewell	120l	0.012
12	Kapurthala	Mand Bandu Jadid	Handpump	90	0.011
13	Kapurthala	Kaulpur	Handpump	90	0.011
14	Patiala	Balheri	Hand pump	70	0.010
15	Ludhiana	Jhande	Tubewell	80	0.009
16	Ludhiana	Dad	Tubewell	80	0.009
17	Ludhiana	Tharika	Tubewell	85	0.009
18	Patiala	Raisal	Tubewell	90	0.009
19	Patiala	Sirinagar	Tubewell	72	0.009
20	Ludhiana	New Raj Guru Nagar	Tubewell	115	0.009
21	Barnala	Dhurkot	Tubewell	122	0.009
22	Barnala	Dhurkot	Tubewell	122	0.009
23	Moga	Mehron	Tubewell	113	0.009
24	Patiala	Ghanurki	Tubewell	95	0.009
25	Patiala	Bhoglan	Tubewell	275	0.009
26	Patiala	Kaidupur	Tubewell	133	0.009
27	Patiala	Jandoli	Tubewell	286	0.009
28	Patiala	Ladha Heri	Tubewell	125	0.009
29	Kapurthala	Patti Sardar Nabi Baksh	Handpump	80	0.008
30	Patiala	Rohti Mouran	Tubewell	150	0.008
31	Patiala	Rohti Basta Singh	Tubewell	150	0.008
32	Sangrur	Shergarh	Handpump	140	0.008
33	Patiala	Sakrali	Tubewell	110	0.008
34	Patiala	Shivgarh	Tubewell	155	0.008
35	Ludhiana	New Raj Guru Nagar	Tubewell	140	0.008
36	Patiala	Bridwal	Tubewell	120	0.008
37	Patiala	Tungan	Tubewell	65	0.008
38	Patiala	Hassanpur	Tubewell	65	0.008
39	Patiala	Achal	Tubewell	65	0.008
40	Ludhiana	Phulanwal	Handpump	110	0.007
41	Ludhiana	Guru Nanak Colony	Handpump	125	0.007
42	Ludhiana	Jand	Tubewell	125	0.007
43	Ludhiana	Mehtabgarh	Handpump	125	0.007
44	Moga	Kore Wala Kalan	Tubewell	128	0.007
45	Patiala	Ramgarh near Bhadson	Tubewell	155	0.007
46	Patiala	Jhambali Sahni	Tubewell	155	0.007
47	Patiala	Ghaniawal	Tubewell	95	0.007
48	Patiala	Lubana Karmoo	Tubewell	120	0.007
49	Patiala	Lubana Teku	Tubewell	120'	0.007
50	Patiala	Tarkheri	Tubewell	160	0.007

Chromium Concentration in Groundwater of Punjab

Chromium (Cr) belongs to the group of chemical elements like Iron, Cobalt, Nickel, Copper and Zinc. DWSS report reveals Cr contamination of groundwater in 76 habitations above the AL value of 0.05 mg/l (ppm). Chromium concentration is widespread in Hoshiarpur district, out of 76 QA habitations, 60 belong to Hoshiarpur district. Ludhiana, Tarn Taran, and Amritsar districts have some pockets where Cr contamination is found higher than AL. However, the highest conc. of Cr (0.308 mg/l) is detected in the water drawn from a handpump of Walipur Khurd village of Ludhiana district (Table 4).

A Tribune report of 20th May 2024 [41] highlights the high levels of Cr in areas around the Kala Sanghian drain in Jalandhar district of Punjab. The Cr levels found in the soil are nearly 7 times higher than the WHO recommended values (100 mg/kg). Exposure to high levels of Chromium can cause respiratory problems, kidney and liver damage, skin irritation and digestive problems. Long-term exposure can even lead to cancer, the prevalence of which has been repeatedly pointed out by environmentalist Balbir Singh Seechewal, a prominent Member of Indian Parliament. Human health risk assessment of Chromium in drinking water has been reported in India by Aliya Naz et al. [42] and in Pakistan by Safia Aziz et al. [43].

Table 4. Chromium Contamination in Groundwater of Punjab (AL = 0.05 mg/l).

S.N.	Name of district	Name of Village	Source of Groundwater	Depth (meter)	Chromium (mg/l)
1	Ludhiana	Walipur Khurd	Handpump	70	0.308
2	Hoshiarpur	Haler	Tubewell	310	0.210
3	Hoshiarpur	Talwara	Tubewell	310	0.210
4	Hoshiarpur	Dhesian	Tubewell	100	0.144
5	Hoshiarpur	Shrakowal	Tubewell	100	0.144
6	Hoshiarpur	Sudharian	Tubewell	100	0.144
7	Hoshiarpur	Bigowal	Tubewell	100	0.144
8	Hoshiarpur	Dhesian	Tubewell	100	0.144
9	Hoshiarpur	Kasrawan	Tubewell	100	0.144
10	Hoshiarpur	Bohran	Tubewell	100	0.140
11	Hoshiarpur	Pandori Baghel Singh	Tubewell	100	0.140
12	Hoshiarpur	Sanial	Tubewell	100	0.140
13	Hoshiarpur	Abadi Tote	Tubewell	122	0.137
14	Hoshiarpur	Gera	Tubewell	122	0.137
15	Hoshiarpur	Handwal	Tubewell	122	0.137
16	Hoshiarpur	Ladhiari	Tubewell	122	0.137
17	Hoshiarpur	Ulaha	Tubewell	122	0.137
18	Hoshiarpur	Khatigarh	Tubewell	122	0.137
19	Hoshiarpur	Lalota	Tubewell	122	0.137
20	Hoshiarpur	Chakerial	Tubewell	122	0.137
21	Hoshiarpur	Andwar Patti	Tubewell	150	0.135
22	Hoshiarpur	Dohar	Tubewell	145	0.132
23	Hoshiarpur	Raoli	Tubewell	145	0.132
24	Hoshiarpur	Bhera	Tubewell	145	0.132

25	Hoshiarpur	Ajmer	Tubewell	172	0.129
26	Hoshiarpur	Dhade Katwal	Tubewell	172	0.129
27	Hoshiarpur	Sandhwal	Tubewell	125	0.127
28	Hoshiarpur	Sibbo Chak	Tubewell	125	0.127
29	Hoshiarpur	Hajipur	Tubewell	125	0.127
30	Hoshiarpur	Niku Chak	Tubewell	125	0.127
31	Hoshiarpur	Panjdhera Rahia	Tubewell	122	0.115
32	Hoshiarpur	Panjdhera Gazi	Tubewell	122	0.115
33	Hoshiarpur	Singhowal	Tubewell	122	0.115
34	Hoshiarpur	Panjdhera Kalan	Tubewell	122	0.115
35	Hoshiarpur	Abadi Sadhani	Tubewell	40	0.114
36	Gurdaspur	Dhande	Tubewell	45	0.113
37	Amritsar	Thathi	Tubewell	50	0.109
38	Hoshiarpur	Miani Malahan	Tubewell	100	0.109
39	Hoshiarpur	Jahanpur	Tubewell	100	0.109
40	Hoshiarpur	Mehtabpur	Tubewell	100	0.109
41	Hoshiarpur	Ladpur	Tubewell	100	0.109
42	Amritsar	Thathi	Tubewell	1101	0.095
43	Hoshiarpur	Pohari	Tubewell	20	0.091
44	Hoshiarpur	Narangpur	Tubewell	20	0.091
45	Hoshiarpur	Natholi	Tubewell	20	0.091
46	Hoshiarpur	Kothi	Tubewell	20	0.091
47	Hoshiarpur	Ghagwal	Tubewell	71	0.090
48	Hoshiarpur	Badala	Tubewell	71	0.090
49	Hoshiarpur	Kando Karora	Tubewell	71	0.090
50	Hoshiarpur	Narnaul	Tubewell	71	0.090

Lead Concentration in Groundwater of Punjab

Lead (Pb) is another dangerous toxic heavy metal reported in groundwaters of Punjab. The AL for Pb has been set at 0.01 mg/l (ppm). Out of 7009 habitations covered under Pb survey, 710 have been found QA which fail to qualify the safety limit. In the total list of QA habitations, Gurdaspur district has highest Lead contamination with 128 habitations followed by Jalandhar district (98). The maximum reported value of Lead content (0.479 ppm) has been found in Chhaura village, followed by a cluster of villages in Jalandhar district, namely, Dhuleta, Patti Kamalpur, and Bara Pind (Table 5). Lead contamination has been found mostly in water drawn from handpumps.

US Environment Protection Agency (US-EPA) [44] has set the maximum contaminant level goal for Lead in drinking water at zero because lead is a toxic metal that can be harmful to human health even at low exposure levels. Lead is persistent and it can bioaccumulate in the body over time. Young children and infants are particularly vulnerable to lead at lower exposure levels in comparison to adults. An overview of carcinogenic pollutants of groundwater in India has been made by Malyan et al. [45]. A report published in 'Down to Earth' [46] blames overexploitation of groundwater resulting in contamination from geological sources, causing highly toxic elements such as uranium, arsenic, manganese, zinc, copper, lead and iron to leach from aquifer rock or sediment into the water.

Table 5. Lead Contamination in Groundwater of Punjab (AL = 0.01 mg/l).

S.N.	Name of district	Name of Village	Source of Groundwater	Depth (meter)	Lead (mg/l)
1	Jalandhar	Chhauha	Handpump	75	0.479
2	Jalandhar	Dhuleta	Handpump	75	0.467
3	Jalandhar	Patti Kamal Pur	Handpump	75	0.467
4	Jalandhar	Patti Nasand Pur	Handpump	75	0.467
5	Jalandhar	Bara Pind	Handpump	75	0.467
6	Jalandhar	Harijan Basti	Handpump	75	0.441
7	Jalandhar	Achan Chak	Handpump	75	0.432
8	Jalandhar	Katana	Handpump	75	0.401
9	Jalandhar	Dasmesh Nagar	Handpump	75	0.391
10	Jalandhar	Bhanda Sahib Rai	Handpump	75	0.387
11	Jalandhar	Daroli Ke Sunderpur	Tubewell	125	0.365
12	Jalandhar	Jajjo Majara	Handpump	75	0.343
13	Jalandhar	Burj Kela	Handpump	75	0.337
14	Jalandhar	Hardo Sangha	Handpump	75	0.320
15	Jalandhar	Phillaur Dehati	Handpump	75	0.303
16	Jalandhar	Burjpukhta	Handpump	75	0.301
17	Jalandhar	Dusanjh Kalan	Handpump	75	0.301
18	Jalandhar	Lehal	Handpump	75	0.301
19	Jalandhar	Nanu Majra	Handpump	75	0.301
20	Jalandhar	Ladian	Handpump	75	0.301
21	Jalandhar	Chhokeran	Handpump	75	0.292
22	Ropar	Gobindpur	Handpump	50	0.291
23	Jalandhar	Bachhowal	Handpump	75	0.274
24	Jalandhar	Nurewal	Handpump	75	0.236
25	Jalandhar	Gidder Pindi	Handpump	75	0.233
26	Jalandhar	MotipurKhalsa	Handpump	75	0.221
27	Jalandhar	Balmiki Nagar	Handpump	75	0.217
28	Patiala	Punia Khana	Tubewell	234.5	0.190
29	Gurdaspur	Baje Chack	Handpump	65	0.187
30	Jalandhar	Phillaur Killa	Handpump	75	0.182
31	Jalandhar	Butran	Tubewell	125	0.180
32	Jalandhar	Dugri	Hand Pump	75	0.180
33	Ludhiana	Gehlewal	Handpump	80	0.180
34	Jalandhar	Lutera Khurd	Hand Pump	75	0.168
35	Jalandhar	MiranPur	Handpump	75	0.167
36	Jalandhar	Chanian	Handpump	75	0.164
37	Moga	Abadi of Baje Ke	Handpump	90	0.154
38	Jalandhar	Jagraal	Handpump	75	0.152
39	Bathinda	Jajjal	Handpump	75	0.149
40	Jalandhar	Makhi	Handpump	75	0.143
41	Tarn Taran	Malmohri	Handpump	92	0.137
42	Jalandhar	Bir Phillaur	Handpump	75	0.135

43	Kapurthala	Shahpur Dogra	Hand Pump	75	0.134
44	Jalandhar	Jal pot	Hand Pump	75	0.123
45	Jalandhar	Sitalpur	Handpump	75	0.117
46	Jalandhar	Bhundri	Handpump	75	0.103
47	Gurdaspur	Rarewali	Handpump	70	0.092
48	Ludhiana	ITI Samrala	Handpump	70	0.091
49	Jalandhar	Khanke Fatehgarh	Handpump	75	0.087
50	Hoshiarpur	Kotla Maruf Jhiri	Handpump	155	0.084

MITIGATION MEASURES FOR HEAVY METALS IN GROUNDWATER

Heavy metals are highly toxic beyond the safe limit in groundwater and their mitigation is on top priority of Punjab government. Mitigation of Iron and Arsenic from groundwater of Amritsar district has been discussed in our Paper [12]. World Bank Project Report [21] implemented by DWSS clearly mentions strategies for monitoring groundwater contaminants and the measures to be taken for their mitigation. Punjab government initiated setting up of Reverse Osmosis (RO) plants for supply of potable water to rural areas during the earlier phases of the project, but this scheme has been almost abandoned at the state level due to fund crunch. It is still in operation in some households who are willing to pay for it.

Department of Water Supply and Sanitation (DWSS), Punjab in its report [47] "Water Quality Mitigation Strategy" gives top priority to mitigation of mandatory parameters, namely, Arsenic, Fluoride, TDS, Nitrate and Iron. Uranium, Aluminium, Selenium and other heavy metals (Nickel, Cadmium, Chromium, Lead) are classified under 'Emerging Parameters' and given lesser importance for purpose of mitigation.

DWSS report [47] mentions that out of 1540 habitations, affected with Emerging Parameters, 494 habitations are covered/being covered with RO plants, 34 are being covered under surface water projects. And thus, a balance of 1012 habitations affected with Emerging Parameters is left to be covered. In the year 2019–20, 15 habitations affected with Mercury, 113 habitations affected with Uranium and 16 habitations affected with Selenium will be provided with treatment technologies. At present, DWSS has shifted its focus from routine measures of mitigation to supply of canal water to rural and urban population of Punjab, which is found to be economical. Our investigations reveal that canal water is free from heavy metals and Uranium [9] and its use will be commendable as a mitigation measure.

CONCLUSIONS

1. The source and origin of heavy metals (Ni, Cd, Cr, and Pb) in groundwaters of Punjab needs to be investigated further. It is being attributed to geogenic origin primarily but augmented by anthropogenic sources such as fertilizers, pesticides, and weedicides.
2. Patiala district is a "Hot Spot" for Nickel and Cadmium contamination of groundwater.
3. Hoshiarpur district is a "Hot Spot" for Chromium contamination of groundwater, accounting for 80% of Chromium affected habitations in Punjab.
4. Lead contamination is more widely distributed in Punjab. Gurdaspur and Jalandhar districts account for highest number of QA habitations in Punjab.
5. Mitigation measures for both mandatory and emerging parameters in groundwater need to be implemented on war footing in Punjab.
6. Epidemiological surveys need to be undertaken to assess health hazards due to heavy metals contamination of groundwater in Punjab.
7. Heavy metal contamination has been established to be a man-made curse in Punjab; there is an urgent need to avoid over-exploitation of groundwater resources by implementing shift in

cropping pattern of agriculture. Paddy is found to be a guzzling crop for water and its cultivation needs to be curbed in Punjab.

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APPENDIX I

RAWTL facilities used by the author at Department of Water Supply and Sanitation (DWSS), Mohali, Punjab, India

AGILENT 7700 X ICP-MS

Parameters to be tested by ICP-MS : Uranium (U), Aluminium (Al), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Arsenic (As), Nickel (Ni), Lead (Pb), Selenium (Se), Iron (Fe), Sodium (Na), Magnesium (Mg), Potassium (K), Calcium (Ca)

COMPONENT DETAILS



Inductively Coupled Plasma Mass Spectrometer
Main machine with facility to analyse metal content in the water samples.



ASX520 Auto-sampler
Auto sampler with facility to run 180 samples automatically. 20 slots for standards & 7 additional slots for washing and rinsing the injection probe of auto-sampler.



Agilent Chiller
For cooling the electronics, RF coil, vacuum system and RF generator.



Rough Pump
To maintain the vacuum of the order of 10^{-4} bars in analyser, ICP section.



Exhaust
For taking the burnt fumes from the system to the outer environment with the flow of 5-7 m³/min.

TESTING PROCEDURE

- ◆ Take the sample and acidify it with Ultrapure Nitric acid to obtain a final strength of 5%.
- ◆ In case of turbid samples, digest the samples using Microwave digestion system.
- ◆ Take the prepared/diluted standards for the desired parameters with ultrapure water in ICP-MS.
- ◆ Take sample/standards in to the vials of Auto-sampler and run in ICP-MS.
- ◆ Extract results from the software Masshunter.

TESTING CAPACITY

- ◆ 300 samples per day @ 3 min for each sample including the time required for the digestion.
- ◆ The device can be put on Auto-shutdown mode which will automatically shut down the device after the analysis is complete.



Gas control panel
For maintaining the pressure of gases like Argon, Oxygen, Helium & Hydrogen in the system.



Microwave Digestion System
To digest the samples or extracting the metal content from the sample so as to make it suitable to be used in the ICP-MS.

STANDARDS, CHEMICALS AND ACCESSORIES

Sr.	Item
1.	Tarson tubes (50 ml and 15 ml)
2.	Standards for Uranium, Arsenic, Aluminium, Mercury, Cadmium, Chromium, Nickel, Lead, Selenium, Iron
3.	Waste disposal unit cans (50 L)
4.	Ultra pure Nitric Acid
5.	Filter paper (Whatman Filter Papers 541, 40, 45 no.)
6.	Ultrapure water
7.	Wash bottles (500 ml)
8.	Citranox (citrate) (5 L)
9.	Skimmer cone opener

**REGIONAL ADVANCE WATER TESTING LABORATORY, S.A.S. NAGAR
CCDU, DEPARTMENT OF WATER SUPPLY & SANITATION, PUNJAB**

Not for Distribution, Uploading, or Publication on Any Other Website (or Online Platform)
Except Journals Official Website.

APPENDIX II

Inside view of inhouse RAWTL facility of DWSS at Mohali, Punjab, India



APPENDIX III

RAWITY RM/01



Agilent Technologies

Certificate of Analysis

Multi-element Calibration Standard 2A

Agilent Part Number: 8500-6940

Lot Number: 51-042CRY2

Analyte	CAS#	Labeled Conc.	Measured Conc.	SRM	Start Mat'l Formula	Start Mat'l Purity	Analyte	CAS#	Labeled Conc.	Measured Conc.	SRM	Start Mat'l Formula	Start Mat'l Purity
Ag	7440-22-4	10.0 µg/mL	10.0 µg/mL	3151*	AgNO ₃	99.99+	Li	7439-93-2	10.0 µg/mL	9.95 µg/mL	3129a*	Li ₂ CO ₃	99.99+
Al	7429-90-5	10.0 µg/mL	9.94 µg/mL	3101a*	Al	99.99+	Mg	7439-95-4	10.0 µg/mL	9.95 µg/mL	3131a*	Mg(NO ₃) ₂ · 6H ₂ O	99.99+
As	7440-38-2	10.0 µg/mL	10.1 µg/mL	3103a*	As	99.99+	Mn	7439-96-5	10.0 µg/mL	9.94 µg/mL	3132*	Mn	99.99+
Ba	7440-39-3	10.0 µg/mL	10.0 µg/mL	3104a*	Ba(NO ₃) ₂	99.99+	Na	7440-23-5	10.0 µg/mL	10.1 µg/mL	3152a*	NaHCO ₃	99.99+
Be	7440-41-7	10.0 µg/mL	10.0 µg/mL	3105a*	BeO(CH ₃ COO) ₂	99.99+	Ni	7440-02-0	10.0 µg/mL	10.1 µg/mL	3136*	Ni	99.99+
Ca	7440-70-2	10.0 µg/mL	9.95 µg/mL	3109a*	CaCO ₃	99.99+	Pb	7439-92-1	10.0 µg/mL	10.1 µg/mL	3128*	PbO	99.99+
Cd	7440-43-9	10.0 µg/mL	10.1 µg/mL	3108*	Cd	99.99+	Rb	7440-17-7	10.0 µg/mL	9.93 µg/mL	3145a*	RbNO ₃	99.99+
Co	7440-48-4	10.0 µg/mL	10.0 µg/mL	3113*	Co	99.99+	Se	7782-49-2	10.0 µg/mL	9.86 µg/mL	3149*	Se	99.99+
Cr	7440-47-3	10.0 µg/mL	10.1 µg/mL	3112a*	Cr(NO ₃) ₃ · 9H ₂ O	99.99+	Sr	7440-24-6	10.0 µg/mL	10.0 µg/mL	3153a*	Sr(NO ₃) ₂	99.99+
Cs	7440-46-2	10.0 µg/mL	10.0 µg/mL	3111a*	CsNO ₃	99.99+	Ti	7440-28-0	10.0 µg/mL	10.2 µg/mL	3158*	TiNO ₂	99.99+
Cu	7440-50-8	10.0 µg/mL	9.97 µg/mL	3114*	Cu	99.99+	U	7440-61-1	10.0 µg/mL	9.95 µg/mL	3164*	UO ₂ (NO ₃) ₂ · 6H ₂ O	99.99+
Fe	7439-89-6	10.0 µg/mL	9.96 µg/mL	3126a*	Fe	99.99+	V	7440-62-2	10.0 µg/mL	9.91 µg/mL	3165*	NH ₄ VCl ₆	99.99+
Ga	7440-55-3	10.0 µg/mL	9.98 µg/mL	3119a*	Ga	99.99+	Zn	7440-66-6	10.0 µg/mL	9.95 µg/mL	3168a*	Zn	99.99+
K	7440-09-7	10.0 µg/mL	9.93 µg/mL	3141a*	KNO ₃	99.99+							

* - indicates NIST SRM

† - indicates CRM (when NIST SRM is not available)

Purity grades:

Starting Materials: Shown above

Matrix:

5% HNO₃: HNO₃ (CAS No. 7697-37-2) high purity grade

Traceability:

This standard has been produced gravimetrically and volumetrically using ISO 9001 quality procedures. Agilent ICP / ICP-MS Spectrometer was used to determine the concentration of the main elements via NIST SRMs shown above, as well as the impurities. Other reference standards used: CL51-014CR, CL51-016CR.

Trace Metallic Impurities in the Actual Solution, in µg/L, via Agilent ICP-MS Analysis, results are accurate to ±10%:

Element	Conc.	Element	Conc.	Element	Conc.	Element	Conc.	Element	Conc.	Element	Conc.
Au	<0.03	Gd	0.05	La	0.1	Pr	<0.01	Si	<100	Ti	10
B	2	Ge	0.5	Lu	<0.01	Pt	<0.2	Sm	<0.3	Tm	0.06
Bi	0.2	Hf	<0.01	Mo	2	Re	<0.02	Sr	0.4	W	<0.2
Ce	0.2	Hg	0.7	Nb	0.1	Rh	<0.1	Ta	<0.04	Y	0.2
Dy	<0.01	Ho	<0.01	Nd	<0.04	Ru	0.5	Tb	<0.01	Yb	0.01
Er	<0.01	In	0.08	P	<100	Sb	0.4	Te	0.5	Zr	0.3
Eu	<0.1	Ir	0.3	Pd	<10	Sn	<0.05	Th	0.03		

Balances are calibrated regularly with weight sets traceable to NIST.

Density: 1.025 g/mL @ 20°C

Agilent reference standards are guaranteed stable and accurate to ±0.5% of measured analyte concentration. This uncertainty is at 95% confidence interval, a coverage factor of 2. For these solutions we use the highest purity acids applicable, 18 megohm double deionized water and acid-leached, triple rinsed bottles. All glassware used is class A. This standard was manufactured following the guidelines set forth under ISO 17025 and ISO 17034 regulations.

Date of release: April 30, 2020

Date of expiration: October 31, 2021

[Signature]

[Signature]
QC Coordinator

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