Assessment of heavy metals concentrations from surface water sources in urban areas of Himachal Pradesh, India

Kartikey Sahil and SK Bhardwaj

DOI: https://doi.org/10.22271/chemi.2021.v9.i1h.11289

Abstract
Surface water forms the major source of drinking water and supportive in maintaining the ground water levels in urban areas of most of the developing nation of the world. The surface water sources are mainly used for drinking and domestic purposes by urban population of India. In the last few decades, due to rapid increase in population and urbanization, we have been witnessing alarming surface water pollution all over the world. The present study was conducted with an objective to assess the concentrations of heavy metals on surface water sources in urban areas of Himachal Pradesh, India. In the study area 12 surface water samples have been collected and analyzed for the heavy metals such as nickel (Ni), iron (Fe), arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), zinc (Zn), mercury (Hg) and copper (Cu). The study revealed that heavy metals concentrations of surface waters sources were within the prescribed standard limits for drinking purposes (IS 10500: 2012) and WHO. Further, the investigation showed that the water quality of the selected urban areas possibly impacted due to increase of anthropogenic activities and improper or illegal release of sewage water and agricultural effluents.

Keywords: Urban areas, surface water quality, heavy metals, urbanization

Introduction
Water pollution is not a new problem except in dimensions which we face today. Man has been using water around him for dumping wastes. In the early stages of human history, domestic discharges probably posed no problem as nature has the capacity to degrade waste and restore normal conditions. Nature still does, but with the advent of urbanization and industrialization we have been overloading the systems beyond their tolerance limit. Consequently, our water bodies such as rivers, streams and lakes are increasingly getting polluted, threatening the safety, welfare and the very existence of mankind. In recent years the newer environmental issues regarding hazardous waste, global climate change, stratospheric ozone depletion, groundwater contamination, disaster mitigation and removal of pollutant have become the focus of environmental attention. Because of the anthropogenic activities, fresh water resources are deteriorating day-by-day at a very fast rate (Ramadhan, 2007) [29]. Anthropogenic influences like urbanization, industrialization, agricultural activities as well as natural sources like precipitation rate, weathering processes and soil erosion degrade the surface water (Ramadhan, 2007; Najafpour et al., 2008; Bu et al., 2010; Shimba and Jonah, 2016) [29, 20, 8, 33]. Thus, the water quality of these water resources is a subject of ongoing concern and has resulted in an increasing demand for monitoring surface water sources. Most cities in India are facing severe water scarcity. Changes such as rapid urbanization, economic growth, increasing populations, and evolving consumption patterns are individually and collectively stressing water supplies. Securing urban water supply is crucial, since the number of urban dwellers living with seasonable water shortages is expected to grow from close to 500 million people in 2000 to 1.9 billion in 2050 (McDonald et al. 2011) [19]. It is expected that about 70 percent of urban water requirement will be met by surface water sources and remaining from groundwater (Kumar et al., 2005) [17]. Almost 200 million people in India do not have access to safe and clean drinking water and 90 percent of the country’s water resources are polluted. In India, only 29 percent of the wastewater generated is being treated in urban centers having a population of more than 50,000 and 71 percent as untreated wastewater is being discharged to our rivers, streams, and
lakes, making them highly polluted (CPCB, 2011) [13]. Even some of our developed cities in India like Pune, Nagpur, and Nashik are treating only 70 to 80 percent of city sewage, so the sewage pollution caused by ordinary Indian towns and villages can be imagined.

Water pollution has now become a growing hazard in many developing countries. A more serious aspect of water-pollution is being caused by human activity and industrialization (Park, 2009) [22]. In India, almost 70 per cent of its surface water resources and a growing percentage of its groundwater reserves are contaminated by biological, toxic, organic and inorganic pollutants (CPCB, 2008) [12]. The quality of surface water has become a critical issue in many countries especially due to the concern that freshwater will be a scarce resource in the future so a water quality monitoring program is necessary for the protection of freshwater resources (Pesce and Wunderlin, 2000) [23].

Materials and Methods
The study was conducted in major urban areas of the Himachal Pradesh namely Shimla, Dharamshala, Mandi and Kullu with the objective of assessing the impacts of urbanization on surface water quality status. The water samples were collected at different sampling stations during 2017 and 2018 in three seasons viz., summer, monsoon and winter. The samples were analyzed for toxic elements like As, Cd, Cu, Cr, Ni, Pb, Zn, Fe and Hg. The standard methods and procedures were used for quantitative estimation of water quality parameters and followed as in, “Standard methods of analysis of water and waste water” (APHA, 1998) [3]. In water sampling analysis, the samples were first filtered using Whatman filter paper (No.1). The heavy metals in the water samples were estimated by using Inductively Coupled Plasma Emission Spectrometer (iCAP 6000 Series, Model No. 6300) duo of thermo make and expressed as mg l⁻¹.

Results and Discussion
Arsenic
The different urban areas were found to exhibit significant variations in distribution of As content in surface water sources. The perusal of the data presented in Table 1 indicated that the As content of surface water sources in different urban areas ranged from 0.003 to 0.006 mg l⁻¹ which was normal and within the permissible limits as prescribed by BIS. During first year (2018) significantly highest As content of 0.006 was noticed in the surface water sources of Kullu followed by Shimla, Dharamshala and Mandi with respective values of 0.003, 0.003 and 0.003 mg l⁻¹. The data presented in Table 1 further indicated that the highest As of 0.005 mg l⁻¹ was discerned in pre-monsoon months followed by post-monsoon (0.004 mg l⁻¹) and lowest of 0.002 mg l⁻¹ in monsoon season. The interaction of urban areas and seasons exhibited non-significant variation with respect to As content of surface water sources. The pooled analysis of both the years also indicated the similar trend with respect to As content of surface water sources which followed the order: Kullu (0.005 mg l⁻¹) > Shimla (0.003 mg l⁻¹) > Dharamshala (0.003 mg l⁻¹) > Mandi (0.003 mg l⁻¹). The values of Shimla, Dharamshala and Mandi were found to be at par with each other. The As was found to be within the permissible limits of BIS in all the urban areas, therefore, indicating that As concentration has not influenced the surface water quality of major towns.
low As content in surface water sources. However, the concentration of As was found higher in Kullu town which may be due to the rapid urbanization, excessive use of pesticides in the horticultural and agricultural practices in the vicinity of the town in comparison to other urban areas. The other sources of As in Kullu might be the erosion of natural deposits and runoff from nearby orchards (Rahmanian et al., 2015) [27]. Season-wise pooled analysis also revealed As distribution in surface water bodies in the order of pre-monsoon (0.005 mg l⁻¹) > post-monsoon (0.003 mg l⁻¹) > monsoon (0.002 mg l⁻¹).

| Table 1: Seasonal distribution of arsenic (mg l⁻¹) in surface water sources of urban areas |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| **Urban areas**                          | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** |
|                                | 2018          |          |              |         | 2019          |          |              |         | 2019          |          |              |         | 2019          |          |              |         |
| Shimla                        | 0.005        | 0.001   | 0.002        | 0.003   | 0.005        | 0.001   | 0.003        | 0.003   | 0.005        | 0.001   | 0.002        | 0.003   | 0.002        | 0.003   |
| Dharamshala                  | 0.004        | 0.002   | 0.002        | 0.003   | 0.004        | 0.002   | 0.002        | 0.003   | 0.004        | 0.002   | 0.002        | 0.003   | 0.002        | 0.003   |
| Mandi                        | 0.004        | 0.002   | 0.003        | 0.003   | 0.004        | 0.002   | 0.003        | 0.003   | 0.004        | 0.002   | 0.003        | 0.003   | 0.003        | 0.003   |
| Kullu                        | 0.009        | 0.004   | 0.005        | 0.006   | 0.008        | 0.005   | 0.007        | 0.007   | 0.009        | 0.005   | 0.006        | 0.006   | 0.006        | 0.006   |
| Mean                         | 0.006        | 0.002   | 0.003        |         | 0.005        | 0.002   | 0.004        |         | 0.005        | 0.002   | 0.003        |         | 0.002        | 0.003   |
| **CD_0.65**                  | Urban areas  | 0.003   |         |         | 0.003        |         |         |         | 0.003        |         |         |         | 0.002        |         | 0.003        |         |
|                             | Seasons      | 0.002   |         |         | 0.002        |         |         |         | 0.002        |         |         |         | 0.002        |         | 0.002        |         |
|                             | Seasons × Urban areas | NS |         |         | NS          |         |         |         | NS          |         |         |         | NS          |         | NS          |         |

The values of monsoon and post-monsoon months were found to be at par with each other. Higher concentration in pre-monsoon may probably be because of increase in the rate of evaporation at high temperature and decrease in volume of water in the sources and due to rapid oxidation of organic materials and increase in anthropogenic activities (Lashari et al., 2009) [18], whereas the comparatively less concentration in monsoon season attributed to the dilution of pollutants in surface water bodies due to high rainfall during this season.

**Cadmium**

The different urban areas were found to exhibit significant variations in distribution of Cd content in surface water sources. The perusal of the data presented in Table 2 indicated that the surface water Cd in different urban areas ranged from 0.000 to 0.003 mg l⁻¹ which was within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Cd content of 0.003 mg l⁻¹ was noticed in the surface water sources of Shimla followed by Dharamshala (0.000 mg l⁻¹), Mandi (0.000 mg l⁻¹) and Kullu (0.000 mg l⁻¹). The data presented in Table 2 further stipulated that irrespective of the urban areas the seasons exerted significant influence on surface water Cd. The water sources registered highest Cd of 0.001 mg l⁻¹ in pre-monsoon season followed by post-monsoon (0.001 mg l⁻¹) and lowest of 0.000 mg l⁻¹ in monsoon months. The urban areas and season interaction observed to induce non-significant variation in surface water Cd.

Similarly, during second year the highest Cd of 0.003 mg l⁻¹ was recorded in Shimla, followed by Dharamshala with respective value of 0.001 mg l⁻¹. The lowest Cd was recorded in Mandi with value of 0.001 mg l⁻¹ which was found to be at par with Kullu (0.001 mg l⁻¹). The data presented in Table 2 further indicated that the highest Cd of 0.002 mg l⁻¹ was discerned in pre-monsoon months followed by post-monsoon (0.001 mg l⁻¹) and lowest of 0.000 mg l⁻¹ in monsoon season. The interaction of urban areas and seasons exhibited non-significant variation with respect to the Cd of surface water sources.

The pooled analysis of both the years also indicated the similar trend with respect to Cd of surface water sources which followed the order: Shimla (0.003 mg l⁻¹) > Dharamshala (0.001 mg l⁻¹) > Mandi (0.000 mg l⁻¹) > Kullu (0.000 mg l⁻¹). The values of Dharamshala,

| Table 2: Seasonal distribution of cadmium (mg l⁻¹) in surface water sources of urban areas |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| **Urban areas**                          | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** | **Pre-monsoon** | **Monsoon** | **Post-monsoon** | **Mean** |
|                                | 2018          |          |              |         | 2019          |          |              |         | 2019          |          |              |         | 2019          |          |              |         |
| Shimla                        | 0.004        | 0.002   | 0.002        | 0.003   | 0.004        | 0.001   | 0.004        | 0.003   | 0.004        | 0.001   | 0.002        | 0.003   | 0.002        | 0.003   | 0.003        | 0.003   |
| Dharamshala                  | 0.000        | 0.000   | 0.000        | 0.000   | 0.002        | 0.000   | 0.000        | 0.001   | 0.001        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.001        | 0.001   |
| Mandi                        | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   |
| Kullu                        | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   | 0.000        | 0.000   |
| Mean                         | 0.001        | 0.000   | 0.001        |         | 0.002        | 0.000   | 0.001        |         | 0.002        | 0.000   | 0.000        |         | 0.000        |         | 0.001        |         |
| **CD_0.65**                  | Urban areas  | 0.001   |         |         | 0.001        |         |         |         | 0.001        |         |         |         | 0.001        |         |         |         |
|                             | Seasons      | 0.001   |         |         | 0.001        |         |         |         | 0.001        |         |         |         | 0.001        |         |         |         |
|                             | Seasons × Urban areas | NS |         |         | NS          |         |         |         | NS          |         |         |         | NS          |         |         |         |

Mandi and Kullu were found to be at par with each other. The concentration of Cd was found to be within the permissible limits of BIS in all the urban areas, therefore, inferring that Cd concentration has not influenced the surface water quality of selected towns. However, the concentration of Cd was found higher in Shimla town which may be due to the rapid urbanization, population pressure, tourist inflow, municipal waste water and rampant increase in construction activities in the surrounding areas of the town. According to Hanan et al. (2000) [15], Cd occurs naturally in rocks and soils and enters water when there is contact with soft groundwater or surface water. Moreover, it may be introduced by paints, pigments,
plastic stabilizers, fossil fuel, fertilizer and sewage sludge disposal (Rahmanian et al., 2015) [27]. Season-wise pooled analysis also revealed Cd distribution in water bodies in the order of pre-monsoon (0.002 mg l\(^{-1}\)) > post-monsoon (0.001 mg l\(^{-1}\)) > monsoon (0.000 mg l\(^{-1}\)). The values of monsoon and post-monsoon months were found to be at par with each other. The higher values of Cd content during pre-monsoon months may be ascribed to less rains and relatively higher retention of the chemicals in soils compared to post-monsoon season where dilution effect of high rains during monsoon might have reduced its concentration in the water sources. The results are in line with findings of Rajmohan and Elango (2005) [28], Sankar et al. (2010) [31] and Kumar et al. (2012) [16] who have also noticed similar trend in Cd content under the influence of seasons.

**Copper**

The different urban areas were found to exhibit significant variations in distribution of Cu content in surface water sources. The perusal of the data presented in Table 3 indicated that the surface water Cu in different urban areas ranged from 0.002 to 0.096 mg l\(^{-1}\) which was normal and within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Cu of 0.003 mg l\(^{-1}\) was noticed in the surface water sources of Dharamshala followed by Mandi (0.003 mg l\(^{-1}\)). Whereas the lowest surface water Cu of 0.002 mg l\(^{-1}\) was observed in Shimla which was found to be at par with Kullu (0.002 mg l\(^{-1}\)). The data presented in Table 3 further stipulated that irrespective of the urban areas the seasons exerted significant influence on Cu content of surface water sources. The water sources registered highest Cu of 0.039 mg l\(^{-1}\) in pre-monsoon season followed by post-monsoon (0.019 mg l\(^{-1}\)) and lowest of 0.016 mg l\(^{-1}\) in monsoon months. The urban areas and season interaction also induced significant variation in surface water Cu. The highest Cu of 0.148 mg l\(^{-1}\) was noticed in Dharamshala in pre-monsoon season and lowest value of 0.001 mg l\(^{-1}\) was observed in Shimla and Kullu in monsoon months.

Similarly, during second year, the highest Cu of 0.098 mg l\(^{-1}\) was recorded in Dharamshala, followed by Mandi with respective value of 0.003 mg l\(^{-1}\). The lowest Cu was recorded in Shimla with value of 0.002 mg l\(^{-1}\) which was found to be at par with Kullu (0.002 mg l\(^{-1}\)). The data presented in Table 3 further indicated that the highest Cu of 0.041 mg l\(^{-1}\) was discerned in pre-monsoon months followed by post-monsoon (0.021 mg l\(^{-1}\)) and lowest of 0.016 mg l\(^{-1}\) in monsoon season. The interaction of urban areas and seasons was found to be significant with respect to the Cu of surface water sources. The highest Cu of 0.158 mg l\(^{-1}\) was noticed in Dharamshala in pre-monsoon season and lowest value of 0.001 mg l\(^{-1}\) was observed in Shimla and Kullu in monsoon months.

The pooled analysis of both the years also indicated the similar trend with respect to Cu content of surface water sources which followed the order: Dharamshala (0.096 mg l\(^{-1}\)) > Mandi (0.003 mg l\(^{-1}\)) > Shimla (0.002 mg l\(^{-1}\)) > Kullu (0.002 mg l\(^{-1}\)). The values of Mandi, Shimla and Kullu were found to be at par with each other. Since, the level of Cu has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. The elevated concentration of Cu in Dharamshala town may be due to the construction and mining activities which exposed the Cu in soil to water sources. Ashraf et al. (2011) [4] and Rahmanian et al. (2015) [29] Metal mining is found to be the second largest source of metal contamination in soil which includes metals such as Zn, Cu, Pb and Sn. The higher concentration may also be due to the natural deposits of Cu in surrounding areas of Dharamshala town. Season-wise pooled analysis revealed similar trend with respect to Cu content of surface water sources which followed the order: pre-monsoon (0.040 mg l\(^{-1}\)) > post-monsoon (0.020 mg l\(^{-1}\)) > monsoon (0.016 mg l\(^{-1}\)). The values of monsoon and post-monsoon months were found to be at par with each other. The interaction between urban areas and season also induced significant variation in Cu of surface water sources. The highest Cu of 0.153 mg l\(^{-1}\) was noticed in Dharamshala in pre-monsoon season and lowest value of 0.001 mg l\(^{-1}\) was observed in Shimla and Kullu in monsoon months. The higher values of Cu content during pre-monsoon months may be ascribed to less rains and relatively higher retention of the chemicals in soils compared to post-monsoon season where dilution effect of high rains during monsoon might have reduced its concentration in the water sources (Sankar et al., 2010) [31].

**Chromium**

The different urban areas were found to exhibit significant variations in distribution of Cr content in surface water sources. The perusal of the data presented in Table 4 indicated that the surface water Cr in different urban areas ranged from 0.001 to 0.020 mg l\(^{-1}\) which was normal and within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Cr of 0.019 mg l\(^{-1}\) was noticed in the surface water sources of Shimla followed by Mandi (0.011 mg l\(^{-1}\)) and Kullu (0.004 mg l\(^{-1}\)). Whereas the lowest surface water Cr of 0.001 mg l\(^{-1}\) was observed in Dharamshala. The data presented in Table 4 further stipulated that irrespective of the urban areas the seasons exerted significant influence on Cr of surface water sources. The water sources registered highest Cr of 0.015 mg l\(^{-1}\) in pre-monsoon season followed by post-monsoon (0.006 mg l\(^{-1}\)) and lowest of 0.005 mg l\(^{-1}\) in
monsoon months. The urban areas and season interaction also induced significant variation in surface water Cr. The highest Cr of 0.025 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Dharamshala (0.001 mg l\(^{-1}\)) in all the months. Similarly, during second year the highest Cr of 0.021 mg l\(^{-1}\) was recorded in Shimla, followed by Mandi and Kullu with respective values of 0.012 and 0.004 mg l\(^{-1}\). The lowest Cr was recorded in Dharamshala with value of 0.001 mg l\(^{-1}\). The data presented in Table 4 further indicated that the highest Cr of 0.016 mg l\(^{-1}\) was discerned in pre-monsoon months followed by post-monsoon (0.007 mg l\(^{-1}\)) and lowest of 0.005 mg l\(^{-1}\) in monsoon season. The interaction of urban areas and seasons was also found to be significant with respect to the Cr of surface water sources. The highest Cr of 0.026 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Dharamshala (0.001 mg l\(^{-1}\)) in all the months. The pooled analysis of both the years also indicated the similar trend with respect to Cr of surface water sources which followed the order: Shimla (0.020 mg l\(^{-1}\)) > Mandi (0.011 mg l\(^{-1}\)) > Kullu (0.004 mg l\(^{-1}\)) > Dharamshala (0.001 mg l\(^{-1}\)). The values of Kullu and Dharamshala were found to be at par with each other. Since, the concentration of Cr has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. The elevated concentration of Cr in Shimla town may be due to the population pressure, construction activities which leads to the erosion of natural deposits from the surrounding areas.

| Seasons | Urban areas | 2018 Mean | 2019 Mean | Pooled Mean |
|---------|-------------|-----------|-----------|-------------|
| Pre-monsoon | Shimla | 0.025 | 0.014 | 0.019 |
| Monsoon | 0.001 | 0.001 | 0.001 |
| Post-monsoon | 0.001 | 0.001 | 0.011 |
| Monsoon | 0.011 | 0.000 | 0.000 |
| Monsoon | 0.004 | 0.004 | 0.004 |
| Mean | 0.015 | 0.05 | 0.006 |
| CD\(_{0.05}\) | 0.005 | 0.010 | 0.006 |

It is in line with the findings of (Rahmanian et al., 2015)\(^{[27]}\). Season-wise pooled analysis also depicted Cr distribution in water bodies in the order of pre-monsoon (0.016 mg l\(^{-1}\)) > post-monsoon (0.006 mg l\(^{-1}\)) > monsoon (0.005 mg l\(^{-1}\)). The values of monsoon and post-monsoon months were found to be at par with each other. The urban areas and season interaction of both years also induced significant variation in surface water Cr. The highest Cr of 0.026 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Dharamshala (0.001 mg l\(^{-1}\)) in all the months. The results are in consonance with the findings of Ravichandran and Jayaprakash (2011)\(^{[30]}\) who reported that the high concentration of chromium during pre-monsoon season could be due to increase in temperature and high rate of evaporation leaving behind heavy metals and lowest value in monsoon season may be due to dilution in the water sources due to the rainfall.

Nickel
The different urban areas were found to exhibit significant variations in distribution of Ni content in surface water sources. The perusal of the data presented in Table 5 indicated that the surface water Ni in different urban areas ranged from 0.002 to 0.006 mg l\(^{-1}\) which was within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Ni of 0.006 mg l\(^{-1}\) was noticed in the surface water sources of Kullu followed by Mandi (0.005 mg l\(^{-1}\)) and Shimla (0.003 mg l\(^{-1}\)). Whereas the lowest surface water Ni of 0.002 mg l\(^{-1}\) was observed in Dharamshala. The data presented in Table 5 further stipulated that irrespective of the urban areas the seasons exerted significant influence on surface water Ni. The water sources registered highest Ni of 0.005 mg l\(^{-1}\) in pre-monsoon season followed by post-monsoon (0.004 mg l\(^{-1}\)) and lowest of 0.003 mg l\(^{-1}\) in monsoon months. The urban areas and season interaction were found to induce non-significant variation in Ni of surface water sources. Similarly, during second year the highest Ni of 0.007 mg l\(^{-1}\) was recorded in Kullu followed by Mandi and Shimla with respective values of 0.005 and 0.003 mg l\(^{-1}\). The lowest Ni was recorded in Dharamshala with value of 0.002 mg l\(^{-1}\). The data presented in Table 5 further indicated that irrespective of the urban areas the seasons exerted non-significant influence on surface water Ni. The interaction of urban areas and seasons was also found to be non-significant with respect to the Ni of surface water sources.

| Seasons | Urban areas | 2018 Mean | 2019 Mean | Pooled Mean |
|---------|-------------|-----------|-----------|-------------|
| Pre-monsoon | Shimla | 0.005 | 0.002 | 0.003 |
| Monsoon | 0.003 | 0.002 | 0.002 |
| Post-monsoon | 0.003 | 0.002 | 0.002 |
| Monsoon | 0.006 | 0.004 | 0.005 |
| Monsoon | 0.007 | 0.006 | 0.006 |
| Mean | 0.005 | 0.003 | 0.004 |
| CD\(_{0.05}\) | 0.003 | 0.004 | 0.003 |
The pooled analysis of both the years also indicated the similar trend with respect to Pb content in surface water sources which followed the order: Kullu (0.006 mg l\(^{-1}\)) > Mandi (0.005 mg l\(^{-1}\)) > Shimla (0.003 mg l\(^{-1}\)) > Dharamshala (0.002 mg l\(^{-1}\)). The values of Dharamshala and Shimla were found to be at par with each other. Since, the level of Ni has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. The higher concentration of Ni in Kullu town may be due to its natural occurrence in the surroundings rocks or varied geology which might get exposed to the surface water bodies due to the construction activities, agricultural practices nearby the town, further illegal discharge of municipal waste water effluents, sewage sludge, commercial and various anthropogenic activities enhanced its concentration in water sources. Cempel & Nikel (2006) \(^{[9]}\) advocated natural sources of atmospheric Ni as wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation. The ambient air also reported to contain Ni due the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage and miscellaneous sources (Clayton and Clayton, 1994; Grandjean, 1984; Clarkson, 1998; Anonymous, 1991; Von Burg, 1997; Cempel & Nikel, 2006 and Spectrum, 1998. Bencko 1983) \(^{[11, 14, 10, 2, 35, 9, 34, 6]}\), Scott-Fordsmand (1997) \(^{[32]}\) and Von Burg (1997) \(^{[35]}\) reported that Ni may pose a major problem in land near towns, industrial areas, or even in agricultural land receiving wastes such as sewage sludge and varies in soil in a wide range from 3 to 1000 mg kg\(^{-1}\). Scott-Fordsmand (1997) \(^{[32]}\); Anonymous, (1991) \(^{[2]}\) and Bennett (1982) \(^{[7]}\) also observed several forms of Ni in soils such as inorganic crystalline minerals or precipitates, complexed or adsorbed on organic cation surfaces or on inorganic cation exchange surfaces, water soluble, free-ion or chelated metal complexes in soil solution which may be released into the surface water bodies. Season-wise pooled analysis also revealed Ni distribution in water bodies in the order of pre-monsoon (0.005 mg l\(^{-1}\)) > post-monsoon (0.003 mg l\(^{-1}\)) > monsoon (0.004 mg l\(^{-1}\)). The higher values of Ni content during pre-monsoon months may be ascribed to less rains and relatively higher retention of the chemicals in soils compared to post-monsoon season where dilution effect of high rains during monsoon might have reduced its concentration in the water sources (Lashari et al., 2009) \(^{[18]}\).

**Lead**

The different urban areas were found to exhibit significant variations in distribution of Pb content in surface water sources. The perusal of the data presented in Table 6 indicated that the surface water Pb in different urban areas ranged from 0.003 to 0.006 mg l\(^{-1}\) which was normal and within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Pb of 0.006 mg l\(^{-1}\) was noticed in the surface water sources of Shimla followed by Mandi (0.005 mg l\(^{-1}\)). Whereas the lowest surface water Pb of 0.003 mg l\(^{-1}\) was observed in Dharamshala town which was found to be at par with Kullu (0.003 mg l\(^{-1}\)). The data presented in Table 6 further stipulated that irrespective of the urban areas the seasons exerted significant influence on surface water Pb. The water sources registered highest Pb of 0.006 mg l\(^{-1}\) in pre-monsoon season followed by post-monsoon (0.003 mg l\(^{-1}\)) and monsoon (0.003 mg l\(^{-1}\)) months. The urban areas and season interaction also induced significant variation in Pb content of surface water sources. The highest Pb of 0.006 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Kullu (0.001 mg l\(^{-1}\)) in monsoon months. Similarly, during second year the highest Pb of 0.007 mg l\(^{-1}\) was recorded in Shimla, followed by Mandi with respective value of 0.004 mg l\(^{-1}\). The lowest Pb of 0.003 mg l\(^{-1}\) was recorded in Dharamshala which was found to be at par with Kullu (0.003 mg l\(^{-1}\)). The data presented in Table 6 further indicated that the highest Pb of 0.008 mg l\(^{-1}\) was discerned in pre-monsoon months followed by post-monsoon (0.003 mg l\(^{-1}\)) and lowest of 0.002 mg l\(^{-1}\) in monsoon season. The interaction of urban areas and seasons was found to be significant with respect to the Pb of surface water sources. The highest Pb of 0.015 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Kullu (0.001 mg l\(^{-1}\)) in monsoon months.

The pooled analysis of both the years also indicated the similar trend with respect to Pb content of surface water sources which followed the order: Shimla (0.006 mg l\(^{-1}\)) > Mandi (0.005 mg l\(^{-1}\)) > Dharamshala (0.003 mg l\(^{-1}\)) > Kullu (0.003 mg l\(^{-1}\)). The values of Dharamshala and Kullu were found to be at par with each other. Since, the level of Pb has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. The higher concentration of Pb in surface water sources of Shimla town may be due to high transport activities, increased rate of urbanization and population pressure in comparison to the other major towns. The elevated concentrations of Pb in surface water sources of urban areas have also been reported in literature due to high combustion of leaded gasoline (Bannat et al., 1998) \(^{[5]}\). The lowest Pb content in surface water sources of Dharamshala and Kullu may be ascribed to less transport and anthropogenic activities.

| Seasons × Urban areas | Pre-monsoon (Mean) | Monsoon (Mean) | Post-monsoon (Mean) | NS | NS | NS | NS |
|----------------------|-------------------|---------------|---------------------|----|----|----|----|
| **Urban areas**       | 0.005             | 0.004         | 0.004               | 0.005 | 0.004 | 0.008 | 0.011 | 0.004 | 0.005 | 0.006 |
| Shimala               | 0.004             | 0.002         | 0.005               | 0.003 | 0.004 | 0.002 | 0.003 | 0.003 | 0.004 | 0.002 | 0.003 |
| Mandi                 | 0.005             | 0.004         | 0.005               | 0.005 | 0.005 | 0.003 | 0.005 | 0.005 | 0.004 | 0.005 | 0.005 |
| Kullu                 | 0.008             | 0.001         | 0.002               | 0.003 | 0.006 | 0.001 | 0.002 | 0.003 | 0.007 | 0.001 | 0.002 |
| Mean                  | 0.006             | 0.003         | 0.003               | 0.008 | 0.002 | 0.003 | 0.007 | 0.003 | 0.003 | 0.003 | 0.003 | 0.003 |

- **Table 6**: Seasonal distribution of lead (mg l\(^{-1}\)) in surface water sources of urban areas
Season-wise pooled analysis also revealed similar trend with respect to Pb of surface water sources which followed the order: pre-monsoon (0.007 mg l\(^{-1}\)) > post-monsoon (0.003 mg l\(^{-1}\)) > monsoon (0.003 mg l\(^{-1}\)). The values of post-monsoon and monsoon were found to be at par with each other. The interaction between urban areas and season for both years also induced significant variation in surface water Pb. The highest Pb of 0.011 mg l\(^{-1}\) was noticed in Shimla in pre-monsoon season and lowest was observed in Kullu (0.001 mg l\(^{-1}\)) in monsoon months. The results are in collaboration with the findings of Rahman et al. (2013) who have also reported high concentration of lead during pre-monsoon months due to elevated temperature and rate of evaporation which might have enriched its heavy metal concentrations in water due to decrease in its volume.

**Zinc**

The different urban areas were found to exhibit significant variations in distribution of Zn in surface water sources. The perusal of the data presented in Table 7 indicated that the surface water Zn in different urban areas ranged from 0.000 to 0.044 mg l\(^{-1}\) which was normal and within the permissible limits as prescribed by BIS. During first year (2018) significantly highest Zn of 0.045 mg l\(^{-1}\) was noticed in the surface water sources of Kullu followed by Mandi (0.024 mg l\(^{-1}\)) and Shimla (0.004 mg l\(^{-1}\)). Whereas the lowest surface water Zn of 0.000 mg l\(^{-1}\) was observed in Dharamshala. The data presented in Table 7 further stipulated that irrespective of the urban areas the seasons exerted significant influence on surface water Zn. The water sources registered highest Zn of 0.029 mg l\(^{-1}\) in pre-monsoon season followed by post-monsoon (0.016 mg l\(^{-1}\)) and lowest of 0.012 mg l\(^{-1}\) in monsoon months. The urban areas and season interaction also induced significant variation in surface water Zn. The highest Zn of 0.076 mg l\(^{-1}\) was noticed in Kullu in pre-monsoon season and lowest was observed in Dharamshala (0.000 mg l\(^{-1}\)) in all the months.

Similarly, during second year surface water Zn in different urban areas was found to exhibit significant variations. The highest Zn of 0.047 mg l\(^{-1}\) was recorded in Kullu, followed by Mandi and Shimla with respective values of 0.032 and 0.000 mg l\(^{-1}\). The lowest Zn was recorded in Dharamshala with value of 0.000 mg l\(^{-1}\). The data presented in Table 7 further indicated that irrespective of locations, seasons exerted significant influence on surface water Zn. The highest Zn of 0.032 mg l\(^{-1}\) was pre-monsoon in summer months followed by post-monsoon (0.018 mg l\(^{-1}\)) and lowest of 0.011 mg l\(^{-1}\) in monsoon season. The interaction of urban areas and seasons was also found to be significant with respect to the Zn of surface water sources.

**Table 7:** Seasonal distribution of zinc (mg l\(^{-1}\)) in surface water sources of urban areas

| Urban areas | Pre-monsoon | Monsoon | Post-monsoon | Mean | Pre-monsoon | Monsoon | Post-monsoon | Mean | Pre-monsoon | Monsoon | Post-monsoon | Mean | Pooled |
|-------------|-------------|---------|-------------|------|-------------|---------|-------------|------|-------------|---------|-------------|------|--------|
| Shimla      | 0.004       | 0.003   | 0.004       | 0.004 | 0.004       | 0.003   | 0.004       | 0.004 | 0.004       | 0.003   | 0.004       | 0.004 | 0.004   |
| Dharamshala | 0.000       | 0.000   | 0.000       | 0.000 | 0.000       | 0.000   | 0.000       | 0.000 | 0.000       | 0.000   | 0.000       | 0.000 | 0.000   |
| Mandi       | 0.035       | 0.019   | 0.027       | 0.027 | 0.044       | 0.016   | 0.037       | 0.029 | 0.039       | 0.017   | 0.032       | 0.029 | 0.029   |
| Kullu       | 0.076       | 0.025   | 0.034       | 0.045 | 0.079       | 0.027   | 0.033       | 0.046 | 0.078       | 0.026   | 0.034       | 0.046 | 0.046   |
| Mean        | 0.029       | 0.012   | 0.016       | 0.032 | 0.032       | 0.011   | 0.018       | 0.030 | 0.030       | 0.012   | 0.017       | 0.017 | 0.017   |

The highest Zn of 0.079 mg l\(^{-1}\) was noticed in Kullu in pre-monsoon season and lowest was observed in Dharamshala (0.000 mg l\(^{-1}\)) in all the months. The pooled analysis of both the years also indicated the similar trend with respect to Zn of surface water sources which followed the order: Kullu (0.046 mg l\(^{-1}\)) > Mandi (0.029 mg l\(^{-1}\)) > Shimla (0.004 mg l\(^{-1}\)) > Dharamshala (0.000 mg l\(^{-1}\)). The values of Shimla and Dharamshala were found to be at par with each other. Since, the level of Zn has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. The highest Zn concentration in surface water sources may be attributed to the higher exposure of these sources to road construction and expansion activities (Polkowaska et al., 2007). The highest Zn content in Kullu town might be due to the construction and expansion of the highway and heavy flow of tourists towards Manali hill station and population pressure and due to rapid rise in urbanization and construction activities. Also, the illegal discharge of sewage into the water bodies and its mixing might have also enhanced its concentration in water sources of Kullu. It is in agreement with the findings of Shivaraju (2016). Season-wise pooled analysis also revealed similar trend with respect to ground water Zn which followed the order: pre-monsoon (0.030 mg l\(^{-1}\)) > post-monsoon (0.017 mg l\(^{-1}\)) > monsoon (0.012 mg l\(^{-1}\)). The interaction between urban areas and season also induced significant variation in Zn content of surface water sources. The highest Zn of 0.078 mg l\(^{-1}\) was noticed in Kullu in pre-monsoon season and lowest was observed in Dharamshala (0.000 mg l\(^{-1}\)) in all the months. The results are in conformity with the findings of Ndeda and Manohar (2014) who have also reported high concentration of Zn during pre-monsoon season due to elevated temperature and rate of evaporation leaving behind heavy metals and lowest value in monsoon season may be due to dilution effect during rainfall in the surface water sources.

**Iron**

The different urban areas were found to exhibit significant variations in distribution of Fe content in surface water sources. The perusal of the data presented in Table 8 indicated that the surface water Fe in different urban areas ranged from 0.15 to 0.42 mg l\(^{-1}\) which was normal and within the permissible limits as prescribed by BIS. During first year
(2018) significantly highest Fe of 0.42 mg l$^{-1}$ was noticed in the surface water sources of Kullu followed by Mandi (0.29 mg l$^{-1}$) and Shimla (0.27 mg l$^{-1}$). Whereas the lowest surface water.

| Seasons | Urban areas | Pre-monsoon Mean | Monsoon Mean | Post-monsoon Mean | 2018 (Mean), 2019 (Mean), Pooled (Mean) |
|---------|-------------|------------------|--------------|-------------------|-----------------------------------------|
|        |             | 0.18             | 0.28         | 0.27              | 0.37, 0.37, 0.30                         |
| Shimla  |             | 0.36             | 0.18         | 0.27              | 0.37, 0.19, 0.30                         |
| Dharamshala |       | 0.18             | 0.13         | 0.15              | 0.18, 0.13, 0.16                         |
| Mandi   |             | 0.37             | 0.25         | 0.26              | 0.38, 0.22, 0.30                         |
| Kullu   |             | 0.50             | 0.35         | 0.41              | 0.50, 0.34, 0.43                         |
| Mean    |             | 0.35             | 0.23         | 0.27              | 0.36, 0.23, 0.30                         |
| CDIO:I  |             | 0.06             | 0.05         | 0.04              | 0.05, 0.05, 0.03                         |
| Seasons |             |                  |              |                   |                                         |
| Urban areas |       |                  |              |                   |                                         |
| Nearest |             |                  |              |                   |                                         |
| NS      |             |                  |              |                   |                                         |

Fe of 0.15 mg l$^{-1}$ was observed in Dharamshala. The data presented in Table 8 further stipulated that irrespective of the urban areas the seasons exerted significant influence on Fe of surface water sources. The water sources registered highest Fe of 0.35 mg l$^{-1}$ in pre-monsoon season followed by post-monsoon (0.27 mg l$^{-1}$) and lowest of 0.23 mg l$^{-1}$ in monsoon months. The urban areas and season interaction exhibited non-significant variation in surface water Fe. Similarly, during second year surface water Fe in different urban areas was found to exhibit significant variations. The highest Fe of 0.42 mg l$^{-1}$ was recorded in Kullu, followed by Mandi and Shimla with respective values of 0.30 and 0.28 mg l$^{-1}$. The lowest Fe was recorded in Dharamshala with value of 0.16 mg l$^{-1}$. The data presented in Table 8 further indicated that irrespective of locations, seasons exerted significant influence on surface water Fe. The highest Fe of 0.36 mg l$^{-1}$ was discerned in pre-monsoon months followed by post-monsoon (0.30 mg l$^{-1}$) and lowest of 0.22 mg l$^{-1}$ in monsoon season. The interaction of urban areas and seasons was found to be non-significant with respect to the Fe of surface water sources.

The pooled analysis of both the years also indicated the similar trend with respect to surface water Fe which followed the order: Kullu (0.42 mg l$^{-1}$) > Mandi (0.30 mg l$^{-1}$) > Shimla (0.28 mg l$^{-1}$) > Dharamshala (0.15 mg l$^{-1}$). The values of Mandi and Shimla were found to be at par with each other. Since, the level of Fe has not exceeded the permissible limits prescribed by the BIS and hence resulted no harmful effect on surface water sources and environmental ecosystem as a whole. Elevated concentration of Fe at Kullu town may be due to the presence of large number of automobiles repairing workshops which uses iron material for various operations. Similar, results are also reported by Puri (2011) [35] who also found an increase in the concentration of Fe in surface water sources which might be attributed to seepage of Fe containing waste water effluents to surface water sources. High concentration of Fe may also be attributed to the dissolution of iron bearing minerals from the soil strata in the study area. Season-wise pooled analysis also revealed similar trend with respect to ground water Fe which followed the order: pre-monsoon (0.35 mg l$^{-1}$) > post-monsoon (0.29 mg l$^{-1}$) > monsoon (0.22 mg l$^{-1}$). The higher concentration of Fe during pre-monsoon months may be ascribed to less rains and relatively higher retention of the chemicals in soils as compared to post-monsoon season where dilution effect of high rains during monsoon might have reduced its concentration in the water sources. The present trend of results is in line with findings of Sankar et al. (2010) [31] who have also noticed similar trend of Fe content under the influence of seasons.

**Mercury**

The analysis of water samples had been carried out for measuring mercury (Hg) content of surface water sources in selected towns. However, the concentration of Hg was not detected in any of water samples collected from the surface water sources.

**Conclusion**

The study inferred that the major urban areas of Himachal Pradesh have started impacting water quality however it was still within the permissible limits. The study inferred that the current activities in urban areas has started impacting the heavy metals concentration of surface water quality which at present is in good to excellent category. Further, evinced by the fact that the urban areas having high population, vehicular density and rate of urbanization experienced elevated levels of heavy metals in surface water quality parameters. Therefore, in order to maintain the quality of the important natural resources within the safe limits, urbanization on ecological principles is recommended for sustainable development in the state.

**References**

1. Ahmed A, Ghosh PK, Hasan M, Rahman A. Surface and groundwater quality assessment and identification of hydrochemical characteristics of a south-western coastal area of Bangladesh. Environmental Monitoring and Assessment 2020;192(4):258. https://doi.org/10.1007/s10661-020-8227-0
2. Anonymous. Environmental Health Criteria 108. Nickel. WHO, Geneva 1991.
3. APHA. Standard methods for the examination of waste water. Washington DC. 1998, 161.
4. Ashraf MA, Maah MJ, Yussof I. Heavy metals accumulation in plants growing in ex tin mining catchment. International Journal of Environmental Science and Technology 2011;8(2):401-416.
5. Bannat IM, Hussain ES, EL-Shahawi MS, Abu Hilal AH. Post-gulf war assessment of nutrients, heavy metal ions, hydrocarbons and bacterial pollution level in the United Arab Emirates coastal waters. Environment International 1998;24:109-116.
6. Bencko V. Nickel: A review of its occupational and environmental toxicology. Journal of Hygiene,
Epidemiology, Microbiology and Immunology 1983;27:237.

7. Bennett BG. Exposure of man to environmental nickel--an exposure commitment assessment. Science of the Total Environment 1982;22(3):203.

8. Bu H, Tan X, Li S, Zhang Q. Temporal and spatial variations of water quality in the Jinshui River of the South Qinling Mts., China. Ecotox. Environ. Safe. 2010;73:907-913.

9. Cempel M, Nikel G. Nickel: A review of its sources and environmental toxicology. Polish Journal of Environmental Studies 2006;15(3):375-382.

10. Clarkson TW. Biological Monitoring of Toxic Metals; plenum press: New york. 1998, 265-282.

11. Clayton GD, Clayton FE. Patty’s Industrial Hygiene Toxicology, 4th ed.; A wiley-Interscience publication: New York. 1994, 2157-2173.

12. CPCB. Status of ground water quality in India Part-II, Ground water quality series: GWQS/10/2007-2008. Central Pollution Control Board, Ministry of Environment and Forests, Government of India. Parivesh Bhawan, East Arjun Nagar Delhi – 110 032. 2008, 334. www.cppc.nic.in

13. CPCB. (Central Pollution Control Board). Guidelines for the measurements of Ambient Air Pollution, New Delhi. India 2011:(1);55.

14. Grandjean P. Human exposure to nickel. IARC Scientific Publications 1984;53:469.

15. Hanaa M, Eweida EA, Azza F. Heavy metals in drinking water and their environmental impact of human health 2000.

16. Kumar J, Puri A. A review of permissible limits of drinking water. Indian Journal of Occupational and Environmental Medicine 2012;16:40-44.

17. Kumar R, Singh RD, Sharma KD. Water resources of India. Current Science 2005;89(5):794-811.

18. Lashari KH, Korai AL, Sahato GA, Kazi TG. Limnological studies of Keenjar Lake, District, Thatta, Sindh, Pakistan. Pakistan Journal of Analytical & Environmental Chemistry 2009;10:39-47.

19. McDonald R, Green P, Balk D, Fekete BM, Revenga C, Todd M et al. Urban Growth, Climate Change, and Freshwater Availability. Proceedings of the National Academy of Sciences 2011;108(15):6312-6317.

20. Najafpour SH, Alkarkhi AFM, Kadir MOA, Najafpour GD. Evaluation of Spatial and Temporal Variation in River Water Quality. Int. J. Environ. Res. 2008;2:349-358.

21. Ndeta LA, Manohar S. Determination of heavy metals in Nairobi dam water, Kenya. Journal of Environmental Science, Toxicology and Food Technology 2014;8:68-73.

22. Park K. Preventive and Social Medicine. Jabalpur, India: M/S Banarsidas Bhanot Publishers 2009.

23. Pesce SF, Wunderlin DA. Use of water quality indices to verify the impact of Cordoba city (Argentina) on Suquia river. Water Research 2000;34:2915-2926.

24. Polkowska Z, Skarzynska K, Dubiella-Jackowska A, Staszek W, Namiesnik J. Evaluation of pollutant loading in the runoff water from a major urban highway (Gdansk Beltway, Poland). Global Nest Journal 2007;9:269-275.

25. Puri R. Study Regarding Lake Water Pollution with Heavy Metals in Nagpur City (India). International Journal of Chemical, Environmental and Pharmaceutical Research 2011;2(1):34-39.