



Spatio-Temporal Distribution, Ecological Risk Assessment, and Multivariate Analysis of Heavy Metals in Bathinda District, Punjab, India

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Abstract The pollution of agricultural soil due to heavy metals is a serious environmental problem throughout the world due to their persistence and toxicity. The present study was carried out on agricultural soils of district Bathinda, Punjab where a total of 120 soil samples were collected from 40 different locations during pre-monsoon, monsoon, and post-monsoon season. The total mean concentration of heavy metals (arsenic (As), chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg), lead (Pb)) was estimated by ThermoScientific–iCAP Qc (Germany) inductively coupled plasma–mass spectrometry (ICP-MS). The concentration of heavy metals was of the order of $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$, $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$, and $Fe > Zn > Cr > Ni > Cu > Co > Pb > As > Hg > Cd$ in pre-monsoon, monsoon, and post-monsoon seasons, respectively. The metals such as Fe, Zn, Cr, and Ni indicated higher concentrations at most of the sites, whereas Hg and Cd showed lower concentrations throughout the region. The total mean concentrations (mg/kg) of the metals were found to be lower than their natural background concentration values. Based on enrichment factor (EF), the soils were moderately

contaminated at most of the sites with a few cases where the soil was minimally enriched with heavy metals. Other pollution indices such pollution load index (PLI) and degree of contamination (C_d) also indicated low to moderate level of soil contamination. Besides, risk assessment of heavy metals was also determined using potential ecological risk factor (E_i) and ecological risk index (R_i) which indicated low E_i and R_i in the region for most of the metals. Spatial distribution using interpolation technique, Inverse Distance Weighted (IDW) in ArcGIS 10.6.1 software, showed a significant spatial and seasonal variability of heavy metals throughout the region. Pearson's correlation coefficient (r) between heavy metal variables was found to be significant at $p < 0.05$ significance level (As-Cr ($r = 0.769$), As-Fe ($r = 0.760$), As-Co ($r = 0.883$), As-Ni ($r = 0.886$), As-Cu ($r = 0.859$), As-Hg ($r = 0.678$) in pre-monsoon samples; As-Fe ($r = 0.613$), As-Co ($r = 0.669$), As-Ni ($r = 0.619$), As-Cu ($r = 0.639$) in monsoon samples and As-Cr ($r = 0.631$), As-Fe ($r = 0.715$), As-Co ($r = 0.710$), As-Cu ($r = 0.690$) in post-monsoon samples) indicated a strong relationship between different variables. Principal component analysis (PCA) technique also proved to be significant in studying the behavioral pattern of variables, where PCA biplots showed different behavior as revealed from some strong associations. Finally, continuous monitoring of the sites is suggested to avoid further contamination and degradation of soil quality, despite low contamination levels in the region.

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1 Introduction

The soil is a complex system which is composed of organic matter, minerals, air, and water (Chavre 2017; Morillas et al. 2020). It is also a mediator of many pollutants to plants because of plant's ability to uptake toxic substances through their roots (Youssef and Chino 1991). Environmental pollution particularly of soil due to heavy metals has been one of the most challenging issues because of widespread distribution, severe toxicity, long-term persistence, and soil–plant exchangeability compared with other contaminants that leads to different diseases (Jean-Philippe et al. 2012; Prajapati 2014; Huang et al. 2015a, 2016; Cao et al. 2009; Du et al. 2018). According to a report of the Central Pollution Control Board, the states such as Andhra Pradesh and Maharashtra of India contribute to 80% of potentially hazardous wastes along with heavy metals (Marg 2011). The hazardous environmental problems occur due to hasty developmental activities across the world (Agarwal et al. 2016; Kord Mostafapour et al. 2018) mostly in developing countries. Heavy metals enter into the soil system through natural means (e.g., rocks) (Erel and Morgan 1992) or by human activities (Yang et al. 2016; Jiang et al. 2017). Naturally, the soil contamination occurs as a result of lithogenesis, soil erosion, desertification, weathering process, and geological courses (Stafilov et al. 2010). Rapid growth of industries and subsequent increase in effluent discharge, fertilizers and pesticides, atmospheric deposition, and other anthropogenic activities in agriculture have increased the heavy metal accumulation in soil (Naghipour et al. 2016a; Yousefi et al. 2017; Dayani and Mohammadi 2010; Bolan et al. 2013; Lin et al. 2017). Some reports also suggested that population explosion in the past few decades have also increased the toxic heavy metals in soil through large-scale agricultural activities (Niu et al. 2013; Huang et al. 2015b). The soil is a long-term natural sink for potential toxicants including nickel, lead, zinc, cadmium, copper, and chromium (Nedelescu et al. 2017). From the soil, the contaminants enrooted through food chain enter into biota causing health issues (Naghipour et al. 2016b; Asghari et al. 2018). Ingestion, inhalation, and dermal contact are the three main routes which allow heavy metals from soil to be transferred into the human body (De Miguel et al. 1998; Li et al. 2013; Wu et al. 2015). In urban areas, the heavy metal contaminants (arsenic, lead, copper, zinc, and nickel) have been found in elevated concentrations which are mostly originated

from industries (Waldron 1980; Harte et al. 1991). Huang et al. (2018) assessed heavy metal contamination in agricultural soils of southeast China where the main risk was linked with arsenic, cadmium and chromium contamination. Table 1 shows different possible sources of contamination of soil due to heavy metals in the region.

Though the heavy metals play a role in maintaining the health of the soil system, a small fluctuation above permissible limits of metal concentration can cause negative impacts on soil biota, soil chemistry, and hydrology, besides socio-economic consequences (Cerdà et al. 2017; Antonelli et al. 2018). As a result, many countries have

Table 1 Heavy metals and their sources of contamination

Metal	Sources of pollution	References
As	Industrial effluents, sewage sludge, bricks and agricultural practices; coal combustion	Nriagu and Pacyna 1988; Dantu 2009; Navas and Machín 2002
Cr	Industrial wastes and sewage sludge; mining activities	Yaylali-Abanuz 2011; Krishna et al. 2013
Fe	Municipal and industrial effluent discharges; product of corrosion in soil and water	Bhagure and Mirgane 2011; Smith 1981
Co	Industrial effluents, coal burning and open ground dumping of solid wastes	Govil et al. 2001; Krishna and Govil 2005
Ni	Fuel combustion or industrial waste discharge	Krishna and Govil 2005; Bhagure and Mirgane 2011
Cu	Commercial fertilizers; agricultural and municipal wastes, industrial emissions, and effluent discharge; Cu-based fungicides, phosphate fertilizers and pesticides	Acosta et al. 2011; Machender et al. 2011; Yaylali-Abanuz 2011; Xiong et al. 2016; Wang et al. 2015
Zn	Industrial waste, composted materials, liquid manures, agro-chemicals; lignite coal mine tailings	Wang et al. 2015; Romić and Romić 2003; Ladwani et al. 2012
Cd	Industrial effluents, sewage effluents, phosphate fertilizers	Williams and David 1973; Jiao et al. 2012; Peris et al. 2008; Cai et al. 2012
Hg	Fungicides, sewage wastes	Yaylali-Abanuz 2011
Pb	Phosphate fertilizers and pesticides; industrial effluents; vehicular emission	Wang et al. 2015; Machender et al. 2011; Adachi and Tainosho 2004

Table 2 Maximum allowable limits (MAL) for heavy metals in soil (mg/kg) in different countries (Lacatusu 2000; Kabata-Pendias 2000, 2001; Duressa and Leta 2015; He et al. 2015)

	Austria	Canada	Germany	Britain	China	Japan	India	Poland	USA
As	50	20	20	–	20–40	–	–	30	14
Cr	100	75	100	50	150–300	–	50	50–80	1500
Fe	–	–	–	–	–	–	–	–	–
Co	50	25	–	–	–	50	–	50	–
Ni	100	100	100	50	40–60	100	75–150	100	210
Cu	100	100	50	100	50–200	125	135–270	100	750
Zn	300	400	300	300	200–300	250	250–500	300	1400
Cd	5	5	1.5–3.0	3	0.3–0.6	–	3–5	1–3	1.6
Hg	5	0.8	2	–	0.3–1.0	–	–	5	0.5
Pb	100	200	100	100	80	400	250–500	70–150	50–300

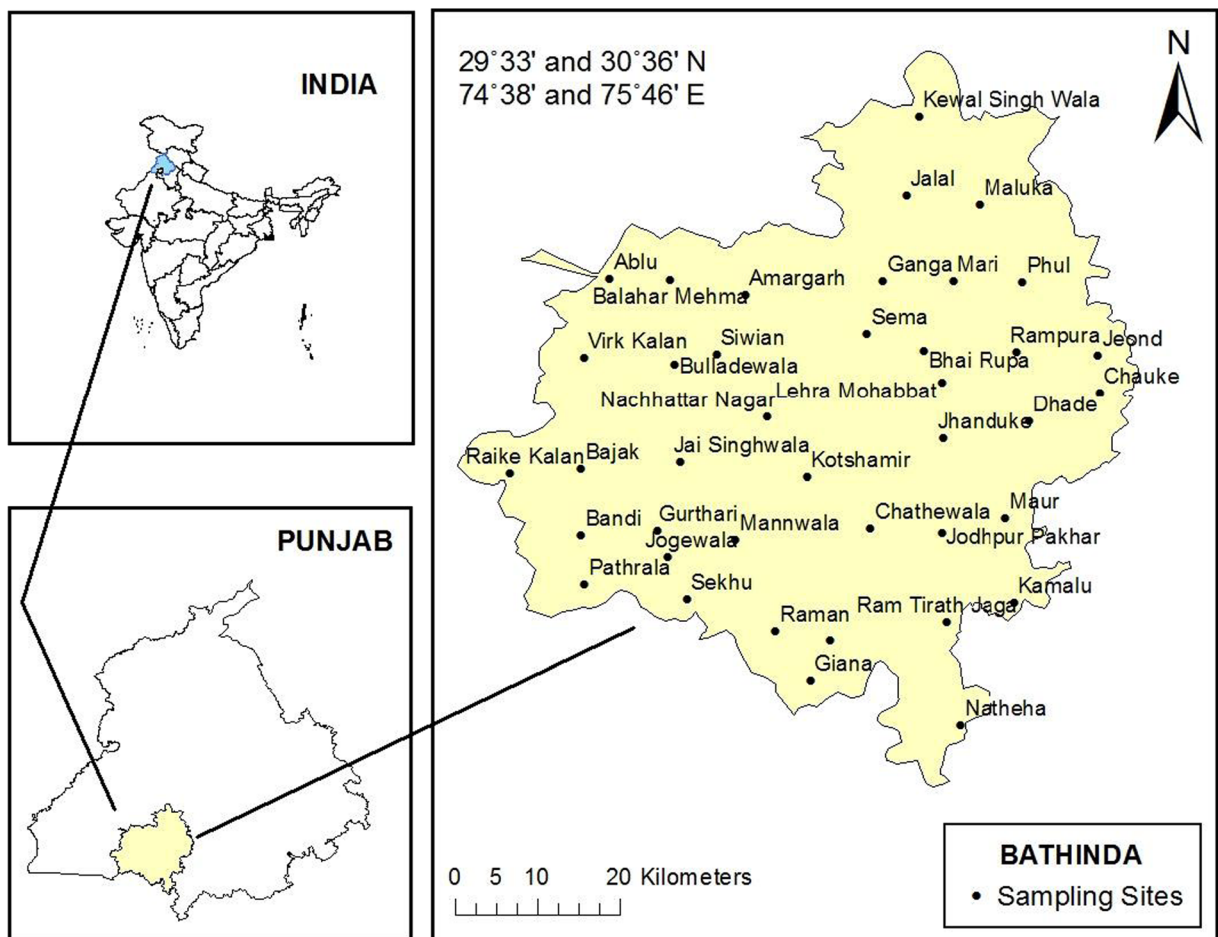


Fig. 1 Study area map of Bathinda, Punjab showing sampling sites and geographical location

started various programs to monitor and control the use of different chemicals in addition to check their passage into the soil system (Sidhu 2016; Sidhu et al. 2017). Therefore, considering such consequences, researchers can develop effective strategies and design sustainable technologies to improve soil health, to restore polluted areas, and to avoid further deterioration (Keesstra et al. 2018).

For better results, comparative analysis, and quality interpretation, it is essential to integrate field-based study with Geographical Information System (GIS) to explore the problems efficiently with better predictions. In the

present study, it was done using Inverse Distance Weighted (IDW) interpolation technique and multivariate tools. Studies have been carried out where GIS-based approach and multivariate analysis were integrated with field base data in order to estimate heavy metals in soil and delineate the sources of contamination (Cheng et al. 2009; Gong et al. 2010). There are various methods conventionally used for the determination of concentration of heavy metals in soil such as acid digestion-based techniques—inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy

Table 3 Details of sampling sites (site number, site name, latitude–longitude, nature–rural, urban, sub-urban)

Site number	Site name	Geographical coordinates	Nature	Site number	Site name	Geographical coordinates	Nature
1	Maluka	30°26'.480"N 75°2'.55.11"E	Rural	21	Natheha	29°84'.468"N 75°17'.228"E	Rural
2	Jalal	30°48'.490"N 75°15'.957"E	Rural	22	Jogewala	29°55'.680"N 74°45'.040"E	Rural
3	Kewal Singh Wala	30°51'.133"N 75°12'.722"E	Rural	23	Giana	29°89'.403"N 75°00'.791"E	Rural
4	Bhai rupa	30°25'.436"N 75°13'.173"E	Sub-urban	24	Malkana	29°93'.679"N 75°02'.890"E	Rural
5	Phul	30°32'.936"N 75°24'.106"E	Rural	25	Raman	29°94'.740"N 74°96'.967"E	Rural
6	Rampura	30°25'.390"N 75°23'.407"E	Rural	26	Sekhu	29°98'.267"N 74°87'.303"E	Rural
7	Jeond	30°24'.964"N 75°32'.273"E	Rural	27	Pathrala	29°99'.838"N 74°76'.078"E	Rural
8	Chauke	30°20'.836"N 75°32'.609"E	Rural	28	Bandi	30°05'.214"N 74°75'.748"E	Rural
9	Dhade	30°17'.695"N 75°24'.793"E	Rural	29	Raike Kalan	30°12'.051"N 74°67'.989"E	Rural
10	Jhanduke	30°15'.887"N 75°15'.310"E	Sub-urban	30	Bajak	30°12'.456"N 74°75'.671"E	Rural
11	Lehra Mohabbat	30°21'.930"N 75°15'.152"E	Sub-urban	31	Gurthari	30°05'.752"N 74°84'.043"E	Rural
12	Mari	30°33'.161"N 75°16'.415"E	Rural	32	Mannwala	30°04'.745"N 74°92'.538"E	Sub-urban
13	Ganga	30°33'.172"N 75°08'.724"E	Sub-urban	33	Jai Singhwala	30°13'.280"N 74°86'.539"E	Urban
14	Sema	30°27'.316"N 75°06'.918"E	Sub-urban	34	Siwian	30°25'.081"N 74°90'.562"E	Urban
15	Kotshamir	30°11'.612"N 75°00'.410"E	Urban	35	Amargarh	30°31'.615"N 74°93'.728"E	Urban
16	Chathewala	30°05'.973"N 75°07'.322"E	Sub-urban	36	Balahar Mehma	30°33'.283"N 74°85'.448"E	Rural
17	Jodhpur Pakhar	30°05'.538"N 75°15'.135"E	Rural	37	Ablu	30°33'.329"N 74°78'.779"E	Rural
18	Maur	30°07'.141"N 75°22'.194"E	Rural	38	Virk Kalan	30°24'.722"N 74°76'.050"E	Rural
19	Kamalu	29°97'.845"N 75°23'.145"E	Rural	39	Bulladewala	30°24'.001"N 74°85'.999"E	Urban
20	Ram Tirath Jaga	29°95'.708"N 75°15'.657"E	Rural	40	Nachhattar Nagar	30°18'.248"N 74°96'.118"E	Urban

Table 4 Mean concentrations (mg/kg) of heavy metals in pre-monsoon season ($n = 40$)

As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
5.26±0.04	30.52±0.24	16,123.7±174.56	5.82±0.003	20.24±0.26	9.55±0.34	59.29±0.71	0.09±0.00006	0.02±0.0003	5.45±0.03
6.38±0	33.18±0.18	17,552.06±186.29	6.63±0.002	22.62±0.24	11.1±0.13	93.93±0.25	0.06±0.00003	0.02±0.002	4.72±0.01
5.16±0.02	24.78±0.24	14,427.6±147.47	5.21±0.001	17.59±0.38	8.53±0.11	44.19±0.73	0.07±0.00004	0.03±0.002	5.15±0.01
6.98±0.09	33.32±0.19	19,033.46±152.61	7.28±0.002	26.73±0.35	13±0.2	45.4±0.47	0.08±0.00002	0.02±0.001	5.92±0.06
5.87±0.05	28.95±0.23	16,583.46±242.33	6.18±0.001	21.3±0.36	10.05±0.15	83.56±0.26	0.06±0.00001	0.02±0.002	5.51±0.02
4.93±0.01	25.61±0.26	13,858.18±164.5	4.87±0.004	16.9±0.24	9.11±0.42	32.81±1.02	0.08±0.00007	0.02±0.001	5.33±0.06
4.15±0.07	25.31±0.29	13,277.11±95.56	4.7±0.005	16.73±0.22	8.18±0.08	72.06±0.42	0.05±0.00006	0.02±0.001	4.09±0.01
5.96±0.04	24.43±0.26	14,293.31±179.33	5.32±0.001	17.07±0.11	9.64±0.05	39.07±0.89	0.04±0.00002	0.02±0.002	3.8±0.02
6.4±0.02	31.7±0.27	16,718.7±152.64	6.14±0.002	21.4±0.36	11.1±0.12	45.77±0.46	0.06±0.00002	0.04±0.002	5.38±0.02
5.09±0.06	27.97±0.26	14,257.53±180.41	5.0±0	17.19±0.31	8.17±0.04	41.68±0.42	0.04±0.00003	0.02±0.003	3.8±0.03
4.71±0.05	24.94±0.24	13,564.91±232.24	4.76±0.008	16.61±0.33	7.43±0.25	37.32±0.54	0.06±0.00004	0.02±0.001	4.5±0.04
4.5±0.04	25.86±0.25	13,407.64±178.85	4.67±0.001	16.98±0.37	7.63±0.13	26.05±0.96	0.06±0	0.01±0.002	3.55±0.01
5.38±0.09	26.1±0.25	13,778.05±158.71	5.07±0.005	17.82±0.31	8.3±0.17	27.95±0.62	0.05±0.00008	0.02±0.001	4.42±0.02
6.17±0.07	31.48±0.23	17,860.07±186.59	6.61±0	22.07±0.22	12.28±0.09	53.84±0.91	0.08±0.00005	0.01±0.001	4.64±0.05
5.05±0.05	29.79±0.21	15,933.57±193.32	5.84±0.002	20.51±0.39	11.63±0.16	50.09±0.29	0.09±0.00003	0.01±0.003	6.69±0.01
5.05±0.04	32.7±0.22	16,719.32±146.66	6.12±0.001	20.86±0.31	11.52±0.11	78.67±0.58	0.09±0.00005	0.01±0.001	5.04±0.03
4.68±0.03	25.01±0.25	13,150.65±182.51	4.48±0.003	15.85±0.1	6.93±0.06	67.85±0.25	0.04±0.00002	0.01±0.004	3.28±0.03
6.41±0.05	33.54±0.11	19,547.58±147.96	7.33±0.004	24.21±0.19	13.4±0.11	41.59±0.26	0.08±0.00001	0.01±0.002	5.38±0.01
5.4±0.03	36.45±0.15	19,435.4±111.54	7.36±0.001	24.64±0.17	12.61±0.24	85.88±0.42	0.12±0.0003	0.01±0.001	5.59±0.02
3.26±0.01	20.27±0.15	10,440.39±142.78	3.51±0.001	12.21±0.23	5.48±0.09	26.28±0.65	0.13±0.00004	0.02±0.003	3.86±0.06
10.26±0.04	77.44±0.18	39,630.07±196.25	15.68±0.001	56.08±0.26	28.82±0.13	89.5±0.53	0.03±0.00006	0.12±0.002	1.28±0.05
9.21±0.05	57.57±0.19	36,020.88±148.29	14.14±0.004	50.22±0.16	24.35±0.07	93.81±0.36	0.11±0.00009	0.3±0.002	3.63±0.01
8.6±0.06	47.58±0.27	29,635.22±236.65	12.07±0.002	41.96±0.18	21.86±0.12	89.08±0.68	0.08±0.00002	0.26±0.001	3.2±0.01
8.57±0.05	41.49±0.29	27,059.94±147.39	10.82±0.001	38.13±0.11	18.59±0.36	97.42±0.75	0.11±0.00006	0.19±0.001	2.6±0.02
9.5±0.01	43.9±0.31	29,867.7±205.6	12.06±0.004	41.34±0.21	22.73±0.04	87.86±1.12	0.05±0.00003	0.19±0.004	3.14±0.03
8.42±0.05	38.2±0.11	25,146.7±147.36	10.33±0.001	36.51±0.19	19.7±0.23	35.72±0.83	0.09±0	0.19±0.003	3.74±0.02
8.95±0.05	40.59±0.24	26,011.73±132.35	11.12±0.002	38.1±0.28	22.86±0.12	85.44±0.41	0.07±0.00006	0.13±0.002	3.18±0.01
6.3±0	33.92±0.21	22,777.34±96.65	9.36±0	31.7±0.35	18.98±0.35	114.7±0.85	0.11±0.00005	0.18±0.001	3.79±0.02
5.51±0.05	31.15±0.35	20,108.1±149.76	8.18±0.002	28.34±0.36	15.39±0.32	87.14±0.91	0.07±0.00003	0.19±0.002	3.27±0.05
7.09±0.02	34.02±0.31	21,055.27±179.34	8.44±0.001	29.47±0.34	18.55±0.08	74.01±0.78	0.07±0.00002	0.14±0.002	3.53±0.09
4.81±0.03	35.28±0.33	20,238.53±162.63	7.97±0.003	26.57±0.28	15.27±0.16	91.85±0.69	0.06±0.00008	0.11±0.003	2.56±0.04
7.16±0	36.64±0.23	22,640.34±179.21	9.18±0.002	31.78±0.25	27.1±0.03	96.74±0.36	0.06±0.00007	0.13±0.001	4.7±0.02
9.05±0.04	34.44±0.47	21,186.81±144.23	8.78±0	30.84±0.09	16.97±0.11	64.79±0.49	0.05±0.00002	0.15±0.001	3.22±0.06
7.9±0.05	32.33±0.33	20,485.98±212.69	8.28±0.001	28.03±0.11	15.14±0.17	56.41±0.47	0.03±0.00001	0.12±0.002	2.04±0.04
6.71±0.08	27.91±0.14	17,614.19±265.1	6.73±0.002	24.08±0.13	12.41±0.05	63.69±0.61	0.06±0.00006	0.18±0.001	3.4±0.01
7.64±0	36.39±0.41	21,148.48±189.23	8.36±0.001	29.74±0.25	14.72±0	71.22±0.52	0.05±0.00004	0.12±0.005	2.88±0.02
6.94±0.07	37.81±0.22	22,83.19±183.42	8.77±0.004	29.8±0.16	15.85±0.22	69.41±0.79	0.05±0	0.11±0.004	2.6±0.03
7.6±0.01	39.27±0.43	24,338.6±164.81	9.87±0.001	34.58±0.26	19.61±0.1	108.5±0.78	0.06±0.00002	0.16±0.003	3.76±0.03
10.07±0.04	39.7±0.13	21,789.59±152.34	9.93±0.001	35.09±0.24	20.86±0.25	67.52±0.63	0.07±0.00003	0.11±0.001	4.94±0.01
8.61±0.03	35.53±0.33	21,214.21±170.54	8.76±0.001	30.58±0.21	23.14±0.15	72.81±0.61	0.07±0.00005	0.1±0.002	4.13±0.02

00—below detection limit (BDL)

Table 5 Mean concentrations (mg/kg) of heavy metals in monsoon season (*n* = 40)

As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
6.47 ± 0.09	32.18 ± 0.34	20,673.52 ± 234.16	8.53 ± 0.062	29.31 ± 0.18	16.66 ± 0.12	77.68 ± 0.56	0.08 ± 0.0001	0.13 ± 0	3.98 ± 0.01
7.47 ± 0.1	31.73 ± 0.48	20,784.41 ± 146.28	8.89 ± 0.052	30.16 ± 0.13	17.24 ± 0.02	68.20 ± 0.23	0.07 ± 0	0.13 ± 0	4.01 ± 0
5.87 ± 0	26.84 ± 0.65	17,845.46 ± 157.46	7.33 ± 0.061	24.80 ± 0.14	14.18 ± 0.18	66.99 ± 0.71	0.07 ± 0.0007	0.13 ± 0.003	3.59 ± 0.03
5.01 ± 0.04	16.44 ± 0.09	11,430.11 ± 142.31	4.12 ± 0.001	14.55 ± 0.32	7.33 ± 0.16	36.17 ± 0.41	0.02 ± 0.0011	0.15 ± 0.003	2.36 ± 0.02
5.46 ± 0.15	30.99 ± 0.53	19,898.68 ± 232.43	8.71 ± 0.06	34.89 ± 0.31	17.08 ± 0.05	68.78 ± 0	0.05 ± 0.0008	0.11 ± 0	3.42 ± 0.01
6.93 ± 0.06	36.19 ± 0.76	22,616.19 ± 114.5	9.75 ± 0.045	40.23 ± 0.14	18.71 ± 0.21	70.13 ± 0.09	0.06 ± 0.0001	0.11 ± 0.002	4.18 ± 0.05
5.49 ± 0.07	26.86 ± 0.19	16,800.60 ± 95.46	6.84 ± 0.06	30.51 ± 0.02	12.73 ± 0.08	74.08 ± 0.12	0.06 ± 0.0004	0.20 ± 0.001	3.51 ± 0
7.49 ± 0.14	26.98 ± 0.56	18,822.24 ± 169.23	7.81 ± 0.51	29.05 ± 0.01	14.23 ± 0.02	66.78 ± 0.81	0.06 ± 0	0.17 ± 0	3.58 ± 0.03
6.24 ± 0.12	25.39 ± 0.17	17,528.53 ± 182.44	6.97 ± 0.082	26.97 ± 0	12.30 ± 0.12	63.64 ± 0.16	0.05 ± 0	0.19 ± 0.003	2.94 ± 0.01
6.16 ± 0.16	28.85 ± 0.46	18,247.38 ± 156.11	7.10 ± 0	26.90 ± 0.11	12.05 ± 0.04	67.23 ± 0.4	0.04 ± 0.0008	0.17 ± 0.001	2.71 ± 0.02
6.44 ± 0.05	27.62 ± 0.34	16,957.58 ± 232.34	6.86 ± 0.018	29.67 ± 0.23	15.52 ± 0.04	65.47 ± 0.34	0.06 ± 0.0003	0.19 ± 0.004	3.20 ± 0.07
5.76 ± 0.04	29.65 ± 0.45	16,988.32 ± 188.25	6.76 ± 0.009	31.78 ± 0.32	12.96 ± 0.14	59.86 ± 0.16	0.04 ± 0.0021	0.14 ± 0.005	2.23 ± 0
8.14 ± 0.02	33.83 ± 0.15	21,096.92 ± 158.72	9.16 ± 0.005	36.30 ± 0.31	16.99 ± 0.18	62.11 ± 0.12	0.04 ± 0.0002	0.11 ± 0.002	3.06 ± 0.02
6.67 ± 0.01	29.35 ± 0.73	17,615.71 ± 206.58	7.20 ± 0	31.94 ± 0.2	13.40 ± 0.09	68.96 ± 0	0.04 ± 0.0012	0.15 ± 0	3.31 ± 0.01
5.80 ± 0.05	32.94 ± 0.91	18,563.95 ± 193.32	7.36 ± 0.052	30.63 ± 0.31	15.41 ± 0.11	76.88 ± 0.12	0.05 ± 0.0005	0.11 ± 0.001	2.66 ± 0.02
7.87 ± 0.04	31.59 ± 0.62	18,830.18 ± 116.61	7.57 ± 0.06	35.93 ± 0.21	15.16 ± 0	50.06 ± 0.18	0.03 ± 0.0001	0.12 ± 0.004	2.51 ± 0.01
7.68 ± 0.02	29.15 ± 0.35	18,050.34 ± 152.53	7.25 ± 0.043	28.75 ± 0.1	13.08 ± 0	48.07 ± 0.56	0.04 ± 0	0.10 ± 0.001	3.02 ± 0.03
8.16 ± 0.03	28.80 ± 0.51	17,497.45 ± 127.91	6.99 ± 0.31	30.05 ± 0.11	12.67 ± 0.13	48.10 ± 0.06	0.04 ± 0.0006	0.09 ± 0	3.31 ± 0.02
8.46 ± 0.03	34.26 ± 0.25	21,403.46 ± 131.52	9.07 ± 0.052	33.12 ± 0.14	20.99 ± 0.04	63.73 ± 0.23	0.07 ± 0.0007	0.07 ± 0.004	4.34 ± 0
8.42 ± 0.02	36.24 ± 0.85	20,347.13 ± 122.72	8.36 ± 0.023	33.99 ± 0.26	16.72 ± 0.09	52.21 ± 0.34	0.04 ± 0.0005	0.08 ± 0.001	2.68 ± 0.01
1.47 ± 0.04	6.89 ± 0.28	2751.87 ± 106.21	2.26 ± 0.043	9.64 ± 0.16	5.73 ± 0.03	26.39 ± 0.31	0.03 ± 0.0002	0.08 ± 0.001	1.39 ± 0.01
2.51 ± 0.05	9.19 ± 0.79	3469.49 ± 118.23	3.22 ± 0.074	13.93 ± 0	7.61 ± 0	29.76 ± 0.11	0.05 ± 0.0012	0.11 ± 0.001	2.41 ± 0
3.34 ± 0.01	16.43 ± 0.07	3716.45 ± 206.61	4.12 ± 0.053	13.70 ± 0	11.52 ± 0.11	28.66 ± 0	0.05 ± 0	0.10 ± 0.004	3.08 ± 0.02
2.08 ± 0.05	9.93 ± 0	2449.20 ± 117.31	2.52 ± 0.021	8.92 ± 0.01	6.48 ± 0.36	16.76 ± 0.34	0.02 ± 0.0004	0.07 ± 0	1.28 ± 0.07
2.36 ± 0.01	13.93 ± 0.41	3202.31 ± 205.6	3.12 ± 0.011	13.81 ± 0.11	6.15 ± 0.04	18.79 ± 1.11	0.04 ± 0.0007	0.10 ± 0	2.25 ± 0.01
5.20 ± 0.01	79.13 ± 0.11	22,142.72 ± 156.36	5.70 ± 0.001	29.82 ± 0.19	10.06 ± 0.23	44.67 ± 0.79	0.04 ± 0.0024	0.08 ± 0.002	1.46 ± 0.01
6.41 ± 0.05	94.02 ± 0.04	28,803.71 ± 132.35	7.99 ± 0.008	26.63 ± 0.08	21.66 ± 0.02	34.76 ± 0.4	0.02 ± 0.0014	0.04 ± 0.001	1.47 ± 0.02
6.40 ± 0.01	86.33 ± 0.61	18,471.15 ± 96.65	5.57 ± 0	22.34 ± 0.15	12.29 ± 0.15	31.03 ± 0	0.03 ± 0.0003	0.05 ± 0.003	1.97 ± 0.04
4.62 ± 0.05	32.50 ± 0.45	16,918.06 ± 119.76	6.30 ± 0.004	26.78 ± 0.32	11.04 ± 0.02	53.08 ± 0.51	0.07 ± 0.0001	0.06 ± 0.002	2.26 ± 0.07
6.58 ± 0.02	26.74 ± 0.21	14,987.53 ± 149.33	6.05 ± 0.002	23.67 ± 0.51	12.07 ± 0.08	41.31 ± 0.71	0.06 ± 0.0001	0.07 ± 0.001	2.53 ± 0.02
8.06 ± 0.23	34.22 ± 0.73	20,447.58 ± 162.61	8.40 ± 0	31.05 ± 0	13.54 ± 0.04	43.26 ± 0.71	0.04 ± 0	0.05 ± 0	2.49 ± 0.01
5.50 ± 0.08	30.83 ± 0.33	14,673.30 ± 129.11	6.79 ± 0.002	26.84 ± 0.43	12.43 ± 0.03	52.93 ± 0.86	0.05 ± 0.0002	0.08 ± 0	3.02 ± 0.02
15.05 ± 0.01	28.99 ± 0.47	16,613.44 ± 154.23	6.72 ± 0.003	28.14 ± 0.69	15.67 ± 0	50.88 ± 0.79	0.04 ± 0.005	0.07 ± 0.005	2.96 ± 0.02
6.20 ± 0.05	29.77 ± 0.53	17,990.39 ± 112.64	7.24 ± 0.001	35.74 ± 0.11	14.92 ± 0.17	56.51 ± 0.27	0.05 ± 0	0.07 ± 0.002	3.77 ± 0.01
7.66 ± 0.08	39.39 ± 0.64	18,671.29 ± 165.1	7.52 ± 0.081	28.74 ± 0.03	14.22 ± 0.03	69.42 ± 0.81	0.26 ± 0.0004	0.07 ± 0.001	2.77 ± 0.01
6.40 ± 0.05	32.01 ± 0.31	19,120.76 ± 239.21	7.65 ± 0.002	28.14 ± 0.35	12.72 ± 0.1	42.75 ± 0.59	0.03 ± 0.0014	0.06 ± 0.001	2.21 ± 0.02
5.82 ± 0.07	26.78 ± 0.72	15,825.49 ± 123.42	6.22 ± 0.004	25.85 ± 0.16	10.40 ± 0	42.26 ± 0.74	0.03 ± 0	0.10 ± 0.004	2.69 ± 0.03
6.33 ± 0.09	56.31 ± 0.43	18,610.70 ± 264.81	7.74 ± 0.003	29.71 ± 0.16	16.74 ± 0.1	84.06 ± 0.72	0.06 ± 0.0002	0.07 ± 0.001	3.04 ± 0
6.57 ± 0.02	33.82 ± 0.68	19,335.21 ± 162.39	7.61 ± 0.001	29.18 ± 0.23	14.48 ± 0.25	51.97 ± 0.29	0.05 ± 0.0014	0.06 ± 0.001	3.18 ± 0.01
8.38 ± 0.04	36.69 ± 0.33	20,801.10 ± 141.51	8.49 ± 0.002	35.13 ± 0.11	19.35 ± 0.15	68.05 ± 0	0.04 ± 0.0015	0.05 ± 0.001	3.63 ± 0.03

00—below detection limit (BDL)

Table 6 Mean concentrations (mg/kg) of heavy metals in post-monsoon season (*n* = 40)

As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
4.18 ± 0	25.24 ± 0.14	12,841.96 ± 124.11	4.52 ± 0.02	15.99 ± 0.12	9.70 ± 0	40.71 ± 0.34	0.05 ± 0	0.53 ± 0.001	5.97 ± 0.04
4.88 ± 0.01	27.29 ± 0	13,784.81 ± 66.21	5.11 ± 0.01	16.30 ± 0	8.74 ± 0.03	40.01 ± 0.14	0.07 ± 0.0001	0.33 ± 0.005	4.27 ± 0.02
5.73 ± 0.01	31.06 ± 0.15	16,449.20 ± 107.23	6.19 ± 0.04	22.07 ± 0.11	11.19 ± 0.06	53.27 ± 0	0.07 ± 0.0002	0.21 ± 0	4.17 ± 0
5.78 ± 0.03	28.82 ± 0.02	15,879.93 ± 82.29	5.83 ± 0.001	20.47 ± 0.31	10.50 ± 0	45.19 ± 0	0.21 ± 0	0.20 ± 0.001	4.74 ± 0.01
4.22 ± 0.09	24.23 ± 0.13	12,854.29 ± 122.24	4.54 ± 0.02	15.48 ± 0	7.07 ± 0.02	43.84 ± 1.01	0.07 ± 0.0002	0.18 ± 0.001	4.26 ± 0.05
5.19 ± 0.01	23.43 ± 0.25	12,586.38 ± 94.24	4.56 ± 0.041	15.12 ± 0.21	7.93 ± 0.11	42.57 ± 1.02	0.05 ± 0.0002	0.15 ± 0.003	3.93 ± 0.06
4.45 ± 0.02	25.58 ± 0.11	13,674.66 ± 105	5.11 ± 0.02	17.81 ± 0.01	9.22 ± 0.02	35.36 ± 0.1	0.07 ± 0	0.13 ± 0.002	4.79 ± 0.04
4.68 ± 0.12	23.42 ± 0.23	12,909.32 ± 23.41	4.68 ± 0.25	14.64 ± 0.02	8.34 ± 0.01	30.48 ± 0.23	0.07 ± 0.0001	0.10 ± 0.004	3.41 ± 0
2.48 ± 0.15	17.92 ± 0.12	9459.78 ± 102.41	3.21 ± 0.02	10.58 ± 0	5.73 ± 0.11	24.85 ± 0.11	0.05 ± 0.0002	0.23 ± 0.001	3.60 ± 0.03
3.93 ± 0.14	27.62 ± 0.14	13,559.44 ± 96.1	4.82 ± 0	15.86 ± 0.04	8.96 ± 0.03	36.89 ± 0.96	0.06 ± 0.0002	0.11 ± 0	4.28 ± 0.07
3.85 ± 0.01	26.30 ± 0.02	13,306.60 ± 142.31	4.80 ± 0.02	16.24 ± 0.18	8.00 ± 0.01	37.20 ± 0	0.07 ± 0.0001	0.10 ± 0.002	4.62 ± 0.06
3.04 ± 0.01	26.87 ± 0	12,747.31 ± 158.2	4.47 ± 0.001	15.03 ± 0.21	8.09 ± 0.03	49.78 ± 0.04	0.07 ± 0.0003	0.09 ± 0.001	4.67 ± 0.01
4.35 ± 0.02	23.57 ± 0.12	12,365.37 ± 108.72	4.28 ± 0.001	15.38 ± 0.21	7.32 ± 0.12	24.07 ± 0.12	0.05 ± 0.0001	0.09 ± 0.003	3.77 ± 0
3.91 ± 0.01	33.42 ± 0.13	11,464.03 ± 56.58	4.08 ± 0	35.78 ± 0.1	6.59 ± 0.01	21.39 ± 0	0.05 ± 0	0.07 ± 0.001	5.85 ± 0
3.84 ± 0.02	23.66 ± 0.21	12,189.74 ± 46.32	4.13 ± 0.01	14.53 ± 0.09	6.04 ± 0.13	27.96 ± 0.12	0.11 ± 0.0002	0.08 ± 0.002	4.72 ± 0.08
5.11 ± 0.01	28.43 ± 0.22	13,898.85 ± 86.61	5.03 ± 0.02	17.57 ± 0.2	8.71 ± 0.11	30.33 ± 0.05	0.09 ± 0.0003	0.06 ± 0.002	4.93 ± 0.02
3.79 ± 0.05	21.10 ± 0.15	10,873.80 ± 122.53	3.62 ± 0.01	12.55 ± 0.11	6.07 ± 0	19.71 ± 0.24	0.05 ± 0.0003	0.07 ± 0.002	4.39 ± 0.01
4.63 ± 0.02	28.70 ± 0.21	13,784.55 ± 77.91	4.82 ± 0.04	16.55 ± 0.12	7.63 ± 0	20.11 ± 0.01	0.06 ± 0.0002	0.05 ± 0.001	4.19 ± 0.03
2.84 ± 0	21.11 ± 0	10,067.20 ± 61.52	3.40 ± 0.04	12.10 ± 0.11	4.82 ± 0.01	20.13 ± 0.21	0.05 ± 0.0004	0.05 ± 0	3.36 ± 0.06
4.35 ± 0.01	26.87 ± 0.35	12,692.91 ± 180.11	4.28 ± 0.02	14.27 ± 0.15	7.11 ± 0.02	43.88 ± 0	0.08 ± 0	0.04 ± 0.002	3.90 ± 0
6.17 ± 0	35.89 ± 0.18	16,702.86 ± 96.21	5.91 ± 0	20.75 ± 0.08	10.67 ± 0.01	40.18 ± 0.42	0.07 ± 0.0001	0.03 ± 0.003	4.92 ± 0.04
3.65 ± 0.02	27.12 ± 0.16	11,897.77 ± 88.27	3.70 ± 0.04	13.17 ± 0	6.21 ± 0.14	39.55 ± 0.12	0.06 ± 0.001	0.08 ± 0.002	4.03 ± 0.09
5.75 ± 0.01	46.70 ± 0.02	20,977.31 ± 0	4.01 ± 0	13.76 ± 0	8.45 ± 0.12	46.90 ± 0	0.09 ± 0.0002	0.06 ± 0.002	4.42 ± 0.02
5.98 ± 0.03	54.05 ± 0.23	24,724.60 ± 37.3	4.37 ± 0.01	15.88 ± 0.02	7.51 ± 0.14	71.12 ± 1.32	0.05 ± 0.0003	0.05 ± 0.001	4.36 ± 0.01
4.74 ± 0.01	36.22 ± 0.5	16,935.19 ± 0	4.85 ± 0.01	16.24 ± 0.09	6.68 ± 0	33.13 ± 0.25	0.05 ± 0.0004	0.04 ± 0	3.24 ± 0
4.09 ± 0.02	27.87 ± 0.05	13,216.56 ± 126.28	4.36 ± 0.002	14.48 ± 0.09	5.63 ± 0.12	21.65 ± 0.63	0.05 ± 0.0015	0.03 ± 0.001	3.29 ± 0.01
3.12 ± 0.04	30.16 ± 0.24	13,750.61 ± 102.31	4.67 ± 0.002	16.04 ± 0.23	8.17 ± 0.01	35.87 ± 0.41	0.15 ± 0.0012	0.03 ± 0.003	4.43 ± 0
4.89 ± 0	33.60 ± 0.31	15,236.23 ± 76.56	5.31 ± 0	17.51 ± 0.14	8.37 ± 0.11	37.14 ± 0.12	0.04 ± 0.0001	0.03 ± 0.001	3.89 ± 0.04
3.11 ± 0.01	25.95 ± 0.15	12,579.2 ± 89.16	4.26 ± 0.001	13.50 ± 0.12	5.73 ± 0.01	26.31 ± 0.42	0.05 ± 0	0.03 ± 0.001	4.52 ± 0.02
5.32 ± 0.01	33.67 ± 0	14,462.92 ± 89.31	4.83 ± 0.001	16.33 ± 0.24	7.04 ± 0.03	39.32 ± 0	0.04 ± 0.0002	0.03 ± 0	3.95 ± 0.01
5.90 ± 0.21	37.97 ± 0	17,397.37 ± 0	6.17 ± 0	22.23 ± 0	10.34 ± 0.01	31.91 ± 0.84	0.07 ± 0.0001	0.02 ± 0.002	5.16 ± 0.02
5.12 ± 0.02	34.45 ± 0.13	15,814.24 ± 119.06	5.59 ± 0.01	18.91 ± 0.24	12.21 ± 0.01	43.92 ± 0.74	0.09 ± 0	0.03 ± 0	5.85 ± 0.03
3.70 ± 0.02	28.81 ± 0.17	13,641.36 ± 74.21	4.47 ± 0.02	15.59 ± 0.12	7.97 ± 0.1	60.25 ± 0.14	0.06 ± 0.002	0.03 ± 0.004	4.29 ± 0.01
4.80 ± 0.02	37.27 ± 0.51	17,362.82 ± 92.44	6.22 ± 0.003	20.92 ± 0.11	10.81 ± 0.12	56.30 ± 0.49	0.06 ± 0.0004	0.02 ± 0.003	5.44 ± 0.02
2.80 ± 0	26.34 ± 0.14	12,815.20 ± 95.1	4.35 ± 0	14.43 ± 0.03	6.78 ± 0.1	48.66 ± 0.78	0.08 ± 0.0007	0.02 ± 0.001	4.29 ± 0.02
3.67 ± 0.02	29.27 ± 0	12,864.31 ± 19.2	4.40 ± 0.01	15.08 ± 0.21	7.92 ± 0.1	56.30 ± 0.49	0.09 ± 0.0054	0.02 ± 0.002	3.95 ± 0
2.07 ± 0.01	23.95 ± 0.12	9941.73 ± 105.34	3.05 ± 0.01	9.92 ± 0.11	5.13 ± 0	40.10 ± 0.64	0.04 ± 0.01	0.03 ± 0.001	3.91 ± 0.05
3.69 ± 0.02	25.59 ± 0.13	11,800.37 ± 104.21	3.92 ± 0	13.03 ± 0.09	6.03 ± 0.1	75.57 ± 0.14	0.04 ± 0.0002	0.03 ± 0	3.67 ± 0
3.47 ± 0.01	30.57 ± 0.18	13,736.52 ± 62.31	4.81 ± 0.01	15.74 ± 0	6.76 ± 0.05	56.98 ± 0	0.06 ± 0	0.03 ± 0.004	3.47 ± 0
3.93 ± 0.01	28.82 ± 0.33	12,248.03 ± 21.45	4.22 ± 0	13.92 ± 0.11	6.79 ± 0.04	47.40 ± 0.12	0.20 ± 0.0041	0.05 ± 0.001	4.18 ± 0.01

00—below detection limit (BDL)

(ICP-AES), atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS) (McComb et al. 2014; Paulette et al. 2015; King et al. 2019), and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Nirola et al. 2018). Spatial interpolation techniques such as IDW and Kriging; integrated with GIS have been widely used for soil quality survey (Kelepertzis 2014; Moore et al. 2016) in order to determine the spatial variability of soil contaminants. In addition to geospatial methods and techniques, *pollution indices* (Li et al. 2014; Tianlik et al. 2016), such as enrichment factor (EF), contamination factor (CF), and potential contamination index (Cp) (Sakram et al. 2015; Khorshid and Thiele-Bruhn 2016; Ahmed et al. 2016; Tian et al. 2017), and *multivariate analysis* (Mehrabi et al. 2015; Lv et al. 2015; Ielpo et al. 2017; Song et al. 2018; Mohammadi et al. 2018), such as principal component analysis (PCA) and cluster analysis (CA) (Herojeet et al. 2016; Kowalska et al. 2018), have been widely used for the assessment of contamination levels of heavy metals with reference to background concentrations and source of contamination,

respectively. Table 2 shows maximum allowable limits (MAL) for heavy metals in soil in different countries.

To the best of authors' knowledge, there is a dearth of literature with respect to heavy metal contamination of soil in Bathinda district of Punjab, India. The soil in Bathinda, a semi-arid region, is affected by various degradation processes such as soil erosion, water logging, and salinization (Ahmad and Pandey 2018). Both salinity and water-logging are widespread in Bathinda which act as a major constraint in irrigated agricultural lands (Koshal 2012). Further, the soil texture is predominantly sandy loam to silt (Kumar et al. 2016) and the sandy texture of soils makes the region prone to nutrient losses through leaching during heavy rainfall (Zenawi and Mizan 2019). A number of studies have reported about the arid soil's characteristics such as soil texture, conductivity, cation exchange capacity, organic carbon, and pH (Sidhu and Sharma 1990; Sharma et al. 1992; Kumar et al. 2005). Such properties including bulk density and porosity act as soil indicators (Schoenholtz et al. 2000; Dexter 2004) used for assessment of soil degradation (Dominati et al. 2010).

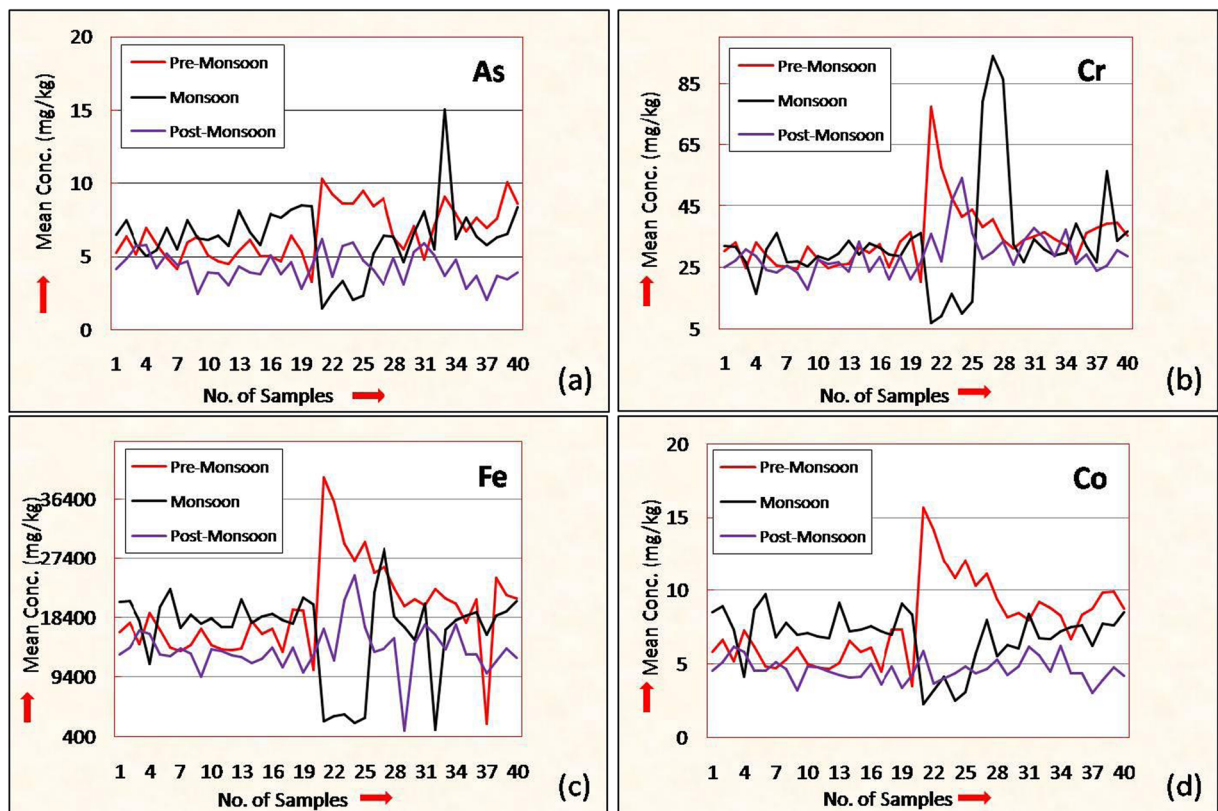


Fig. 2 Mean concentrations (mg/kg) of heavy metals in soil. (a) Arsenic. (b) Chromium. (c) Iron. (d) Cobalt

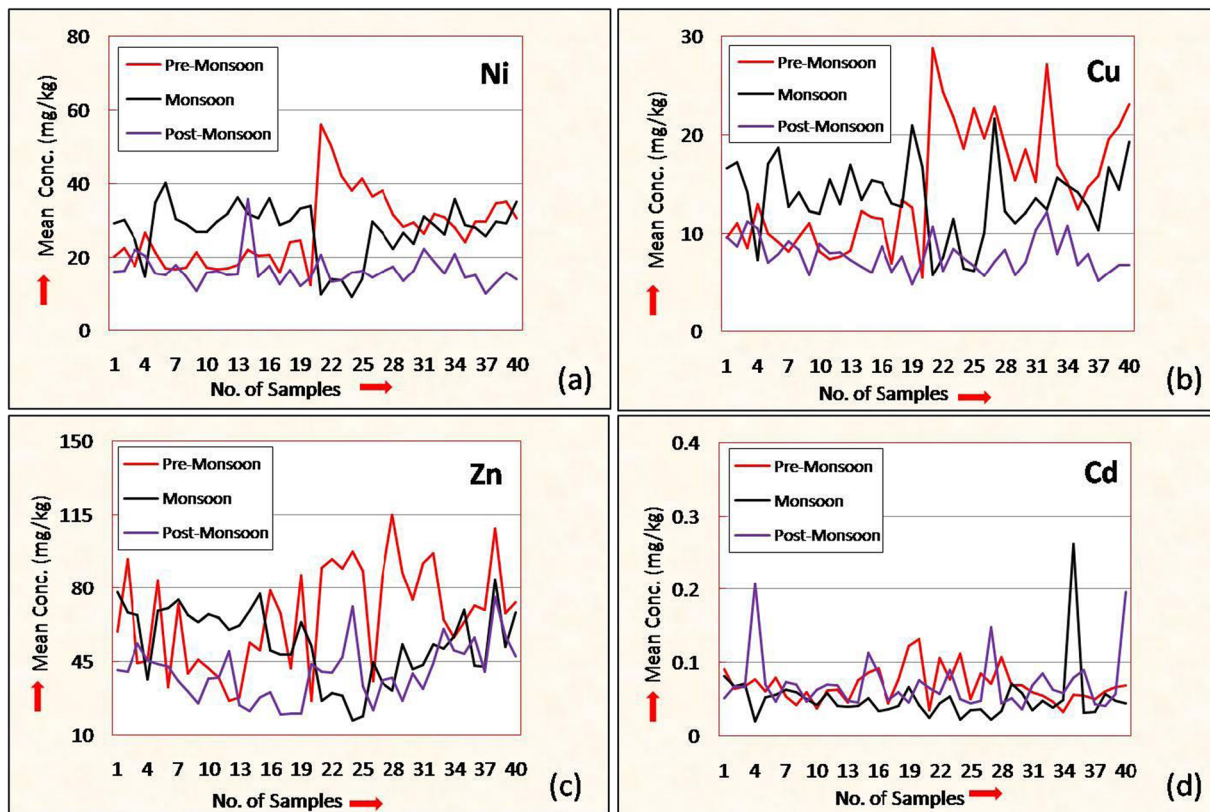


Fig. 3 Mean concentrations (mg/kg) of heavy metals in soil: (a) nickel, (b) copper, (c) zinc, (d) cadmium

Recently, physico-chemical parameters of the soil such as pH, electrical conductivity, and alkalinity in view of land degradation assessment were studied in the region along with their spatial variability in the region using geospatial

techniques—remote sensing (RS), GPS, and GIS (Ahmad and Pandey 2018). Therefore, as part of the land degradation assessment, the study was conducted to gain detailed information about the status of heavy metal pollution for

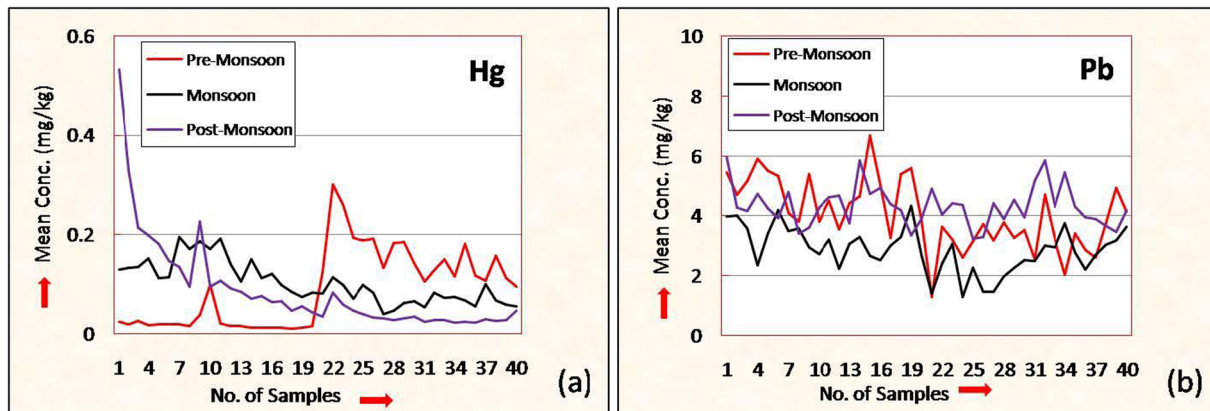


Fig. 4 Mean concentrations (mg/kg) of heavy metals in soil: (a) mercury, (b) lead

arsenic (As), copper (Cu), nickel (Ni), chromium (Cr), mercury (Hg), cobalt (Co), zinc (Zn), cadmium (Cd), iron (Fe), and lead (Pb) in agricultural soils of the district during pre-monsoon, monsoon, and post-monsoon seasons. Geochemical mapping of the selected heavy metals using IDW technique aided by ArcGIS 10.6.1 software was done to reveal the spatial as well as seasonal pattern of distribution throughout the region. Multivariate analysis such as Pearson's correlation (r) and PCA was carried out to determine the correlation or association between the variables besides their pattern of behavior with each other. Besides, risk assessment of heavy metals was also determined using potential ecological risk factor (E_i) and ecological risk index (R_i).

2 Materials and Methods

2.1 Study Area

A total of 120 soil samples were collected from 40 different locations (0–15 cm depth) of the Bathinda district, in the southern part of Punjab (north-western state of India) in

three seasons (pre-monsoon, monsoon, and post-monsoon). The study area covering an area of 3327.523 km² was divided into number of grids (size of each grid 10 × 10 km), and from each selected grid 2–2.5 kg of soil was collected from seven different points of agricultural fields, representing a composite sample at each sampling location. The study area (Fig. 1) is located between 29°33' and 30°36' North latitude and between 74°38' and 75°46' East longitude in the Malwa region. The detailed description (site name, latitude and longitude, nature of the site) of the study area is given in Table 3.

2.2 Methodology

Acid digestion method 3050B was used (HNO₃/H₂O₂) (EPA 1996) for sample digestion through *microwave digestion*. For each sample, a mixture of 8 mL of HNO₃ and 2 mL of H₂O₂ was used in pre-treatment process of soil samples. The mixture was added to 0.5 g of each sample in digestion tubes which were then placed in a *microwave digester* for at least 12 h for complete digestion of the soil samples. After digestion, each sample was filtered with the help of polysulfone (PSF) autoclaved syringe filters

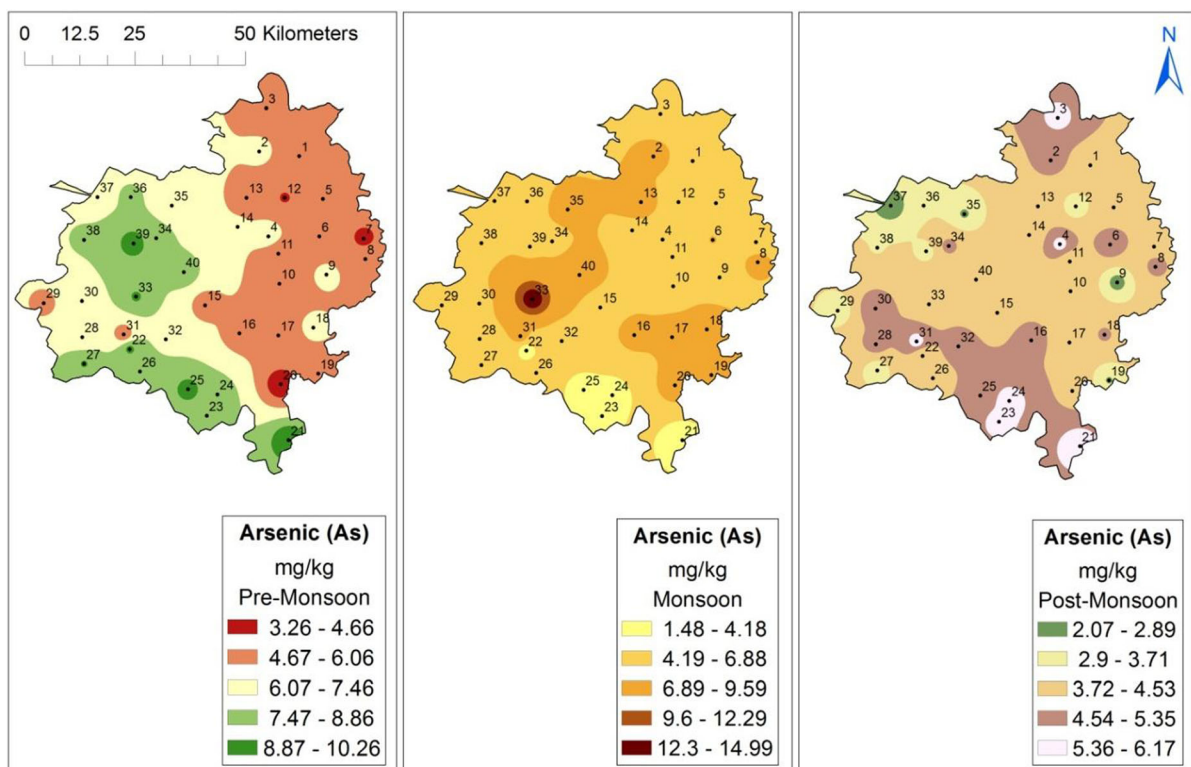


Fig. 5 Spatial and seasonal variability pattern of arsenic (As)

(47 mm pore size). For the current study, Thermo Scientific–iCAP Qc (Germany) inductively coupled plasma–mass spectrometry (ICP-MS) was used to analyze all the samples prepared for heavy metal estimation. ICP multi-element standard (Lobachemie UN No-3264) was used to calibrate the system. The concentrations of six standards used were 25, 50, 100, 250, 500, and 1000 ppb. Argon plasma rate (14 L/min) and nebulizer plasma flow rate (1.05 mL/min) were taken into consideration during analysis.

Bir Talab is a zoo established in 1978, where animals and birds are taken care of by the Forest and Department of Wildlife Protection of the Punjab government. Since its establishment, there has been no human interference such as agrarian practices, spray of chemicals and pesticides, industries, and municipal waste. Therefore, the site was treated as least contaminated area for our study. The current land use of the Bir Talab consists of the forest cover, vegetation, animal habitat, and parks. It is pertinent to mention that the soil samples were collected from forest areas that were least disturbed.

The soil samples were analyzed for reference value in order to estimate pollution indices for each of the element.

The results obtained were used to calculate the total mean concentration of heavy metals and pollution indices such as enrichment factor (EF), pollution load index (PLI), degree of contamination (C_d), and ecological risk assessment (potential ecological risk factor— E_i and ecological risk index— R_i). Pearson’s correlation (r) and PCA were also applied to estimate the strength of linear relationship between variables. Statistical Package for the Social Sciences (SPSS 18.0) software and XLSTAT (2018 version) tools were used for statistical analysis of the datasets.

3 Results and Discussions

3.1 Concentrations of Heavy Metals

The agricultural soil samples collected in pre-monsoon, monsoon, and post-monsoon were analyzed

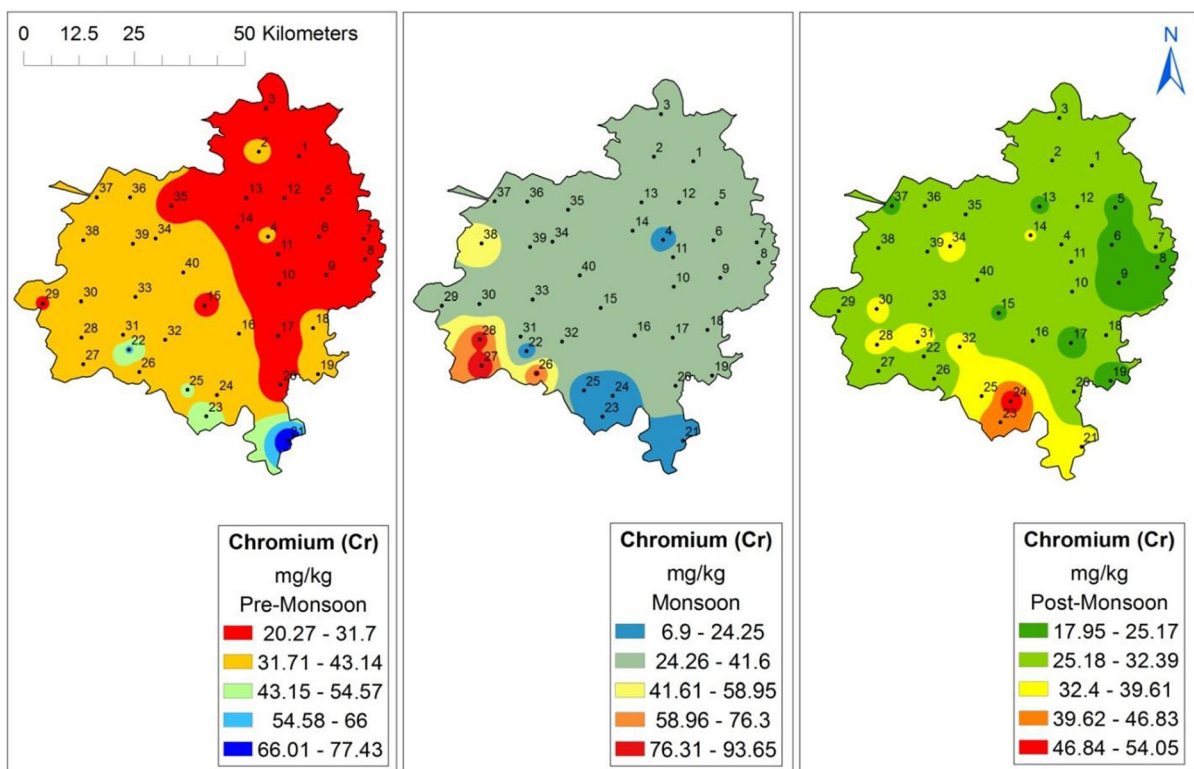


Fig. 6 Spatial and seasonal variability pattern of chromium (Cr)

by ICP-MS for the estimation of heavy metal concentration and their contamination levels. The total mean concentrations (mg/kg) of heavy metals in soil collected from 40 different locations of the study area in different seasons are given in Tables 4, 5, and 6 which are graphically represented in Figs. 2, 3, and 4.

The total mean concentration (mg/kg) of metals in pre-monsoon season was of the order of $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$.

The total mean concentration (mg/kg) of metals in monsoon season was of the order of $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$.

The total mean concentration (mg/kg) of metals in post-monsoon season was of the order of $Fe > Zn > Cr > Ni > Cu > Co > Pb > As > Hg > Cd$.

From the results, a uniform trend of heavy metal concentrations was observed in three different seasons. In other words, the order of the concentrations in all the three season was of the order of $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$ with slightly higher mean concentration of Pb (4.33 mg/kg) in

post-monsoon season compared with pre-monsoon Pb (4.02 mg/kg) and monsoon Pb (2.86 mg/kg) with respect to that of arsenic (As). It was also observed that the iron content in the soil system was much higher than the rest of the metals. The possible reasons for this could be its crustal abundance (Hussain et al. 2017) where ferrous (Fe^{2+}) or ferric (Fe^{3+}) states are readily available (Morrissey and Guerinot 2009), industrial discharges, and product of corrosion in soil and water (Smith 1981; Bhagure and Mirgane 2011). In soil, the iron is attributed by weathering of ferro-magnesium (biotite, hornblende) (Walker 1967; Watts 1980) and ferruginous minerals (hematite, magnetite, and sulfide) (Krishan et al. 2015). Further, the high content of iron in the soil was found consistent with some previous studies where the concentration of iron was found more than 25 mg/L in districts such as Faridkot, Rupnagar, Hoshiarpur, Sangrur, Fatehgarh, Mansa, and Bhatinda (Krishan et al. 2015). General trend showed higher metal concentration in rural areas as compared with soils in urban areas except Pb. Urban areas showed higher

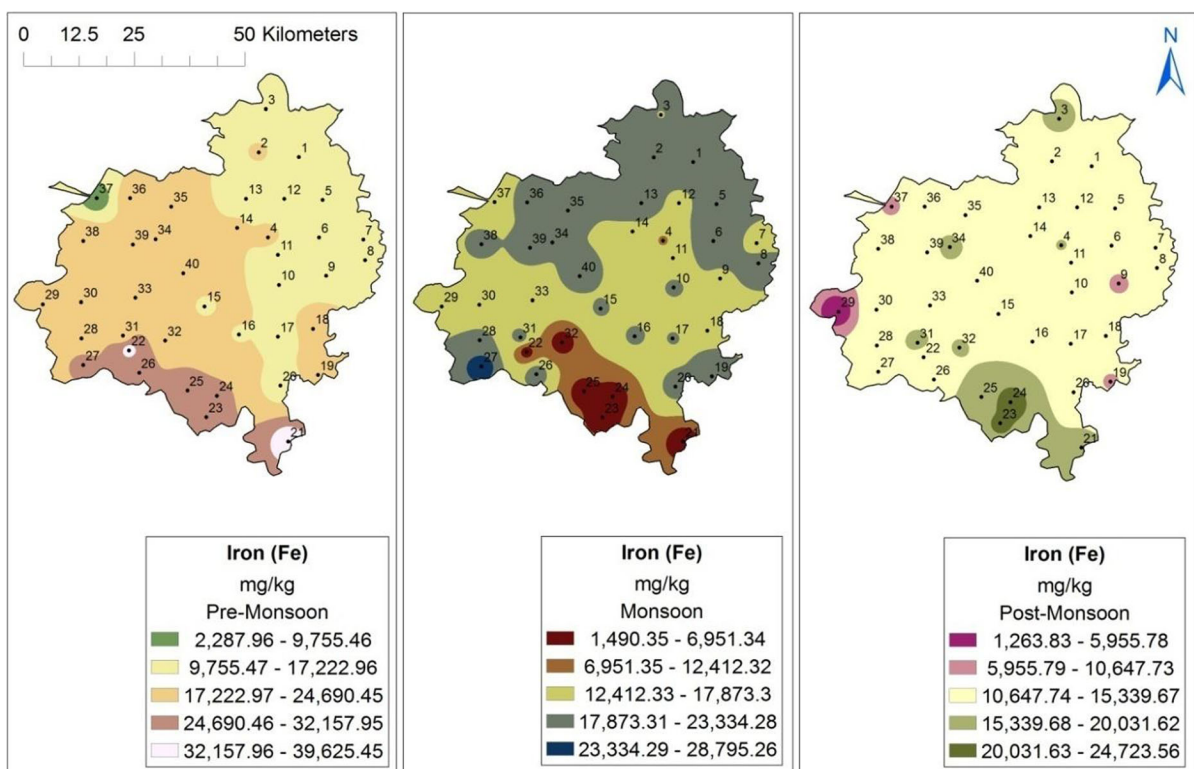


Fig. 7 Spatial and seasonal variability pattern of iron (Fe)

concentration of metals like Pb as compared with rural areas because urban soils have more potential for Pb than rural including road networks, vehicular emissions, and industrial activities (Adachi and Tainosho 2004; Machender et al. 2011; Aelion et al. 2012; Wang et al. 2015). In rural areas, the higher concentration of most of the heavy metals was due to large-scale application of agro-chemicals, fungicides, fertilizers, agricultural wastes, fuel combustion, municipal sewage wastes, and industrial waste effluents (Krishna and Govil 2005; Acosta et al. 2011; Machender et al. 2011; Yaylali-Abanuz 2011; Wang et al. 2015).

3.2 Spatial Distribution/Variability of Heavy Metals Using Inverse Distance Weighted (IDW) Technique

The information regarding the spatial distribution of heavy metals was obtained through interpolation technique (Inverse Distance Weighted IDW), useful in estimating the distribution pattern (Kelepertzis 2014; Moore et al. 2016) of different variables using ArcGIS

10.6.1 software. Figures 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 depict the spatial and seasonal variability pattern of heavy metals in different seasons (pre-monsoon, monsoon, and post-monsoon).

Thus, IDW technique is significant in assessing the heavy metal contamination by recognizing their background information in the soil system (Zhou and Xia 2010) which also helps in determining the variations in concentrations of heavy metals in different parts of the region including known (sampling points) and unknown sampling locations. Spatial distribution through soil mapping is significant in estimating the links with geological factors and also trace out sources of contamination (Xie et al. 2008; Lancianese and Dinelli 2015; Reimann and de Caritat 2017; Salomão et al. 2019) for the variables under investigation. Although no specific pattern of distribution was observed, majority of metals showed higher concentrations toward rural areas as compared with urban areas except lead (Pb) as a result of agricultural practices and frequent use of agro-chemicals, fungicides, and fertilizers (Dantu 2009; Yaylali-

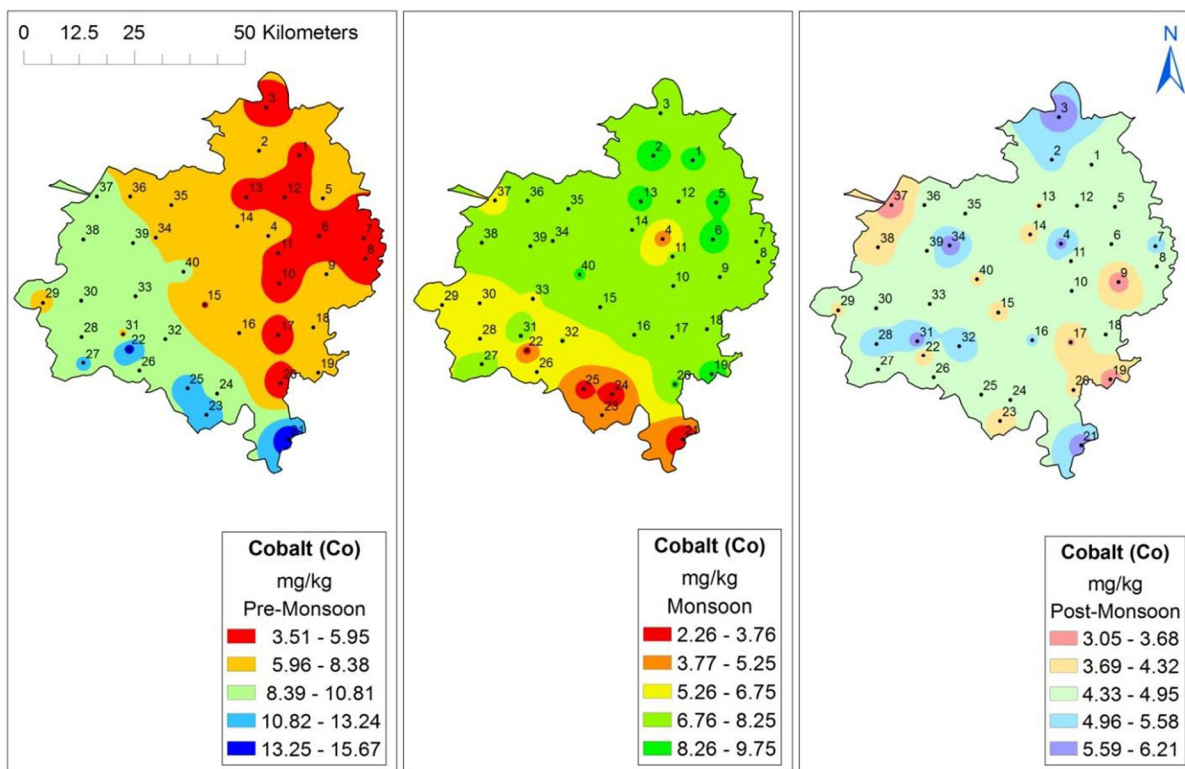


Fig. 8 Spatial and seasonal variability pattern of cobalt (Co)

Abanuz 2011; Machender et al. 2011; Wang et al. 2015). Pb showed higher concentration in sub-urban and urban areas which could be due to various industrial activities (Machender et al. 2011; Wang et al. 2015), vehicular emissions (Adachi and Tainosho 2004), or may be due to phosphate fertilizer and pesticide applications (Adachi and Tainosho 2004; Wang et al. 2015). Zinc showed minimum values at some rural places in monsoon season, whereas Cd showed slightly higher concentration in urban areas as seen from post-monsoon spatial variability map. Northeastern region in rural and few locations near urban and sub-urban parts of the district showed higher values for Ni (sites 5, 6, 13, 14, 16, 21, 22, 23, 25, 34, and 40) while higher values were also observed for Hg in rural areas (sites 1, 7, 8, 9, 10, 11, 22, and 23) which could be due to frequent use of agro-chemicals, fungicides, fertilizers, agricultural wastes, fuel combustion, municipal sewage wastes, and industrial waste effluents (Krishna and Govil 2005; Acosta et al. 2011; Machender et al. 2011; Yaylali-Abanuz 2011; Wang et al. 2015). Thus,

spatial distribution was significant in offering valuable information related to sources of contamination and routes followed by contaminants to reach the soil, and also the knowledge about deposition of minerals in the region (de Caritat et al. 2017; Sahoo et al. 2019). The complexity in spatial variability of heavy metals and their routes can be further explained by integrating geochemical or digital soil mapping with multivariate techniques such as PCA (Wang et al. 2018).

3.3 Evaluation of Pollution Indices

3.3.1 Enrichment Factor (EF)

Enrichment factor (EF) estimates the level of concentration of contaminant in the surrounding system (Zahran et al. 2015). It is commonly used in calculating the concentration of metals in surface soils adding through human activities (Jiao et al. 2015). The index is used to distinguish between natural and anthropogenic sources (Pan et al. 2016) where the level of contamination is

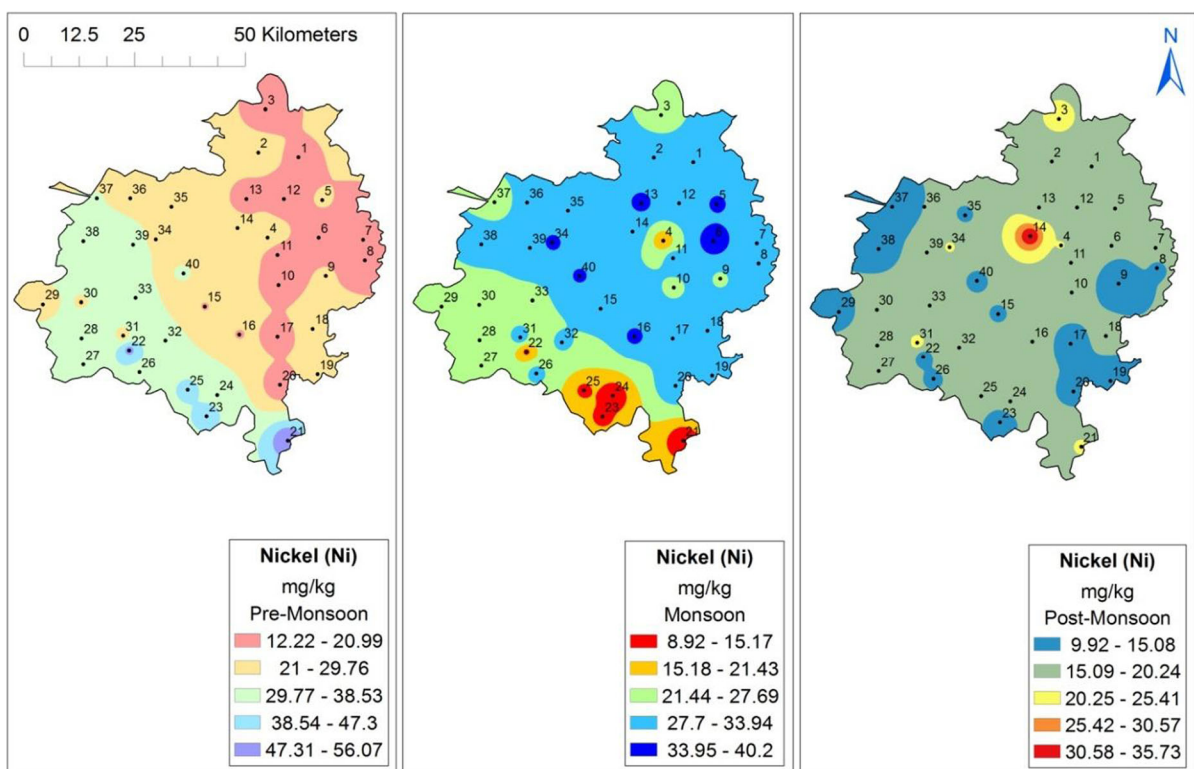


Fig. 9 Spatial and seasonal variability pattern of nickel (Ni)

estimated with respect to the background levels (Selvaraj et al. 2004). Iron (EF) was used as a reference element (Likuku et al. 2013) for the reason that its input is largely dominated through natural means (1.5%) (Tippie 1984). The formula given by Loska et al. (2004) for estimation of EF is actually suggested by Buat-Menard and Chesselet (1979) as in Eq. (1).

$$EF = \frac{C_n(\text{Sample})/C_{ref}(\text{Sample})}{B_n(\text{Background})/B_{ref}(\text{Background})} \quad (1)$$

where

C_n (sample) is the amount of the examined element in the examined environment,

C_{ref} (sample) is the amount of the reference element in the examined environment,

B_n (background) is the amount of examined element in the reference environment; and,

B_{ref} (background) is the amount of the reference element in the reference environment (Armah et al. 2010).

Table 7 shows five different levels of enrichment factor ranging between <2 and >40 along with descriptions of enrichment or pollution levels

related to heavy metals, whereas Table 8 reveals the values of enrichment factor calculated for selected heavy metals in the soil based on datasets generated through ICP-MS as well as the background concentration of both sample and the reference element (i.e., iron) in the examined and reference environment respectively.

For reference values or geochemical background concentration of each element, the soil samples were selected from a selected reference site (*Bir Talab*) to be analyzed for reference value in order to estimate pollution indices for each of the element.

If the value of EF for a particular metal is lower than 2, it means that the source of contamination is natural, whereas the value greater than 2 indicates contamination sources are exclusively anthropogenic (Abreu et al. 2016).

The results (Table 8) indicated that the soils in Bathinda district were enriched with heavy metals to a certain level. The soil enrichment due to heavy metals ranged between minimum to moderate level.

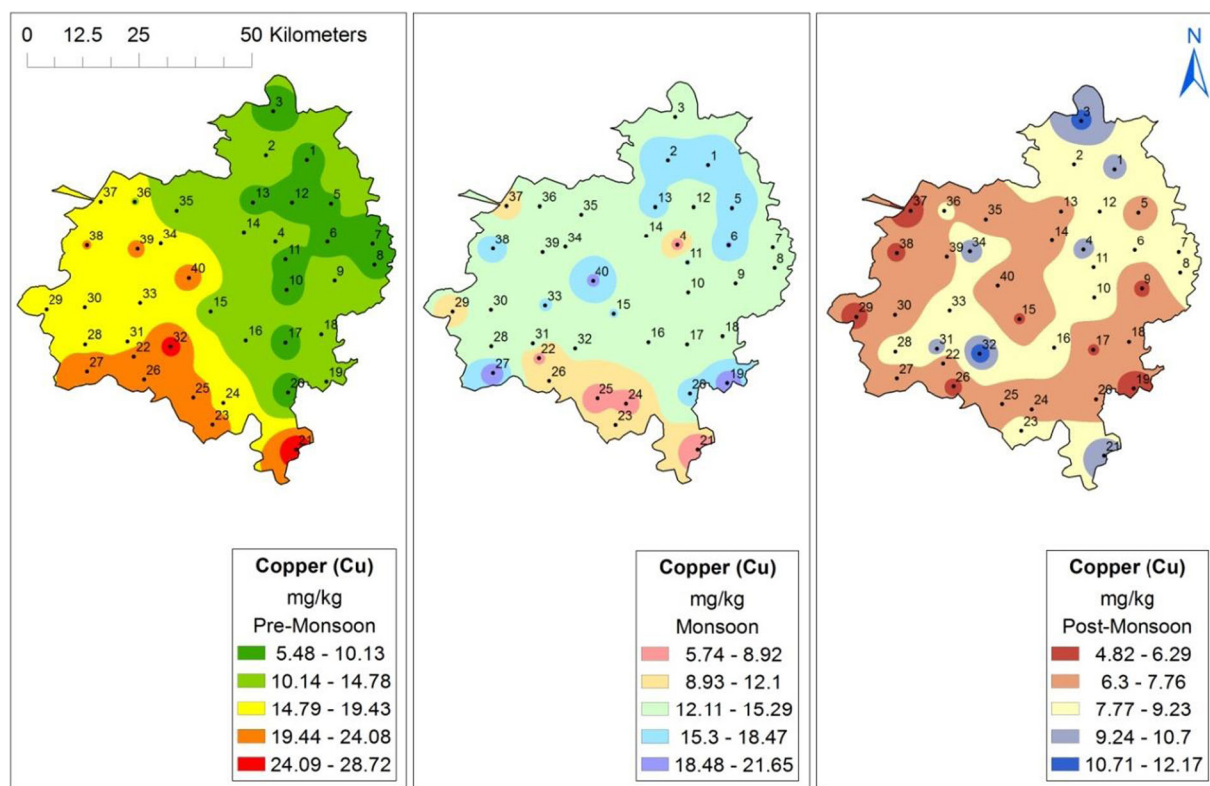


Fig. 10 Spatial and seasonal variability pattern of copper (Cu)

Metals such as Cr, As, Zn, Cu, Ni, and Co were reported with moderate level of contamination, whereas Cd, Hg, and Pb were observed to be with minimum enrichment.

3.3.2 Pollution Load Index (PLI)

Pollution load index (PLI) compares the level of contamination of soil system at different sampling locations (Tomlinson et al. 1980) where the severity and variation of contamination is assessed (Rabee et al. 2011). Divided into different classes (Tomlinson et al. 1980) given in Table 9, the index is computed by estimating the contamination factor (CF) (Hakanson 1980; Pekey et al. 2004) that is expressed as the n -root from the n - C_{fs} obtained for the contaminant. The PLI is calculated by the formula, originally developed by Tomlinson et al. (1980), given in Eq. (2) as

$$PLI = \sqrt[n]{C_f^1 * C_f^2 * C_f^3 * \dots * C_f^n} \quad (2)$$

where n denotes number of metals and C_f is contamination factor.

3.3.3 Degree of Contamination (C_d)

The C_d is a measure of the degree of contamination taken as a whole at a particular sampling location in surface layers. Classified into four classes (Hakanson 1980) as shown in Table 11, C_d is defined as the sum of the contamination factor (C_f^i) values of each element (Hakanson 1980). The C_d was enumerated by the formula given in Eq. (3).

$$C_d = \sum_{i=1}^n C_f^i \quad (3)$$

From the results, pollution load index (PLI) and degree of contamination (C_d) reported low to moderate contamination due to heavy metals in maximum cases as shown in Tables 10 and 12. The study suggested continuous monitoring of the sites as per the results obtained and level of contamination (Table 9). Some of the sites exceptionally reported considerable to very high level of

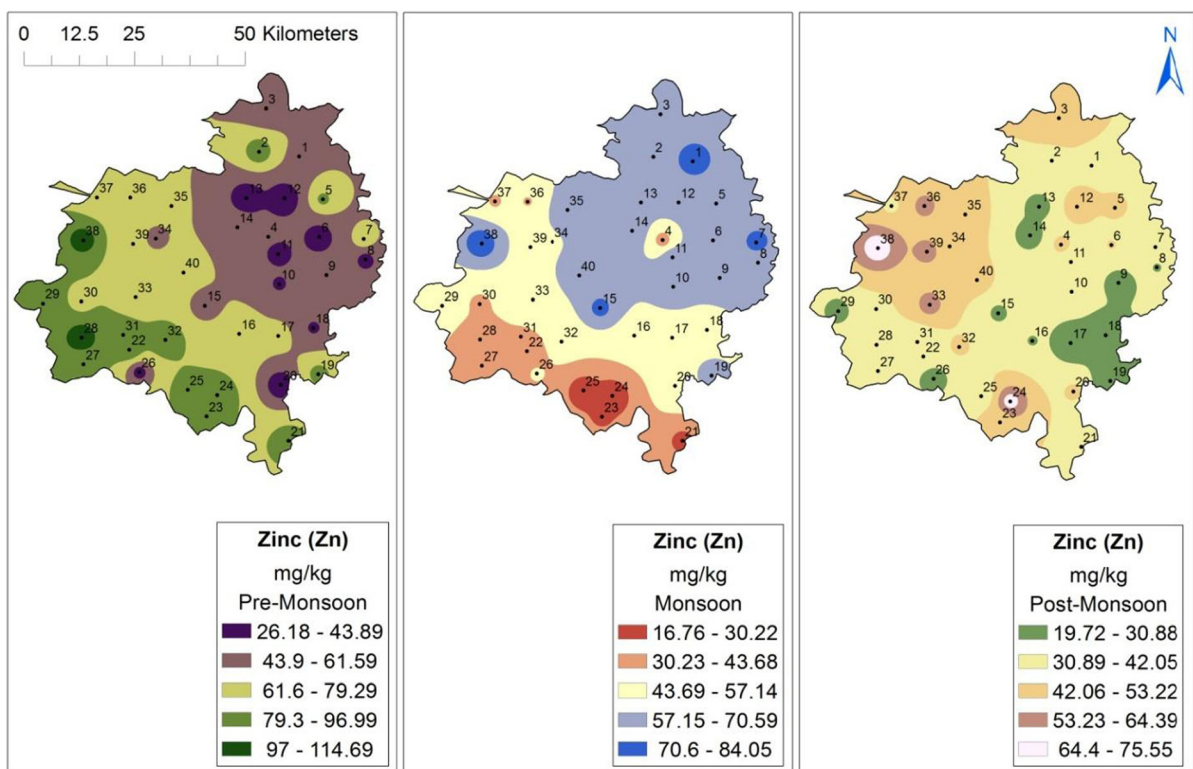


Fig. 11 Spatial and seasonal variability pattern of zinc (Zn)

contamination (Table 12) for metals such as nickel (Ni). On the basis of pollution indices, the study signifies that the soil system in the region was not highly contaminated, implying the land degradation was not severe in the region. However, to restrict the contamination of the soil from becoming worse, it was suggested to take appropriate measures to combat the soil contamination problems in the region in order to maintain soil health for better crop growth.

3.3.4 Ecological Risk Assessment

The potential ecological risk factor (E_i) developed by Hakanson (1980) was originally used to assess the ecological risk associated with heavy metal pollution in the aquatic ecosystem. Hakanson (1980) classified the E_i into five categories as shown in Table 13 which is used to calculate the ecological risk index (R_i) which in turn is divided into four categories (Table 14). Like enrichment factor (EF) (Reimann and de Caritat 2005; Pekey 2006; Zhu et al. 2011)

and degree of contamination (C_d), E_i (Hakanson 1980) also plays an important role in determining the potential ecological risk assessment from different anthropogenic activities (Zhang et al. 2009; Nobil et al. 2010). Since the value of ecological risk index (E_i) for iron (Fe) is less than 1 ($E_i < 1$), it cannot be considered for the evaluation of potential ecological risk factor (R_i) (Pobi et al. 2019). The ecological risk index (E_i) is calculated as the summation of potential ecological risk factor (R_i), where R_i is the product of toxic response factor (T_i) and contamination factor (C_f) of each element taken into consideration (Kumar et al. 2018). The calculation for E_i and R_i was made according to the equations (Eq. 4 and Eq. 5) given below as

$$E_i = T_i(C_i/C_0) \tag{4}$$

$$R_i = \sum_{i=1}^n E_i \tag{5}$$

where,

R_i is calculated as the sum of potential ecological risk factor for heavy metals in sediments;

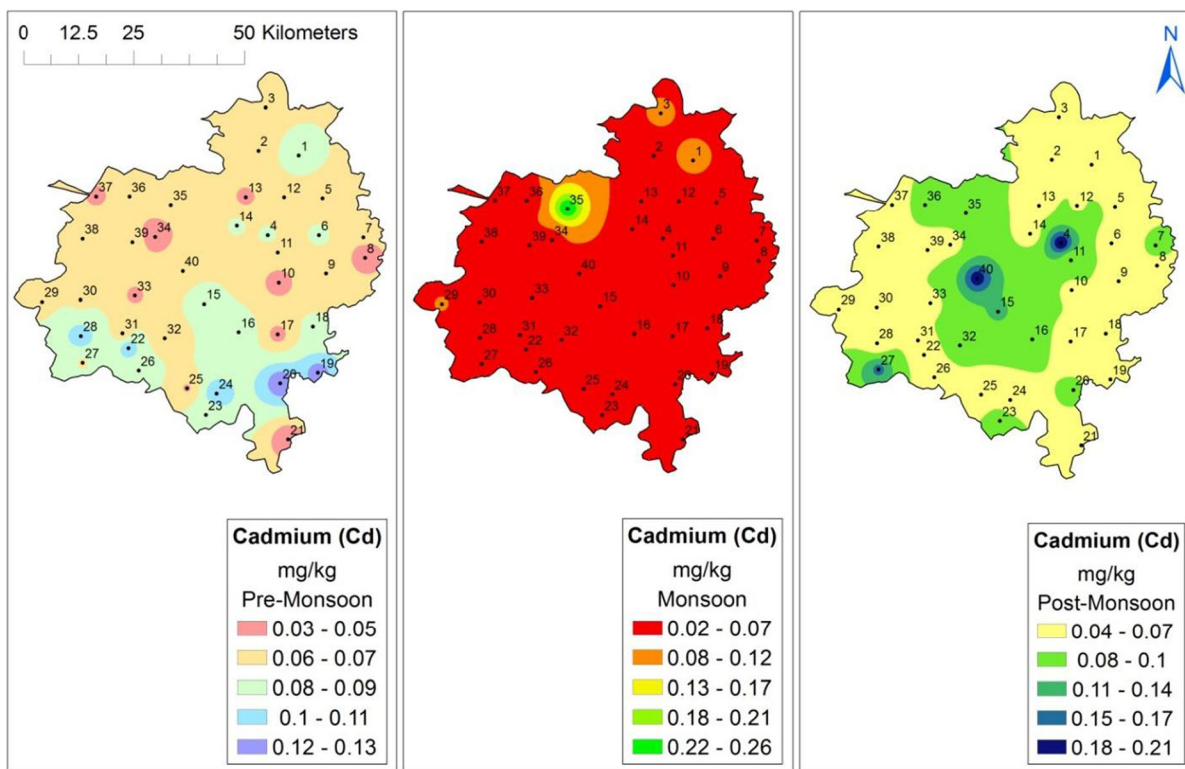


Fig. 12 Spatial and seasonal variability pattern of cadmium (Cd)

E_i is the monomial potential ecological risk factor;

T_i is the toxic response factor of a certain metal.

$C_f = C_i/C_0$ is the ratio of content of the metal in the examined environment and reference value of the metal in the reference environment.

The potential ecological risk factor (E_i) was calculated using toxicity response factor (T_i) and contamination factor ($C_f = C_i/C_0$) of each element at 40 different sampling sites. The toxicity response factor (T_i) for the selected elements (Hakanson 1980; Swarnalatha et al. 2013; Wang et al. 2015; Bhutiani et al. 2017) is given in Table 15. From the results estimated from potential ecological risk factor (E_i) and ecological risk index (R_i) in three different seasons (pre-monsoon, monsoon, post-monsoon) (Tables 16, 17, 18), low potential ecological risk ($E_i < 40$) and low ecological risk ($R_i < 150$) were found at most of the sampling sites except for Hg at few sites where E_i ranged between 40 and 80 ($40 \leq E_i \leq 80$) depicting moderate potential ecological risk, such as pre-monsoon—Hg = 48 (Giana), 41.6 (Malkana) and post-monsoon—Hg = 85.2 (Maluka),

52.8 (Jalal). The lowest and highest values for ecological risk index (R_i) in the region during pre-monsoon, monsoon, and post-monsoon seasons include Ganga ($R_i = 13.28$), Maur ($R_i = 12.3$), Giana ($R_i = 74.82$), and Malkana ($R_i = 64.57$); Jogewala ($R_i = 18.41$), Raman ($R_i = 16.57$), Jeond ($R_i = 46.57$), and Lehra Mohabbat ($R_i = 46.89$); and Ablu ($R_i = 11.47$), Virk Kalan ($R_i = 13.34$), Maluka ($R_i = 95.69$), and Jalal ($R_i = 64.43$), respectively. The results of E_i and R_i showed that the soil system in the region is not contaminated by As, Cr, Co, Ni, Cu, Zn, Cd, Hg, and Pb. However, mercury (Hg) exhibited moderate potential ecological risk at a few locations in the study area (Maluka and Jalal). Similar results were reported by a number of studies worldwide that showed the contamination of the soil was not high enough and the elements analyzed were associated with low ecological risk (Liu et al. 2015; Mohseni-Bandpei et al. 2017; Keshavarzi and Kumar 2019). The potential ecological risk factor (E_i) for heavy metals in the soil was found in the order of $Hg > Ni > As > Co > Cd > Cu > Cr > Zn > Pb$ (pre-monsoon), $Hg > Ni > As > Co >$

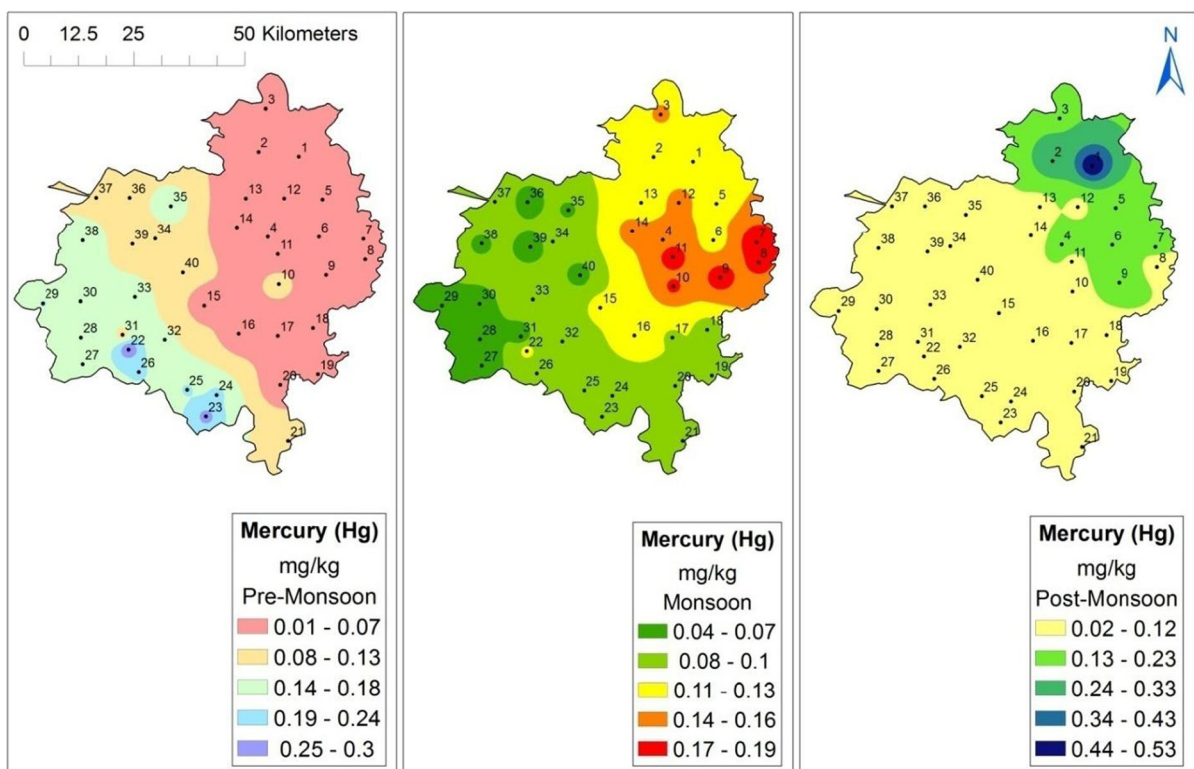


Fig. 13 Spatial and seasonal variability pattern of mercury (Hg)

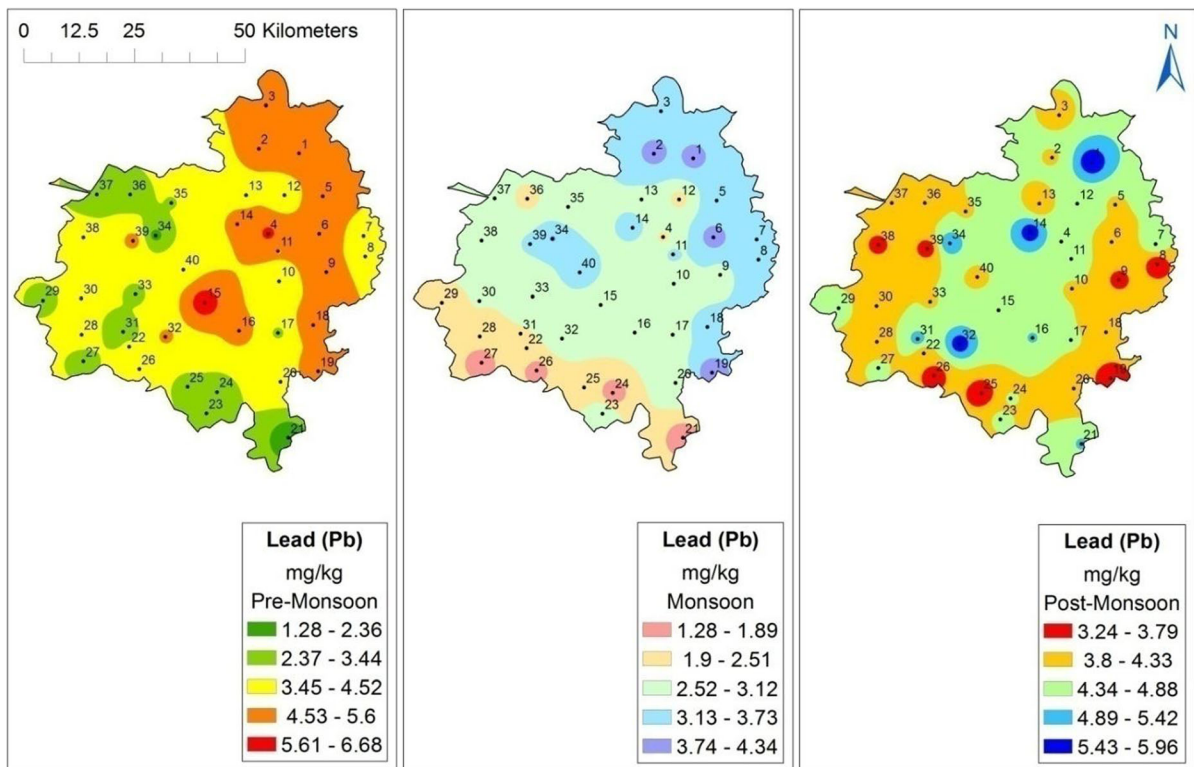


Fig. 14 Spatial and seasonal variability pattern of lead (Pb)

Cd > Cu > Cr > Zn > Pb (monsoon), and Hg > Ni > As > Cd > Co > Cu > Cr > Pb > Zn (post-monsoon), whereas overall ecological risk index (R_i) was found in the order of Hg > Ni > As > Cd > Co > Cu > Cr > Zn > Pb.

(Cr, iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg), and lead (Pb).

The results revealed a strong positive correlation existed between As-Cr ($r = 0.769$), As-Fe ($r = 0.760$), As-Co ($r = 0.883$), As-Ni ($r = 0.886$), As-Cu ($r = 0.859$), and As-Hg ($r = 0.678$) at 5% level

3.4 Multivariate Analysis Using Pearson’s Correlation

Pearson’s correlation (r) and PCA are some essential multivariate techniques which were executed (Kwon et al. 2017; Reimann and de Caritat 2017) on the datasets of heavy metal variables in order to estimate the correlation and also to determine their behavior with each other (Tables 19, 20, 21, 22, 23, 24).

For the purpose of correlation between different metals in three different seasons, Pearson’s correlation (r) coefficient was used ($p < 0.05$). For each season (pre-monsoon, monsoon, and post-monsoon), a total of 40 values (mean concentrations) were used for each of the metals studied which include arsenic (As), chromium

Table 7 Enrichment factor and pollution levels of heavy metals (Sutherland 2000; Zahran et al. 2015)

Level	Enrichment factor
< 2	Depletion to minimal enrichment suggestive for or minimal pollution
2–5	Moderate enrichment, suggestive of moderate pollution
5–20	Significant enrichment, suggestive of a significant pollution signal
20–40	Very highly enriched, indicating a very strong pollution signal
> 40	Extremely enriched, indicating an extreme pollution signal

Table 8 Estimated average enrichment factor (EF) of heavy metals

Metals	Pre-monsoon	Monsoon	Post-monsoon	Enrichment level
As	2.79	3.47	2.5	Moderate
Cr	2.27	2.78	2.76	Moderate
Co	3.12	3.8	2.75	Moderate
Ni	3.27	4.67	2.9	Moderate
Cu	1.07	1.43	0.82	Minimal
Zn	2.78	3.09	2.3	Moderate
Cd	0.000004	0.00001	0.00001	Minimal
Hg	0.06	0.11	0.08	Minimal
Pb	0.59	0.63	0.94	Minimal

of significance during pre-monsoon season (Table 12). The rest of the metals showed either moderate or negative correlation with As at 0.05 significance level. From the samples of monsoon season, a strong correlation at 5% significance level explained between As and other heavy metals (As-Fe ($r=0.613$), As-Co ($r=0.669$), As-Ni ($r=0.619$), As-Cu ($r=0.639$)) as shown in Table 20. Also, from the post-monsoon season, a similar type of observation was exhibited by heavy metals with a strong positive correlation between As-Cr ($r=0.631$), As-Fe ($r=0.715$), As-Co ($r=0.710$), and As-Cu ($r=0.690$) at $p < 0.05$ (two-tailed) significance level. Between As-Ni ($r=0.443$), As-Zn ($r=0.157$), As-Cd ($r=0.127$), As-Hg ($r=0.075$), and As-Pb ($r=0.264$), positively moderate level of correlation was found (Table 21).

Pearson's correlation studies were very significant in determining the relationship between datasets of different variables. It was concluded

Table 9 Pollution load index (PLI) and levels of contamination (Tomlinson et al. 1980; Chakravarty and Patgiri 2009)

PLI values	Soil quality designation
PLI = 1	Heavy metal loads close to the background level/baseline levels of pollutants
$0.5 \leq \text{PLI} < 1$	Monitoring of site is needed
PLI > 1	Deterioration of quality at the site
PLI < 0.5	No need for drastic rectification measures to be taken

that metals such as Cr, Fe, Co, Ni, and Cu showed a strong positive correlation with arsenic (As) from the samples of pre-monsoon, monsoon, and post-monsoon seasons. Such commonality in correlation in all the three seasons revealed that the source of contamination was mostly anthropogenic in nature.

3.5 Multivariate Analysis Using PCA

PCA was executed over the datasets generated through ICP-MS technique. Such multivariate tools are indispensable at local and regional scales in clustering of soil characteristics with respect to those factors that influence parent material (bedrock) and formation of soils (Kabata-Pendias and Mukherjee 2007; Zuo et al. 2009; Wang et al. 2018). Tables 22, 23, and 24 indicate the PCA loadings of heavy metals in three different seasons along with Eigen values, total variance, and cumulative variance. Two factors F1 and F2 with Eigen value greater than 1 and total variance accounted for 12.77, 18.70, and 16.99%, respectively.

From the results obtained by PCA technique as shown in pre-monsoon (Table 22), a strong positive correlation with high factor loadings was observed for the variables such as Cr, As, Fe, Co, Ni, Cu, Zn, and Hg. Similarly, from monsoon and post-monsoon (Tables 23 and 24), majority of the variables showed strong correlation with high factor loadings except for Cd, Hg, and Pb where a moderate or negative correlation was observed in all the three seasons. The variables showed different behavior with each other where some strong associations were

Table 10 Estimated average pollution load index (PLI) of heavy metals

Metals	Pre-Monsoon	Monsoon	Post-Monsoon	Soil quality designation
As	0.98	0.99	0.96	Monitoring of site is required
Cr	0.98	0.98	0.97	Monitoring of site is required
Fe	1	1	0.98	Metal load close to background; monitoring of site is required
Co	0.98	0.98	0.97	Monitoring of site is required
Ni	1	1	0.99	Metal load close to background; monitoring of site is required
Cu	0.97	0.97	0.96	Monitoring of site is required
Zn	0.98	0.97	0.96	Monitoring of site is required
Cd	0.94	0.93	0.96	Monitoring of site is required
Hg	0.97	0.98	0.97	Monitoring of site is required
Pb	0.93	0.92	0.93	Monitoring of site is required

generated based on PCA technique represented through PCA biplots. The associations between variables based on PCA were Cr-As-Fe-Ni-Cu-Cd-Hg in pre-monsoon; Zn-Cd-Pb-Hg, As-Fe-Cu-Ni-Co in monsoon; and Hg-Pb-Ni-Cd-Cu-Co, As-Zn-Cr-Fe in post-monsoon. It was also observed that the variables behaved in a similar fashion in the respective associations established from the datasets. The

Table 11 Degree of contamination (C_d) for heavy metals in soil (Hakanson 1980)

C_d class	Degree of contamination level
$C_d < 8$	Low degree of contamination
$8 \leq C_d \leq 16$	Moderate degree of contamination
$16 \leq C_d \leq 32$	Considerable degree of contamination
$C_d > 32$	Very high degree of contamination

Table 12 Estimated average degree of contamination (C_d) of heavy metals

Metals	Pre-Monsoon	Monsoon	Post-Monsoon	Contamination level
As	17.71	16.86	11.41	Moderate to considerable
Cr	15.26	14.66	12.99	Moderate
Fe	31.13	26.24	21.71	Considerable
Co	17.32	15.22	10.28	Moderate to considerable
Ni	38.65	39.19	23.28	Considerable to very high
Cu	11.77	10.89	6.24	Low to moderate
Zn	15.26	12.24	9.09	Moderate
Cd	2.77	2.07	2.85	Low
Hg	14.4	16.43	14.22	Moderate to considerable level
Pb	2.31	1.64	1.92	Low

factor loadings were found to be consistent with that of Pearson’s correlation matrix. These groups (principal components or factor loadings) and associations are significant in categorization of selected variables based on pedogenesis and mineralization, parent material, lithology, geology, and geochemical factors (Facchinelli et al. 2001; Burak et al. 2010). From the PCA biplots (Fig. 15a), almost all the variables showed strong correlation with each other except Cd and Pb that were poorly significant with respect to other variables. Similarly, in Fig. 15b and c, the variables showed strong positive correlation with each other except Hg which was fairly apart

Table 13 Potential ecological risk factor (E_i) and its classification levels (Hakanson 1980; MacDonald et al. 2000; Guo et al. 2010; Mohseni-Bandpei et al. 2017; Kolawole et al. 2018; Keshavarzi and Kumar 2019)

E_i value	Classification level
$E_i < 40$	Low potential ecological risk
$40 \leq E_i \leq 80$	Moderate potential ecological risk
$80 \leq E_i \leq 160$	Considerable potential ecological risk
$160 \leq E_i \leq 320$	High potential ecological risk
$E_i > 320$	Very high ecological risk at hand for the substance in question

Table 14 Ecological risk index (R_i) and its classification levels (Hakanson 1980; MacDonald et al. 2000; Wang et al. 2015; Pobi et al. 2019)

R_i value	Classification level
$R_i < 150$	Low ecological risk
$150 \leq R_i \leq 300$	Moderate ecological risk
$300 \leq R_i \leq 600$	Considerable ecological risk
$R_i > 600$	Very high ecological risk index

from the rest. Such strong correlations and their pattern of behavior between these variables as indicated from the results of PCA technique could be very helpful in providing information related to their sources of contamination in the region (Ahmed et al. 2016; Moore et al. 2016; Mohammadi et al. 2018; Dogra et al. 2019).

4 Conclusions

Heavy metal contamination assessment and monitoring is essential to ensure better health and quality of soils and the crops grown. The results indicated that the total mean concentration of heavy metals was of the order of $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$, $Fe > Zn > Cr > Ni > Cu > Co > As > Pb > Hg > Cd$, and $Fe > Zn > Cr > Ni > Cu > Co > Pb > As > Hg > Cd$ in pre-monsoon, monsoon, and post-monsoon seasons, respectively. Enrichment factor (EF), pollution load index (PLI), and degree of contamination (C_d) were very significant in determining the contamination levels of different metals in the study area. Spatial distribution mapping technique was very helpful in

Table 15 Toxicity response factor (T_i) of different heavy metals (Hakanson 1980; Swarnalatha et al. 2013; Wang et al. 2015; Bhutiani et al. 2017)

Element	As	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb
T_i	10	2	5	5	5	1	30	40	5

Table 16 Potential ecological risk factor (E_i) in pre-monsoon season and ecological risk index (R_i)

E_i	R_i								
	As	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb
3.5	0.68	1.6	3.6	0.95	0.34	2.7	4.0	0.4	17.77
4.3	0.74	1.85	4.05	1.1	0.54	1.8	3.2	0.35	17.93
3.4	0.56	1.45	3.15	0.85	0.25	2.1	4.0	0.35	16.11
4.7	0.74	2.0	4.75	1.3	0.26	2.4	2.8	0.4	19.35
3.9	0.64	1.7	3.8	1.0	0.48	1.8	3.2	0.4	16.92
3.3	0.56	1.35	3.0	0.9	0.19	2.4	3.2	0.4	15.3
2.8	0.56	1.3	3.0	0.8	0.41	1.5	3.2	0.3	13.87
4.0	0.54	1.5	3.05	0.95	0.22	1.2	2.4	0.25	14.11
4.3	0.7	1.7	3.8	1.1	0.26	1.8	6.0	0.4	20.06
3.4	0.62	1.4	3.05	0.8	0.24	1.2	16	0.25	26.96
3.1	0.56	1.3	2.95	0.75	0.21	1.8	3.2	0.3	14.17
3.0	0.58	1.3	3.05	0.75	0.15	1.8	2.4	0.25	13.28
3.6	0.58	1.4	3.2	0.85	0.16	1.5	2.4	0.3	13.99
4.1	0.7	1.85	3.95	1.25	0.31	2.4	2.0	0.35	16.91
3.4	0.66	1.6	3.65	1.15	0.29	2.7	2.0	0.5	15.95
3.4	0.72	1.7	3.7	1.15	0.45	2.7	2.0	0.35	16.17
3.1	0.56	1.25	2.85	0.7	0.39	1.2	2.0	0.25	12.3
4.3	0.74	2.05	4.3	1.35	0.24	2.4	1.6	0.4	17.38
3.6	0.8	2.05	4.4	1.25	0.49	3.6	1.6	0.4	18.19
2.2	0.46	1.0	2.2	0.55	0.15	3.9	2.4	0.3	13.16
6.8	1.72	4.35	10	2.9	0.51	0.9	19.6	0.1	46.88
6.1	1.28	3.95	8.95	2.45	0.54	3.3	48	0.25	74.82
5.7	1.06	3.35	7.5	2.2	0.51	2.4	41.6	0.25	64.57
5.7	0.92	3.0	6.8	1.85	0.56	3.3	31.2	0.2	53.53
6.3	0.98	3.35	7.4	2.25	0.5	1.5	30	0.2	52.48
5.6	0.84	2.85	6.5	1.95	0.2	2.7	30.4	0.25	51.29
6.0	0.9	3.1	6.8	2.3	0.49	2.1	21.2	0.25	43.14
4.2	0.76	2.6	5.65	1.9	0.66	3.3	29.2	0.25	48.52
3.7	0.7	2.25	5.05	1.55	0.5	2.1	29.6	0.25	45.7
4.7	0.76	2.35	5.25	1.85	0.42	2.1	22.8	0.25	40.48
3.2	0.78	2.2	4.75	1.55	0.52	1.8	16.8	0.2	31.8
4.8	0.82	2.55	5.65	2.7	0.55	1.8	20.4	0.35	39.62
6.0	0.76	2.45	5.5	1.7	0.37	1.5	24	0.25	42.53
5.3	0.72	2.3	5.0	1.5	0.32	0.9	18.4	0.15	34.59
4.5	0.62	1.85	4.3	1.25	0.36	1.8	28.8	0.25	43.73
5.1	0.8	2.3	5.3	1.45	0.41	1.5	18.8	0.2	35.86
4.6	0.84	2.45	5.3	1.6	0.4	1.5	17.2	0.2	34.09
5.1	0.88	2.75	6.2	1.95	0.62	1.8	25.2	0.25	44.75
6.7	0.88	2.75	6.25	2.1	0.39	2.1	18	0.35	39.52
5.7	0.78	2.45	5.45	2.3	0.42	2.1	15.2	0.3	34.7

Table 17 Potential ecological risk factor (E_i) in monsoon season and ecological risk index (R_i)

E_i									R_i
As	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb	
4.3	0.72	2.35	5.25	1.65	0.44	2.4	20.8	0.3	38.21
5.0	0.7	2.45	5.4	1.7	0.39	2.1	21.2	0.3	39.24
3.9	0.6	2.05	4.45	1.4	0.38	2.1	21.6	0.25	36.73
3.3	0.36	1.15	2.6	0.75	0.21	0.6	24.4	0.15	33.52
3.6	0.68	2.4	6.25	1.7	0.39	1.5	18	0.25	34.77
4.6	0.8	2.7	7.2	1.85	0.4	1.8	18.4	0.3	38.05
3.7	0.6	1.9	5.45	1.25	0.42	1.8	31.2	0.25	46.57
5.0	0.6	2.15	5.2	1.4	0.38	1.8	27.2	0.25	43.98
4.2	0.56	1.95	4.8	1.25	0.36	1.5	30	0.2	44.82
4.1	0.64	1.95	4.8	1.2	0.38	1.2	27.6	0.2	42.07
4.3	0.62	1.9	5.3	1.55	0.37	1.8	30.8	0.25	46.89
3.8	0.66	1.9	5.65	1.3	0.34	1.2	22.4	0.15	37.4
5.4	0.76	2.55	6.5	1.7	0.35	1.2	16.8	0.2	35.46
4.4	0.66	2.0	5.7	1.35	0.39	1.2	24	0.25	39.95
3.9	0.74	2.05	5.45	1.55	0.44	1.5	18	0.2	33.83
5.2	0.7	2.1	6.4	1.5	0.29	0.9	19.2	0.2	36.49
5.1	0.64	2.0	5.15	1.3	0.27	1.2	15.6	0.2	31.46
5.4	0.64	1.95	5.35	1.25	0.27	1.2	13.6	0.25	29.91
5.6	0.76	2.5	5.9	2.1	0.36	2.1	11.6	0.3	31.22
5.6	0.8	2.3	6.05	1.65	0.3	1.2	13.2	0.2	31.3
1.0	0.16	0.65	1.7	0.55	0.15	0.9	13.2	0.1	18.41
1.7	0.2	0.9	2.5	0.75	0.17	1.5	18	0.15	25.87
2.2	0.36	1.15	2.45	1.15	0.16	1.5	15.6	0.2	24.77
1.4	0.22	0.7	1.6	0.65	0.1	0.6	11.2	0.1	16.57
1.6	0.3	0.85	2.45	0.6	0.11	1.2	16	0.15	23.26
3.5	1.76	1.6	5.35	1.0	0.26	1.2	13.2	0.1	27.97
4.3	2.08	2.2	4.75	2.15	0.2	0.6	6.4	0.1	22.78
4.3	1.92	1.55	4.0	1.25	0.18	0.9	7.6	0.15	21.85
3.1	0.72	1.75	4.8	1.1	0.3	2.1	10	0.15	24.02
4.4	0.6	1.7	4.25	1.2	0.24	1.8	10.8	0.2	25.19
5.4	0.76	2.35	5.55	1.35	0.25	1.2	8.8	0.2	25.86
3.7	0.68	1.9	5.15	1.25	0.3	1.5	13.2	0.2	27.88
10	0.64	1.85	4.65	1.55	0.29	1.2	11.6	0.2	31.98
4.1	0.66	2.0	6.4	1.5	0.32	1.5	12	0.25	28.73
5.1	0.88	2.1	5.15	1.4	0.4	7.8	10.8	0.2	33.83
4.3	0.72	2.15	5.05	1.25	0.24	0.9	8.8	0.15	23.56
3.9	0.6	1.75	4.6	1.05	0.24	0.9	16	0.2	29.24
4.2	1.26	2.15	5.3	1.65	0.48	1.8	10.8	0.2	27.84
4.4	0.76	2.1	5.2	1.45	0.3	1.5	9.2	0.25	25.16
5.6	0.82	2.35	6.25	1.95	0.39	1.2	8.8	0.25	27.61

Table 18 Potential ecological risk factor (E_i) in post-monsoon season and ecological risk index (R_i)

E_i									R_i
As	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb	
2.8	0.56	1.25	2.85	0.95	0.23	1.5	85.2	0.35	95.69
3.3	0.6	1.4	2.9	0.85	0.23	2.1	52.8	0.25	64.43
3.8	0.7	1.7	3.95	1.1	0.3	2.1	34.4	0.25	48.3
3.9	0.64	1.6	3.65	1.05	0.26	6.3	32	0.25	49.65
2.8	0.54	1.25	2.75	0.7	0.25	2.1	28.8	0.25	39.44
3.5	0.52	1.25	2.7	0.8	0.24	1.5	23.6	0.2	34.31
3.0	0.56	1.4	3.2	0.9	0.2	2.1	21.6	0.25	33.21
3.1	0.52	1.3	2.6	0.85	0.17	2.1	15.2	0.2	26.04
1.7	0.4	0.9	1.9	0.55	0.14	1.5	36	0.2	43.29
2.6	0.62	1.35	2.85	0.9	0.21	1.8	15.2	0.25	25.78
2.6	0.58	1.35	2.9	0.8	0.21	2.1	17.2	0.25	27.99
2.0	0.6	1.25	2.7	0.8	0.28	2.1	14.8	0.25	24.78
2.9	0.52	1.2	2.75	0.75	0.14	1.5	13.6	0.2	23.56
2.6	0.74	1.15	6.4	0.65	0.12	1.5	11.6	0.35	25.11
2.6	0.52	1.15	2.6	0.6	0.16	3.3	12.4	0.25	23.58
3.4	0.64	1.4	3.15	0.85	0.17	2.7	10	0.25	22.56
2.5	0.46	1.0	2.25	0.6	0.11	1.5	10.4	0.25	19.07
3.1	0.64	1.35	2.95	0.75	0.11	1.8	7.6	0.25	18.55
1.9	0.46	0.95	2.15	0.5	0.12	1.5	8.8	0.2	16.58
2.9	0.6	1.2	2.55	0.7	0.25	2.4	6.8	0.2	17.6
4.1	0.8	1.65	3.7	1.05	0.23	2.1	5.6	0.25	19.48
2.4	0.6	1.05	2.35	0.6	0.23	1.8	13.2	0.2	22.43
3.8	1.04	1.1	2.45	0.85	0.27	2.7	9.2	0.25	21.66
4.0	1.2	1.2	2.85	0.75	0.41	1.5	7.6	0.25	19.76
3.2	0.8	1.35	2.9	0.65	0.19	1.5	6.4	0.2	17.19
2.7	0.62	1.2	2.6	0.55	0.12	1.5	5.2	0.2	14.69
2.1	0.68	1.3	2.85	0.7	0.2	4.5	5.2	0.25	17.78
3.3	0.74	1.45	3.15	0.85	0.21	1.2	4.4	0.2	15.5
2.1	0.58	1.2	2.4	0.55	0.15	1.5	4.8	0.25	13.53
3.5	0.74	1.35	2.9	0.7	0.22	1.2	5.6	0.2	16.41
3.9	0.84	1.7	3.95	1.05	0.18	2.1	3.6	0.3	17.62
3.4	0.76	1.55	3.4	1.2	0.25	2.7	4.4	0.35	18.01
2.5	0.64	1.25	2.8	0.8	0.34	1.8	4.4	0.25	14.78
3.2	0.82	1.75	3.75	1.1	0.29	1.8	3.6	0.3	16.61
1.9	0.58	1.2	2.6	0.7	0.28	2.4	4.0	0.25	13.91
2.4	0.66	1.2	2.7	0.8	0.32	2.7	3.6	0.2	14.58
1.4	0.54	0.85	1.75	0.5	0.23	1.2	4.8	0.2	11.47
2.5	0.56	1.1	2.35	0.6	0.43	1.2	4.4	0.2	13.34
2.3	0.68	1.35	2.8	0.7	0.33	1.8	4.4	0.2	14.56
2.6	0.64	1.15	2.5	0.7	0.27	6.0	7.2	0.25	21.31

Table 19 Pearson's correlation coefficient (*r*) matrix of heavy metals (pre-monsoon season)

	As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
As	1									
Cr	0.769*	1								
Fe	0.760	0.843*	1							
Co	0.883	0.927*	0.880*	1						
Ni	0.886	0.932*	0.884*	0.998*	1					
Cu	0.859	0.822*	0.810*	0.933*	0.928*	1				
Zn	0.431	0.543*	0.554*	0.630*	0.613*	0.637*	1			
Cd	-0.136	-0.026	0.093	0.028	0.025	0.004	0.085	1		
Hg	0.678	0.582*	0.677*	0.786*	0.786*	0.738*	0.552*	0.074	1	
Pb	-0.411	-0.451	-0.366	-0.507	-0.505	-0.416	-0.315	0.381	-0.581	1

*Correlation is significant at the 0.05 level

Table 20 Pearson's correlation coefficient (*r*) matrix of heavy metals (monsoon season)

	As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
As	1									
Cr	0.260	1								
Fe	0.613*	0.623*	1							
Co	0.669*	0.359*	0.829*	1						
Ni	0.619*	0.348*	0.773*	0.918*	1					
Cu	0.639*	0.462*	0.769*	0.887*	0.777*	1				
Zn	0.430*	0.104	0.575*	0.756*	0.737*	0.639*	1			
Cd	0.129	0.003	0.121	0.215	0.153	0.164	0.386*	1		
Hg	-0.098	-0.37*	-0.030	0.022	0.056	-0.112	0.396*	-0.009	1	
Pb	0.420*	-0.194	0.317*	0.643*	0.571*	0.582*	0.696*	0.262	0.312*	1

*Correlation is significant at the 0.05 level

Table 21 Pearson's correlation coefficient (*r*) matrix of heavy metals (post-monsoon season)

	As	Cr	Fe	Co	Ni	Cu	Zn	Cd	Hg	Pb
As	1									
Cr	0.631*	1								
Fe	0.715*	0.802*	1							
Co	0.710*	0.401*	0.481*	1						
Ni	0.443*	0.371*	0.274	0.554*	1					
Cu	0.690*	0.379*	0.527*	0.862*	0.482*	1				
Zn	0.157	0.405*	0.426*	0.170	-0.073	0.245	1			
Cd	0.127	0.032	0.119	0.217	0.071	0.232	0.106	1		
Hg	0.075	-0.284	-0.053	0.043	0.011	0.245	-0.048	0.018	1	
Pb	0.264	0.256	0.154	0.401*	0.594*	0.590*	0.002	0.182	0.254	1

*Correlation is significant at the 0.05 level

Table 22 Weight of two factor loadings of heavy metals (pre-monsoon season)

Metals	F1	F2
As	0.883	-0.105
Cr	0.906	0.032
Fe	0.893	0.162
Co	0.990	0.049
Ni	0.989	0.046
Cu	0.939	0.053
Zn	0.673	0.210
Cd	-0.03	0.920
Hg	0.828	-0.013
Pb	-0.561	0.583
Eigen values	6.69	1.277
Total variance (%)	66.901	12.766
Cumulative variance (%)	66.901	79.667

providing information about the distribution of heavy metals and finding the possible pollution factors in the region that could be treated as baseline study for soil quality survey and natural resource management. It was concluded that the concentrations of metals obtained in all the three seasons were lower than their natural background

Table 23 Weight of two factor loadings of heavy metals (monsoon season)

Metals	F1	F2
As	0.729	-0.142
Cr	0.411	-0.762
Fe	0.857	-0.308
Co	0.969	-0.014
Ni	0.917	-0.006
Cu	0.907	-0.156
Zn	0.813	0.420
Cd	0.294	0.231
Hg	0.067	0.774
Pb	0.669	0.566
Eigen values	5.236	1.870
Total variance (%)	52.365	18.697
Cumulative variance (%)	52.365	71.062

Table 24 Weight of two factor loadings of heavy metals (post-monsoon season)

Metals	F1	F2
As	0.848	-0.099
Cr	0.724	-0.525
Fe	0.772	-0.463
Co	0.843	0.172
Ni	0.643	0.356
Cu	0.869	0.271
Zn	0.339	-0.527
Cd	0.234	0.134
Hg	0.072	0.602
Pb	0.568	0.557
Eigen values	4.215	1.699
Total variance (%)	42.155	16.986
Cumulative variance (%)	42.155	59.141

concentration values. Pearson's correlation (r) studies and PCA technique were helpful in determining the relationship between datasets of different variables. Pearson's correlation established at $p < 0.05$ (As-Cr ($r = 0.769$), As-Fe ($r = 0.760$), As-Co ($r = 0.883$), As-Ni ($r = 0.886$), As-Cu ($r = 0.859$), As-Hg ($r = 0.678$) in pre-monsoon; As-Fe ($r = 0.613$), As-Co ($r = 0.669$), As-Ni ($r = 0.619$), As-Cu ($r = 0.639$) in monsoon samples; and As-Cr ($r = 0.631$), As-Fe ($r = 0.715$), As-Co ($r = 0.710$), As-Cu ($r = 0.690$) in post-monsoon samples) indicated strong relationship between different variables. The associations between variables based on PCA were Cr-As-Fe-Ni-Cu-Cd-Hg in pre-monsoon; Zn-Cd-Pb-Hg, As-Fe-Cu-Ni-Co in monsoon; and Hg-Pb-Ni-Cd-Cu-Co, As-Zn-Cr-Fe in post-monsoon indicating a similar behavior of variables in the respective associations. Finally, it was revealed that the study of heavy metal contamination along with pollution indices and ecological risk assessment was very significant in determining the quality of the soil, and this study would be very useful for future studies where the data generated can be used as a baseline to determine the status of soil quality and also to ensure conservation of soil resources. Regular monitoring and formulation of appropriate policies are also suggested to avoid further deterioration of the soil.

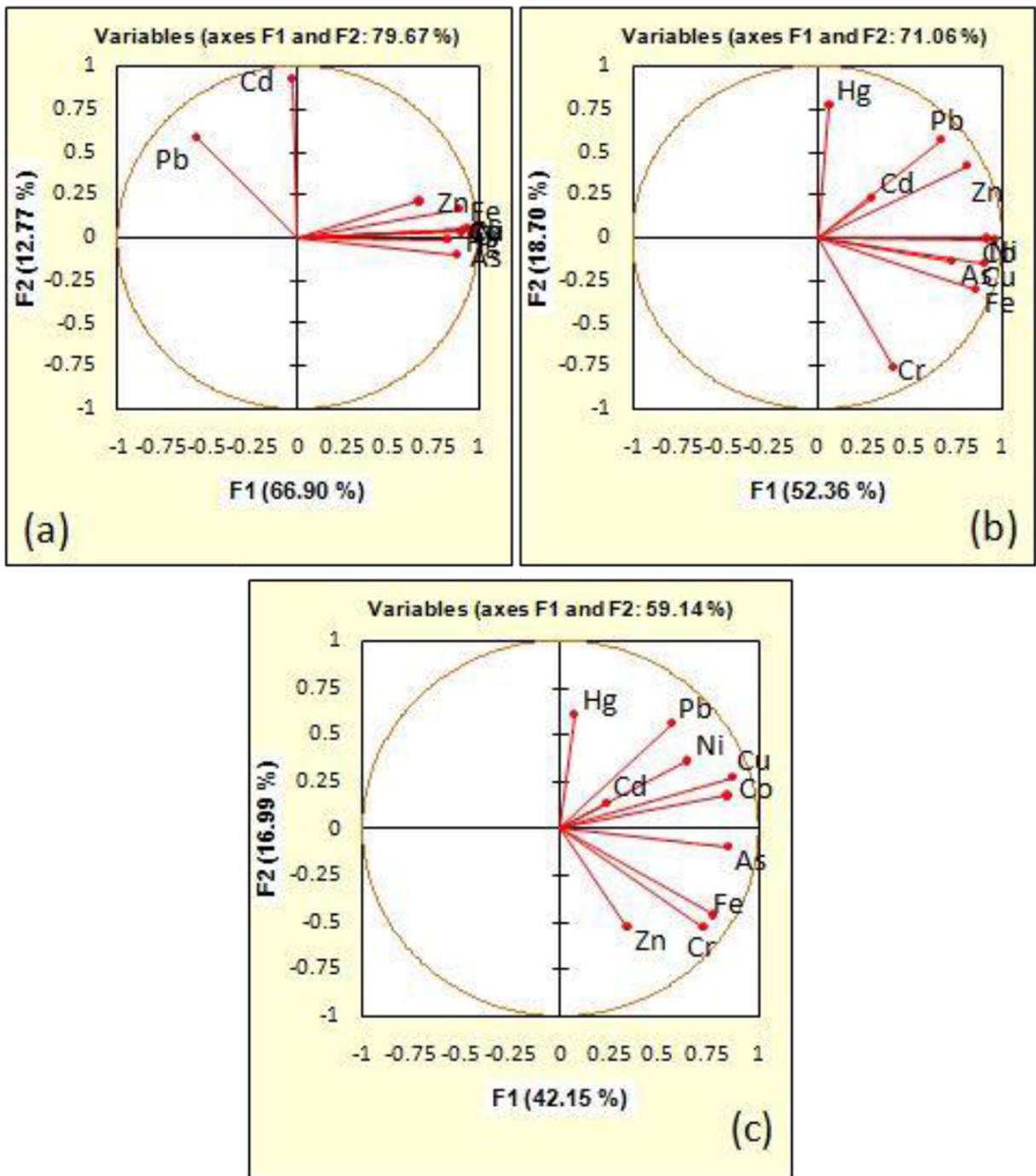


Fig. 15 PCA biplots, (a) pre-monsoon, (b) monsoon, (c) post-monsoon, showing the relationship of variables and factor loadings

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