RESEARCH PAPER



Evaluation of Metal Contamination in the Groundwater of the Aosta Valley Region, Italy

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Abstract One hundred and sixty-two groundwater samples were collected from eighteen locations of the Aosta Valley region during the years 2007-2015 to determine the concentrations of Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn. A heavy pollution index (HPI) model was used to evaluate the metal contamination status in the groundwater of the study area. Spatial distribution maps of the HPI values were prepared using a geographic information system (GIS) technique so that the groundwater quality status of the area could easily be recognized. The concentrations of As, Ba, Cd, Cu, Pb, and Zn did not exceed the drinking water permissible limits for years considered. However, the concentrations of Al, Cr, Fe, Mn, Ni, and Se were above the drinking water permissible limits established by the World Health Organization (WHO 2006). The HPI values were above the critical pollution index of 100 during the years 2011 and 2012. The groundwater in this study area was contaminated with some metals and urgently requires treatment to control current and future contamination problems.

Keywords Metals \cdot Water quality \cdot Sources of pollution \cdot HPI \cdot GIS

Introduction

Metal contamination in groundwater is one of the most serious environmental concerns in the present world scenario, wherein metal contamination is a major problem due to its high toxicity, even at low concentration levels (Singh and Kamal 2016). Metals enter groundwater from a variety of sources such as natural (derived from mineralogy and weathering) or anthropogenic (Adaikpoh et al. 2005; Karbassi et al. 2007). The main anthropogenic source of natural water contamination is industrialization, mining, indiscriminate use of heavy metal-containing fertilizers, pesticides used in agriculture, and sewage discharge (Ammann et al. 2002; Nouri et al. 2008). The concentrations of metals beyond permissible limits in groundwater can harm ecosystems, plants, animals, and cause human health problems (Bhagure and Mirgane 2011).

In recent times, many researchers from all over the globe have shown keen interest in evaluating metal contamination in water resources using the HPI model (Giri et al. 2010; Sheykhi and Moore 2012; Kumar et al. 2012; Prasanna et al. 2012; Giri and Singh 2014; Protano et al. 2014; Varghese and Java 2014; Singaraja et al. 2015; Chidambaram et al. 2015; Kumwimba et al. 2016; Milivojević et al. 2016; Ewaid 2016). The present study aimed to evaluate metal contamination status and assess the groundwater quality for its suitability for drinking and domestic purposes in the Aosta Valley region, Italy. A HPI model and GIS technique were used to assess the influence of overall metal pollution and illustrate the spatial distribution of the HPI values in the groundwater of the study area. Information on metal contamination level is very useful for deciding on the utilization of groundwater resources. It may also help policy makers in future water resource planning for the area.

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Study Area

The study area lies in the northwestern part of the Italian peninsula, located within the latitude 45°42'00"-45°46'00" N and longitude $7^{\circ}16'00''-7^{\circ}26'00''$ E of the Aosta Valley region, Italy (Fig. 1). The region is an area in the valley formed by the Dora Baltea River, which flows from east to west, and its twelve tributary valleys. It is the smallest region in Italy and one of the main alpine valley systems of the Po River, bordered by the major peaks of the Pennine and Graie Alps. The Aosta Valley region has a typical alpine climate characterized by cold winters and cool summers. Monthly rainfall reaches its highest annual peaks in the spring and autumn seasons, while the minimum annual values are recorded in the summer and winter seasons. In particular, the highest mean precipitation value by month is roughly 140 mm of rainfall, while the minimum is 30 mm (Mercalli et al. 2003). The study area has one steel factory situated in the SE part of the city of Aosta. Its main products are stainless steel wire rods, stainless steel bars, semi-finished products, valve steel, tool steel, and atomised powders. The geology of the Aosta Valley region, from

Fig. 1 Groundwater sampling locations in the Aosta Valley region, Italy

NW to SE, is a natural cross section through the structural block of the Alps. The stacked relics of the ancient European and African continental margins, with wrecked portions of the ocean floor between them, emerge in this area of the Alps (Dal Piaz 1992). In particular, this region contains several structural geological domains, such as the Elvetico–Ultraelvetico Domain, Pennidic Domain, Piemontese Zone, and Austroalpine Domain. The depth to the water table below ground level is minimal in the eastern area of the Aosta plain (<5 m in all seasons) and highest in the northern area (>20–25 m) (Regione Valle d'Aosta 2006).

Materials and Methods

For the estimation of metal contamination in the groundwater of the Aosta Valley region, systematic samplings were carried out during the years 2007–2015. A total of one hundred and sixty-two (eighteen in each year) groundwater samples were collected from different wells in the study area in pre-washed high-density polyethylene bottles



(Fig. 1). Before the sampling phase, the wells were subjected to pumping for a sufficient amount of time to drag the water from the aquifer. Samples were filtered with a Millipore filtration unit, filter paper (pore size 0.45 μ m) and preserved by adjusting the pH <2 with 6 N ultrapure nitric acid (Radojevic and Bashkin 1999). Concentrations of metals were analyzed by inductively coupled plasmamass spectroscopy (ICP-MS) (Thermo Scientific, X Series 2). Reagent blank determinations were used to correct the instrument readings. The SPSS (version 20), a commercial statistical software package, was used for computing interelemental correlations analysis of the metals database.

The heavy metal pollution index (HPI) is a rating technique that provides the composite influence of individual heavy metals on the overall quality of water. The rating system is an arbitrary value between zero and one and its selection depends upon the compression of individual quality considerations. Alternatively, it can be assessed by making values inversely proportional to the recommended standard for the corresponding parameter (Horton 1965; Mohan et al. 1996).

Prasad and Bose (2001) considered unit weightage (W_i) to compute the heavy metal pollution index (HPI). This value is inversely proportional to the recommended standard (S_i) of the corresponding parameter proposed by Reddy (1995). The critical pollution index of HPI value for drinking water as given by Prasad and Bose (2001) is 100. In the present study, we used the modified scale suggested by Edet and Offiong (2002), with three classes: low, medium, and high for HPI values <15, 15–30 and >30, respectively.

For this study, the concentration limits [i.e., highest permissive value for drinking water (S_i) and maximum desirable value (I_i) for each parameter] were taken from the World Health Organization drinking water specifications (WHO 2006). The highest permissive value for drinking water (S_i) refers to the maximum allowable concentration in drinking water in the absence of any alternative water source. The desirable maximum value (I_i) indicates the standard limits for the same parameters in drinking water. The HPI values of the groundwater water samples were computed as per the following equation, which was provided by Mohan et al. (1996),

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i},$$
(1)

where Q_i is the sub-index of the ith parameter. W_i is the unit weightage of ith parameter, and n is the number of parameters considered.

The sub-index (Q_i) of the parameter is calculated by the following equation:

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)},$$
(2)

where M_i is the monitored value of heavy metal of the ith parameter, I_i is the ideal value (maximum desirable value for drinking water) of the ith parameter, and S_i is the standard value (highest permissive value for drinking water) of the ith parameter. The sign (-) indicates the numerical difference of the two values, ignoring the algebraic sign.

Spatial distribution maps of the HPI values were prepared using ARC GIS-10.2 software (Environmental Systems Research Institute, Redlands 380 New York Street 92373, California, United States). An inverse distance weighted (IDW) interpolation technique was used for spatial modeling.

Results and Discussion

The statistical results of the metal analysis are provided in Table 1 and compared with the drinking water guideline of the World Health Organization (WHO 2006). It was observed that concentrations of As, Ba, Cd, Cu, Pb, and Zn did not exceed the limits for drinking water. However, the concentrations of Al, Cr, Fe, Mn, Ni, and Se were above the drinking water limit of the WHO (2006). The mean concentrations for the studied nine years (2007-2015) are presented in Table 1. The total concentrations of all of the studied elements in the groundwater averaged a minimum of 142.3 μ g L⁻¹ in 2014 and averaged a maximum of 341.3 μ g L⁻¹ in 2012 (Fig. 2). The yearly metal concentration variations in the study area groundwater were far higher during the years 2012, 2010, 2009, 2008, and 2011 compared to the years 2014, 2015, 2007, and 2013 (Fig. 2).

The results, as shown in Table 1, indicate that the maximum Cr level in the groundwater was reached in 2007 and the minimum in 2011. We observed that the concentrations of Cr in the groundwater samples were 1.43-5.56 times higher than the drinking water limit of 50 µg L⁻¹ (WHO 2006). High concentration levels of Cr were found at some locations in the study area. This was as a result of the leaching of superficial slag deposits in the area. A recent study of the Aosta Valley region by Bonomi et al. (2015) indicates that Cr contamination in the groundwater due to the leaching of superficial slag deposits has accumulated for decades in a deregulated way.

The concentration of Ni in the groundwater was well within the drinking water limit of 20 μ g L⁻¹ (WHO 2006) during the years 2007 and 2008, respectively. However, the concentration of Ni exceeded the drinking water limit

| Year | Range | Al | As | Ва | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Se | Zn |
|----------|------------|---------|------|-------|------|-------|------|-------|-------|-------|------|-----|------|
| 2007 | Min. | 0.5 | 0.1 | 0.9 | 0.02 | 0.9 | 11.3 | 14.6 | 0.1 | 0.2 | 0.1 | 0.5 | 4.7 |
| | Max. | 93.4 | 2.8 | 50 | 0.7 | 278 | 30 | 143.6 | 174.3 | 11.6 | 3.9 | 16 | 31 |
| | Mean | 13 | 0.6 | 37.1 | 0.1 | 25.7 | 23.7 | 33.1 | 13.0 | 1.6 | 0.9 | 2.5 | 11.1 |
| | Std. error | 6.6 | 0.1 | 3.1 | 0.1 | 15.2 | 1.5 | 7.7 | 9.7 | 0.6 | 0.2 | 0.8 | 1.4 |
| 2008 | Min. | 0.5 | 0.2 | 36 | 0.02 | 0.6 | 1.7 | 11.7 | 0.4 | 0.4 | 0.7 | 0.5 | 5.4 |
| | Max. | 289.6 | 2.1 | 751.4 | 1.2 | 168.5 | 30 | 339.6 | 1116 | 19.4 | 4.0 | 9.0 | 11.6 |
| | Mean | 21.1 | 0.6 | 100.2 | 0.3 | 17.1 | 23.7 | 38.4 | 63.9 | 2.1 | 1.6 | 2.7 | 8.9 |
| | Std. error | 1.0 | 0.1 | 18.6 | 0.1 | 5.0 | 1.6 | 6.2 | 109.6 | 7.4 | 0.05 | 0.3 | 0.5 |
| 2009 | Min. | 0.4 | 0.4 | 48 | 0.02 | 0.4 | 8.9 | 11.1 | 0.2 | 0.6 | 0.3 | 0.4 | 3.4 |
| | Max. | 16.5 | 2.2 | 391 | 1.2 | 89.6 | 30 | 130.1 | 1974 | 132.8 | 1.0 | 5.1 | 10 |
| | Mean | 2.9 | 0.8 | 86.5 | 0.1 | 10.4 | 23 | 26.4 | 111.1 | 10 | 0.7 | 1.9 | 8.1 |
| | Std. error | 1.0 | 0.1 | 18.6 | 0.1 | 5.0 | 1.6 | 6.2 | 109.6 | 7.4 | 0.05 | 1.0 | 0.1 |
| 2010 | Min. | 0.6 | 0.3 | 25.4 | 0.02 | 0.5 | 2.5 | 14.2 | 0.3 | 0.5 | 0.5 | 0.5 | 4.4 |
| | Max. | 74.4 | 9.0 | 80.9 | 0.6 | 109.4 | 123 | 172.5 | 2999 | 78.9 | 8.9 | 6.4 | 74 |
| | Mean | 10.3 | 1.2 | 44.4 | 0.1 | 10.1 | 13 | 35 | 168.5 | 7.0 | 1.3 | 3.2 | 12 |
| | Std. error | 4.4 | 0.5 | 2.8 | 0.0 | 6.0 | 6.6 | 9.4 | 166.5 | 4.6 | 0.4 | 0.3 | 3.7 |
| 2011 | Min. | 1.0 | 0.6 | 15.4 | 0.1 | 0.6 | 4.3 | 12.5 | 0.4 | 0.4 | 0.7 | 1.0 | 1.5 |
| | Max. | 10.6 | 3.7 | 123.2 | 2.7 | 71.6 | 14.5 | 69 | 3001 | 87.2 | 1.4 | 5.8 | 11.4 |
| | Mean | 3.2 | 1.4 | 32.3 | 0.5 | 8.9 | 5.9 | 29.1 | 168.7 | 8.2 | 1.0 | 3.5 | 7.7 |
| | Std. error | 0.7 | 0.2 | 5.7 | 0.2 | 4.0 | 0.5 | 3.7 | 166.6 | 5.3 | 0.04 | 0.4 | 0.7 |
| 2012 | Min. | 0.9 | 0.2 | 9.4 | 0.0 | 0.1 | 0.5 | 5.4 | 0.2 | 0.3 | 0.2 | 0.9 | 1.1 |
| | Max. | 3.2 | 0.7 | 158.5 | 1.7 | 146.6 | 10.2 | 1074 | 3670 | 85.2 | 1.3 | 3.8 | 11.4 |
| | Mean | 1.7 | 0.5 | 27.1 | 0.2 | 11.8 | 1.5 | 77.5 | 204.3 | 8.6 | 0.8 | 2.4 | 4.8 |
| | Std. error | 0.2 | 0.04 | 7.9 | 0.1 | 8.0 | 0.5 | 58.7 | 203.9 | 5.6 | 0.1 | 0.2 | 0.7 |
| 2013 | Min. | 1.1 | 0.2 | 12.7 | 0.01 | 0.4 | 0.5 | 7.5 | 0.2 | 0.3 | 0.7 | 0.9 | 1.3 |
| | Max. | 5.0 | 3.1 | 113.4 | 0.5 | 168.1 | 10.8 | 57.7 | 2044 | 61.6 | 1.3 | 4.9 | 8.7 |
| | Mean | 3.2 | 0.6 | 30.6 | 0.2 | 13.2 | 1.7 | 20.2 | 114.1 | 6.6 | 0.9 | 3.0 | 3.6 |
| | Std. error | 0.2 | 0.1 | 5.2 | 0.04 | 9.2 | 0.5 | 2.8 | 113.5 | 4.0 | 0.04 | 0.3 | 0.5 |
| 2014 | Min. | 1.4 | 0.4 | 7.9 | 0.0 | 0.1 | 0.1 | 8.4 | 0.2 | 0.2 | 0.4 | 0.5 | 3.9 |
| | Max. | 5.0 | 2.9 | 62.6 | 0.6 | 138.2 | 21 | 39.7 | 1145 | 54.1 | 1.0 | 3.9 | 12.4 |
| | Mean | 3.3 | 1.6 | 22.7 | 0.3 | 12.1 | 1.7 | 21.2 | 64.1 | 4.2 | 0.7 | 1.0 | 9.2 |
| | Std. error | 0.2 | 0.2 | 3.3 | 0.04 | 7.6 | 1.2 | 2.4 | 63.6 | 3.0 | 0.05 | 0.2 | 0.6 |
| 2015 | Min. | 0.5 | 0.4 | 13.4 | 0.0 | 0.1 | 0.1 | 4.1 | 0.4 | 0.3 | 0.3 | 0.5 | 4.7 |
| | Max. | 6.1 | 3.4 | 55.4 | 0.5 | 177.1 | 30 | 52.9 | 1139 | 56.7 | 6.6 | 4.1 | 17 |
| | Mean | 3.0 | 1.6 | 28.4 | 0.3 | 15 | 5.4 | 16.5 | 64 | 3.8 | 1.0 | 1.9 | 9.8 |
| | Std. error | 0.3 | 0.2 | 2.7 | 0.04 | 9.7 | 2.3 | 2.6 | 63.2 | 3.1 | 0.3 | 0.3 | 0.6 |
| WHO 2006 | | 100-200 | 10 | 300 | 3.0 | 50 | 2000 | 300 | 100 | 20 | 10 | 10 | 4000 |

Table 1 Yearly variation in metal concentration ($\mu g L^{-1}$) in the groundwater of the study area and comparison with drinking water guideline values of the WHO (2006)

during the remaining years. We found that the Ni concentrations were 2.70 (in 2014)–6.64 (in 2009) times higher than the drinking water limit (Table 1). High concentration levels of Ni were found at groundwater sampling locations 3 and 10 during most of the years considered. The concentration of Mn was above the drinking water limit of 100 μ g L⁻¹ (WHO 2006) at location 10 in the study area during all the years considered (Table 1). High concentration levels of Ni and Mn were possibly due to municipal solid waste disposal for recycling. Location 10 is in close proximity to the dumping site of municipal solid wastes. A positive correlation between Mn and Ni indicates that they may be derived from similar sources (Table 2). At a few sites, the concentrations of Al, Fe, and Se were above the permissible limit of the WHO (2006). These findings present valuable information for the local population of the Aosta Valley, who utilize groundwater for drinking and domestic purposes.





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A correlation coefficient is a commonly used measure to establish the relationship between two variables. It is simply a measure to exhibit how well one variable predicts the other. Table 2 provides the computed correlation matrix of the 12 analyzed metals in the groundwater of the Aosta Valley region. A number of significant correlations were observed in the metal concentrations in the study area groundwater. Positive correlations were found between Pb and Zn, Pb and Cu, Cd and Mn, Fe and Mn, and Cu and Zn (Table 2). Moreover, moderate correlations were also observed between Mn and Ni, Al and Pb, Fe and Ni, and Fe and Al in the groundwater of the study area.

To evaluate the extent of pollution and suitability of the groundwater, the HPI values were calculated using the mean concentration values of the analyzed metals (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn). The HPI values of the groundwater in the study area and its statistical results are provided in Table 3. The lowest HPI value,

1.7, was found in 2007, while the highest HPI value, 114.6, was observed in 2012 (Table 3). The results, as shown in Table 3, indicate high values of HPI in the groundwater at location 3 and 10 for most of the years considered. Moreover, location 1 only had a high HPI value in 2011 (Table 3). The high concentration levels of Cr, Mn, and Ni are responsible for the high value of HPI in the study area. The higher values of HPI may be attributed to anthropogenic activities of the area. The HPI values of the years 2011 and 2012 exceeded the critical HPI value of 100 (Prasad and Bose 2001). However, for all the other years the HPI values were found to be below the critical pollution index (100). Moreover, a modified scale using three classes was used in the present study after Edet and Offiong (2002). The classes were demarcated as low, medium, and high for HPI values <15, 15-30 and >30, respectively (Edet and Offiong 2002). The groundwater samples of the study area varied between all of the above classes (Table 4,

Table 2 Pearson's correlation matrix between different metals in the groundwater (n = 162) of the Aosta Valley region

| Metals | Al | As | Ba | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Se | Zn |
|--------|-------|-------|--------|--------|--------|--------|-------|--------|--------|--------|--------|---------|
| Al | 1.000 | 0.131 | 0.040 | -0.048 | 0.207 | 0.289 | 0.324 | -0.034 | -0.006 | 0.464 | 0.008 | 0.273 |
| As | | 1.000 | -0.066 | 0.198 | 0.103 | -0.069 | 0.016 | 0.017 | -0.011 | 0.101 | -0.054 | 0.198 |
| Ba | | | 1.000 | 0.123 | 0.261 | 0.263 | 0.129 | 0.311 | 0.181 | 0.073 | 0.063 | 0.049 |
| Cd | | | | 1.000 | -0.018 | -0.088 | 0.289 | 0.551 | 0.211 | 0.034 | 0.127 | 0.024 |
| Cr | | | | | 1.000 | 0.073 | 0.022 | -0.064 | -0.013 | 0.033 | 0.069 | 0.004 |
| Cu | | | | | | 1.000 | 0.132 | 0.034 | 0.002 | 0.588 | -0.026 | 0.663 |
| Fe | | | | | | | 1.000 | 0.519 | 0.325 | 0.233 | 0.031 | 0.088 |
| Mn | | | | | | | | 1.000 | 0.428 | -0.017 | 0.124 | -0.0026 |
| Ni | | | | | | | | | 1.000 | 0.005 | 0.075 | -0.011 |
| Pb | | | | | | | | | | 1.000 | 0.033 | 0.649 |
| Se | | | | | | | | | | | 1.000 | -0.020 |
| Zn | | | | | | | | | | | | 1.000 |

Fig. 3a–i). Fewer groundwater samples belonged to the high HPI class for all the years considered except for 2007 and 2015, while a larger number of the groundwater samples belonged to the medium class except in the year 2009 (Table 4; Fig. 3c). The results, as shown in Table 4 and Fig. 3a–i, indicate that most of the groundwater samples belonged to the low HPI class during the years 2007–2015. We observed that locations 3 and 10 had a high HPI value for most of the years considered. However, locations 1, 2, 3, and 9 belonged mainly to the medium HPI class in the study area (Table 3, Fig. 3a–i). This indicates that the groundwater was contaminated with some metals in the study area and not suitable for direct consumption.

Table 5 compares of the metal concentration in the groundwater of the Aosta Valley region with the WHO guideline values and other studies of groundwater done

Fig. 3 a–i Heavy metal pollution index (HPI) class maps of the Aosta Valley region groundwater during the years 2007–2015 (after Edet and Offiong 2002)

around the globe. Most of the researchers (Table 5) have reported that the high concentrations of metals in their study area groundwater were mainly due to anthropogenic activities. Similarly, the Aosta Valley region groundwater was contaminated with high concentrations of some metals caused by anthropogenic activities. However, several remedial measures have already been implemented to decrease the contamination levels in the Aosta Valley region (Beretta 2015). These include the positioning of geomembranes in 2012, which may have caused the noticeable reduction of metal concentrations. In fact, these membranes provide the final line of defense against groundwater

Table 3 HPI values of the groundwater in the Aosta Valley region during the years 2007-2015

| Sample code | HPI (2007) | HPI (2008) | HPI (2009) | HPI (2010) | HPI (2011) | HPI (2012) | HPI (2013) | HPI (2014) | HPI (2015) |
|-------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 1 | 27.2 | 15.8 | 7.5 | 18.6 | 42.7 | 8.5 | 8.4 | 16.2 | 15.2 |
| 2 | 22.3 | 19.1 | 14.3 | 19.6 | 27.9 | 15.7 | 19.6 | 25 | 22.4 |
| 3 | 16.6 | 17.1 | 52.3 | 35.8 | 44.9 | 29.5 | 28.1 | 27 | 27.7 |
| 4 | 6.7 | 8.3 | 3.9 | 7.2 | 13.7 | 7.8 | 5.9 | 4.6 | 11 |
| 5 | 4.4 | 8.2 | 3.7 | 6.1 | 7.7 | 7.2 | 5.1 | 10.3 | 8.6 |
| 6 | 4.5 | 8.7 | 5.1 | 7.2 | 9.9 | 8.4 | 10.7 | 3.3 | 13.1 |
| 7 | 2.9 | 7.2 | 4.1 | 6.5 | 12.6 | 6.4 | 11.5 | 10.4 | 10.5 |
| 8 | 4.5 | 8.3 | 5.9 | 5.7 | 11.3 | 22.9 | 9.4 | 6.0 | 13.3 |
| 9 | 4.1 | 27.7 | 5.4 | 9.1 | 15 | 6.0 | 9.1 | 8.2 | 15.8 |
| 10 | 7.4 | 31.6 | 65.2 | 70.8 | 110.8 | 114.6 | 55.7 | 31.9 | 23.2 |
| 11 | 7.9 | 8.3 | 7.1 | 6.9 | 14.1 | 4.1 | 6.4 | 13 | 13.1 |
| 12 | 5.8 | 6.2 | 4.9 | 7.5 | 11.3 | 5.7 | 7.8 | 6.3 | 3.9 |
| 13 | 3.9 | 6.8 | 7.5 | 8.0 | 9.8 | 7.7 | 7.9 | 12.4 | 9.4 |
| 14 | 4.4 | 7.9 | 8.7 | 27.8 | 13.2 | 4.3 | 13.5 | 10.1 | 9.1 |
| 15 | 16.8 | 7.7 | 6.1 | 15 | 8.1 | 8.4 | 7.8 | 6.3 | 4.8 |
| 16 | 25.7 | 6.2 | 7.8 | 14.1 | 13.4 | 8.1 | 7.7 | 13.7 | 14 |
| 17 | 3.09 | 27.6 | 5.2 | 9.3 | 12.9 | 4.1 | 11.3 | 13.7 | 12.3 |
| 18 | 1.7 | 17.9 | 3.2 | 3.6 | 8.3 | 8.7 | 11.5 | 8.7 | 15 |
| Min. | 1.7 | 6.2 | 3.2 | 3.6 | 7.7 | 4.1 | 5.1 | 3.3 | 3.9 |
| Max. | 27.2 | 31.6 | 65.2 | 70.8 | 110.8 | 114.6 | 55.7 | 31.9 | 27.7 |
| Mean | 9.4 | 13.4 | 12.1 | 15.5 | 21.6 | 15.5 | 13.2 | 12.6 | 13.5 |
| Std. error | 2.0 | 2.0 | 4.1 | 3.8 | 5.9 | 6.0 | 2.8 | 1.9 | 1.4 |

| T-LL 4 | T1 | (07) = C IIDI | -1 | · · · · · · · · · · · · · · · · · · · | - 41 · | 2007 2015 | (. ft 1. | 000 | • ` |
|----------|----------------|---------------|----------------|---------------------------------------|------------|--------------|-----------------|-------------------|-----|
| I anie 4 | The nercentage | (%) of HPL | classes in the | groundwater durin | σ ine veai | rs /UU/-/ULD | latter Edet and | U_{IIII} | 1 |
| Lable I | The percentage | (,0) 01 111 1 | ciusses in the | Stoulia mater durin | s the year | 10 2007 2010 | anter Duct und | | • • |

| HPI classes | 2007 (%) | 2008 (%) | 2009 (%) | 2010 (%) | 2011 (%) | 2012 (%) | 2013 (%) | 2014 (%) | 2014 (%) |
|--------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Low class (HPI <15) | 72 | 61 | 89 | 72 | 72 | 77 | 83 | 77 | 72 |
| Medium class (HPI 15-30) | 28 | 33 | - | 17 | 17 | 17 | 11 | 17 | 28 |
| High class (HPI >30) | - | 6 | 11 | 11 | 11 | 6 | 6 | 6 | - |



| Table 5 Co. | mparison of the | metals in | the groundwa | tter of the A | osta Valley re | gion, Italy wit | h other studie | es done aroun | d the world | | | | |
|---|--|--|---|---|--|---|---|--|--|---|---|---|---|
| Locations | Al | \mathbf{As} | Ba | Cd | Cr | Cu | Fe | Mn | Ni | Ъb | Se | Zn | References |
| Aosta Valley region, Italy | 0.4-289.6 | 0.1–9.0 | 0.9–751.4 | 0.0–2.7 | 0.1–278 | 0.1–123 | 4.1–1074 | 0.1–3670 | 0.2–132.8 | 0.1–8.9 | 0.4–16 | 1.1-74 | Present study (during the years 2007–2015) |
| Goa mining, India | I | I | I | <0.2–1.7 ^a 0.3–2.3 ^b | <0.5–11.8 ^a <3.0–30 ^b | <0.2–2.1 ^a <0.3–19.3 ^b | <12–500 ^a <8–65.6 ^b | <8–264 ^a 1–29.0 ^b | I | <6–20 ^a <2-9.8 ^b | I | <0.24-45.2 ^a 0.30-65.2 ^b | Singh and Kamal (2016) |
| Ardabil area Iran | I | 0.0–9.42 | I | I | 0.0–12.8 | 0.0-11.4 | 0.95–181 | 0.0–16.43 | I | I | I | I | Aghazadeh et al (2016) |
| West Bokaro coalfield, | 13.7–174.4 ^b 14.3–679 ^c | 0.1–0.7 ^b 0.2–1.3 ^c | 29.4–98.7 ^b 38–236 ^c | 1 | 0.04–6.4 ^b 0.4–9.5 ^c | 0.3- 5.7 ^b 0.4–29.5 ^b | 308–895 ^b 491–1321 ^c | 1.3–139 ^b 2.6–191 ^c | 0.5–36 ^b 1.0–44 ^c | I | 0.24–2.0 ^b 0.3–2.8 ^c | 5.4-45.5 ^b 9.8-117.4 ^c | Tiwari et al. (2016) |
| India Ethiopia | I | I | 14.2–152.4 | 0.09–1.59 | 0.5–5.2 | 2.3-41.3 | 1–21,675 | 6.96-184.7 | I | 1.2–26.9 | I | 4.1–73.7 | Haileslassie and Gebremedhin |
| North West Bank, Dalastine | I | I | I | 0.0–2.19 | 22.6-165.5 | 21.93–925.5 | I | 4.56–552.3 | 9.15-87.28 | I | I | 22.19–302.98 | (2015) Malassa et al. (2014) |
| Miduk copper complex, | 130–1000 | I | I | 0.02-0.29 | I | 0.05-545.3 | 40-710 | 1 | 0.2–35.3 | 0.5–16.1 | I | I | Kargar et al. (2012) |
| Iran Densu Basin, Ghana | I | I | I | 2.0-7.0 | I | I | 2.0-1190 | 2.0–34,000 | I | 5.0-34 | I | 2.0–353 | Amoako et al. (2011) |
| Drinking water quality standard, WHO | 100–200 | 10 | 300 | 3.0 | 50 | 2000 | 300 | 100 | 20 | 10 | 10 | 4000 | WHO (2006) |
| Unit µg L ⁻¹ ^a Moncoon (| | | | | | | | | | | | | |

contamination including metals. The effect of the use of remedial measures is visible in the values of HPI and the concentrations of metals. There is a continuous decrease in the HPI values and total concentrations of metals (Fig. 2) after the year 2012. A recovery of the metal levels in the groundwater of the study area by the year 2015 as compared to the levels of the year 2007 is also obvious (Fig. 3a, i).

Conclusion

The concentrations of Al, Cr, Fe, Mn, Ni, and Se were above the drinking water permissible limit established by the WHO (2006). The high concentration level of Cr was observed in some locations near the industrial area. The HPI values within the study area were below the critical pollution index (100), except in the years 2011 and 2012. The HPI values belonged to low class, medium class as well as high class during the years 2008–2014, while in the years 2007 and 2015 it ranged from low class to medium class. The groundwater in the study area was contaminated with metals (especially Cr, Mn, and Ni) caused by anthropogenic activities. This water requires urgent suitable treatment before its utilization for drinking and domestic purposes. Finally, from the environmental degradation point of view, only a few significant metals were observed which would have a detrimental effect on the environment. Thus, this study could be very useful for the current and future groundwater management in the Aosta Valley region, Italy.

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