



## Speciation of selenium in groundwater: Seasonal variations and redox transformations

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### ABSTRACT

Speciation of selenium in groundwater is essential from the viewpoint of toxicity to organisms and biogeochemical cycling. Selenium speciation in groundwater is controlled by aquifer redox conditions, microbial transformations, dissolved oxygen (DO) and other redox couples. A suburban area of Chennai city in India, where improper waste disposal measures have been practiced is selected for this study. Se(IV), Se(VI) and other hydrochemical parameters were monitored in shallow ground water during pre- and post-monsoon seasons for a period of three years. The objective of the study was to investigate the effect of groundwater recharge on selenium speciation. The concentration of Se(IV), and Se(VI) ranged between 0.15–0.43  $\mu\text{g L}^{-1}$  and 0.16–4.73  $\mu\text{g L}^{-1}$ , respectively. During post-monsoon period the concentration of Se(IV), and Se(VI) ranged between 0.15–1.25  $\mu\text{g L}^{-1}$  and 0.58–10.37  $\mu\text{g L}^{-1}$ , respectively. Se(VI) was the dominant species of selenium during the pre- and post-monsoon periods. During the post-monsoon periods, leaching of selenium from soil was more effective due to the increased oxidizing nature of the groundwater as indicated by the DO and redox potential (Eh) measurements. This finding has important implications on the behavior of selenium in groundwater, and also on the health of people consuming groundwater from seleniferous areas.

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### 1. Introduction

Selenium has been attracting some interest because it is an essential nutrient to humans in a limited range of daily intake, but will turn into a toxin at elevated amounts. In humans and other organisms, the concentration range between essentiality and toxicity is narrow; hence selenium is designated as an ‘essential toxin’ [1]. Selenium has been reported to have anti-carcinogenic activity [2], and it also prevents heavy metal toxic effects [3], especially arsenic toxicity [4]. Several studies have shown that low selenium levels in soils could be a factor in the origin of some diseases such as cancer, cardiovascular sclerosis, cirrhosis, diabetes etc. [5]. In order to increase dietary selenium levels, sodium selenate has been added to fertilizers in Finland [6]. In China, some regions with low level of selenium in soil had high prevalence rate of endemic juvenile cardiomyopathy (Keshan disease) and a type of osteoarthritis (Kashin–Beck disease), which can be corrected and prevented by Se supplementation [7,8]. On the other hand, chronic selenium poisoning of plants, animals, and humans has been reported in northwestern India [9], and in some parts of China [10].

In groundwater, selenium occurs due to weathering and leaching of rocks, and dissolution or oxidation of soluble salts in soils. Se exists in groundwater as Se(-II), Se(IV), and Se(VI) oxidation states. Thermodynamic calculations show that Se(-II) species should be found in reducing environments, Se(IV) species in moderately oxidizing environments, and Se(VI) species in oxidizing environments [11]. These species differ in their mobility in the aquatic environment; i.e., Se(IV) tends to be adsorbed on soil particles, whereas Se(VI) is less adsorbed hence more mobile. Also, these species differ in their toxicity towards organisms i.e., Se(IV) is more toxic than Se(VI) due to the higher bioavailability of Se(IV) [12].

The speciation of Se in groundwater is influenced by redox potential (Eh), dissolved organic matter, microbial activity, and other redox couples such as Fe(III)/Fe(II) and Mn(IV)/Mn(II). Leaching of soil selenium is enhanced by anionic constituents such as nitrate, sulphate and phosphate [13,14]. Besides geogenic sources, a major portion of these anions originate from anthropogenic activities; hence, possibility of selenium leaching into groundwater is high in areas where improper waste disposal is practiced. As rainfall is the main source of groundwater recharge, its influence on the species distribution is important from the viewpoint of biogeochemical cycling. Previous investigations of selenium in groundwater have focused on its occurrence, speciation and its mobilization due to nitrate, phosphate and sulphate introduced

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due to agricultural activities [6,14,15]. The occurrence of high selenium and its behavior in groundwater of the Kesterson reservoir site in central California has been extensively studied [16–18]. Several studies have also been carried out in the low-selenium belt of China [7,10,19]. Studies on selenium species transformations due to groundwater recharge and its associated factors are in fact not addressed. Therefore, monitoring the levels of selenium species and other factors that influence the speciation will provide better understanding of the behavior of selenium in groundwater environment. Consequently, the objectives of this study were (1) to survey the background level of selenium in groundwater of a sub-urban area which is contaminated due to tanneries and open sewerage system, (2) to study the pattern (if any) of variation of selenium species during pre- and post-monsoon periods, and (3) to study the influence of nitrate, sulphate and phosphate on the occurrence of selenium in groundwater.

## 2. Materials and methods

### 2.1. Study area

The study area is located at the southwestern part of Chennai City (erstwhile Madras), the capital of Tamil Nadu state, India (Fig. 1). It has an aerial extent of 45 km<sup>2</sup> and lies between N latitude 12°56'12" to 12°59'56" and E longitude from 80°06'14" to 80°11'30". The area is underlain by charnockite rocks of archaic age. Groundwater occurs in the shallow weathered zone as well as in the deeper fractured zones. Leather tanning is an established industry in the area. The area was away from residential areas when the tanneries came up nearly a century ago, but now it has become part of Chennai City. About 152 tanneries existing in the area produce about 3000 m<sup>3</sup> day<sup>-1</sup> of effluents and are treated at the common effluent treatment plant (CETP). Before the establishment of CETP during 1995, the effluents were discharged untreated into low-lying areas and ponds. Also, the area lacks adequate domestic sewerage system; hence the domestic wastes are disposed into the unlined open sewers and ponds. This resulted in widespread groundwater contamination in the area.

### 2.2. Sample collection and preservation

Groundwater samples were collected from 65 open dug wells representing the phreatic aquifer during the months of May (pre-monsoon) and January (post-monsoon) for a period of three years (i.e., 2004–2007). The sampling wells were selected to represent the industrial and domestic sewage contamination. The depth of sampled wells ranged between 3.32 m and 14.15 m below ground level (bgl). The depth to water table (DWT) ranged between 0.70 m and 13.77 m bgl (May 2004). DWT was measured during all sampling seasons in order to assess the effect of rainfall on groundwater table.

Water samples were collected separately for major ions, total dissolved metals, and for selenium speciation analysis. Samples for major ions and other inorganics were collected in 1 L pre-cleaned polypropylene bottles. Samples for total dissolved metals were filtered (0.45 μm, Millipore) and acidified with HNO<sub>3</sub> to pH < 2. Samples for selenium speciation analysis were filtered (0.45 μm, Millipore), collected in 500 mL polypropylene bottles and acidified with HCl (ultra-pure grade, BDH) to pH < 2 [20,21]. As stability of selenium species is a crucial issue and often depends on matrix [22], we carried out a preliminary study to find out the maximum holding time using the same samples. We found that this preservation procedure stabilized selenium species at least for 30 days. The samples were immediately transported to the laboratory under low-temperature conditions in ice-boxes and stored in the labora-

tory at 4 °C until analysis. Field blanks and field-spiked samples were prepared and treated exactly as samples.

### 2.3. Analytical methods

All reagents used were of analytical grade or higher and were prepared in de-ionized water of resistivity 18 MΩ cm obtained from a Milli-Q (Millipore) water purification system. The sample pH, electrical conductivity (EC), redox potential (Eh) and dissolved oxygen (DO), were measured onsite. Dissolved Fe(II) and Fe(III) concentrations were determined onsite by the modified ferrozine procedure [23] using a portable spectrophotometer (HACH DR 2010). Major ionic constituents were determined following APHA procedures [24]. Total dissolved manganese concentration was determined using ET-AAS (GBC Avanta). Total Se, and Se(IV) concentrations were determined by the HGAAS method reported earlier [25]. Se(VI) concentrations were calculated by difference. An ICP-MS (Perkin Elmer, Elan 4000) was also used for total selenium determination. The method of determining Se(VI) by difference, may bias the results if non-volatile organic selenium exist [26]. To verify this, samples were subjected to alkaline digestion (pH 10) with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.4 mmol L<sup>-1</sup>) and MnSO<sub>4</sub> (0.6 mmol L<sup>-1</sup>) at 80 °C for 20 min. Under alkaline conditions, the added MnSO<sub>4</sub> prevents the oxidation of Se(IV) to Se(VI), thus eliminates the necessity of pre-reduction before analysis as in the case of HCl–K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> digestion. In addition, alkaline digestion provides a more accurate check on the contribution of organic selenium [26]. The digested samples were analyzed for total selenium and the results showed no significant contribution of organic selenium towards total selenium.

### 2.4. Quality control

Analysis of five field blanks showed no evidence of contamination. The recoveries of Se(IV) and Se(VI) from 15 field spikes ranged between 96.0–104.5% and 94.0–103.0%, respectively. The accuracy of the analytical results was verified by an independent method of analysis using ICP-MS. Regression analysis of total selenium values obtained from HGAAS and ICP-MS methods showed that the calculated slope (1.0035) and intercept (0.0017) values were not significantly differed from the ideal values of 1 and 0, respectively. Recovery of Se from the analysis of certified reference material SRM 1640 was satisfactory (certified value: 22.0 ± 0.5 μg L<sup>-1</sup>; analytical result: 24.1 ± 0.9 μg L<sup>-1</sup>; recovery: 109%).

## 3. Results and discussion

### 3.1. Hydrochemistry of groundwater

The range, mean and standard deviation of the various parameters monitored are presented in Table 1. It shows that the groundwater pH is circumneutral to slightly alkaline (pH range: 6.96–8.18) during the pre-monsoon period May 2004. Except one sample, the pH of remaining 64 samples were >7.00. The EC, which indicates the total ionic content of the groundwater ranged between 605 μS cm<sup>-1</sup> and 11,660 μS cm<sup>-1</sup> at 25 °C. The high EC values indicate that the groundwater was highly mineralized. Most of the wells located near drainage channels and waste disposal sites showed higher EC values, which indicate that the contamination is due to the improper waste disposal measures being practiced. The Eh and DO ranged between 65–322 mV and 0.25–5.00 mg L<sup>-1</sup>, respectively. These values indicate that the groundwater was slightly oxidizing in nature, which is due to the shallow water table of the area. The predominant water type of the area is Ca/NaCl. A few samples collected from the unpolluted area are of Ca/NaHCO<sub>3</sub> type. The change of anionic facies from HCO<sub>3</sub> to Cl showed the influence of groundwater contamination from anthropogenic sources. As the

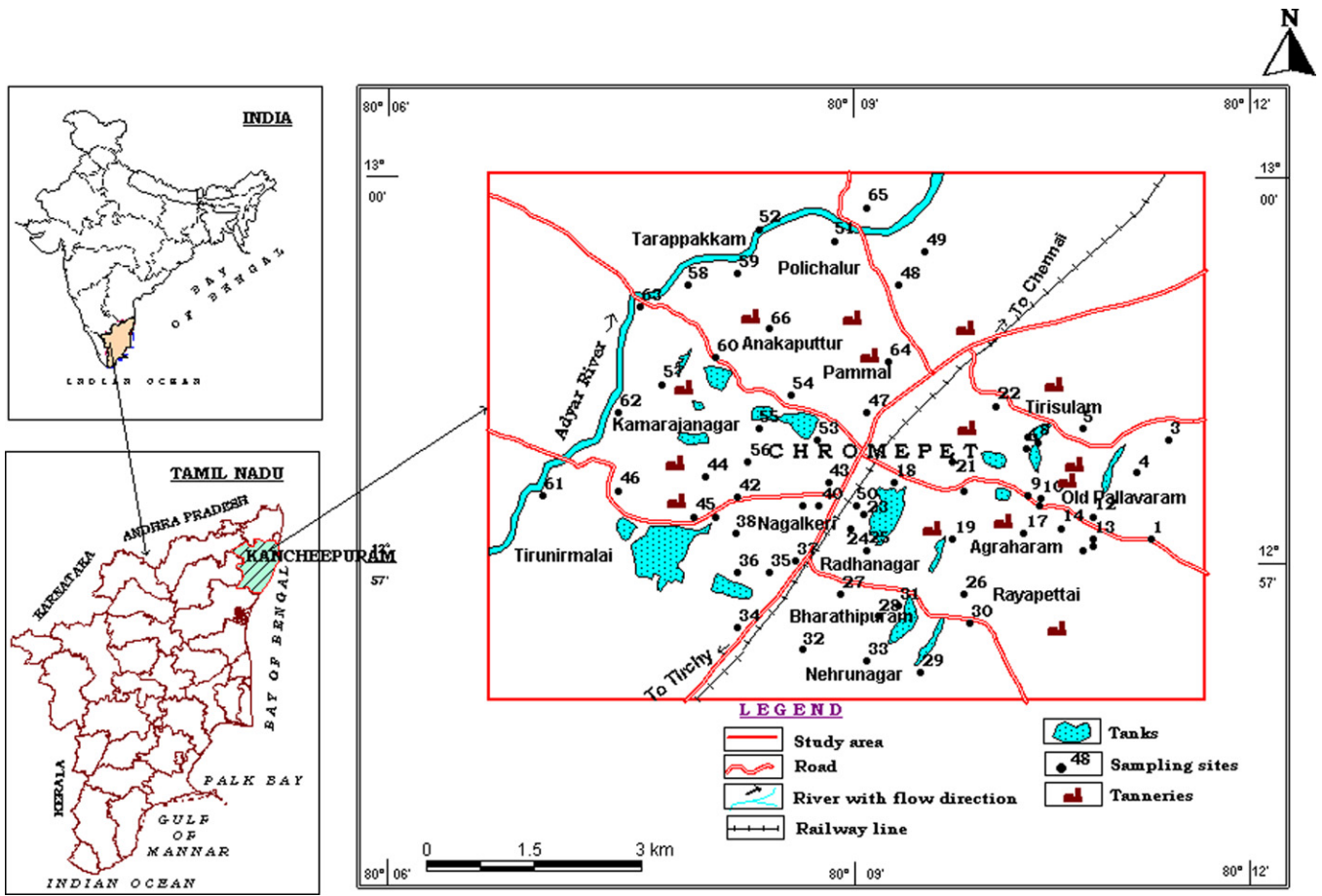


Fig. 1. Study area showing the sampling points and other features.

sources of pollution are spread throughout the area, no pattern of spatial distribution of any of the constituents was observed.

### 3.2. Speciation of selenium

Selenium existed as Se(IV) and Se(VI) species. Non-volatile organic selenium species was not detected. The analytical results of some of the representative samples are given in Table 2. Also, the average values of the relative distribution of Se(IV) and Se(VI) found during the pre- and post-monsoon periods is shown in Fig. 2. During the pre-monsoon period (May 2004), Se(IV) was detected in 16 samples in the range of 0.15–0.43  $\mu\text{g L}^{-1}$ . On the other hand, Se(VI) was detected in 55 samples in the range of 0.16–4.73  $\mu\text{g L}^{-1}$ . In all these samples, Se(VI) was the dominant species of Se. This is in agreement with other published results [9,16,27,28], and also in accordance with the thermodynamic predictions for oxidizing groundwaters. Another reason for the predominance of Se(VI) species is the alkaline sample pH with high bicarbonate concentrations (73–650  $\text{mg L}^{-1}$ ). Studies have shown that unlike transition metal ions, oxyanionic forms of elements are stable under alkaline pH [29].

### 3.3. Temporal variations in selenium speciation

The temporal variation of selenium species is due to groundwater recharge. Fig. 2 shows the temporal variation of Se species in the groundwater. Although the average values are plotted, the results shown in Table 2 give more realistic picture of the change in Se speciation due to groundwater recharge. Most of the samples showed an increase of Se(IV) and Se(VI) concentrations during the

post-monsoon periods. During January 2005, Se(IV) was detected in 23 samples in the range of 0.15–1.25  $\mu\text{g L}^{-1}$ . Se(VI) was detected in all 65 samples in the range between 0.58  $\mu\text{g L}^{-1}$  and 10.37  $\mu\text{g L}^{-1}$ . Except one sample (well no. 40), all the other samples had Se(VI) concentration  $>1.00 \mu\text{g L}^{-1}$ . The number of samples containing Se(IV) and Se(VI) was more during the post-monsoon periods. In the subsequent pre-monsoon period (May 2005), however, Se(IV) and Se(VI) concentrations decreased. This pattern of decrease during

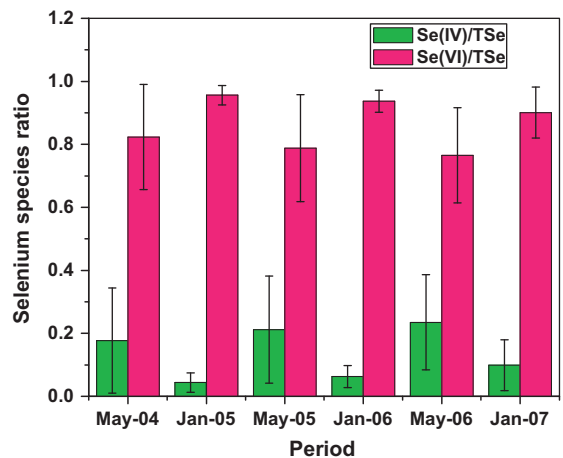
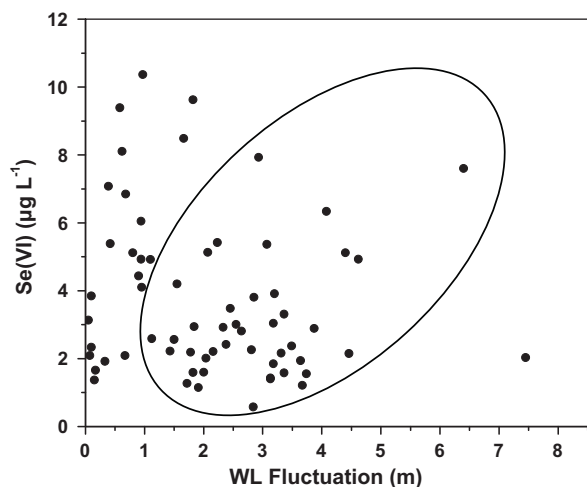


Fig. 2. Comparison of Se(IV)/TSe and Se(VI)/TSe ratios of groundwater samples during the study period May 2004–January 2007. The months May and January represent pre- and post-monsoons, respectively. The y error bars indicate standard deviations.



**Fig. 3.** Scatter plot of Se(VI) vs. water level fluctuations (Post-monsoon WL–Pre-monsoon WL). The plot shows both positive (shown separately) and negative correlations of water level fluctuations with Se(VI) concentrations.

pre-monsoon period and increase during the post-monsoon was observed during the remaining periods.

As rainfall is the source of groundwater recharge, it is expected that the quantum of recharge should have a positive correlation with the Se concentration. Due to the lack of the various hydrogeological parameters required for the computation of quantum of recharge of the aquifer, we have considered the fluctuation in the water level (post-monsoon DTW – pre-monsoon DTW) as a rough measure of recharge. As Se(VI) is the predominant species present in all the samples, we have plotted the Se(VI) concentration and water level (WL) fluctuation (May 2004 and January 2005) in Fig. 3. As can be seen, Se(VI) levels and WL fluctuations are positively correlated in most of the samples (shown separately). However, in some of the samples Se(VI) levels and WL fluctuations are negatively correlated. These wells have shown less WL fluctuations (<2 m) and are shallow in depth (<7 m). Rainfall recharge had not changed considerable WL rise in these wells, because the aquifer had already been saturated. The shallow water table enhances the solubility of soil organic matter more effectively [15]. The data presented in Fig. 3 support this hypothesis as shallow wells have more Se(VI) concentration than the deeper ones (depth > 7 m). In the case of deeper wells, considerable fraction of dissolved selenium might

have lost due to adsorption onto mineral surfaces and redox transformations before it reached the water table.

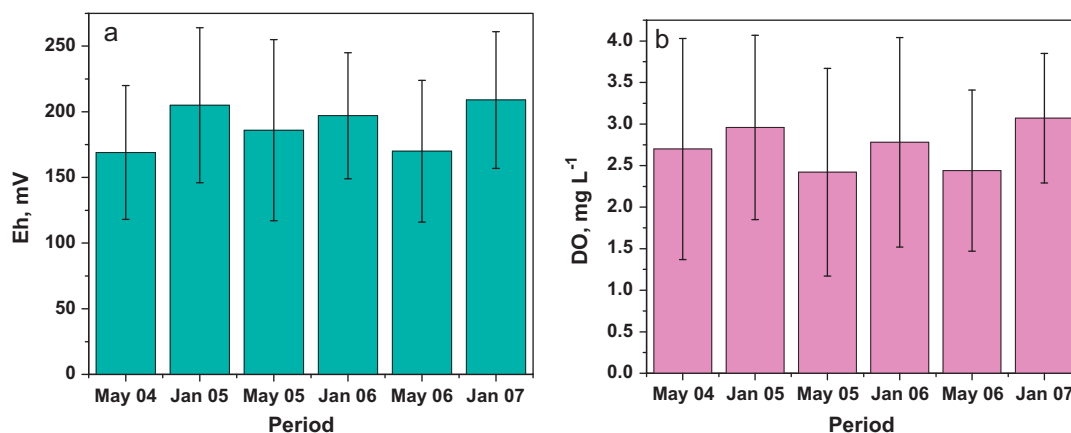
#### 3.4. Relationship between selenium speciation and groundwater redox chemistry

Because of the dependence of Se speciation and solubility on Eh, correlations are expected between Se and other chemical parameters which are indicative of either oxidizing or reducing conditions in the groundwater. Platinum electrode measurements, which represent at best a semi-quantitative representation of Eh, produced a potential range between 65 mV and 322 mV. This range is indicative of mildly reducing to moderately oxidizing conditions.

The presence of DO and  $\text{NO}_3$  are indicative of groundwater oxidizing conditions. Half-cell potentials ( $E^0$ ) for these redox species indicate that the presence of DO and  $\text{NO}_3$  would prevent the reduction of Se(VI) and the precipitation of elemental Se [18]. It is observed that samples containing higher Se(VI) concentrations always contained higher DO. Though, this qualitative relationship was evident in most of the samples, correlations between these indicator parameters are very poor. For example, DO and Eh ( $r=0.168$ ); Eh and  $\text{NO}_3$  ( $r=0.224$ ); DO and  $\text{NO}_3$  ( $r=-0.140$ ) (May 2004). Such observations have also been noticed in the groundwater of Kesterson site [18]. It is also to be noted that platinum electrode measurements do not respond quantitatively to DO [30].

The role of Eh and DO on the distribution of selenium species is more pronounced during post-monsoon periods. During post-monsoon periods, the groundwater was more oxidizing than the respective pre-monsoon periods as indicated by the increased DO and Eh values (Fig. 4a and b). This resulted in the increased mobilization of Se(IV) and Se(VI) species [17]. Fe(II) and Mn are chemical species which are indicative of reducing groundwater conditions. In general, the concentrations of these species are higher during pre-monsoon periods than the post-monsoon periods, because the groundwater was more oxidizing due to groundwater recharge. Hence, as expected, a negative correlation between Se(VI) and Fe(II) and Mn is observed (Fig. 5).

Attempts to employ measured Eh values to predict the observed Se(IV) and Se(VI) concentrations were unsuccessful, which indicate platinum electrode measurements are completely insensitive to the relative distribution of selenium species as observed by Runnells and Lindberg [31]. Redox potentials calculated using PHREEQC program [32], based on Se(IV) and Se(VI) concentrations are compared with measured Eh values in Fig. 6. The calculated Eh values are generally higher than the measured values, indicating that the



**Fig. 4.** Average values ( $n=65$ ) of (a) Eh (mV) and (b) DO ( $\text{mg L}^{-1}$ ) of groundwater during pre- (May) and post-monsoon (January) periods. The y error bars indicate standard deviations.



**Table 1**

Basic statistics of groundwater samples collected from the study area during the period May 2004–January 2007.

| Variables          | May 2004   |      |      | January 2005 |       |      | May 2005   |      |      | January 2006 |      |      | May 2006   |      |      | January 2007 |      |      |
|--------------------|------------|------|------|--------------|-------|------|------------|------|------|--------------|------|------|------------|------|------|--------------|------|------|
|                    | Range      | Mean | SD   | Range        | Mean  | SD   | Range      | Mean | SD   | Range        | Mean | SD   | Range      | Mean | SD   | Range        | Mean | SD   |
| pH                 | 6.96–8.18  | 7.59 | 0.26 | 6.5–8.20     | 7.38  | 0.32 | 6.95–7.94  | 7.43 | 0.20 | 6.67–7.57    | 7.17 | 0.21 | 6.90–7.84  | 7.42 | 0.17 | 6.81–7.85    | 7.24 | 0.22 |
| Eh                 | 65–322     | 171  | 49   | 110–330      | 204   | 58   | 95–395     | 185  | 68   | 105–305      | 197  | 48   | 78–320     | 169  | 53   | 118–351      | 209  | 51   |
| EC                 | 605–11660  | 3171 | 1851 | 600–10260    | 2677  | 1585 | 745–10540  | 3011 | 1646 | 250–10735    | 2276 | 1687 | 355–11950  | 2633 | 1715 | 320–8500     | 2149 | 1288 |
| Alk                | 60–533     | 309  | 104  | 23–740       | 326   | 135  | 60–870     | 320  | 136  | 53–580       | 284  | 116  | 55–725     | 340  | 138  | 60–435       | 290  | 84   |
| DO                 | 0.25–5.00  | 2.74 | 1.29 | 0.38–5.05    | 2.96  | 1.11 | 0.22–6.16  | 2.45 | 1.32 | 0.60–6.10    | 3.00 | 1.26 | 0.81–4.21  | 2.44 | 0.97 | 0.85–5.12    | 3.32 | 1.06 |
| SO <sub>4</sub>    | 46–1606    | 306  | 294  | 28–1090      | 201   | 196  | 34–1487    | 282  | 302  | 10–1160      | 220  | 203  | 34–1850    | 242  | 263  | 10–800       | 178  | 159  |
| NO <sub>3</sub>    | 2–452      | 133  | 116  | 0.26–381     | 105   | 92   | 0.86–769   | 109  | 116  | BDL–644      | 107  | 126  | 3–436      | 98   | 85   | BDL–644      | 91   | 101  |
| PO <sub>4</sub> -P | BDL–0.30   | 0.07 | 0.05 | BDL–0.41     | 0.06  | 0.09 | 0.06–0.99  | 0.20 | 0.18 | BDL–1.19     | 0.28 | 0.28 | 0.03–0.68  | 0.18 | 0.14 | 0.02–1.19    | 0.28 | 0.28 |
| Mn                 | BDL–2.05   | 0.22 | 0.40 | BDL–0.8      | 50.09 | 0.17 | BDL–3.05   | 0.30 | 0.57 | BDL–1.00     | 0.08 | 0.17 | BDL–4.23   | 0.34 | 0.69 | BDL–0.85     | 0.11 | 0.19 |
| Fe(II)             | BDL–1543   | 173  | 232  | BDL–1462     | 143   | 310  | BDL–2000   | 262  | 366  | BDL–1560     | 189  | 344  | BDL–2650   | 239  | 382  | BDL–1450     | 173  | 314  |
| Fe(III)            | BDL–377    | 64   | 58   | BDL–958      | 76    | 153  | BDL–561    | 87   | 76   | BDL–190      | 37   | 42   | BDL–311    | 57   | 49   | BDL–200      | 23   | 31   |
| WL                 | 0.85–13.77 | 5.53 | 2.66 | 0.38–8.56    | 2.34  | 1.71 | 1.40–11.96 | 5.75 | 2.46 | 0.02–5.98    | 0.86 | 1.00 | 1.80–10.52 | 5.18 | 2.12 | 0.02–5.98    | 0.78 | 0.86 |

BDL: below detection limit (Fe(II) and Fe(III): 2 µg L<sup>-1</sup>; Mn: 1 µg L<sup>-1</sup>; NO<sub>3</sub>: 1 mg L<sup>-1</sup>; PO<sub>4</sub>-P: 0.01 mg L<sup>-1</sup>); Eh (mV): redox potential; EC: electrical conductivity; Alk: alkalinity as CaCO<sub>3</sub> mg L<sup>-1</sup>; DO: dissolved oxygen (mg L<sup>-1</sup>); SO<sub>4</sub>: sulphate (mg L<sup>-1</sup>); NO<sub>3</sub>: nitrate (mg L<sup>-1</sup>); PO<sub>4</sub>-P: phosphate phosphorus (mg L<sup>-1</sup>); Mn: manganese (mg L<sup>-1</sup>); WL: water level (m).

**Table 2**Representative analytical results (mean ± SD µg L<sup>-1</sup>, n = 3) of selenium(IV) and selenium(VI) found in groundwater during May 2004 (pre-monsoon) to January 2007 (post-monsoon).

| Well no. | May 2004    |             | January 2005 |              | May 2005    |             | January 2006 |             | May 2006    |             | January 2007 |              |
|----------|-------------|-------------|--------------|--------------|-------------|-------------|--------------|-------------|-------------|-------------|--------------|--------------|
|          | Se(IV)      | Se(VI)      | Se(IV)       | Se(VI)       | Se(IV)      | Se(VI)      | Se(IV)       | Se(VI)      | Se(IV)      | Se(VI)      | Se(IV)       | Se(VI)       |
| 3        | BDL         | 3.06 ± 0.26 | 0.23 ± 0.04  | 3.91 ± 0.07  | BDL         | 2.95 ± 0.12 | 0.25 ± 0.08  | 2.25 ± 0.12 | BDL         | 1.01 ± 0.10 | BDL          | 2.05 ± 0.12  |
| 4        | 0.15 ± 0.09 | 1.96 ± 0.04 | BDL          | 3.01 ± 0.09  | BDL         | 1.31 ± 0.09 | BDL          | 1.85 ± 0.10 | BDL         | 0.85 ± 0.10 | BDL          | 1.23 ± 0.12  |
| 6        | BDL         | 1.78 ± 0.09 | BDL          | 6.34 ± 0.15  | BDL         | 0.41 ± 0.10 | BDL          | 2.05 ± 0.12 | BDL         | 0.75 ± 0.21 | BDL          | 1.75 ± 0.12  |
| 16       | BDL         | 0.69 ± 0.14 | BDL          | 2.26 ± 0.21  | 0.15 ± 0.08 | 2.38 ± 0.12 | 0.20 ± 0.07  | 2.70 ± 0.12 | 0.25 ± 0.09 | 1.33 ± 0.17 | BDL          | 1.62 ± 0.12  |
| 17       | BDL         | 2.27 ± 0.35 | BDL          | 9.63 ± 0.28  | BDL         | BDL         | 0.31 ± 0.1   | 4.94 ± 0.25 | 0.26 ± 0.08 | 1.00 ± 0.08 | 0.35 ± 0.08  | 5.94 ± 0.12  |
| 18       | BDL         | BDL         | BDL          | 4.10 ± 0.07  | BDL         | 0.15 ± 0.11 | 0.15 ± 0.10  | 3.32 ± 0.23 | BDL         | 0.41 ± 0.08 | 0.48 ± 0.10  | 3.13 ± 0.25  |
| 20       | BDL         | 0.82 ± 0.10 | BDL          | 7.60 ± 0.19  | 0.17 ± 0.06 | 0.71 ± 0.11 | 0.21 ± 0.12  | 5.00 ± 0.24 | BDL         | 0.35 ± 0.12 | 0.64 ± 0.09  | 4.64 ± 0.19  |
| 21       | BDL         | 0.84 ± 0.14 | BDL          | 5.12 ± 0.19  | 0.15 ± 0.10 | 0.60 ± 0.18 | 0.23 ± 0.08  | 3.39 ± 0.09 | BDL         | 0.25 ± 0.10 | 0.35 ± 0.08  | 2.23 ± 0.18  |
| 23       | BDL         | 4.72 ± 0.09 | 0.20 ± 0.07  | 4.92 ± 0.12  | 0.21 ± 0.08 | 1.96 ± 0.13 | 0.26 ± 0.07  | 3.69 ± 0.21 | 0.32 ± 0.18 | 0.86 ± 0.12 | 0.28 ± 0.07  | 4.04 ± 0.12  |
| 25       | 0.18 ± 0.10 | 4.69 ± 0.23 | 0.21 ± 0.09  | 5.39 ± 0.12  | 0.28 ± 0.07 | 3.59 ± 0.23 | BDL          | 4.20 ± 0.09 | 0.28 ± 0.10 | 2.24 ± 0.09 | 0.39 ± 0.07  | 4.19 ± 0.20  |
| 27       | 0.18 ± 0.08 | 4.45 ± 0.21 | BDL          | 7.93 ± 0.13  | 0.17 ± 0.09 | 3.44 ± 0.12 | 0.45 ± 0.12  | 5.49 ± 0.20 | BDL         | 1.77 ± 0.08 | 0.45 ± 0.10  | 6.14 ± 0.30  |
| 29       | BDL         | 2.56 ± 0.14 | BDL          | 9.39 ± 0.20  | BDL         | 2.30 ± 0.20 | 0.56 ± 0.07  | 6.31 ± 0.31 | BDL         | 1.72 ± 0.08 | BDL          | 10.05 ± 0.20 |
| 33       | BDL         | 1.98 ± 0.14 | BDL          | 8.49 ± 0.13  | 0.32 ± 0.12 | 2.92 ± 0.12 | 0.65 ± 0.12  | 4.99 ± 0.12 | BDL         | 0.58 ± 0.10 | 0.88 ± 0.08  | 5.50 ± 0.20  |
| 40       | BDL         | 1.48 ± 0.17 | BDL          | 0.58 ± 0.12  | 0.45 ± 0.12 | 5.06 ± 0.10 | 0.95 ± 0.14  | 5.43 ± 0.07 | BDL         | 1.16 ± 0.12 | 0.18 ± 0.11  | 5.38 ± 0.11  |
| 41       | BDL         | 3.11 ± 0.14 | BDL          | 8.11 ± 0.23  | BDL         | 1.82 ± 0.20 | 0.28 ± 0.14  | 5.37 ± 0.12 | 0.25 ± 0.10 | 2.29 ± 0.09 | 0.20 ± 0.11  | 6.05 ± 0.11  |
| 42       | 0.18 ± 0.10 | 1.43 ± 0.13 | BDL          | 4.44 ± 0.12  | BDL         | 0.24 ± 0.09 | 0.15 ± 0.13  | 2.26 ± 0.11 | BDL         | 0.86 ± 0.11 | BDL          | 1.79 ± 0.14  |
| 45       | 0.24 ± 0.10 | 0.89 ± 0.12 | 1.25 ± 0.08  | 10.37 ± 0.30 | 0.21 ± 0.07 | 1.05 ± 0.10 | 0.39 ± 0.14  | 4.17 ± 0.10 | BDL         | 0.28 ± 0.10 | 0.50 ± 0.08  | 3.15 ± 0.12  |
| 46       | 0.42 ± 0.12 | 4.20 ± 0.16 | 0.41 ± 0.07  | 6.05 ± 0.18  | 0.35 ± 0.12 | 0.83 ± 0.10 | 0.21 ± 0.10  | 3.64 ± 0.13 | BDL         | 0.21 ± 0.10 | 0.25 ± 0.11  | 3.03 ± 0.14  |
| 48       | BDL         | 0.78 ± 0.06 | BDL          | 4.93 ± 0.10  | BDL         | 0.50 ± 0.10 | BDL          | 2.95 ± 0.11 | BDL         | 0.52 ± 0.09 | BDL          | 2.97 ± 0.14  |
| 62       | BDL         | 0.65 ± 0.10 | 0.16 ± 0.06  | 5.12 ± 0.16  | 0.25 ± 0.09 | 1.52 ± 0.11 | BDL          | 1.95 ± 0.12 | BDL         | 0.61 ± 0.09 | 0.26 ± 0.09  | 1.13 ± 0.20  |
| 63       | BDL         | 4.73 ± 0.20 | BDL          | 6.85 ± 0.12  | BDL         | 0.94 ± 0.11 | 0.18 ± 0.12  | 2.97 ± 0.13 | BDL         | 0.15 ± 0.08 | 0.45 ± 0.08  | 5.00 ± 0.21  |
| 64       | 0.43 ± 0.09 | 0.55 ± 0.12 | BDL          | 2.89 ± 0.16  | BDL         | 0.39 ± 0.11 | BDL          | 1.63 ± 0.10 | BDL         | 0.16 ± 0.08 | BDL          | 1.86 ± 0.10  |

BDL: below detection limit (0.15 µg L<sup>-1</sup>).

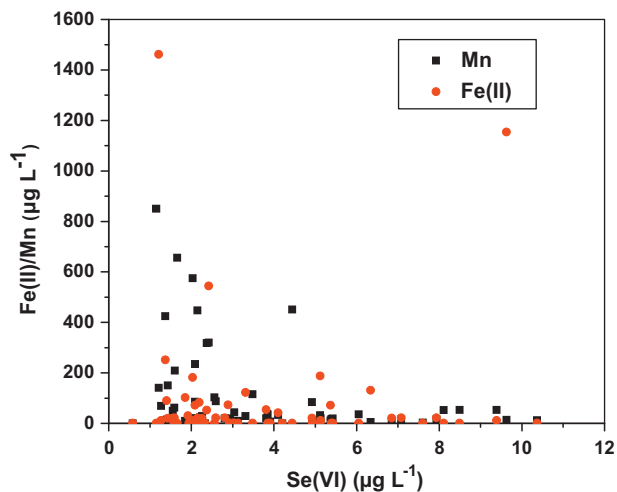


Fig. 5. Scatter plot of Fe(II) and Mn vs. Se(VI) concentrations of groundwater samples collected during May 2004 showing negative relationships.

measured Se(VI)/Se(IV) concentration ratios are higher than the predicted based on the measured Eh values. Further, Fig. 6 shows that the calculated Eh values based on Fe(III)/Fe(II) concentrations are close to measured Eh values.

### 3.5. Effect of nitrate and phosphate

The groundwater of the area contains high concentration of nitrate (range 2–452 mg L<sup>-1</sup>). Out of the 65 samples, 36 samples contained nitrate >100 mg L<sup>-1</sup>. The level of nitrate found is even more than that observed in the Kesterson reservoir area [18]. However, there was no correlation between nitrate levels and Se(VI) either during pre- or during the post-monsoon periods. Due to groundwater recharge, generally all the major ionic constituents showed decreasing trend during post-monsoon periods. However, nitrate did not follow this trend. Since leaching effect would be more after rainfall, most of the samples showed higher concentration of nitrate during post-monsoon periods. In all the reports that observe enhanced mobilization of Se due to nitrate, the source of nitrate is agricultural drainage (i.e., inorganic fertilizers) [14,18,33]. However, in the present study the sources of nitrate are domestic and tannery wastes, that are predominantly organic in nature. We

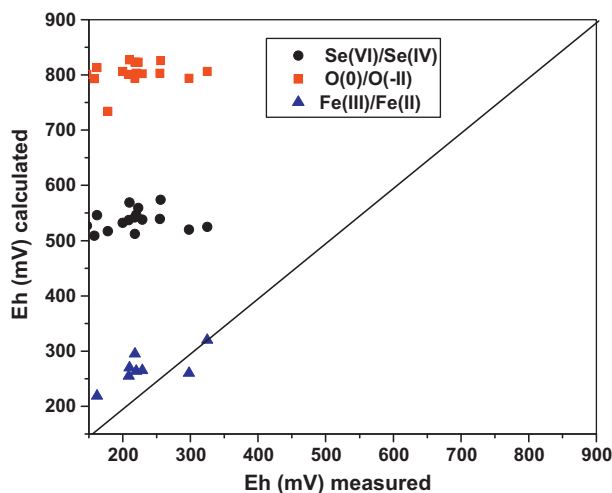


Fig. 6. Comparison between measured redox potentials (Eh) and calculated potentials based on measured concentrations of redox couples. The diagonal line represents the 1:1 line.

could not make any valid conclusion on the influence of nitrate and selenium mobilization, and it requires further investigation.

The concentration of phosphate was <0.5 mg L<sup>-1</sup> during all the pre- and post-monsoon periods. The low solubility and high adsorption onto soil particles control its occurrence in groundwater. We have not observed any relationship between Se(VI) levels and phosphate. Similarly, though some reports [13] support the increased mobilization of selenium due to sulphate, no such behavior is observed in this study. Unlike nitrate, sulphate concentration decreased in most of the wells like other major ions during all the post-monsoon periods.

### 3.6. Probable mechanism of selenium speciation changes

Selenium speciation is influenced by both biotic and abiotic transformations. Though we have not investigated the biotic transformations, in the light of other published results, and from the pattern of variation of selenium species, the following could be inferred. Biotic transformations generally reduce Se(IV) and Se(VI) to Se<sup>0</sup>. While the remobilization of selenium through oxidation does occur, the rates are three to four orders of magnitude less than the reductive part of the cycle [34,35]. Column experiments has demonstrated that selenium uptake by microorganisms is effectively suppressed by the presence of nitrate [33]. Abiotic transformations are mainly mediated by Fe(III)/Fe(II) couple [36], and in the present work, the concentration of Fe(II) was higher during pre-monsoon than during post-monsoon periods. The negative relationship between Fe(II) and Se(VI) implies that Fe(II) acted as a potential reductant for Se(VI) more effectively during pre-monsoon periods. Due to the increased oxidizing nature of the groundwater during post-monsoon period, the concentration Fe(II) decreased, consequently, Se(VI) concentration increased. Thus unlike biotic reduction, which removes selenium from the dissolved state, abiotic transformations maintain total selenium concentration. Thus, the abiotic transformations seem to be dominating in groundwater of the study area.

## 4. Conclusions

The results of this monitoring study indicate that in oxidizing groundwaters selenium exists predominantly as Se(VI). Shallow groundwater is prone to selenium enrichment than deeper ones due to the contribution from soil organic matter. DO and Eh play a major role in the occurrence of Se(VI). Groundwater recharge increases the oxidizing nature; hence mobilization of selenium species is enhanced during post-monsoon periods. Though nitrate and sulphate were present at higher concentrations it did not enhance the leaching of soil selenium. Increase of DO and Eh after monsoon enhances the mobilization of soil selenium into groundwater. This finding has important implications on the behavior of selenium in groundwater and on the health of the people consuming groundwater from seleniferous areas.

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