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ORIGINAL PAPER

Temporal changes in trace elements in brown soil and soybean after long-term fertilization

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Abstract In agricultural production, specific elements in soil and plants are very important for the soil quality and plant productivity. Trace elements and rare earth elements enter in agri-environment by the application of fertilizers and, through anthropogenic activities, pose important health impacts even at low concentration due to non-biodegradable nature with long half-life. The micro nutrients are essential for human body in a quantity most of less than 100 mg/day. The nutritional element uptake by plants is regulated by availability of the required elements and element accumulation ability of the plants. Therefore, this study was aimed to investigate the accumulation of trace and rare earth elements after long-term application of different fertilizers in soil and soybean uptake. The inorganic fertilizers (NKP) and pig manure were applied to maize-maize-soybean rotation in Alfisols (brown) soil since 1979. Atomic emission spectrometry along with inductively coupled plasma technique was applied to determine trace and rare earth elements. The accumulation pattern of trace elements (TEs) observed in soil was Ni > Co > Se > Mo and rare earth elements (REEs) was found as La > Nd > Tb > Y > Pr > Gd > Er > Yb > Lu. In soybean stem, the TE and REE concentrations were Se > Ni > Co > Mo and Pr > Gd > Er > Yb > Tb > Nd > Lu > La > Y, respectively. Elemental concentrations in the seed samples were Ni > Se > Mo > Co and Pr > Gd > Er > Yb > Tb > Nd > Lu > Y > La. The seed of soybean accumulated Co, Mo, Ni, Gd, Pr, Er, Lu, and Tb more than the stem. Higher concentrations of Se, Nd, Y, and Yb were found in soil. These elements were higher in soybean stem followed by the seed. However, these elements are within safe toxic level and light pollution level.

Keywords Elements · Fertilizers · Accumulation · ICP-OES

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Introduction

The trace elements are significant when exploiting environmental quality of soil for crop productivity (Wang et al. 2014). The improvements of mineral status of agricultural system are essential for human benefits. Suitable mineral concentrations are essential for development and growth of all animals as well. Some of the trace elements have been identified as vital nutrients for the plant metabolism (Cu, Mn, Mo, Zn) while some others are micronutrients for human (Mn, Mo, Se, Zn) (Kloss et al. 2014). Some of these elements such as Co and Se are not necessary for plant growth but essential for animals, and Cd, Pb, Cr, Ni, Hg, and As have not been recognized as required by both plants and animals. It has also been reported that Co, Ni, Cu, and Cr are essential in biological structures up to a certain limits (Khan et al. 2014) while the deficiency of Se creates implications in many serious diseases in the human body (Wei et al. 2014).

In agro-ecosystem, the sources of trace and rare earth elements are geological distribution in parent soil and atmospheric deposition from industrial air emissions (Tang et al. 2015) through rain water, agricultural amendments like organic/inorganic fertilizers, and application of pesticides (Avci and Deveci 2013). Trace elements pose important health impacts on human and other mammals and involve in physiochemical

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activities in the body when they are present in accessible forms and are toxic at concentrations exceeding the limits in uninterrupted environments as a result of accumulation due to pedogenic, biogenic, and geogenic processes. The micro nutrients including cobalt, selenium, zinc, manganese chromium, and vanadium are essential for the human body in a quantity of less than 100 mg/day (Karadaş and Kara 2012). In nutrition, micronutrients are considered to be involved in the formation of metalloprotein, polyphenol, phosphate, chelate, and phytate compounds. These compounds take part in enzymatic activities with specific functions or transport proteins from manufacturing site to target site (Fraga 2005a). Beyond to the quantitative concentration limits of their functions, the trace elements are toxic (Khan et al. 2014). Even at low concentration, due to non-biodegradable nature with long half-life, some of the trace elements are very toxic and accumulate potentially inside the body (Behbahaninia et al. 2009). Their availability in the soil affects the safety and food quality by plant uptake at elevated levels (Muchuweti et al. 2006). Under ideal irrigation and cultivation conditions, the absorption of elements by plants through the roots is affected by some factors like soil type, pH of soil, plant species, and soil organic matter (Maathuis 2009), and these factors determine the uptake of the elements and bio-accumulation in the plant tissues.

The element uptake by plant is affected by some factors like soil type, pH of soil, plant species, and soil organic matter. Studies reflect that the exposure time and entry path of the cobalt affect animal health adversely. Molybdenum is vital for life due to its involvement in metabolism of organisms and in biogeochemical cycles. Molybdenum also plays an important role in environmental stresses (Wu et al. 2014). Nickel releases in agri-environment as a result of groundwater contamination and polluted particulate matter. Nickel accumulation in soil at higher concentration impedes the chemical process. In human and animal, the antioxidant protection is provided by the selenoproteins that take part in metabolism of thyroid hormone. Various studies prove that the consumption of vegetables, cereals, mushrooms, meat, and sea food is an important selenium source which reduces the cancer risk (Funes-Collado et al. 2015).

Based on literature, it was hypothesized that application of mineral fertilizers and manure would affect the accumulation of micronutrients in soil and plants. Limited study is available on the accumulation, speciation, and temporal changes of trace and rare earth elements after long-term application of organic and mineral fertilizers. The speciation and accumulation of micronutrients/trace elements in maize and soybean including As, Cd, Cr, Cu, Fe, Hg, Mn, and Zn have been studied on the under consideration study area in the previous work. This study was focused on accumulation of trace and rare earth elements, i.e., Ni, Mo, Co, Se, Er, Gd, La, Lu, Nd, Pr, Tb, Y, and Yb, in soil and soybean plants after long-term application of chemical fertilizers and pig manure. The usage of manure along with chemical fertilizers for a reasonable improvement and optimization of soil physical and chemical properties improves soil C/N ratio and soil beneficial protein and enzyme activity in the low-yield farmland. The aim of the present study was to determine temporal variations in soil micronutrients and also to obtain insight into the concentrations of selected micronutrients in soybean crop which is a major cash crop in many countries.

Materials and methods

Geo-physical description of study site

The eight experimental plots for long-term application of fertilizers on brown soil were located at Shenyang Agricultural University in Shenyang, Shenhe District of Liaoning Province, China (40° 48′ N, 123° 33′ E). The eight experimental plots, each with four replicates randomly (32 plots, 10 × 5 m each), were established in 1979. The area is semi-humid and rain-fed with the mean annual precipitation and temperature 574–684 mm and 7.0–8.1 °C, respectively. Geology of the experimental field is 23% clay, 48% sand, and 29% silt (clay brown loam) at 0–20-cm depth and classified as Alfisols dominated with hydromica clay mineral (Luo et al. 2014). Tillage is being done up to 20 cm deep by machine generally at the time of planting or the day before.

Fertilization approach

The study was conducted on eight treatment plots (in triplicates) (160 m^2 each with maize-maize-soybean rotation). Based on the previous record and recommendations, the current study included all the previously studied parameters. The treatments were T_1 (NP), T_2 (NPK), T_3 (N), T_4 (MNP), T_5 (MNPK), T_6 (MN), T_7 (M), and T_8 (no fertilizers). The notations N, P, K, and M were used for proportion of nitrogen, phosphorus, potassium fertilizers, and pig manure, respectively. The details of fertilizers applied were, for soybean, nitrogen fertilizer = 22.5 kg/hm^2, phosphorus fertilizer (P_2O_5) = 90 kg/hm^2, potassium fertilizer (K_2O) = 90 kg/hm^2, and pig manure = 0 kg/hm^2).

Sampling

The top soils of eight treatments were sampled up to 20-cm depth between the rows with an auger of 5-cm diameter. The randomly taken five samples of individual treatment were mixed to make a composite sample. The same procedure was adopted for soybean plant (stem and seed) samples. These soil and plant samples were sealed in plastic bags and transferred to laboratory. The collected soil samples were dried at room temperature and homogenized by grinding with wooden mortar and pestle, passed through 63-μm nylon sieve, and stored at 25 °C till elemental analysis. The soil samples for the years of 1979, 1989, 2002, and 2014 and the plant samples (stem and seed) for the following years: 1989, 2002, and 2014 were selected for this study.

Analytical procedure

Several techniques have been applied to determine the macro- and micro-elements in the soil and plant samples including atomic absorption spectrometry (AAS) (Barbosa et al. 2014), inductively coupled plasma mass spectrometry (ICP-MS) (Santato et al. 2012), and atomic emission spectrometry with inductively coupled plasma (ICP-OES/AES) (Barbosa et al. 2014). However, the technique with multi-element detection capability provided with much lower detection limits and wider linear dynamic range is ICP-based technique (Barbosa et al. 2014).

The soil and fertilizer samples were prepared in suprapure HNO_3 (65%), HCl (37%), and HF (GR) (6:2:2 mL) according to US EPA 3051A method for microwave-assisted acid digestion. However, the plant samples were digested in suprapure HNO_3 (65%) only. Blank digests for the soil and plant samples were also prepared.

A Milestone ETHOS One (high-performance microwave digestion) equipped with MPR-600/12 HT high-pressure segmented rotor used for the soil samples and DRN-41 rotor used for the plant samples. All Teflon vessels had been pre-cleaned with 5% HNO_3 in a hot acid bath and then rinsed with Milli-Q water. Ultrapure (Milli-Q) water obtained (18.2 MΩ cm TC, 25 °C) from Milli-Q (Milipore, Billerica, MA). Water purification system was used in the experiments. Ultrapure HNO_3, HCl, and HF supplied by Sinopharm Chemical Reagent Co. Ltd., China, were used. Standard solutions for external calibration were prepared from solutions of 100–1000-μg/mL concentrations supplied by "analytical measurement center of national nonferrous metals and electronic material, China." The soil reference material (GBW07403) and plant reference material (GBW10012) supplied by the National Center for Reference Materials, China, were used in these experiments.

Trace elements (Co, Mo, Ni, and Sc) and rare earth elements (Er, Gd, La, Lu, Nd, Pr, Tb, Y, and Yb) were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (VISTA-MPX, VARIAN, Germany).

Statistical analysis

Data were statistically analyzed at the significant differences ($p < 0.05$) using one-way analysis of variance (ANOVA) following Tukey's post-hoc test (HSD) and Duncan test, using SPSS version 22 (IBM Corp.).

Results

The soil organic carbon and pH of the soil samples of the years 1979, 1989, 2002, and 2014 are displayed below in Table 1 while the concentrations of trace elements (TEs) and rare earth elements (REEs) of the fertilizers applied in 2014 are also determined and cited below in the Table 2.

The pH of the soil samples in 1989 was slightly acidic to neutral with a range of 6.67 to 7.29. The pH of the various soil samples in 2014 was more acidic, which might be due to addition of increments of organic matter (Table 1). Although, the amount of organic matter added in various soils was similar, it seems that organic matter could not be efficiently utilized by cropping systems which might have lowered soil pH in 2014.

T_1 treatment

The concentration of cobalt (Co) increased significantly after the application of fertilizer as compared to the start of the experiment. Cobalt was mostly accumulated in soil (Fig. 1). A very small concentration is bio-accumulated in soybean plant (both in the stem and seed) in 1989 but in 2002, Co was higher in the stem (Table 3). Molybdenum (Mo) was significantly higher in concentration in 2014 soil sample (Fig. 1) and its concentration 0.617 and 0.466 μg/g was determined in the stem and seed in the years 1989 and 2014, respectively (Tables 3 and 4). However, the concentration of nickel (Ni) enhanced and accumulated in soil after fertilization (Fig. 1) and bio-accumulated with higher concentration in the seeds followed by the stem (Tables 3 and 4). The selenium (Se) element was found lower in soil in 1989 and 2002 (Fig. 1). In 1989 and 2002, the Se was detected higher in the stem and then in the seed (Tables 3 and 4).

Except Y, the concentration of rare earth elements in soil increased and found higher in the year 2014 (Fig. 2). In the stem, the concentrations of Gd, La, Nd, Tb, and Y were almost

Table 1 The soil pH and soil organic carbon (g/kg) in 4-year samples of different treatments

Treatments	1979		1989		2002		2014	
	pH	SOC	pH	SOC	pH	SOC	pH	SOC
T_1	–	–	6.98	8.06	6.48	8.87	5.43	8.93
T_2	–	–	6.90	8.18	6.39	8.58	5.33	8.82
T_3	–	–	7.28	7.25	6.52	7.71	5.43	8.64
T_4	–	–	6.96	11.77	6.14	11.14	5.69	10.61
T_5	–	–	6.67	11.31	5.95	11.19	5.87	12.06
T_6	–	–	6.87	10.90	5.99	9.98	5.90	11.83
T_7	–	–	7.29	12.70	5.97	10.03	5.90	11.77
T_8	6.5	9.22	7.09	8.41	6.26	8.06	5.92	8.29

Table 2 Concentrations of TEs and REEs in fertilizers (μg/g dry wt.)

Elements	Fertilizers			
	N-fertilizer	P-fertilizer	K-fertilizer	Pig manure
Co	ND	53.74 ± 4.31	ND	4.09 ± 1.26
Mo	0.28 ± 0.07	0.60 ± 0.07	0.26 ± 0.05	0.78 ± 0.02
Ni	2.85 ± 5.55	1.04 ± 0.99	ND	62.01 ± 41.51
Se	12.45 ± 0.01	24.60 ± 6.12	12.45 ± 0.01	4.81 ± 2.29
Gd	ND	136.99 ± 1.94	ND	2.92 ± 0.36
La	21.74 ± 0.25	529.37 ± 4.64	20.99 ± 0.18	36.60 ± 1.12
Nd	18.48 ± 0.23	822.21 ± 5.73	17.6 ± 0.53	33.27 ± 1.35
Pr	0.72 ± 0.17	156.87 ± 1.03	1.13 ± 0.39	6.35 ± 0.39
Er	ND	25.43 ± 0.29	ND	0.25 ± 0.19
Lu	ND	2.06 ± 0.07	ND	0.04 ± 0.06
Tb	ND	5.24 ± 0.49	ND	ND
Y	15.26 ± 0.17	260.22 ± 0.84	15.11 ± 0.26	16.83 ± 0.17
Yb	1.08 ± 0.01	15.24 ± 0.09	1.06 ± 0.05	1.57 ± 0.09

ND means none detected

same, and no change was observed after long-term fertilization while the concentration of Pr, Er, Lu, and Yb significantly decreased in 2014 (Table 5). In the seed, the concentration of Gd, Pr, and Y showed a similar pattern to that of the stem samples. Higher Nd was observed in the seed in 1989 (Table 5).

T_2 treatment

Cobalt concentration was significantly higher in the soil (Fig. 1) and stem samples in 1989 and 2002, respectively (Table 3); however, the seeds exhibited higher amount in 1989 (Table 4). Mo was determined in the three soil samples in the order 1.38 < 3.10 μg/g in 1979 and 2014, respectively (Fig. 1), and stem and seed gave higher content in 2014 (Tables 3 and 4). Ni concentration was significantly higher in the soil (Fig. 1), seed samples in 2014 (Table 4), and stem sample in 2002 (Table 3). Se was significantly higher in the soil sample of 2014 (Fig. 1). It is detected in the stem samples of 2002 and 2014 at almost same concentration (Table 3). In the seed, Se was bio-accumulated in the samples of 1989 and 2002 but significantly higher in 1989 (Table 4).

In T_2 treatment, the REEs in soil showed similar pattern as observed in T_1 treatment except Lu. No significant change in concentration of Lu was observed in this treatment (Fig. 2). The concentrations of Nd, Pr, Er, Tb, and Y were decreased yearly except La (Table 5). In the seed, Gd, Pr, Lu, and Yb concentrations reduced with time as 1989 > 2002 > 2014. The concentrations of Nd and Er were significantly higher in 2002. Lower Tb concentration was found in 2002 (Table 6).

T_3 treatment

The Co concentration in T_3 was higher in soil sampled during 1989 than that in soil sample of 2014 (Fig. 1). In the stem, higher Co was noted in 2002 (Table 3). In the seed, higher accumulation was noticed in 2002 than that in 1989 (Table 4). Mo was significantly higher in the soil sample of 2014 (Fig. 1); however, its higher concentration was detected in the stem in 2014 (Table 3) and in the seeds during the 1989 (Table 4). Ni concentration was significantly higher in soil (Fig. 1) and seed during the 2014. Se was significantly higher in the soil sample of the year 1979 (Fig. 1). In the stem and seed samples, it is significantly higher in the sample of the year 1989 and was absent in the year 2014 (Tables 3 and 4).

In T_3 treatment, the concentrations of Gd, Pr, Er, Lu, Tb, and Yb in soil were significantly higher in 2014. The concentration of Y was significantly higher in the years 1979 and 1989 than that in the year 2002 (Fig. 2). In the stem, the concentrations of Gd, Nd, Pr, Tb, and Yb were significantly higher in 1989. The concentrations of La and Y were significantly higher in the sample in the year 2014 while the concentrations of Er and Lu in 2002 (Table 5). In the seed sample of 1989, the concentrations of Gd, Nd, Pr, and Y were significantly higher than those of 2002 and 2014. The concentrations of Er, Lu, and Yb were significantly lower in 2014 than those in other two years.

T_4 treatment

In this treatment, Co concentration in soil was significantly higher in sample of the year 1989 (Fig. 1). In plant, it was detected in the stem sample of the year 2002 (Table 3). Ni concentration was increased in soil in 1989 (Fig. 1). In the stem, Ni contents were 0.661 μg/g in 2002 and 1.152 μg/g in 2014 (Table 3). In the seed, Ni was higher in soil during 2014 (Table 4). Se in soil differed as 1979 > 2002 > 2014 (Fig. 1).

In the T_4 treatment, the concentrations of Gd, Pr, and Lu were significantly higher in the soil during 2014 while Tb, Y, and Er in 1979, 1989, and 2002, respectively (Fig. 2). In the stem, an increase in concentrations of La and Yb was noted in 2002 while Gd and Tb were significantly higher in 2002 and 2014 than those in 1989. Nd was detected in 1989. In the seed, the concentration of Gd and Y was higher in 1989 and a decrease in the concentrations of Lu and Yb was observed in 2014. The concentrations of Pr and Tb were enhanced in 2002. Nd and Er accumulated in the seeds.

T_5 treatment

The concentration of Co in soil showed the pattern of T_4 treatment (Fig. 1). It was determined in the stem samples in 2002 and 2014 (Table 3). In the seed, Co was significantly

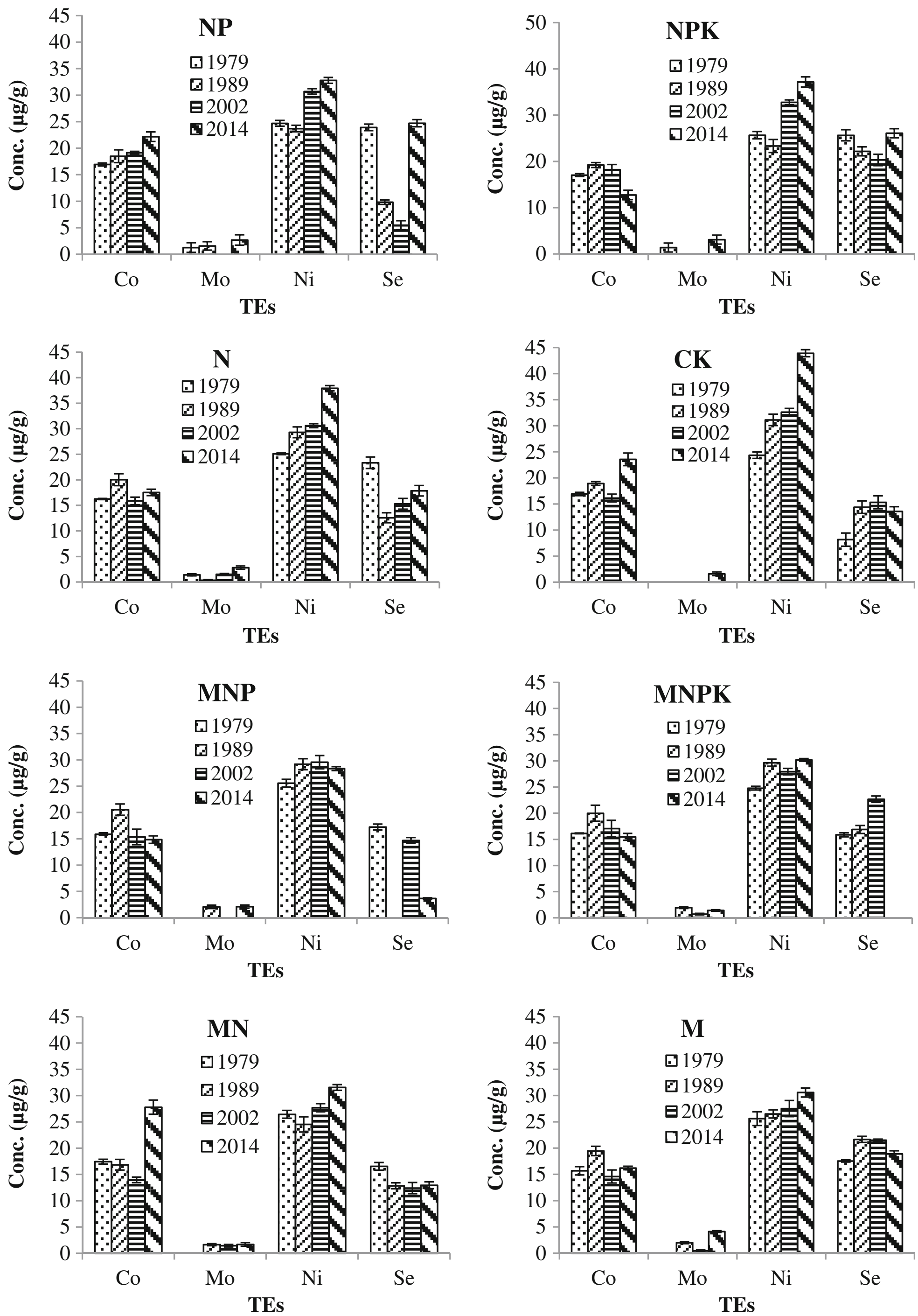

Fig. 1 Trace element (TE) concentrations in eight different soil treatments

higher in 1989 (Table 4). Mo was determined in the soil sample in 1989, 2002, and 2014 and lower in 2002 (Fig. 1). In plant, Mo was higher in the seeds in 2014 (Table 4). Se concentration was significantly higher in the soil sample in 2002 (Fig. 1). Nd in the soil samples of 1989 and 2002, Pr in 2014, Tb in 1979, and Y in 1989 were significantly higher while the concentration of Yb was lower in the soil sample of 2002 (Fig. 2). In the stem samples, all REEs showed the same behavior as in T_4 treatment except La and Nd. La was present in the stem sample of 2014. Nd was detected in the sample of 2014 but in lower concentration (Table 5).

T_6 treatment

Cobalt concentration was significantly higher in the soil sample of 2014 (Fig. 1). Its concentration in the stem was 0.279 μg/g in 2002 and 0.114 μg/g in 2014 (Table 3). In the seed, it was 0.243 μg/g in 1989 and 0.384 μg/g in 2002

Table 3 Concentrations of TEs in the stem of soybean plant (μg/g dry wt.)

Treatments/year		Stem			
		Co	Mo	Ni	Se
T_1	1989	0.386 ± 0.042a	0.617 ± 0.019	0.368 ± 0.020c	5.252 ± 0.205a
	2002	0.289 ± 0.023b	ND	2.144 ± 0.013a	3.705 ± 0.023b
	2014	ND	ND	0.568 ± 0.012b	ND
T_2	1989	0.061 ± 0.001b	ND	1.468 ± 0.10ab	ND
	2002	0.320 ± 0.003a	ND	1.670 ± 0.131a	2.245 ± 0.004
	2014	ND	0.636 ± 0.006	1.375 ± 0.017b	2.242 ± 0.002
T_3	1989	ND	ND	1.118 ± 0.226	7.530 ± 0.002a
	2002	0.393 ± 0.120	ND	1.676 ± 0.261	3.329 ± 0.004b
	2014	ND	0.134 ± 0.001	1.270 ± 0.181	ND
T_4	1989	ND	ND	ND	ND
	2002	0.392 ± 0.002	ND	0.198 ± 0.005b	ND
	2014	ND	ND	0.426 ± 0.018a	ND
T_5	1989	ND	ND	ND	2.833 ± 0.025
	2002	0.179 ± 0.120	ND	0.661 ± 0.187	ND
	2014	0.224 ± 0.061	ND	1.152 ± 0.193	ND
T_6	1989	ND	ND	ND	2.808 ± 0.024b
	2002	0.279 ± 0.025a	ND	0.962 ± 0.013b	8.354 ± 0.016a
	2014	0.114 ± 0.002b	ND	1.290 ± 0.013a	ND
T_7	1989	0.154 ± 0.003	ND	0.332 ± 0.016b	5.777 ± 0.010
	2002	ND	ND	0.252 ± 0.009c	ND
	2014	ND	0.074 ± 0.010	0.472 ± 0.009a	ND
T_8	1989	ND	ND	1.679 ± 0.021a	0.555 ± 0.017
	2002	0.643 ± 0.066a	ND	0.883 ± 0.006b	ND
	2014	0.45 ± 0.064b	ND	ND	ND

ND means none detected

(Table 4). In plant, Mo was determined in the seeds with higher concentration in 2014 (Table 4). Ni concentration was significantly higher in the soil (Fig. 1) and plant samples in 2014 (Tables 3 and 4). Se was significantly higher in 1979 (Fig. 1). It was detected only in the stem samples of the years 1989 and 2002 at the concentration of 2.808 and 8.35 μg/g, respectively (Table 3).

In T_6 treatment, the concentrations of all REEs were significantly higher in the soil sample of the year 2014 except La (Fig. 2). In the stem, the concentrations of La, Nd, Er, Lu, and Yb were higher in the sample of 1989. The concentrations of Gd and Tb were higher in the sample of 2014 (Table 5). In the seed, the Gd, Pr, Lu, Tb, Y, and Yb concentrations were significantly higher in 1989. Nd and Er were accumulated in the seed at higher concentrations in 2002.

T_7 treatment

In T_7 treatment, the Co concentration was significantly higher in soil in 1989 (Fig. 1) and also detected in the same year in the stem (Table 3). In the seed, it was in the pattern of 0.255, 0.172, and 0.278 μg/g in the 1989, 2002, and 2014, respectively (Table 4). Mo was detected in the soil samples of 1989, 2002, and 2014 and significantly higher in 2014 (Fig. 1). In the stem sample of 2014, 0.074 μg/g of Mo was measured (Table 3). However, it was significantly higher in the seed sample of 2014 (Table 4). Se was significantly higher in the soil samples of 1989 and 2002 (Fig. 1). In the stem sample of 1989, it was at the rate of 5.777 μg/g only (Table 3). In the seed, it was at the rate of 3.241 and 2.437 μg/g in 1989 and 2002, respectively (Table 4).

The concentrations of Nd and Tb were higher in the soil samples of 1989 and 1979, respectively. However, the concentrations of Pr and Er were significantly decreased in the soil samples of 1989 and 2002, respectively (Fig. 2). La and Y concentrations were significantly higher in the stem samples of 2002 and 1989, respectively (Table 5). The concentrations of all REEs were significantly higher in the seed sample of 1989 and decreased over the years except Er (Table 6).

T_8 treatment

Co concentration was significantly higher in the soil sample of the year 2014 (Fig. 1). In the stem, it is higher in 2002

Table 4 Concentrations of TEs in the seed of soybean plant (μg/g dry wt.)

Treatments/year		Seed			
		Co	Mo	Ni	Se
T_1	1989	0.311 ± 0.002	ND	9.524 ± 0.237b	4.453 ± 0.061a
	2002	ND	ND	8.036 ± 0.325c	3.373 ± 0.014b
	2014	ND	0.466 ± 0.019	13.090 ± 0.425a	ND
T_2	1989	0.050 ± 0.001	ND	8.879 ± 0.124b	9.515 ± 0.288a
	2002	ND	ND	8.049 ± 0.065b	1.699 ± 0.080b
	2014	ND	1.539 ± 0.011	11.852 ± 0.368a	ND
T_3	1989	0.169 ± 0.085b	0.887 ± 0.006	10.193 ± 0.383a	7.250 ± 0.004a
	2002	0.232 ± 0.120a	ND	6.941 ± 0.141b	1.828 ± 0.003b
	2014	ND	ND	11.872 ± 0.776a	ND
T_4	1989	ND	1.548 ± 0.009b	7.282 ± 0.173b	ND
	2002	ND	ND	7.049 ± 0.009b	ND
	2014	ND	2.300 ± 0.017a	9.107 ± 0.091a	ND
T_5	1989	0.491 ± 0.003a	0.978 ± 0.011b	5.300 ± 0.115c	4.377 ± 0.001a
	2002	0.117 ± 0.001c	0.630 ± 0.018c	7.067 ± 0.057b	2.255 ± 0.012b
	2014	0.275 ± 0.004b	1.628 ± 0.028a	10.300 ± 0.158a	ND
T_6	1989	0.243 ± 0.009	0.844 ± 0.022b	5.723 ± 0.032c	ND
	2002	0.384 ± 0.287	0.656 ± 0.009c	6.797 ± 0.049b	ND
	2014	ND	1.960 ± 0.016a	9.767 ± 0.023a	ND
T_7	1989	0.255 ± 0.023a	2.662 ± 0.055b	4.991 ± 0.169c	3.241 ± 0.006a
	2002	0.172 ± 0.009b	2.771 ± 0.019b	5.930 ± 0.011b	2.437 ± 0.056b
	2014	0.278 ± 0.018a	3.509 ± 0.130a	6.541 ± 0.017a	ND
T_8	1989	0.323 ± 0.004b	ND	5.965 ± 0.039b	9.437 ± 0.162
	2002	0.297 ± 0.001c	ND	5.182 ± 0.001c	ND
	2014	0.349 ± 0.005a	0.975 ± 0.005	8.992 ± 0.025a	ND

ND means not detected

(Table 3). In the seed, it was significantly higher in 2014 (Table 4). Mo was present only in the soil sample of 2014 (Fig. 1). It was detected in the seed sample of 2014 (Table 4). Ni concentration was significantly higher in the soil (Fig. 1) and seed samples of 2014 (Table 4). In the stem, it was higher in 1989 than that in 2002 (Table 3). In T_8 treatment, the concentrations of Gd, La, Pr, Er, Lu, and Tb in the soil sample were significantly higher in 2014 (Fig. 2). In the stem samples, the concentrations of Gd, Pr, Lu, Tb, and Y were significantly higher in the sample of 2002 and the concentrations of Nd and Er in the sample of 1989. The concentration of La was observed as 1989 < 2002 < 2014 while the concentration of Yb remains almost same during the whole period (Table 5).

Discussions

Industrialization and urban development elevate the level of TEs and REEs in environments (Adriano 2001). Accumulation of trace and rare earth elements in soil and uptake and bio-accumulation in plant is influenced by soil pH, $CaCO_3$ contents, crop rotation, plant species, cultivar, and fertilization approaches like use of compost and manure instead of inorganic fertilizers and avoid using heavy metal-enriched pesticides. Bioavailability, solubility, transportation, and concentration of TEs and REEs are affected by the factors mentioned above (Avci and Deveci 2013; He et al. 2005; Smith 2009). It is also reported by some researchers that root development and growth of plant is restricted by the high concentrations of the trace elements (Gisbert et al. 2006; Parra et al. 2014; Shi et al. 2011; Zheljazkov et al. 2006).

In this study, it is reflected from the result that the overall accumulation of trace element concentration pattern was in soil as Ni > Co > Se > Mo, and rare earth elements were in the pattern La > Nd > Tb > Y > Pr > Gd > Er > Yb > Lu. In the stem, the TE and REE concentration patterns were Se > Ni > Co > Mo and Pr > Gd > Er > Yb > Tb > Nd > Lu > La > Y, respectively. However, Ni > Se > Mo > Co and Pr > Gd > Er > Yb > Tb > Nd > Lu > Y > La pattern was seen in the seeds. The ability of Co, Mo, Ni, Gd, Pr, Er, Lu, and Tb to accumulate in soil and plant parts in our study was ranked as soil > seed > stem, and that of La was soil > stem. However, Se, Nd, Y, and Yb showed soil > stem > seed coinciding with literature

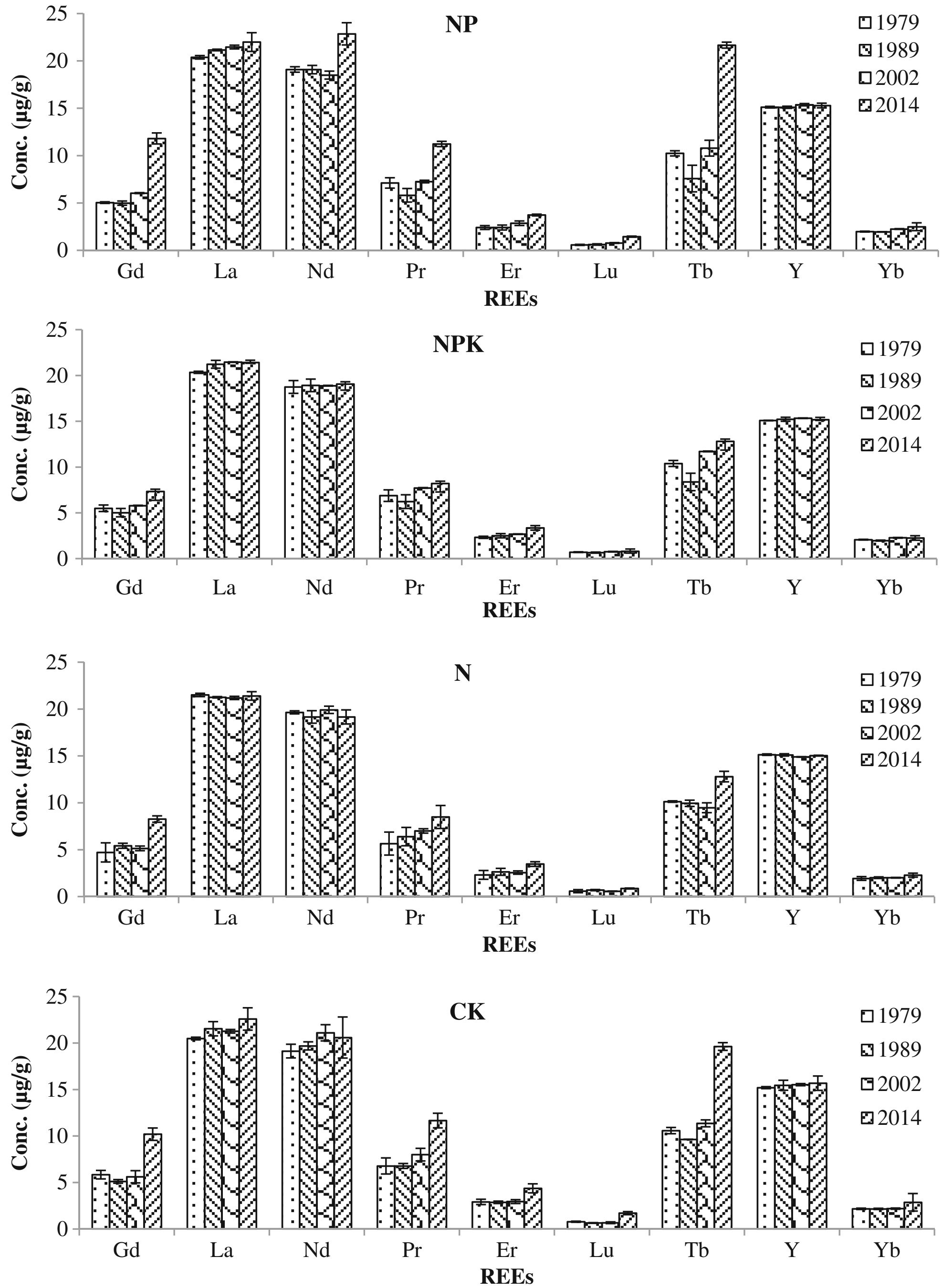

Fig. 2 Rare earth element (REE) concentrations in eight different soil treatments

reported by (Ding et al. 2006; Wang et al. 2001). The organic labile compounds present in pig manure form soluble organic ligands. The increments in accumulation of some trace elements in plants maybe as a result of the formation of these organic ligands (Parra et al. 2014).

The relative higher Mo concentration in plant resulted in its foliar application also. Ni is available in abundance in environment. It is naturally bio-accumulate at higher concentration in many plants to their tissues. Ni concentration in plant tissues depends upon the available form and soil properties (Avci and Deveci 2013; Yusuf et al. 2011). It is reported that SOC affect the trace element availability and speciation and uptake by plant (Cloutier-Hurteau et al. 2014). In this study, the measured Ni concentration was lined with the range reported by the Lorenz and Lal (2009), Ajmone-Marsan and Biasioli (2010), and Vasenev et al. (2013) in soil (Fig. 1), and higher concentration than the WHO/EU (1983) and FAO/WHO (2001) (Wu et al. 2014) limits (0.2 mg/kg) in plant samples may be due to the different uptake characteristics (Kabata-Pendias and Mukherjee 2007) (Table 3). Se is present in

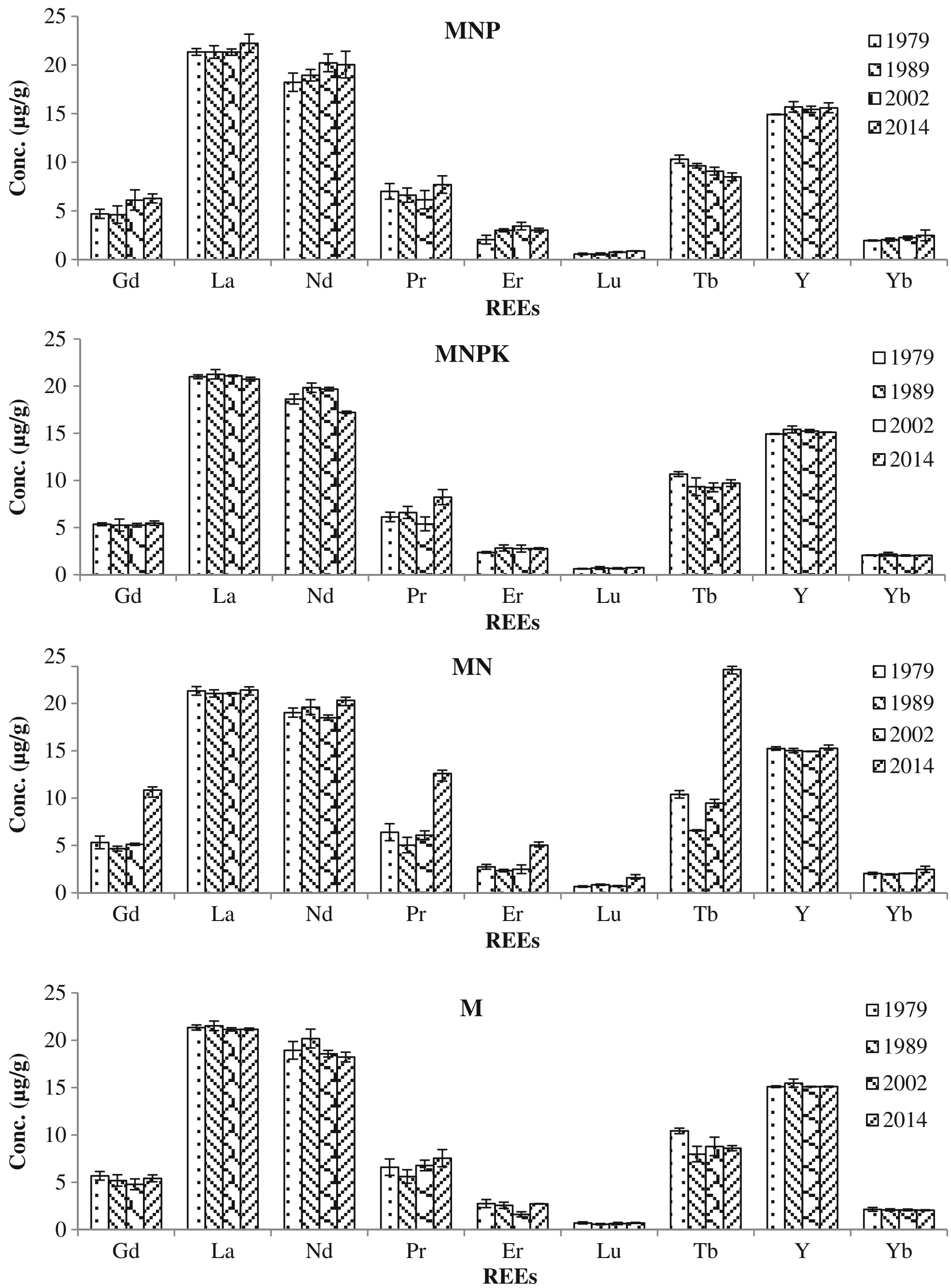

Fig. 2 continued.

environment in Se^{-2}, Se^{0}, Se^{4+}, and Se^{6+} oxidation states. It is present in one of the volatile organic compounds formed in plants escaped through the leaves. Selenite (SeO_3^{2-}) have stronger adsorption affinity than selenite to different soil components and reduce the bioavailability of Se^{4+}, so more Se accumulate in plant from selenate compounds (Kamei-Ishikawa et al. 2007; Songshan et al. 2010; Su and Suarez 2000; Wang et al. 2012; Zhu et al. 2009). Plants uptake selenite through the roots and transport it to the stems while selenite is converted into organic compounds and bio-accumulated in the roots (Li et al. 2008; Terry et al. 2000; Zayed et al. 1998). Se transportation within plant is also affected by climate conditions like humidity, temperature, and soil moisture indirectly by affecting the soil chemical and physical properties that determined its concentration in plants (De Temmerman et al. 2014).

The rare earth elements are almost evenly distributed in soybean plant except La which is accumulated only in the stem of the soybean plant. In literature, the pH-dependent accumulation behavior of REEs has been elaborated. The cell wall structure is changed due to change in osmotic pressure in plant cells with soil pH. The REEs could barely cross the cell

Table 5 Concentrations of REEs in soybean stem (μg/g dry wt.)

Treatments/year		Gd	La	Nd	Pr	Er	Lu	Tb	Y	Yb
T_1	1989	4.547 ± 0.051	0.285 ± 0.061	ND	7.839 ± 0.272a	1.822 ± 0.07a	0.223 ± 0.007b	1.118 ± 0.025	0.034 ± 0.002	1.613 ± 0.011b
	2002	4.454 ± 0.024	0.145 ± 0.014	0.378 ± 0.244	6.669 ± 0.069b	1.972 ± 0.03a	0.251 ± 0.008a	1.417 ± 0.03	0.037 ± 0.001	1.637 ± 0.002a
	2014	4.446 ± 0.018	0.169 ± 0.072	0.514 ± 0.053	6.362 ± 0.186b	1.591 ± 0.009b	0.129 ± 0.002c	1.256 ± 0.192	0.035 ± 0.003	1.526 ± 0.002c
T_2	1989	4.511 ± 0.058	0.119 ± 0.029b	0.837 ± 0.003a	7.695 ± 0.114a	1.972 ± 0.008a	0.281 ± 0.02	1.831 ± 0.009a	0.148 ± 0.001a	1.650 ± 0.016
	2002	4.576 ± 0.048	0.119 ± 0.044b	0.127 ± 0.001c	6.935 ± 0.136b	1.939 ± 0.034a	0.237 ± 0.007	1.19 ± 0.003b	0.053 ± 0.001c	1.645 ± 0.008
	2014	4.542 ± 0.050	0.241 ± 0.025a	0.664 ± 0.005b	7.7229 ± 0.17ab	1.633 ± 0.03b	0.250 ± 0.022	1.147 ± 0.005c	0.138 ± 0.001b	1.649 ± 0.023
T_3	1989	4.63 ± 0.045a	0.239 ± 0.002b	1.39 ± 0.121a	7.804 ± 0.059a	1.770 ± 0.004b	0.233 ± 0.007b	1.297 ± 0.102a	0.118 ± 0.002b	1.618 ± 0.002a
	2002	4.504 ± 0.037b	0.173 ± 0.001c	0.43 ± 0.008b	6.67 ± 0.006b	1.852 ± 0.012a	0.258 ± 0.002a	1.468 ± 0.118a	0.119 ± 0.002b	1.621 ± 0.008a
	2014	4.458 ± 0.020b	0.43 ± 0.001a	0.498 ± 0.006b	6.436 ± 0.014c	1.631 ± 0.009c	0.229 ± 0.001b	0.868 ± 0.038b	0.162 ± 0.002a	1.59 ± 0.007b
T_4	1989	4.259 ± 0.039b	0.049 ± 0.001b	1.263 ± 0.001	7.067 ± 0.309	1.890 ± 0.116a	0.246 ± 0.013	0.263 ± 0.072b	0.456 ± 0.016	1.626 ± 0.014ab
	2002	4.378 ± 0.018a	0.181 ± 0.001a	ND	7.097 ± 0.178	1.609 ± 0.052b	0.260 ± 0.045	0.871 ± 0.168a	0.437 ± 0.012	1.658 ± 0.032a
	2014	4.409 ± 0.021a	0.04 ± 0.001c	ND	6.846 ± 0.181	1.520 ± 0.053b	0.206 ± 0.004	1.046 ± 0.049a	0.663 ± 0.013	1.578 ± 0.002b
T_5	1989	4.196 ± 0.040b	ND	1.219 ± 0.003a	6.535 ± 0.306	1.924 ± 0.028a	0.223 ± 0.012	0.259 ± 0.006c	0.264 ± 0.194	1.623 ± 0.013a
	2002	4.464 ± 0.042a	ND	ND	6.482 ± 0.101	1.595 ± 0.039b	0.220 ± 0.008	0.692 ± 0.037b	0.024 ± 0.001	1.625 ± 0.004a
	2014	4.457 ± 0.021a	0.134 ± 0.001	0.603 ± 0.014b	6.456 ± 0.03	1.645 ± 0.042b	0.214 ± 0.003	0.948 ± 0.007a	0.055 ± 0.001	1.585 ± 0.012b
T_6	1989	4.238 ± 0.006b	0.312 ± 0.004a	0.949 ± 0.004a	6.843 ± 0.014	1.952 ± 0.046a	0.265 ± 0.017a	0.509 ± 0.015c	0.067 ± 0.023	1.622 ± 0.006a
	2002	4.421 ± 0.049a	0.215 ± 0.004b	0.164 ± 0.004b	6.917 ± 0.008	1.462 ± 0.134b	0.225 ± 0.006b	0.647 ± 0.004b	0.052 ± 0.017	1.618 ± 0.006a
	2014	4.417 ± 0.046a	ND	0.123 ± 0.001c	6.833 ± 0.004	1.505 ± 0.180b	0.199 ± 0.006b	0.861 ± 0.02a	0.040 ± 0.013	1.567 ± 0.003b
T_7	1989	4.218 ± 0.016b	ND	1.495 ± 0.069a	6.397 ± 0.297	1.892 ± 0.031a	0.254 ± 0.015	0.273 ± 0.004c	0.036 ± 0.002a	1.621 ± 0.006a
	2002	4.526 ± 0.045a	0.192 ± 0.003a	0.544 ± 0.019b	6.806 ± 0.127	1.582 ± 0.044b	0.243 ± 0.013	0.55 ± 0.022b	0.013 ± 0.001c	1.632 ± 0.007a
	2014	4.427 ± 0.039a	0.06 ± 0.006b	0.42 ± 0.029b	6.877 ± 0.119	1.623 ± 0.019b	0.215 ± 0.004	0.846 ± 0.018a	0.028 ± 0.003b	1.58 ± 0.005b
T_8	1989	4.219 ± 0.023c	0.208 ± 0.001c	1.265 ± 0.007a	7.557 ± 0.02a	1.877 ± 0.012a	0.228 ± 0.002ab	0.341 ± 0.004c	0.092 ± 0.001c	1.618 ± 0.007
	2002	4.565 ± 0.028a	0.239 ± 0.001b	0.475 ± 0.006b	7.644 ± 0.067a	1.765 ± 0.082a	0.247 ± 0.008a	1.551 ± 0.013a	0.119 ± 0.001a	1.627 ± 0.008
	2014	4.445 ± 0.006b	0.287 ± 0.004a	0.109 ± 0.001c	6.494 ± 0.021b	1.542 ± 0.029b	0.218 ± 0.007b	0.935 ± 0.002b	0.108 ± 0.001b	1.591 ± 0.015

ND means none detected

Table 6 Concentrations of REEs in soybean seed (μg/g dry wt.)

Treatments/year		Gd	La	Nd	Pr	Er	Lu	Tb	Y	Yb
T_1	1989	4.703 ± 0.065a	ND	1.553 ± 0.14	7.482 ± 0.143a	1.895 ± 0.063	0.279 ± 0.054	1.37 ± 0.132a	0.077 ± 0.002a	1.661 ± 0.005
	2002	4.292 ± 0.026b	ND	ND	6.807 ± 0.028b	1.908 ± 0.002	0.233 ± 0.004	0.394 ± 0.133b	0.002 ± 0.001b	1.611 ± 0.009
	2014	4.379 ± 0.038b	ND	ND	7.095 ± 0.019b	1.892 ± 0.027	0.200 ± 0.048	1.263 ± 0.036a	0.001 ± 0.001b	1.566 ± 0.054
T_2	1989	4.553 ± 0.033a	ND	0.208 ± 0.001b	7.841 ± 0.05a	1.749 ± 0.027b	0.218 ± 0.008a	1.452 ± 0.016a	0.027 ± 0.001a	1.616 ± 0.008a
	2002	4.27 ± 0.066b	ND	1.316 ± 0.001a	6.787 ± 0.149b	1.847 ± 0.031a	0.226 ± 0.011a	1.269 ± 0.003b	0.024 ± 0.002a	1.618 ± 0.008a
	2014	4.290 ± 0.035b	ND	ND	6.83 ± 0.081b	1.755 ± 0.016b	0.139 ± 0.006b	1.527 ± 0.044a	ND	1.514 ± 0.006b
T_3	1989	4.621 ± 0.001a	ND	0.667 ± 0.005a	7.652 ± 0.008a	1.681 ± 0.026c	0.23 ± 0.003a	1.346 ± 0.02a	0.063 ± 0.001a	1.609 ± 0.007ab
	2002	4.177 ± 0.002c	ND	0.153 ± 0.001b	6.353 ± 0.006b	1.942 ± 0.006a	0.232 ± 0.002a	0.532 ± 0.078b	0.044 ± 0.001b	1.659 ± 0.047a
	2014	4.351 ± 0.006b	ND	0.162 ± 0.001b	6.414 ± 0.030b	1.868 ± 0.02b	0.142 ± 0.002b	1.186 ± 0.05a	ND	1.517 ± 0.004b
T_4	1989	4.610 ± 0.063a	ND	0.231 ± 0.003	7.927 ± 0.008a	1.754 ± 0.033	0.209 ± 0.019a	1.423 ± 0.139a	0.08 ± 0.004a	1.613 ± 0.005a
	2002	4.345 ± 0.006b	ND	0.228 ± 0.009	6.302 ± 0.035b	1.907 ± 0.068	0.21 ± 0.014a	0.704 ± 0.08b	0.023 ± 0.002b	1.604 ± 0.004a
	2014	4.409 ± 0.058b	ND	ND	7.262 ± 0.332a	1.859 ± 0.084	0.144 ± 0.016b	1.267 ± 0.117a	ND	1.525 ± 0.003b
T_5	1989	4.517 ± 0.040a	ND	ND	7.543 ± 0.112a	1.8 ± 0.039b	0.227 ± 0.008a	1.389 ± 0.151a	0.076 ± 0.003	1.604 ± 0.003b
	2002	4.204 ± 0.059b	ND	0.405 ± 0.223	6.041 ± 0.092c	2.116 ± 0.029a	0.205 ± 0.008a	0.711 ± 0.092b	0.023 ± 0.001	1.624 ± 0.009a
	2014	4.291 ± 0.014b	ND	ND	7.034 ± 0.068b	1.703 ± 0.035b	0.146 ± 0.005b	1.175 ± 0.084a	ND	1.522 ± 0.003c
T_6	1989	4.557 ± 0.051a	ND	0.015 ± 0.002b	7.517 ± 0.015a	1.872 ± 0.027b	0.228 ± 0.004a	1.421 ± 0.009a	0.084 ± 0.006a	1.606 ± 0.009a
	2002	4.388 ± 0.016b	ND	0.252 ± 0.004a	6.376 ± 0.01c	2.052 ± 0.003a	0.212 ± 0.005a	1.291 ± 0.034b	0.006 ± 0.023b	1.61 ± 0.004a
	2014	4.393 ± 0.006b	ND	ND	6.573 ± 0.055b	1.710 ± 0.029c	0.148 ± 0.005b	1.317 ± 0.019b	ND	1.523 ± 0.004b
T_7	1989	4.513 ± 0.042a	ND	0.459 ± 0.018a	7.549 ± 0.074a	1.809 ± 0.025	0.225 ± 0.006a	1.376 ± 0.004a	0.057 ± 0.001a	1.614 ± 0.007a
	2002	4.279 ± 0.035b	ND	0.248 ± 0.009b	6.647 ± 0.012b	1.867 ± 0.009	0.227 ± 0.009a	1.251 ± 0.01b	0.017 ± 0.001b	1.608 ± 0.013a
	2014	4.375 ± 0.047ab	ND	0.239 ± 0.021b	6.682 ± 0.127b	1.745 ± 0.072	0.149 ± 0.003b	1.366 ± 0.028a	ND	1.523 ± 0.007b
T_8	1989	4.582 ± 0.048a	ND	0.253 ± 0.007b	7.827 ± 0.019a	1.791 ± 0.068b	0.209 ± 0.002a	1.410 ± 0.011a	0.098 ± a0.001	1.609 ± 0.003a
	2002	4.3 ± 0.030b	0.027 ± 0.001	0.636 ± 0.013a	6.424 ± 0.02c	2.034 ± 0.026a	0.213 ± 0.004a	1.037 ± 0.004c	0.034 ± 0.001b	1.612 ± 0.007a
	2014	4.359 ± 0.065b	ND	ND	6.573 ± 0.018b	1.830 ± 0.029b	0.144 ± 0.006b	1.242 ± 0.001b	ND	1.527 ± 0.004b

ND means not detected

wall to enter in the plant cells in acidic soil resulting in lower accumulation in the stem and seed (Zhang and Shan 2001). Cereals are also a source of essential elements required for the human body. The uptake of metals through consumption of soybean is in safe limits of toxicity as the assessed concentration of trace elements in the seeds of soybean appeared quite low. Considering the pollution level of these elements in edible part is within safe limit and falls under light pollution level.

Conclusions

The results obtained from this study are important as human health is being directly affected by the consumption of cereals/extracted oil. The heavy metals/trace elements in cereals need to be monitored continuously because cereals in any way are sources of food for human and are bioindicators of environmental pollution. It was also concluded that long-term application of mineral and organic fertilizers changed the concentrations of trace and rare earth elements in soil. Fertilizers increased the micronutrient concentrations in plants. Se bioaccumulation was found not associated with Se concentration in soil. This could be due to the pH, SOC, and crop cultivar. The Se uptake increased at higher pH. It also varied among plant species and SOC levels. This study revealed that the REEs were present more abundantly in soil as compared to those in plants.

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