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ORIGINAL PAPER

Assessment of nutrient and heavy metal content and speciation in sewage sludge from different locations in Iran

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Abstract

More than 80% of sewage sludge (SS) produced in Iran is landfilled with high environmental impact. The chemical properties of SS produced from wastewater plants of cites of Arak, Isfahan, Kermanshah, Rasht, Saveh, Shiraz, Sanandaj, Tehran, Takestan, and Toyserkan were studied to assess the potential beneficial effects of their application to agricultural soil as sustainable SS management. The pH and EC values, total content and water-soluble concentration of nutrients and heavy metals, their water-extractable pools were determined, and their speciation was done through the NICA–Donnan model using the Visual MINTEQ software. Relatively high contents of N, P, and physiologically active cations indicated potential beneficial effects of SS for land application in the agro-ecosystems, whereas the heavy metal content depended on the SS production site, with higher levels found in the SS of the Arak and Saveh wastewater treatment plants. The pH value was the main factor controlling the metal speciation, with Cu and Pb having the highest affinity for the organic matter, and Zn and Mn being mainly present as free ions or inorganic species. Results showed that SS from different locations in Iran differed in their main chemical properties and elemental composition and that speciation analysis could be used to predict potential beneficial and harmful effects of SS, particularly upon the modeling of metal–organic complexes by the NICA–Donnan approach. Globally, our results confirmed that while the SS produced in Iran has potential suitable chemical properties for use in agriculture, their heavy metals load should not be ignored.

Keywords Trace elements · Organic matter · Elemental speciation · Visual MINTEQ

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1 Introduction

Progressive increase in world population along with increasing urbanization is leading to an ever-increasing trend of sewage sludge (SS) production, with related problems of disposal strategies. Incorporation of SS into soil is a common agricultural practice accounting for ca. 50% of produced SS in EU countries (Torri et al. 2012), allowing the resupply of nutrients to crops, such as nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn) (Aggelides and Londra 2000; Allison and Richards 1954; Mtshali et al. 2014), and constituting an alternative to SS landfilling or incineration. Estimated SS production in Iran was in the order of 6.5×10^5 metric tons dry matter y^{-1} in 2008 (Mateo-Sagasta et al. 2015), with an estimate treatment 28% of the generated wastewater (Sato et al. 2013). Environmental SS disposal regulation mainly focuses on protection of public health, with less attention to environment protection. The SS production in Iran is increasing due to both increases in the proportion of severe population and implementation of more strict controls on wastewater treatment. Amendment of agricultural soils with SS increases the soil biological activity and nutrient availability to crop plants (Martínez and McBride 1999; Zaman et al. 2002), thus increases crop yield (Latare et al. 2014). The main SS positive effects on crops are due to N content, which generally ranges from 4 to 5% (Pakhnenko et al. 2009), and due to general soil amelioration in terms of structure, water retention and cation exchange capacity by increasing the adsorption sites for essential nutrients (Ashworth and Alloway 2008; Khaleel et al. 1981; Kim and Kim 1999). Latare et al. (2014) reported that the application of 40 t ha^{-1} SS increased grain yield of rice due to enhanced nutrient availability in the amended soils. However, a long-term perspective of sustainable management relying on the regular incorporation of SS in soil, the evaluation of SS quality is necessary to assess the potential effects on microorganisms, plant health, and soil fertility. In fact, SS use in agricultural soils of several world areas including Europe and North America is mainly regulated by the N agronomical dose and heavy metals content (McGrath et al. 1994; Torri et al. 2012) to prevent the release of excessive N into the ground waters and soil pollution. Organic pollutants (e.g., polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates, nonylphenols, surfactants) and pathogenic microorganisms have specific legislation limits in the USA and European countries. Also, SS usually contains elevated contents of heavy metals including Zn, Cu, nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg), and chromium (Cr) which can cause plant toxicity (Oleszczuk and Hollert 2011), reduce the soil microbial activity (Renella et al. 2007) and alter the soil microbial community structure (Gomes et al. 2010). Chemical functional groups such as -COOH and phenolic–OH present in fulvic acids (FA), and in general in the dissolved organic carbon (DOC) (Saar and Weber 1982), can form complexes with heavy metals (Tapia et al. 2010) increasing their solubility and bioavailability (Ashworth and Alloway 2008). Therefore, prediction of heavy metal solubility in SS-amended soils can be done after a characterization of the SS organic C quality. Additional chemical factors in the global evaluation of SS use in the agricultural soils are salinity and the potential macronutrient imbalance; for example, high exchangeable sodium content can hinder Ca uptake in plants (Sumner and Naidu 1998).

Main soil properties such as the pH value, clay, and organic matter (OM) content are factors influencing the heavy metals speciation and availability to plants and microorganisms through their sorption reactions onto the reactive soil solid phases (Alvarez et al. 2002; Naidu et al. 2003). Various analytical techniques have been developed to determine the heavy metals lability and mobility in soil (Fadiran et al. 2014; Roussel 2013; Kumpiene et al. 2017). Modeling of ion binding to humic and fulvic acids (FA and HA) in soil is complex due to their inherent heterogeneity, and the ion-binding dependency upon environmental variables such as pH value, ionic strength and competing ions, metal concentration, and metal speciation in the liquid phase (Milne et al. 2001). These chemical factors significantly influence the ion electrostatic attraction, ion exchange, and chemical complexation (Chang et al. 2006). Among the models that can be used to assess the ion-binding behavior of HAs, the non-ideal competitive adsorption NICA–Donnan model is widely used and has proven to provide reliable results (Kinniburgh et al. 1999; Koopal et al. 2005; Li 2014), as this model combines the use of thermodynamic parameters and Donnan descriptions of the electrostatic behavior of the humic substances (Pedra et al. 2008).

Currently, there is no comprehensive knowledge about principal characteristics of SS in Iran, and because an increase in SS production and in land application in Iran is anticipated, a chemical characterization of SS produced by the wastewater treatment plants of the most densely inhabited areas is advisable. The objectives of this study were to: (i) determine the chemical characterization of SS produced from different cities of Iran, (ii) analyze the speciation of elements in the SS water-soluble phase identifying the dominant soluble metal species and the saturation indices of the solid phases controlling metal solubility, and (iii) evaluate the solid/solution elemental partition to assess the factors influencing the dynamics of heavy metals released by the studied SSs. Results of this study provide information about the quality of SS currently produced from different locations in Iran, that can help local stakeholders (e.g., farmers and policy makers) in the sustainable and safe use of SS in Iranian agriculture.

2 Materials and methods

2.1 Sewage sludge sampling and preparation

Ten wastewater treatment plants of the Iranian cities of Arak, Isfahan, Kermanshah, Rasht, Saveh, Shiraz, Sanandaj, Tehran, Takestan, and Toyserkan were selected for SS sampling, and all SSs were sampled in March 2015. The inhabitants of these cities are as follows: Arak (591,756), Isfahan (2,243,249), Kermanshah (1,083,833), Rasht (956,971), Saveh (283,538), Shiraz (1,869,001), Sanandaj (501,402), Tehran (8,737,510), Takestan (172,636), and Toyserkan (101,666). The studied SSs originated from municipal wastewater treatment plants, except the SSs of Saveh and Arak originating from a treatment plant receiving both municipal and industrial wastewaters. The wastewater treatment processes for all SSs included: settlement tank, waste stabilization pond, constructed wetland, percolating filter, and anaerobic digestion. At each location, 5 SS samples were taken and mixed to obtain a composite SS sample. All SS samples were air-dried at room temperature for 1 month, crushed, and passed through a 2-mm sieve for eliminating plant roots, stones, plastics, grass, and other impurities.

2.2 Determination of total content of cations and anions

Total cations, anions and heavy metals content in the SSs were determined according to Cao et al. (2010). Finely ground SS samples (0.2 g) were digested with concentrated HNO_3 (4 ml) on a hot plate for 1 h at 60 °C, and then the temperature was increased to 100 °C for 90 min.

The SS samples were then added with 0.2 ml of 8.8 M hydrogen peroxide and left at room temperature for 30 min. The mineralized samples were filtered and the extracts were brought to 25 ml volume and the solution samples were stored prior to elemental analysis. The concentration of Cd, Ni, Pb, Cu, Zn, Fe, Mn, cobalt (Co), and Cr was analyzed by atomic absorption spectrophotometry (AAS; Varian, spectra 220). The Ca and Mg contents were quantified by complexometric titration, and K and Na contents were measured by flame emission spectrometry (Sakala et al. 2004). Sulfate (SO_4), chloride (Cl), phosphate (PO_4), and bicarbonate (HCO_3) concentrations were analyzed by $BaSO_4$ gravimetric analysis, $AgNO_3$ titration, ammonium molybdate complexation followed by spectrophotometric quantification, and H^+ titration, respectively (Zhang et al. 2008). Nitrate (NO_3) concentration was determined colorimetrically (Mulvaney 1996). Total organic C (TOC) and N content of all SSs were determined by Kjeldahl digestion (Rowell 2014), and Walkley and Black (1934) methods, respectively.

2.3 Measurement of pH and electrical conductivity (EC) values, DOC, and ion water-extractable concentration

The water-soluble phase of the SS was extracted in duplicate using a dried SS:deionized water ratio of 1:10 by end-over-end shaking for 30 min at 25 °C. After extraction, the suspensions were centrifuged (4200×*g*) for 10 min and filtered using Whatman 0.45-mm cellulose filters. The extracts were analyzed for the pH and EC values, and concentrations of Ca, Mg, K, Na, Cl, HCO_3, PO_4, NO_3, SO_4, and DOC. Cation and anion concentrations were determined by the analytical methods mentioned above, and the DOC content was measured according to Walkley and Black (1934).

2.4 Chemical speciation of elements in the water-soluble phase of SS

Elemental speciation and calculation of the saturation index (SI) of water-soluble phases were conducted using the geochemical speciation program Visual MINTEQ version 3 (Gustafsson 2011). For speciation, the input data were concentration of the cations and anions, pH value, and DOC in the soluble phase of SSs. The speciation was done in temperature 25 °C and CO_2 pressure 3.8×10^{-4} atm (default od MINTEQ program). Modeling of the results was carried out to simulate the formation of complexes between metals and DOC. The prediction was run using the NICA–Donnan model (Kinniburgh et al. 1999), which models complexation of metals to humic materials by two types of binding sites, carboxylic (weak) and phenolic (strong). The SI value for each solid was defined as log IAP (logarithm of the ion activity product)—log Ks (Ks is the temperature-corrected solubility constant). Values of $SI > 0$ indicated oversaturation of the solution with respect to the solid phase, $SI < 0$ indicated undersaturation of the solution as compared to the solid phase, whereas $-0.5 < SI < 0.5$ indicated equilibrium between solid and solution phases (Allison et al. 1991). The PAS 100 standard values of the UK legislation for SS and composts (BSI 2005) were taken as a reference.

3 Results

3.1 Total and water-soluble components of SS

The total content of C, N, cations and anions, and OM content of SSs are reported in Table 1. The OM content of the SSs ranged from 29.6 to 55.7%, with a median of 42.8%, total N content of samples was relatively high, and the C/N ratio values ranged from 7.8 to 17.7 (Table 1), with higher values for the SS originated from both municipal and industrial wastewaters (Kaveh Industrial City—Saveh) than that of the other locations.

Total heavy metals content, along with the PAS 100 standard values, are reported in Table 2. The average of total metal content (mg kg^{-1}) in the studied SSs was as follows: Fe (8584), Zn (1118), Mn (185.6), Pb (120.5), Cu (100.0), Cr (49.2), Ni (31.6), Cd (9.6), and Co (0.83). The Cd content exceeded the PAS 100 limits in all the studied SSs, the Pb and Ni content were higher than the PAS 100 limits only in the Saveh SS, the Zn content was higher than PAS 100 limit in all SSs, except the Isfahan SS, the Cr content was higher than PAS 100 limit in SSs from Saveh and Arak, whereas the Cu content was below the PAS 100 limits in all SS samples (Table 2).

The pH and EC values, and the concentrations of H_2O-soluble DOC and nutrient cations and anions are reported in Table 3. The pH values of the SSs varied from 5.9 (Toyserkan) to 8.9 (Saveh); the EC values of SSs ranged from 1.5 (Tehran) to 4.6 dS m^{-1} (Arak). Concentrations of H_2O-soluble PO_4^{3-} were 143, 124, and 101 mg l^{-1} in the SSs from Tehran, Kermanshah, and Toyserkan, respectively. The DOC content ranged from 1544 (Saveh) to 727 mg l^{-1} (Shiraz). Among the measured heavy metals, Pb had the maximum concentration in the soluble phase of the studied SSs (Table 4).

Table 1 Total content of cations and anions along with C%, OM%, N%, and C/N ratio value in the studied sewage sludges

Sampling place	Ca	Mg	K	Na	Cl	NO_3	SO_4	PO_4	C	OM	N	C/N
	mg g^{-1}								%			
Arak	46.0	26.4	1.7	2.9	27.8	7.5	49.3	13.5	20.9	36.3	2.0	10.3
Isfahan	60.0	24.0	2.5	4.1	49.6	10.4	41.8	12.7	26.2	45.6	2.8	9.4
Kermanshah	52.0	39.6	3.1	2.7	39.4	10.6	79.8	22.6	21.3	37.1	2.5	8.7
Rasht	44.0	27.6	3.6	2.7	59.2	7.6	41.3	20.1	17.0	29.6	2.3	7.4
Sanandaj	40.0	18.0	2.2	2.7	84.6	6.3	40.0	12.7	25.7	44.7	3.3	7.8
Saveh	32.0	4.8	4.6	11.5	233.3	6.5	39.3	7.9	31.0	54.0	1.8	17.7
Shiraz	80.0	12.0	0.9	2.8	71.1	6.3	58.5	7.2	21.3	37.1	2.0	10.5
Takestan	46.0	14.4	4.2	3.5	87.5	8.2	44.3	4.6	22.8	39.7	2.2	10.2
Tehran	40.0	18.0	3.2	4.0	131.3	7.0	34.0	15.2	27.8	48.4	3.4	8.3
Toyserkan	50.0	9.6	5.0	2.4	116.7	24.1	38.0	18.5	32.0	55.7	3.5	9.1
Average	49.0	19.4	3.1	3.9	90.0	9.4	46.6	13.5	24.6	42.8	2.6	9.9

Values are the means of two replicates

Table 2 Total heavy metals content in the studied sewage sludges

Sampling place	Fe mg kg^{-1}	Mn	Cu	Zn	Cd	Ni	Pb	Co	Cr
Arak	16,043.8	275.3	91.3	2077.0	15.3	48.8	98.5	0.0	144.7
Isfahan	5533.8	135.7	127.3	259.6	6.1	17.9	92.5	1.1	30.0
Kermanshah	6897.5	184.2	82.2	909.1	9.1	43.4	118.0	6.6	17.6
Rasht	12,672.5	160.5	116.6	2031.1	11.2	23.3	56.0	0.0	23.5
Sanandaj	7713.8	288.6	78.7	950.6	5.9	23.8	62.5	0.6	12.8
Saveh	5226.3	198.0	162.6	2065.1	9.7	59.3	462.0	0.0	174.1
Shiraz	4317.5	123.7	57.5	442.4	9.5	28.0	137.0	0.0	49.3
Takestan	12,542.5	270.0	102.2	407.9	6.3	29.6	79.5	0.0	10.6
Tehran	5127.5	192.5	56.3	927.3	5.8	12.7	55.0	0.0	0.0
Toyserkan	9765.0	172.4	125.0	1115.4	17.2	29.0	44.5	0.0	29.3
Average	8584.0	185.7	99.9	1118.6	9.6	31.5	120.6	0.8	49.2
UK PAS 100 limits	–	–	200.0	400.0	1.5	50.0	200.0	–	100.0

Values are the means of two replicates

3.2 Speciation of elements in the water-soluble phase

Results of the elemental chemical speciation obtained from the MINTEQ chemical speciation software (using data reported in Tables 3 and 4 as input) are presented in Table 5 as predominant species for each studied SS. The FA1 and FA2 in Table 5 represent the two types of DOC strong and weak sites for bounding cations, whereas species shown as ‘cation + 2D’ are attributed to portion of that cation that is bound to the Donnan gel phase via the counterion accumulation effect, which is in turn controlled by charge balance. Speciation of CO_3^{2-} indicated that this anion in solution was present as HCO_3^-, H_2CO_3, and CO_3^{2-}. The CO_3 species in the Toyserkan and Saveh SSs were different from those of other SSs having acidic and alkaline pH values, respectively, with the Toyserkan SS having 67% of H_2CO_3, and the Saveh SS having 89.8 and 5.9% of HCO_3^- and CO_3^{2-}, respectively (Table 5). The majority of Ca bound to the Donnan gel phase accounted for 17–87% (Table 5), whereas the average Ca^{2+} free ion was 35.7% (Table 5). The percentage of $CaCO_3$ (not reported) was lower than OM, indicating the preferential complexation of Ca with DOC instead of precipitation as $CaCO_3$. Predominant H_2O-soluble Mg species were (6)Mg + 2D(aq) (average 40.6%), whereas K and Na complexation with DOC was low leading to high proportions of free ion concentration for K (85.8%) and Na (85.9%). Among the anions, more than 98% of Cl and NO_3 were in Cl^- and NO_3^- forms, whereas HPO_4^{2-} and $H_2PO_4^-$ accounted for 38.1% and 36.4% of H_2O-soluble P species (as average), respectively (Table 5). The percentage of H_2O-soluble PO_4^{3-} was high only in the SS from Shiraz, whereas it was zero in the other studied SSs. The predominant H_2O-soluble S species was SO_4^{2-}, with an average of 79.2% (Table 5).

Speciation of H_2O-soluble heavy metals showed different values depending on the considered metal (Table 5). Water-soluble Fe 100% bound to DOC, whereas 100% of Mn was present as Mn^{2+} free ion (Table 5) and Zn was mostly present as free ion in SSs from Toyserkan, Arak, Shiraz, Takestan, and Kermanshah. In the Rasht, Tehran, Sanandaj, and Isfahan SSs Zn was present as Zn + 2D(aq) bound to the Donnan gel phase via the counterion accumulation effect, whereas the dominant species of H_2O-soluble Zn of Saveh SS

Table 3 Chemical properties and soluble concentration of some cations and anions of the in the studied sewage sludges

Sampling place	pH	EC ($dS\ m^{-1}$)	Ca $mg\ l^{-1}$	Mg	K	Na	Cl	HCO_3	PO_4	NO_3	SO_4	DOC
Arak	7.4	4.6	440.0	156.0	12.4	63.3	96.3	244.0	1.4	25.4	1456.0	783.1
Isfahan	7.3	3.4	300.0	120.0	62.1	84.5	148.8	1049.2	16.8	47.5	423.0	1484.7
Kermanshah	6.1	4.5	400.0	300.0	66.6	36.5	105.0	463.6	124.0	111.0	443.0	1098.4
Rasht	7.4	1.9	170.0	48.0	42.2	47.1	113.8	366.0	23.3	35.6	283.0	1059.0
Sanandaj	6.7	2.3	160.0	114.0	39.2	45.1	152.3	939.4	37.1	26.4	1070.0	1188.8
Saveh	8.9	2.9	250.0	102.0	73.0	74.9	700.0	671.0	31.7	25.1	750.0	1543.6
Shiraz	7.3	1.9	260.0	60.0	23.3	30.5	113.8	268.4	5.9	30.9	286.0	727.0
Takestan	6.8	5.1	480.0	252.0	10.9	69.4	140.0	109.8	2.3	45.9	1123.0	1054.3
Tehran	7.5	1.5	150.0	30.0	44.2	56.7	105.0	707.6	142.7	16.9	220.0	1285.7
Toyserkan	5.9	4.1	400.0	162.0	68.6	58.8	140.0	366.0	100.7	124.9	1000.0	1480.4
Average	7.14	3.2	301.0	134.4	44.2	56.7	181.5	518.5	48.6	49.0	705.4	1170.5

Values are the means of two replicates

Table 4 Soluble concentration of heavy metals in the studied sewage sludges

Sampling place	Fe mg l^{-1}	Mn	Cu	Zn	Cd	Ni	Pb	Co	Cr
Arak	0.10	0.33	0.08	0.12	0.07	0.10	0.63	0.07	0.08
Isfahan	0.96	0.03	0.35	0.22	0.05	0.11	0.91	0.01	0.05
Kermanshah	0.68	0.26	0.05	0.11	0.02	0.07	0.94	0.08	0.08
Rasht	0.48	0.30	0.13	0.08	0.01	0.06	0.60	0.05	0.12
Sanandaj	0.54	0.29	0.05	0.27	0.02	0.23	0.83	0.03	0.04
Saveh	1.08	0.06	1.25	0.52	0.04	0.44	0.57	0.04	0.09
Shiraz	0.31	0.10	0.06	0.03	0.01	0.04	0.62	0.05	0.04
Takestan	0.29	0.83	0.03	0.01	0.03	0.07	1.00	0.06	0.00
Tehran	0.79	0.03	0.04	0.12	0.03	0.07	0.69	0.03	0.06
Toyserkan	0.26	0.38	0.00	0.56	0.20	0.07	0.55	0.03	0.03
Average	0.55	0.26	0.20	0.20	0.05	0.13	0.73	0.05	0.06

Values are the means of two replicates

was $ZnCO_3$ (aq) (Table 5). In all the studied SSs, more than 98% of Cd species was FA-Cd (6)(aq), indicating binding of Cd to weak sites of humic acid (Table 5). Predominant form of H_2O-soluble Ni was the tightly bound FA1-Ni (6)(aq), with an average of 59.8%, with the exception of the Saveh SS (Table 5). The H_2O-soluble Pb species were dominated by the FA2-Pb(6)(aq) form, with an average of 95.6% (Table 5). The dominant species of H_2O-soluble Cr was $HCrO_4^-$ in the Toyserkan and Kermanshah SSs, whereas in the other SSs most of the Cr was present as chromate anion, CrO_4^{2-} (Table 5). Water-soluble Cu was predominantly (90.2%) bound to the DOC as FA2-Cu (6) (aq), whereas the H_2O-soluble Co was approximately 100% present as $CoOH^+$ (Table 5).

3.3 Calculation of saturation index

Potential precipitation of H_2O-soluble elements in the different SSs was examined by calculating the SI of selected minerals allowed by the Visual MINTEQ software. Results of SI of Ca, Mg, and K minerals for the studied SSs are shown in Fig. 1. Values of SI of Ca, Mg, and K minerals in the soluble phase of SSs showed undersaturation for all SSs with respect to dolomite, except for the Saveh, Arak, and Isfahan SSs where dolomite precipitation was anticipated (Fig. 1). The formation of hydroxyapatite could be attributed to the simultaneous presence of Ca and P in solution. The H_2O-soluble phase of Saveh SS was oversaturated with respect to most of the selected solid phases and only was undersaturated with respect to gypsum (Fig. 1), likely due to high pH value. In contrast, in the H_2O-soluble phase of Tehran SS, all Ca minerals had $SI < 0$, except for hydroxyapatite (Fig. 1). All SSs solutions were undersaturated with respect to all the Mg minerals, except the Saveh SS, which was oversaturated to magnesite (Fig. 1). The soluble phase of all the studied SSs was undersaturated to K minerals (Fig. 1). The SI of Na, Cu, and Cd minerals in the solutions of the studied SSs is shown in Figure S1 (supplementary data). All the SS solutions were undersaturated to Na, Cu, and Cd minerals (Figure S1). The SI of minerals containing Fe, Pb, and Pb was less than zero in all SS samples (Figure S2). The SI of Co indicated oversaturation with respect to $Co(OH)_3$(s) for all the studied SS, with the Saveh SS having the higher values (Figure S3). Chromium and Ni minerals had SI values lower than zero,

Table 5 Speciation of soluble components in the water-extractable phase of the studied sewage sludges

Component	Species name	Arak	Isfahan	Kermanshah	Rasht	Sanandaj	Saveh	Shiraz	Takestan	Tehran	Toyserkan	Average
CO_3^{2-}	CO_3^{2-}	0.2	0.2		0.2		5.9	0.1		0.2		1.1
	HCO_3^-	88.1	89.4	41.7	91.6	72.4	89.5	88.3	74.5	93.3	30.8	76.0
	$H2CO_3$ (aq)	6.6	7.6	54.7	7.3	26.6	0.2	8.3	19.8	6.4	67.8	20.5
Ca^{2+}	Ca^{2+}	50.9	33.2	66.0	16.9	23.4	15.8	51	57.1	0.5	42.5	35.7
	$CaSO_4$ (aq)	27.2	7.4	9.3	4.0	13.6	6.3	8.9	20.8	0.1	18.0	11.6
	(6)Ca + 2D(aq)	16.6	45.4	17.9	67.2	50.8	57.7	32.3	17.3	87.2	32.5	42.5
	FA1-Ca(6)(aq)	3.9	9.1	3.5	10.4	9.7	13.1	5.6	3.9	12.1	5.3	7.7
Mg^{2+}	Mg^{2+}	52.6	32.0	66.6	15.6	23.0	15.1	49.6	58.4	0.4	42.8	35.6
	$MgSO_4$ (aq)	22.3	5.7	7.5	2.9	10.6	4.8	6.8	16.9	0.1	14.4	9.2
	(6)Mg + 2D(aq)	17.2	43.8	18.1	62.2	50.1	55.3	31.4	17.7	77.5	32.8	40.6
	FA1-Mg(6)(aq)	6.6	14.6	5.1	17.9	14.1	20.6	10.2	6.1	21.8	8.6	12.6
K^+	K^{+1}	93.7	89.8	95.6	84.3	87.5	84.5	94.1	94.4	43.2	91.0	85.8
	KSO_4^-	3.3	1.2	0.9	1.0	3.1	2.1	0.9	2.3	0.4	2.4	1.8
	(6)K + 1D(aq)	2.9	8.8	3.2	14.5	9.1	12.8	4.9	3.2	56.1	6.2	12.2
Na^+	Na^{+1}	94.3	89.6	95.7	84.3	87.8	84.2	94.1	94.8	43.1	91.5	85.9
	(6)Na + 1D(aq)	2.9	8.7	3.2	14.5	9.2	12.7	4.9	3.2	56	6.2	12.2
Cl^-	Cl^{-1}	98.6	99.1	97.5	99.7	99.6	99.6	99.1	98.0	99.9	98.7	99.0
PO_4^{3-}	PO_4^{-3}						0.1	42.5				21.3
	HPO_4^{-2}	40.4	47.7	10.2	59.8	31.6	65.2	21.5	25.5	71.7	7.4	38.1
	$H2PO_4^-$	14.8	20.9	65.7	26.3	58.2	0.7		32.9	27.2	81.3	36.4
	MgHPO4 (aq)	18.8	13.2	12	4.5	5.5	6.3	11.2	21	0.1	3.3	9.6
	$CaHPO_4$ (aq)	22.6	15.1	7	7.5	3.4	7.1	21.9	17.2	0.2	3.5	10.6
NO_3^-	NO_3^-	99.1	99.4	98.9	99.7	99.8	99.7	99.3	98.9	99.9	99.2	99.4

Table 5 (continued)

Component	Species name	Arak	Isfahan	Kermanshah	Rasht	Sanandaj	Saveh	Shiraz	Takestan	Tehran	Toyserkan	Average
SO_4^{2-}	SO_4^{2-}	70.3	79.8	59.2	91.4	89.9	91.3	74.6	63.1	99.3	72.6	79.2
	$MgSO_4$ (aq)	9.4	6.4	20.0	2.0	4.5	2.6	5.7	15	0.0	0.0	6.6
	$CaSO_4$ (aq)	19.7	12.6	20.2	5.8	4.9	5.0	19.3	21.3	0.1	9.2	11.8
	$NaSO_4^-$	0.5	0.8	0.2	0.5	0.4	0.7	0.3	0.5	0.4	17.3	2.2
Fe^{3+}	FA2-Fe(III)(6)(aq)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0
Mn^{3+}	Mn^{3+}	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zn^{2+}	Zn^{2+}	43.3	24.8	59.0	13.4	20.9	3.9	39.4	44.6	0.4	40.4	29.0
	FA2-Zn(6)(aq)	2.1	2.4	0.4	2.5	0.6	9.5	3.1	2.7	0.8	0.2	2.4
	$Zn(OH)_2$ (aq)	0.2	0.1	0.2	0.1	0.0	16.9	0.1	0.0			2.5
	$ZnCl^+$	22.1	5.3	8.0	3.0	11.6	0.1	6.5	15.5	0.1	0.2	7.2
	$ZnSO_4$ (aq)	2.1	0.2	0.2	0.1	1.0	1.5	0.1	1.0		16.3	2.5
	$ZnCO_3$ (aq)	3.9	10.3	0.3	2.7	1.4	35.6	4.4	0.4	0.2	0.1	5.9
	(6)Zn + 2D(aq)	14.2	33.9	16	53.4	45.3	14.3	24.9	13.5	75.9	30.9	32.2
Cd^{2+}	Cd^{2+}	1.3	0.2	1.1	0.1	0.1	0.0	0.4	1.0		1.3	0.6
	FA1-Cd(6)(aq)	90.1	92.3	96.1	92.7	96.9	56.4	90.4	93.6	97.8	96.1	90.2
	FA2-Cd(6)(aq)	7.1	6.9	1.9	6.9	2.4	43.2	8.7	4.6	1.7	0.6	8.4
Ni^{2+}	Ni^{2+}	5.2	1.4	11.3	0.7	2.8	0.1	2.7	6.5	0.0	5.2	3.6
	FA1-Ni(6)(aq)	46.3	54.7	70.0	62.9	74.7	13.8	52.8	60.6	82.2	80.1	59.8
	FA2-Ni(6)(aq)	42.9	39.8	11.6	33.3	12.4	84.9	41.3	28.3		8.0	33.6
FA1-Pb(6)(aq)	FA1-Pb(6)(aq)	1.5	2.1	6.5	3	5.7	0.4	2.1		7.6	10.8	4.4
FA2-Pb(6)(aq)	FA2-Pb(6)(aq)	98.4	97.9	93.4	97	94.3	99.6	97.9		92.4	89.2	95.6
Co^{2+}	$CoOH^+$	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
CrO_4^{2-}	CrO_4^{2-}	55.5	66.3	31.2	79.4	65.6	86.7	56.4	46.7	92.1	25.8	60.6
	$HCrO_4^-$	4.2	5.9	41.1	7.2	24.8	0.2	5.8	12.3	7.2	58	16.7
	$CaCrO_4$ (aq)	39.9	27	27.4	12.9	9.1	12.2	37.5	40.6	0.3	15.8	22.3

Table 5 (continued)

Component	Species name	Arak	Isfahan	Kermanshah	Rasht	Sanandaj	Saveh	Shiraz	Takestan	Tehran	Toyserkan	Average
Cu^{2+}	FA1-Cu(6)(aq)	2.1	4.8	16.4	5.6	12.1	0.4	2.9	3.5	14.4		6.9
	FA2-Cu(6)(aq)	97.9	95.2	83.6	94.4	87.9	99.6	97.1	96.5	85.6	100.0	93.8
Pb^{+2}	Pb^{+2}			0.02							0.01	0.02
	$PbSO_4$ (aq)			0.02							0.01	0.02
	FA1-Pb(6)(aq)	1.55	2.13	6.49	2.97	5.67	0.36	2.08		7.55	10.79	4.40
	FA2-Pb(6)(aq)	98.45	97.85	93.45	97.03	94.31	99.63	97.91		92.44	89.17	95.6

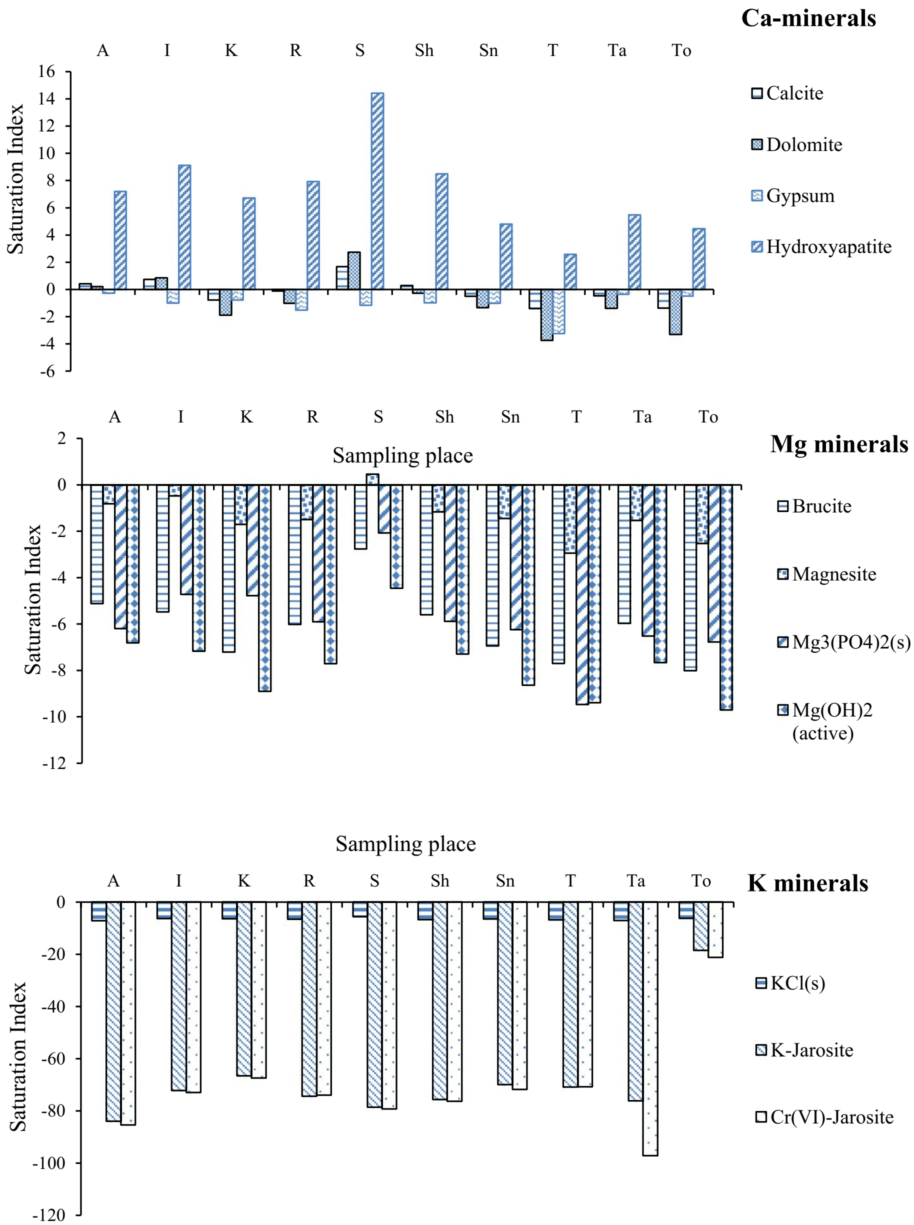

Fig. 1 Saturation index of Ca, Mg, and K minerals in water-soluble phase of different sewage sludges (A: Arak, I: Isfahan, K: Kermanshah, R: Rasht, S: Saveh, Sh: Shiraz, Sn: Sanandaj, T: Tehran, Ta: Takestan, and To: Toyserkan)

indicating the undersaturation of the solution with respect to Ni and Cr minerals (Figure S3).

Analysis of elemental speciation between inorganic and organic forms is reported in Table 6. The average results indicated that more than 60% of Ca in the Saveh, Rasht,

Table 6 Distribution of H2O-soluble components between inorganic and organic phases in the studied sewage sludges

Component	Arak		Isfahan		Kermanshah		Rasht		Saveh	
	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC
Ca^{2+}	79.5	20.5	45.1	54.9	78.5	21.5	22.3	77.7	28.9	71.1
Cd^{2+}	2.4	97.6	0.5	99.5	1.7	98.3	0.1	99.9	0.3	99.7
Cl^{-}	100.0	0.0	99.9	0.1	100.0	0.0	100.0	0.0	100..0	0.0
Co^{3+}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
CO_3^{2-}	99.9	0.1	99.8	0.2	99.9	0.1	99.9	0.1	99.9	0.1
CrO_4^{2-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Cu^{2+}	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0
Fe^{3+}	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0
K^{+}	97.1	2.9	91.2	8.8	96.8	3.2	85.5	14.5	87.2	12.8
Mg^{2+}	76.2	23.9	41.3	58.7	76.7	23.2	19.8	80.2	23.8	76.2
Mn^{3+}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Na^{+}	97.1	2.9	91.3	8.7	96.8	3.2	85.5	14.5	87.3	12.7
Ni^{2+}	9.1	90.9	3.5	96.5	15.2	84.7	1.2	98.8	0.9	99.1
NO_3^{-}	100.0	0.0	99.9	0.1	99.9	0.01	100.0	0.0	100.0	0.0
Pb^{2+}	0.0	100.0	0.0	100.0	0.1	99.9	0.0	100.0	0.0	100.0
PO_4^{3-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
SO_4^{2-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Zn^{2+}	74.7	25.3	48.9	51.2	74.4	25.6	22.7	77.3	69.2	30.8
Ca^{2+}	62.1	37.9	39.3	60.7	0.7	99.3	78.8	21.2	68.8	31.2
Cd^{2+}	0.6	99.4	0.3	99.7	0.0	100.0	1.5	98.5	8.0	92.0
Cl^{-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Co^{3+}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
$CO3^{2-}$	99.8	0.1	100.0	0.1	100.0	0.0	99.8	0.2	100.0	0.0

Table 6 (continued)

Component	Arak		Isfahan		Kermanshah		Rasht		Saveh	
	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC	Dissolved inorganic	Bound to DOC
CrO_4^{2-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Cu^{2+}	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.00	100.0
Fe^{3+}	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.00	100.0
K^+	95.1	4.9	90.9	9.1	43.9	56.1	96.8	3.2	97.1	2.9
Mg^{2+}	58.3	41.7	35.7	64.3	0.6	99.4	76.2	23.8	71.2	28.8
Mn^{3+}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Na^+	95.1	4.9	90.8	9.2	44.1	55.9	96.8	3.2	97.1	2.9
Ni^{+2}	4.1	95.9	6.5	93.5	0.1	99.9	9.1	90.9	5.0	95.0
NO_3^-	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Pb^{2+}	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.1	99.9
PO_4^{3-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
SO_4^{2-}	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
Zn^{2+}	54.9	45.1	40.1	59.9	1.1	98.9	63.0	37.0	12.0	88.0

Data are presented as % of the total element concentrations reported in Table 4

Tehran, and Sanandaj SSs was inorganic, the rest was bound to DOC and 97% of Cd was bound to DOC, whereas > 99% of Co, Cr, Mn, NO_3, PO_4, and SO_4 were present in inorganic form (Table 6). In all the SS samples 100% of the Cu, Pb, and Fe and more than 90% of Ni were bound to DOC. In addition, more than 85% of Na and K in the SS samples were attributed to inorganic form.

4 Discussion

The relatively high average N content of the studied SSs indicated their potential use in the Iranian agro-ecosystems and is in line with previously published values (Mtshali et al. 2014). However, a C/N ratio value was observed for the SS from Kaveh industrial city, and caution should be taken in case of use because incorporation of SS with high C/N ratio values into soil may lead to N immobilization by soil microorganisms (McGrath et al. 1994). The aerobically digested SSs have generally higher N mineralization rates than the anaerobic SSs in the soil (Serna and Pomares 1992), with the predominant N mineralization in SS-amended soils occurring in the first 28 d of incubation (Pakhnenko et al. 2009; Terry et al. 1979). Therefore, using SS in soil can provide N for crops in first weeks of application. Early stages of SS mineralization are dominated by the C and N mineralization by soil microorganisms, but the length of the C-dominated phase also depends on the C availability and can be predicted from the quantification of the DOC content. Among the other macronutrients, soluble PO_4 concentrations in the SSs of Tehran, Kermanshah, and Toyserkan were high enough to meet the plant P requirements for optimal crop production. Phosphorus speciation is important in the perspective of using SS for integrating or even replacing the use of P fertilizers in agricultural soils (Nyamangara and Mzezewa 2001; Torri et al. 2017). The average concentration of macronutrients in the studied SSs were in the same order of magnitude of those of previous studies (Ambily and Jisha 2012; Renella et al. 2007; Zheng et al. 2013). Results of chemical speciation showed that the pH value was the main factor controlling the CO_3 species (Table 5). In particular, in the soluble phase of Toyserkan SS with low pH value (5.9), 30.8% and 67.8% of carbonate was present as HCO_3^- and H_2CO_3, respectively, while for Saveh SS with high pH value (8.9) these values were 89.5% and 0.2%, respectively. In general, the $CaCO_3$ percentage was relatively low indicating the preferential complexation of Ca with DOC (Table 6) instead of precipitation as $CaCO_3$, although Ca, HCO_3^-, and SO_4^{2-}, along with Cl^-, showed relatively high content in all the studied SSs (Tables 3). The results were in agreement with the results of Li (2014). However, during the OM decomposition process, SS can release cations (e.g., Na, K, Ca, and Mg) in soil leading to a shift from organically bound to inorganic cations in soil (Nikolova-Kuscu et al. 2013), which may in turn increase soil salinity and EC values of SS-amended soils to levels that can inhibit plant growth (Allison and Richards 1954).

The studied SSs contained variable amounts of different heavy metals. Elevated heavy metals content in SS is mainly caused by a concentration effect related to drying and composting, but also depends on the quality of local wastewaters and, eventually sewerage connection between household and industrial effluents (Mtshali et al. 2014). Metal-contaminated SS impacts microbial diversity and biochemical functionality of agricultural soils (Liu and Sun 2013; Zhang et al. 2013). High variability of the heavy metals composition and contents in SS from various locations has been reported (Kidd et al. 2007; Ščančar et al. 2000; Usman 2008). Total metals content in SS does not allow predicting their toxic effects to plants and soil microorganisms, as metal toxicity to plants and soil biota is related to their bioavailability, which is related to their solubility and free ion concentration (Renella et al. 2004; Kumpiene et al. 2017). Results of metal speciation confirmed the previously reported high affinity of Cu and Pb for the OM, and the tendency of Zn and Mn to predominantly persist as free ions or inorganic species (Fadiran et al. 2014; Pérez-Esteban et al. 2014; Plaza et al. 2006; Roussel 2013), with a strong influence of the pH value on the metal speciation, e.g., $ZnCl^+$ and $ZnOH^+$ at low pH values, and also $ZnHCO3^+$, $Zn(OH)_2^0$, and $ZnCO_3^0$ at neutral–alkaline pH values. Schaecke et al. (2002) reported that the majority of Cu, Ni, and Cd in SS were bound to the OM. It is important to underline that the metal solubility in SS-amended soils results from the complex interplay of several variables. For example, Zhou and Wong (2001) reported that application of SS decreased Cu sorption in soil due to its complexation by DOC of SS in the soluble phase, especially at alkaline pH values. Also, Ashworth and Alloway (2008) confirmed the relationship between solubility of the Cu and DOC, particularly at high pH value. Therefore, metal speciation results from the dominance of the soil physicochemical properties and the changes occurring in the SS after incorporation into soils (Andrés and Francisco 2008).

Our study on the SI values for different minerals showed that different ion species could potentially form different minerals, controlling the metal bioavailability, solution-to-solid phase partition, and transport into the environment (Hooda 2010). For example, SSs from Saveh, Arak, Shiraz, and Isfahan were supersaturated to calcite, suggesting caution in the application of these SSs to the agricultural calcareous soils, to prevent pore clogging upon carbonate precipitation.

Results of the present study also suggest caution in the use of SS produced by the Arak and Saveh wastewater treatment plants due to their high heavy metals content. In fact, metal–organic complexes with low molecular weight organic ligands can have toxic effects on plants and soil microorganisms through metal solubilization effects, as beside the free hydrated metal ions, also the labile metal complexes formed between metals and fulvic acids may also contribute to the metal bioavailable fraction (Martínez and McBride 1999; Pérez-Esteban et al. 2014). To our knowledge, farmers from the Arak and Saveh in this area apply SS to the agricultural soils to improve soil fertility, with low consideration of their potential toxic effects in the long term.

5 Conclusions

Results from this study showed that SS from different locations in Iran had very different main chemical properties and elemental composition, but confirmed their potential to sustain the fertility of Iranian agricultural soils, owing to their nutrient content. However, the high metal content of the Arak and Saveh SSs, probably formed from effluents generated from industries, may pose environmental risks, thus limiting their use in agriculture. Based on the obtained results, the application of these SSs in agricultural soils is not recommended. The results of metal speciation achieved by chemical modeling confirmed the high affinity of Cu and Pb for the OM and the tendency of Zn and Mn to predominantly persist as free ions or inorganic species. It will be also important to monitor the shift of Na, K, Ca, and Mg cations from the organic to the inorganic forms, which may increase the salinity of in SS-amended soil in the long term. Modeling by the NICA–Donnan approach of the formation and dynamics of metal–organic complexes of nutrients and heavy metals during the SS decomposition into soil allows predicting the nutrient and metal bioavailability, transport, and fate in the environment. Overall, our study showed that a scientific-based perspective is needed for a nationwide plan of SS use in agriculture and evalation the potential beneficial and harmful effects of the SS incorporation into agricultural soils. This can be predicted by the study of metal speciation in the SS solid matrix and H_2O-soluble phase coupled with chemical modeling, not only from the determination of the total elemental content.

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