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Bari : CIHEAM / EU DG Research
Options Méditerranéennes : Série A. Séminaires Méditerranéens; n. 66

2005
pages 185-191

To cite this article / Pour citer cet article

Tawfik T. **Chemical speciation of selected metals in groundwater using geochemical model.** In : Hamdy A. (ed.). *The use of non conventional water resources.* Bari : CIHEAM / EU DG Research, 2005. p. 185-191 (Options Méditerranéennes : Série A. Séminaires Méditerranéens; n. 66)

CHEMICAL SPECIATION OF SELECTED METALS IN GROUNDWATER USING GEOCHEMICAL MODEL

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INTRODUCTION

Groundwater contains a wide variety of dissolved inorganic species in various concentrations, as a result of chemical and biochemical interactions between groundwater and the geological materials through which it flows, and to a lesser extent because of contributions from the atmosphere and surface water bodies.

The availability of various inorganic constituents in groundwater is controlled by the reaction mechanism such as dissolution- precipitation reactions and adsorption in addition to the rates (kinetics) of the geochemical process.

Analytical techniques such as spectrometry and chromatography provide important information about the total metals concentration available in water, but ions in groundwater can form unlimited number of species due to the hydrolysis, complexation, and redox reactions.

The purpose of this study is to estimate the activities of various ionic species of manganese, copper, lead and Zinc in groundwater using geochemical models from the measured total metals concentrations.

The selected four metals are of great importance to water chemistry. Manganese is an essential element in plant metabolism, and its organic compounds may influence its occurrence in natural waters. Copper is used extensively in Modern industry, and consequently disposed in the environment. Zinc is widely used in metallurgy, principally as a constituent of brass and bronze or for galvanizing. Such applications tend to increase its level in the environment. Lead is also produced from various activities specially car emissions and is extensively deposited in the environment.

The Visual MINTEQ speciation model was used to calculate ion activities. The model is a geochemical speciation model that is capable of computing specific equilibrium ion activities among the dissolved and adsorbed species and their equilibrium solid phase. The model is able to consider the interaction of metals with major anions (Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) as a function of temperature and ionic strength and pH.

MATERIALS AND METHODS

Water Quality Data

The investigation of groundwater chemistry in the study area started with the chemical analysis of samples collected from 30 deep groundwater wells (more than 100 m depth) in El-Sadat City; Fig (1). Collected samples were analyzed for major cations; Na^+, K^+, $Ca^{2+}$and Mg^{2+} and four trace metals; Pb, Cu, Mn and Zn according to standard procedures for the Inductively Coupled Plasma Optical Emission Spectrometric (ICP-OES). Major anions (Cl-, SO_4^{2-}, and NO_3^-) were also analyzed according to standard procedures for ion chromatography, the CO_3^{2-} and HCO_3^- were determined by titration and solution pH values were measured using a microprocessor pH meter.

Geochemical modeling

Geochemical modeling of the water composition was conducted with the Visual MINTEQ Model developed for the USEPA. The model is used to perform the calculations necessary to simulate the contact of waste solutions with heterogeneous sediments or the interaction of groundwater with solidified wastes. The computer equilibrium model contains thermodynamic database which contains equilibrium constants for aqueous simple and complex species as well as solubility product and redox potential, in addition to other equilibrium parameters. Visual MINTEQ can calculate ion species/solubility, adsorption, oxidation-reduction, gas phase equilibrium, and precipitation/dissolution of solid phases.

The following parameters were used to formulate the input files for Visual MINTEQ

1. Equilibrium solution pH values.
2. Total concentration of cations and anions
3. Room temperature

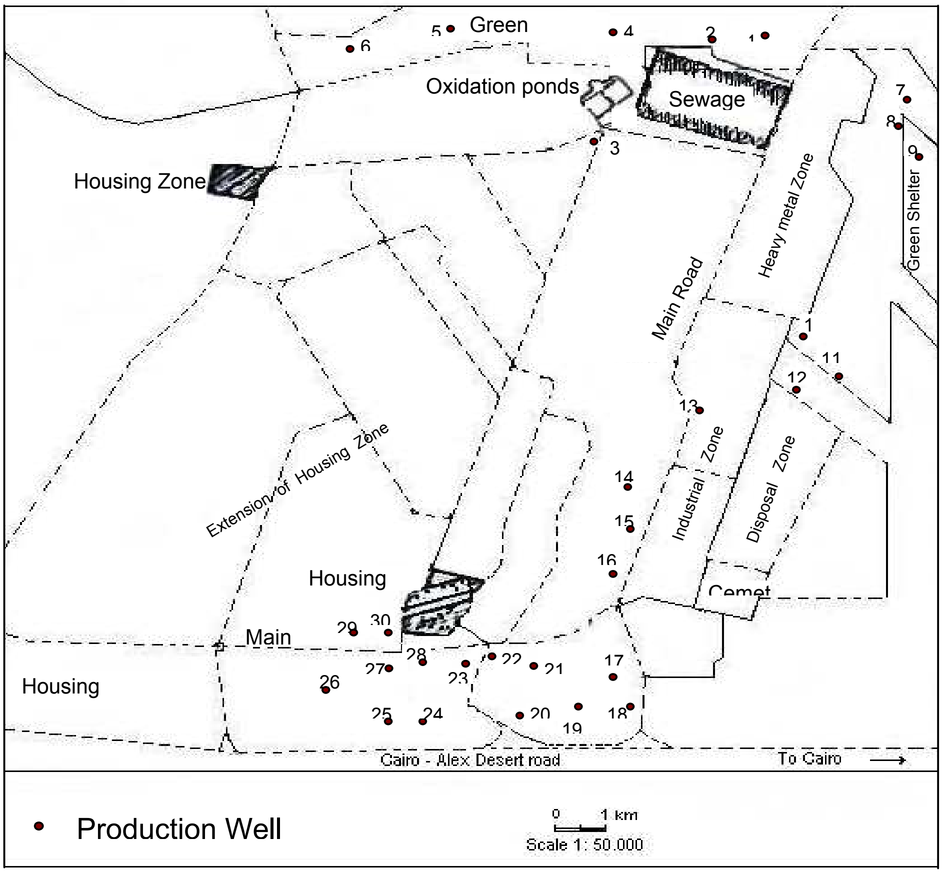

Fig. 1. The distribution of the tested wells in El-Sadat City

RESULTS AND DISCUSSION

Analytical data are provided in Table (I). The pH values for tested samples varied between 7.26 and 8.55. Manganese concentrations range was between 0.011 mg/l and 2 mg/l with an overall average of 0.093 mg/l. Copper was detected in only 13 samples with values less than 0.2 mg/l, and Zinc was detected in 22 samples with values less than 0.5 mg/l while lead was detected in 6 samples only out of the tested 30 well.

Tabulated analytical values of major cations, anions, trace metals and pH were used to create the input data file. Generated output by the model included the calculated ionic strength in analyzed samples and Activities of various metal ionic species whether free or complexed ions (Table 2).

Table 1. Results of chemical analyses for the groundwater wells in the study area

Serial		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pH	-----	8.33	7.57	7.79	7.70	7.58	8.55	7.78	7.39	7.53	7.49	7.34	8.22	7.4	7.61	7.3
Major Cations																
Calcium	mg/l	58.3	42	63.5	88.7	22.3	19.5	35.6	65.5	31.3	41.2	27	39.4	33.5	37	52.5
Potassium	mg/l	6.2	4.92	8.8	7.1	5.55	2.84	4.43	6.28	8.57	7.51	3.96	4.28	13.5	4.18	4.8
Magnesium	mg/l	20.9	26.5	17.2	30.7	18.5	18.5	23.8	18.2	20.3	26.0	15.9	20.7	26.4	29.6	17.8
Sodium	mg/l	55.4	110	118	119	58.5	80.6	61.3	130	87.9	76.2	50.5	75.5	94.3	55.4	52.5
Major Anions																
Chloride	mg/l	58.4	85.7	110	203	61.7	75.5	59.1	116	80.9	63.4	38.1	74.3	72.5	50.2	39.4
Sulfate	mg/l	44.4	168	160	121	13.1	12	25.4	131	50.3	89.1	24.1	54.6	147	43.7	95.5
Bicarbonate	mg/l	281	190	200	223	190	224	261	265	223	250	204	238	186	262	210
Carbonate	mg/l	14.4	0.0	0	0	0.00	16.0	0.0	0.0	0.0	0.0	0.0	7.20	0.00	0	0.0
Nitrate	mg/l	0.75	5.5	5.1	7.0	5.56	6.47	0.99	4.75	10.7	0.82	0.98	1.1	3.78	5.08	1.62
Trace metals																
Copper	mg/l	n.d	0.04	0.01	0.05	0.12	0.05	n.d	n.d	0.19	n.d	0.12	n.d	0.04	0.08	n.d
Manganese	mg/l	0.13	0.09	0.03	0.2	0.02	0.01	n.d	0.08	0.13	0.12	0.08	0.1	0.06	0.06	0.01
Lead	mg/l	n.d	0.01	0.02	n.d	n.d	n.d	n.d	n.d	0.01	0.11	0.01	n.d	n.d	0.01	n.d
Zinc	mg/l	n.d	0.13	0.19	0.38	0.16	0.05	n.d	n.d	0.04	0.04	0.06	n.d	0.02	0.05	0.25
Serial		16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
pH	-----	7.47	7.52	7.53	7.48	8.28	7.59	7.36	8.14	7.62	7.36	7.26	8.12	8.25	7.38	7.44
Major Cations																
Calcium	mg/l	31.5	37.7	29.6	40.6	34.4	35.8	38.2	36.5	45	27.5	29.5	42.5	38.3	23.9	53.5
Potassium	mg/l	3.9	4.20	5.63	5.87	5.40	3.19	4.30	5.98	4.23	2.41	4.07	3.11	2.33	6.23	4.30
Magnesium	mg/l	20.2	14.4	17.5	18.7	20.2	18.6	19.2	10.2	13.6	17.1	14.3	17.7	15.8	27.1	10.2
Sodium	mg/l	42.5	69.8	89.0	77.4	75	60.9	65	48.7	64.6	70.5	55.5	14.2	89.6	34.3	28.7
Major Anions																
Chloride	mg/l	38.6	48.4	69.5	68.9	58.6	60.3	32.6	39.7	72.5	59.6	42.2	12.6	95.7	35.5	39.6
Sulfate	mg/l	22.8	52.5	62.2	35.5	54.6	21	58.8	13	58.5	12.6	45.2	21.6	23.5	10.3	28.3
Bicarbonate	mg/l	210	230	220	260	245	240	251	221	186	235	180	213	239	229	184
Carbonate	mg/l	0.0	0.0	0.0	0.0	9.60	0.00	0.00	12.4	0.00	0.00	0.00	18.4	12.0	13.2	0.00
Nitrate	mg/l	4.6	3.94	5.7	3.83	3.93	0.98	5.06	1.17	3.51	3.92	4.32	3.19	2.23	2.21	3.12
Trace metals																
Copper	mg/l	0.02	0.02	0.11	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.15	n.d	n.d	n.d	n.d
Manganese	mg/l	0.1	0.05	0.03	0.14	0.04	0.09	0.02	0.03	0.01	0.09	0.03	0.05	0.02	0.03	0.05
Lead	mg/l	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Zinc	mg/l	0.01	0.01	0.11	0.11	0.01	0.04	0.15	0.44	n.d	0.1	0.06	n.d	n.d	0.31	n.d

n.d= not detected

Table 2. Summary of Visual MINTEQ output file containing activities and concentrations of metals ionic species

species	Conc. mol/l	Activity mol/l	species	Conc. mol/l	Activity mol/l	species	Conc. mol/l	Activity mol/l
Cu(CO3)2-2	1.323E-07	7.464E-08	Zn+2	1.356E-05	0.000007651	MnOH+	1.423E-09	1.233E-09
Cu(NO3)2(aq)	3.23E-16	3.247E-16	ZnCl+	1.636E-07	1.418E-07	MnSO4 (aq)	1.394E-07	1.401E-07
Cu(OH)2 (aq)	7.74E-09	7.778E-09	ZnCl2 (aq)	1.553E-09	1.561E-09	Pb(CO3)2-2	5.29E-08	2.984E-08
Cu(OH)3-	1.342E-11	1.163E-11	ZnCl3-	1.062E-11	9.201E-12	Pb(NO3)2(aq)	1.513E-14	1.52E-14
Cu(OH)4-2	1.183E-16	6.675E-17	ZnCO3 (aq)	6.243E-06	0.000006274	Pb(OH)2 (aq)	7.122E-10	7.157E-10
Cu+2	4.111E-08	2.319E-08	ZnHCO3+	1.171E-06	0.000001015	Pb(OH)3-	6.021E-13	5.218E-13
Cu2(OH)2+2	1.066E-10	6.015E-11	ZnNO3+	4.203E-09	3.642E-09	Pb(OH)4-2	1.652E-16	9.318E-17
CuCl+	3.109E-10	2.694E-10	ZnOH+	5.657E-07	4.903E-07	Pb(SO4)2-2	9.769E-11	5.512E-11
CuCl2 (aq)	6.392E-13	6.424E-13	ZnOHCl (aq)	1.364E-07	1.371E-07	Pb+2	3.005E-08	1.695E-08
CuCl3-	5.015E-17	4.346E-17	ZnSO4 (aq)	1.723E-06	0.000001732	Pb2OH+3	3.023E-14	8.34E-15
CuCl4-2	3.055E-21	1.723E-21	Mn(NO3)2(aq)	1.071E-13	1.076E-13	Pb3(OH)4+2	2.352E-16	1.327E-16
CuCO3 (aq)	1.936E-06	1.946E-06	Mn(OH)3-	5.318E-18	4.609E-18	Pb4(OH)4+4	1.878E-19	1.902E-20
CuHCO3+	7.084E-09	6.14E-09	Mn(OH)4-2	1.923E-23	1.085E-23	PbCl+	5.082E-09	4.404E-09
CuNO3+	1.602E-11	1.388E-11	Mn+2	1.358E-06	0.000000766	PbCl2 (aq)	1.452E-10	1.459E-10
CuOH+	5.679E-08	4.922E-08	MnCl+	8.314E-09	7.205E-09	PbCl3-	5.101E-13	4.421E-13
CuSO4 (aq)	5.438E-09	5.465E-09	MnCl2 (aq)	7.567E-11	7.605E-11	PbCl4-2	2.61E-15	1.473E-15
Zn(NO3)2(aq)	1.342E-13	1.348E-13	MnCl3-	1.806E-13	1.565E-13	PbCO3 (aq)	7.225E-07	7.261E-07
Zn(OH)2 (aq)	6.414E-08	6.446E-08	MnHCO3+	7.583E-08	6.572E-08	PbHCO3+	6.098E-08	5.285E-08
Zn(OH)3-	2.718E-10	2.355E-10	MnNO3+	2.627E-10	2.276E-10	PbNO3+	5.4E-11	4.68E-11
Zn(OH)4-2	1.212E-14	6.837E-15	MnO4-	1.788E-16	1.55E-16	PbOH+	3.582E-08	3.104E-08
Zn(SO4)2-2	2.847E-08	1.606E-08	MnO4-2	5.177E-18	2.921E-18	PbSO4 (aq)	8.671E-09	8.714E-09

Chemical speciation of Manganese

In natural water system dissolved manganese will be often in +2 oxidation state. The results indicate that Mn^{+2} is predominate in most situations and it is often the most soluble Chemical species of manganese and represented about 91.3 % of the manganese. Complexed species were 4.46 % as carbonates, 3.96 % as sulfates, and less than 0.3 % with other anions Fig. 2.

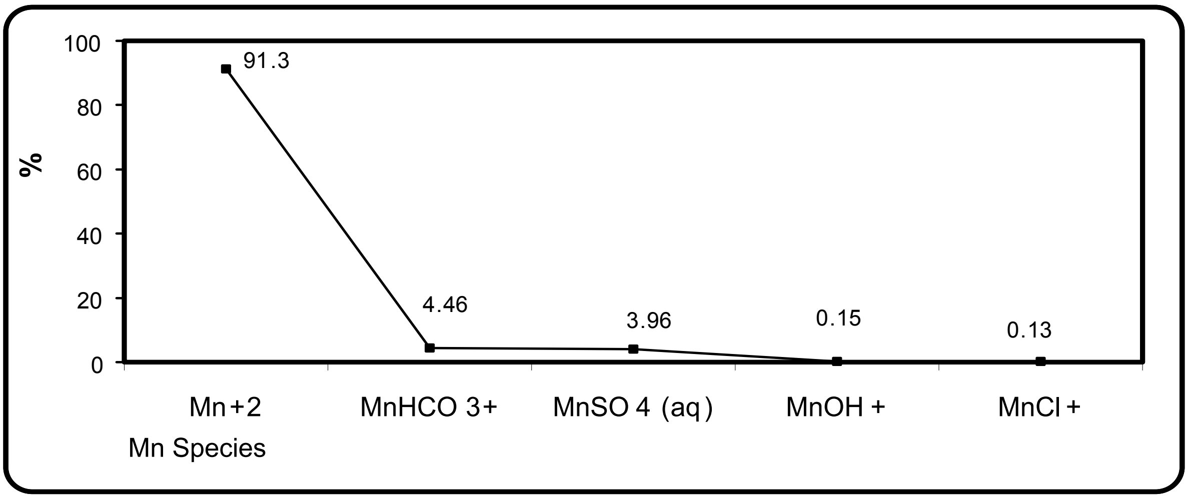

Fig. 2. Percent distribution of manganese ionic species

Chemical speciation of Copper

Copper may occur in solution either as Cu^{+2} or Cu^{+} based on the oxidation state. The redox conditions in oxygenated water favors the more oxidized form (Cu^{+2}). Cupric ions (Cu^{+2}) form complexes with a number of ligands, a strong $CuCO_3$ (aq) appears likely to be the major form in natural water containing dissolved CO_2. Chemical speciation of copper in groundwater samples estimated that 4.8 % of copper is in the free ionic form (Cu^{+2}) and the predominated copper form in groundwater is carbonate (87.9 %), Fig (3).

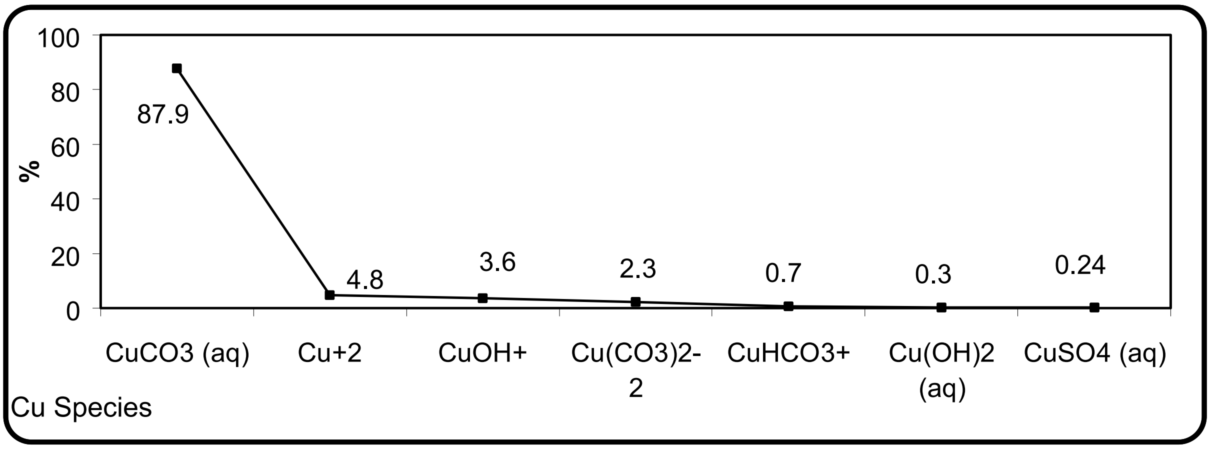

Fig. 3. Percent distribution of copper ionic species

Chemical speciation of Zinc

Zinc has only one significant oxidation state Zn^{+2} and it tends to be soluble in most types of natural waters than copper. Chemical speciation of zinc with different anions is shown in Fig. (4), about 60 %

of zinc exists as free ion (Zn^{+2}), about 31 % as carbonates and bicarbonate, 4.9 % as hydroxides 3.4 % as sulfates, and less than 0.5 % with other anions.

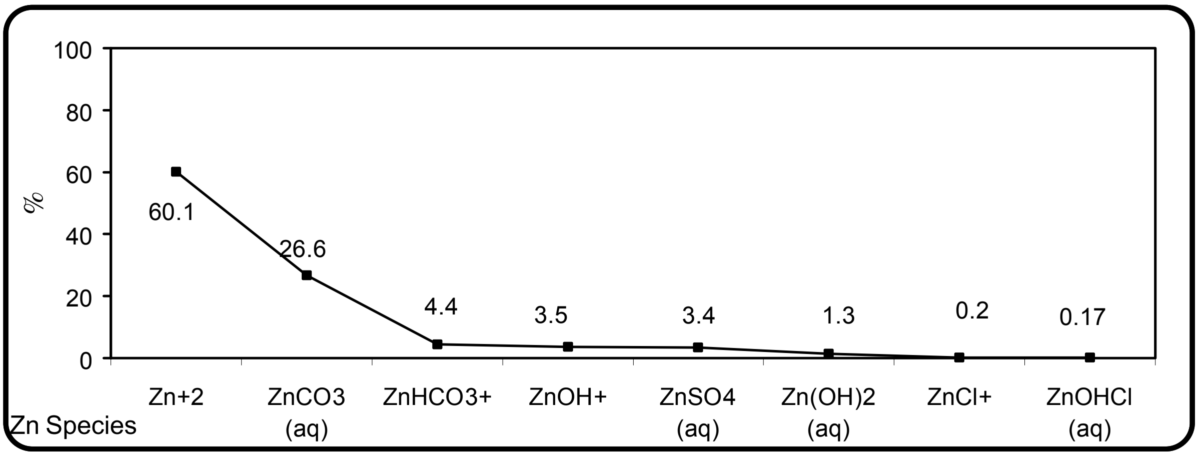

Fig. 4. Percent distribution of zinc ionic species.

Chemical speciation of lead

Chemical speciation of lead with various anions is shown in Fig. 5. About 6.7 % of lead exist in the free ionic form (Pb^{+2}) and the predominate form of lead in groundwater is the carbonate form (73%).

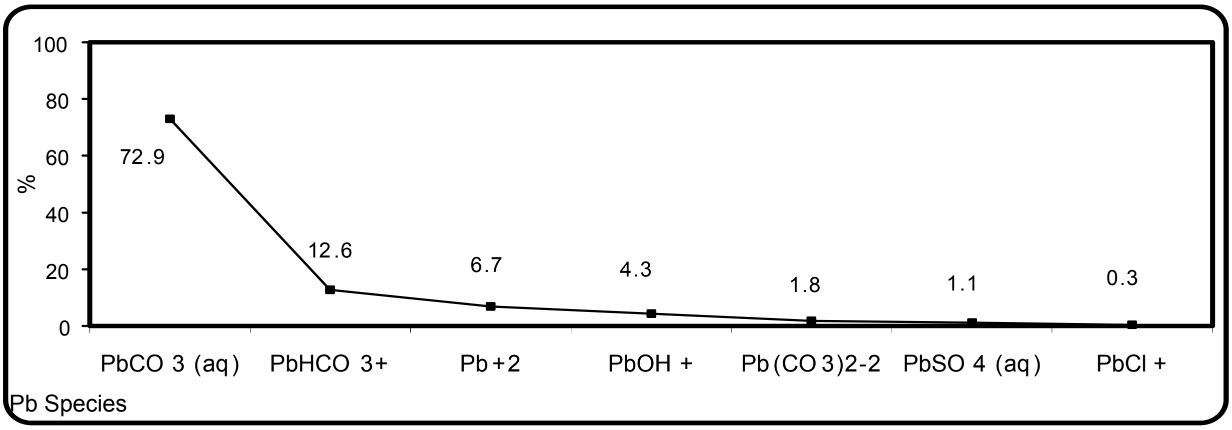

Fig. 5. Percent distribution of lead ionic species

CONCLUSION

The study findings based on model calculations indicated that Mn^{+2} is highly soluble and consequently will be bioavailable at the pH range of tested wells. Zinc is also expected tp be bioavailable as 60% of the total zinc is presented as Zn^{+2}. The law values of Cu^{+2} and Pb^{+2} are highly related to the alkaline pH values and organic complexation of the two ions.

Identifying ionic distributions is of particular importance as pollutants affect the groundwater environment by the chemical behavior of the ionic species and transformation of species than by total concentrations. The adverse effects of highly soluble free Mn^{+2} and Zn^{+2} are important in groundwater chemistry because their inherent toxicities `are related to the bioavailability.

The results suggest that Mn^{+2} and Zn^{+2} at such level would be available for uptake by plants, animals and humans. It is highly possible that such conditions may constitute a negative health impact. The model findings also suggest that Cu^{2+} and Pb^{2+} levels do not represent a health risk.

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