Chemical Speciation of Heavy Metals in Ground and Surface Waters

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Metal speciation in natural waters is of increasing interest and importance because of toxicity, bioavailability, and environmental mobility. Biogeochemical behavior and potential risk in general are strongly dependent on the chemical species of metals. The present study aims to determine the distribution of chemical species of dissolved heavy metals in shallow and deep aquifers and surface waters from Buddha nala stream and Sutlej River of Punjab, north-west India. Attempt was also made to identify different possible minerals that may control the solubility of elements in these aqueous solutions. The study was performed at village Walipur in Ludhiana ($30^0 55^/$N, $75^0 54^/$E) district of Punjab, north-west India, where Buddha nala surface water stream loaded with heavy metals from municipal waste and Industrial effluents contaminate underground water. A sutlej River also flowed a couple of Km from the village site. Ground water samples were collected at four different occasions from the same sites of shallow aquifer (45 feet deep) and deep aquifer (200 feet deep) by the already installed hand pump and tube well adjacent to Buddha nala stream. Before sampling the water was drawn for half an hour to empty the hand pump and tube well pipes in order to collect the fresh water from the shallow and deep aquifers, respectively**.** Surface water samples on four different occasions were also taken from Buddha nala stream and Sutlej River. Polyethylene bottles of 50 ml volumes were used for collection of water samples. These bottles were repeatedly washed with the water to be sampled. Bottles were fully filled with water and closed avoiding air bubbles. Field measurements of redox potential (Eh) were also made at the time of water sampling. The redox meter checked with Zobell's solution several times during the investigation period. Water samples were taken from each location and brought back to Laboratory at Punjab Agricultural University for further analyses. The samples were put in a cooled ice box during transportation and stored in refrigerator until analysis (at 5 ^{0}C). Th**e** pH of water samples was determined using Elico model L 110 glass electrode in combination with calomel as reference electrode on pH meter. The electrical conductivity of water samples was measured by Elico model CM-84 Conductivity Bridge. The carbonates and bicarbonates concentrations were measured by titration a known volume of water against standard sulfuric acid using phenolphthalein and methyl red as indicators respectively. The chloride concentration in water samples were measured by titrating with a known volume against standard N/40 silver nitrate solution using potassium chromate as indicator. All samples were filtered and acidified prior to analysis. The acidified water samples were analyzed for Cadmium, Nickel, Lead, Zinc, copper, Iron, Manganese and sulfur on Inductively Coupled Argon Plasma of Thermo Electron corporation iCAP 6000 series. Mean of Metals and dominant anions composition of waters determined after four occasions for different sites are listed in Table 1. The higher concentration of Cd, Cu,Fe, Mn, Ni, and Pb in waste water of Buddha nala stream must be due to disposal of Industrial effluents. The ionic strength of waste water was also three times more than other water sources. Comparatively high concentration of Zinc (16.10 uM) was measured in water of shallow aquifer than water of deep aquifer and surface water of Buddha nala stream and Sutlej River. The geochemical speciation model Visual MINTEQA2 Version 3.11 was used to calculate the equilibrium concentrations of dissolved species for four solutions, representing the range of water compositions encountered in the shallow and deep aquifers as well as in surface waters of Buddha nala

Table1. Metals and dominant anions composition of waters collected from different sites used in speciation calculations

Element	Shallow aquifer Hand pump	Deep aquifer Tube well	Surface water Buddha nala	Surface water Sutlej River
Cu uM	0.10	0.06	2.14	0.11
Zn uM	16.10	0.79	12.80	0.53
Cd uM	0.03	0.02	0.07	0.01
Pb uM	0.04	0.07	0.55	0.14
Ni uM	0.18	0.13	5.25	0.27
Fe uM	9.39	0.01	250	7.51
Mn uM	0.61	0.20	4.06	0.34
Cl^-	45.71	22.86	170	28.57
CO_3^{2-}	110.20	58.10	190	25.00
SO_4^{2-}	880	340	650	460
Ionic strength (u) ML^{-1}	0.016	0.010	0.034	0.010
pH	7.50	7.90	7.30	8.0
Pe (mV)	47	75	-253	226

stream and sutlej Rivers, respectively. The speciation of trace elements in different sources of waters are summarizes in Table 2. In all water compositions, except waste water of Buddha nala Zn, Cd, Ni, and Mn were predominantly present (93-97%) as divalent cation forms. About 95 % of the total dissolved iron in shallow and deep aquifers was in ferrous (Fe^{2+}) form due the occurrence of reduced status in underground waters. In Sutlej River, 90 % of the total dissolved iron was computed to be in ferric (Fe^{3+}) form due to oxidized (+226 mV) water status. The free activity of Pb^{2+} ion were 52, 33, 39, and 34% of the total dissolved lead in waters of hand pump, tube well and surface waters of Buddha nala and Sutlej River streams, respectively. Significant contribution of $Me(OH)^+$ (29%) and $Me(CO)_3$ aq (27%) complexes were computed for all the metals in Buddha nala water stream and ultimately these complexes eventually contributes to the higher concentration of these elements in this aqueous system. Appreciable fraction of $Me(OH)^+$ were also found for Cu and Pb in shallow and deep aquifers and Sutlej River waters. The $Me(CO_3)$ aq species were also found for Cu and Pb in waters of shallow and deep aquifers abstracted by hand pump and tube well, respectively.

Analyzed heavy metals data were also used in Visual MINTEQA2 to determine geochemical signatures of solute sources in the aquitards of shallow and deep aquifers, and bed sediments of Sutlej River and Buddha Nala stream. In addition to bed sediments, discharges from industrial manufacturing activities into Buddha Nala stream also cause increases in heavy-metal concentrations in Waste water. Selected minerals with saturation indices in the -2 to +2 range are presented in Table 3. The results indicate that various minerals containing of heavy metals have the potential to precipitate or dissolve in surface and ground waters. A positive saturation index indicates that the mineral is super saturated and might be precipitate in solid phase form. A negative saturation indicates that mineral is under saturated and if is present in the aquifers materials or in the bed sediments is dissolving to maintained its equilibrated concentration in the aqueous medium. Among the copper minerals,

Table 2. Percent species distributions of copper, zinc, cadmium, lead, Nickel, Iron and Manganese in shallow, deep aquifers and in surface waters of Buddha Nala stream and Sutlej river in Punjab, North West India

Species	Hand Pump water							Tube Well Water						
	Cu	Zn	Cd	Pb	Ni	Fe	Mn	Cu	Zn	Cd	Pb	Ni	Fe	Mn
Me^{2+}	45	93	96	52	96	95	97	25	87	97	33	97	95	98
$Me(OH)^{+}$	31	2	-	28	-	1	1	49	5	-	50	1	2	-
$Me(OH)_2$	2	1	-	-	-	-	-	7	5	-	1	-	-	-
$Me(OH)_3$	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$Me\ (SO_4)_{aq}$	2	3	4	4	3	4	3	-	2	2	1	2	2	1
$Me\ (CO_3)_{aq}$	20	-	-	13	-	-	-	18	1	-	14	-	-	1
$Me\ HCO_3^{+}$	-	-	-	2	1	-	-	-	-	-	1	-	-	-
Species	Buddha nala stream water							Satlej River Water						
Me^{2+}	39	39	39	39	39	39	39	28	86	95	34	96	90*	97
$Me(OH)^{+}$	29	29	29	29	29	29	29	54	5	-	54	1	-	-
$Me(OH)_2$	3	3	3	3	3	3	3	7	5	-	1	-	-	-
$Me(OH)_3$	-	-	-	-	-	-	-	-	-	-	-	-	4	-
$Me(OH)_4^{-}$	-	-	-	-	-	-	-	-	-	-	-	-	6	-
$Me\ (SO_4)_{aq}$	1	1	1	1	1	1	1	1	3	4	3	3	-	3
$Me\ (CO_3)_{aq}$	27	27	27	27	27	27	27	9	-	-	7	-		-
$Me\ HCO_3^{+}$	-	-	-	-	-	-	-	-	-	-	-	-		-

*Iron is present in ferric form

Table 3 Results from modeling with MINTEQ. All minerals with saturation indices (SI) from –2 to +2 are shown shallow, deep aquifers and Buddha Nala and Sutlej Rivers waters.

Mineral	Handpump	Tubewell	waste	Sutlej	Mineral	Handpump	Tubewell	waste	Sutlej
$Cu(OH)_2$	-1.85	-1.45	-0.47	-1.17	Malachite $Cu_2(OH)_2CO_3$	-1.56	-1.40		-1.19
$CuCO_3$	-	-	-1.50	-	Atacamite $Cu_2(OH)_3Cl$	-	-	-1.21	-
Langite $(Cu)_4(OH)_7HSO_4$	-	-	-1.28	-	Antlerite $Cu_3SO_4\ (OH)_4$	-	-	-1.40	-
Tenorite amp	-1.05	-0.65	0.33	-0.37	Azurite $Cu_3(OH)_2(CO_3)_2$	-	-	0.22	-
Tenorite (c)	-0.20	0.23	1.18	0.48	Brochantite	-	-	0.99	-
Siderite $FeCO_3$	-1.59	-	0.05		$Ni(OH)_2$ (c)	-	-	-1.18	
$Fe(OH)_2$ (c)	-	-	-1.60	-	Rhodochrosite $MnCO_3$	-	-	-1.32	
Smithsonite $ZnCO_3$	-1.05	-	-0.94	-	Hydrocerrusite$(Pb)_3(OH)_2(CO_3)_2$	-	-	0.07	
$Zn(OH)_2$	-1.78	-	-1.75	-1.72	Cerrusite $PbCO_3$	-1.57	-1.35	-0.30	-1.36
$NiCO_3$	-	-	-1.01	-	$Pb(OH)_2$	-1.01	-0.14	0.17	0.19

copper hydroxide [$Cu(OH)_2$], amorphous and crystalline tenorite [CuO] were identified as the solid phase in aquifer materials of shallow and deep waters and in the bed sediments of Buddha Nala and Sutlej River waters. Malachite [$Cu_2(OH)_2CO_3$] mineral was found in materials of shallow, deep water aquifers and in bed sediments of Sutlej Rivers (Table 3). Their could be the possibility of the existence of copper carbonate [$CuCO_3$] and Langite [$(Cu)_4(OH)_7HSO_4$], Atacamite [$Cu_2(OH)_3Cl$], Antlerite [$Cu_3SO_4(OH)_4$] and Brochantite [$CuSO_4 \cdot 3Cu(OH)_2$] in wastewater of Buddha Nala. The occurrence of these different copper minerals in aquifer materials for ground water and bed sediments could eventually be the primary factors for controlling the concentration of copper in water sampled from different sites. Among zinc minerals, Smithsonite [$ZnCO_3$] was found to be present in shallow aquifer materials and in the bed sediments of Buddha Nala waste water (Table 3). Zinc hydroxide [$Zn(OH)_2$] was recorded in aquifer material of shallow water, bed sediments of Buddha Nala and Sutlej river waters. Nickel carbonate [$NiCO_3$] and Nickel hydroxide [$Ni(OH)_2$] mineral were identified in bed sediments of Buddha Nala waste water only. Similarly the Rhodochrosite [$MnCO_3$] mineral for manganese and Hydrocerrusite [$(Pb)_3(OH)_2(CO_3)_2$] mineral for lead solid phases were identified in bed sediments materials of Buddha Nala waste water site. The most common minerals of lead Cerrusite [$PbCO_3$] and lead hydroxide [$Pb(OH)_2$] were found in aquifers material of shallow, deep waters as well as in the sediments of Buddha Nala waste and Sutlej Rivers waters. In case of iron, Siderite [$FeCO_3$] mineral was identified in the shallow aquifer materials and in the sediments under waste water of Buddha Nala (Table 3). The reduced form of mineral for iron as ferrous hydroxide [$Fe(OH)_2$ (c)] was found in the bed sediments of Buddha Nala waste water. The identification of this mineral illustrates that bed sediments under waste water of Buddha Nala were highly reduced conditions. The redox potential recorded for waste water at the time of sampling also showed low value of redox status (-253 mV).