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Effect of Seasonal Variation on Metal Speciation in Leachate from a Thermal Power Plant Ash Pond: Impact on Ground Waters

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Abstract

The concentration and extent of speciation of three environmentally important heavy metals, viz., Cd, Cu and Zn in the form of free ions and labile complex (C+F), slowly labile complex (CS1) and stable complex (CS) has been investigated in terms of percentage (%) in the Leachates from an ash pond of a 720mw thermal power plant in Delhi. The seasonal variations also have great influence on the total concentrations and speciation of these heavy metals in the ground water as well as in the leachates. The total concentration and speciation of these heavy metals is influenced by the physico-chemical parameters of the water column and also on the seasonal variations. For seasonal variation, the study has been carried out on the monsoon(MON) period (June, July and August), pre-monsoon(PRE) period (March, April and May), Post monsoon(POS) period (September, October and November) and the winter (WIN) season (December, January and February). Leachates containing different species of these heavy metals and other contaminants may have a deleterious effect on the receiving waters of the river Yamuna. Lysimeter studies simulating the generation of ash pond leachates have been conducted to ascertain the seasonal variation on leachability of different metal species. This may impart metal toxicity to the water body. Estimation of the speciation of these three heavy metals in the leachates and ground water, a picture of heavy metal distribution and the nature or extent of the speciation may be obtained.

Keywords: Metal speciation, Leachate, Physico-chemical parameters, Ground water, Thermal power plant.

Introduction

Different physico-chemical forms of many elements may exist in water systems. These different forms often exhibit different physical, chemical and biological properties, which have been studied widely in recent years. The total concentrations of the elements alone can not explain the transport, behavior, effects and fate of such elements in the water system. The term "SPECIATION" has become widely accepted, particularly with reference to metals, as appropriate to describe this distribution of an element between different physico-chemical forms or species. Thus, the immediate and long term effects of a metal, discharge to the water system are influenced by its speciation. The detection and determination of different forms of the heavy metals in natural waters are quite essential to establish their influence on various ecosystems as also to monitor and control the pathways by which they reach the hydrosphere.

A substantial amount of ground water pollution is caused by heavy metals leaching from the effluents running through ash pond [1]. The fate and transport of heavy metals in landfill leachates depend upon their variable complexing abilities, the relative concentrations of other constituents and upon the environmental conditions particularly the acidic value. The generation of leachate is a result of percolation of precipitation through open landfill or through cap of the completed site [2].

Leachates contain many contaminants that may have a deleterious effect on ground water. It may bring ecological and health associated risks if poorly managed like contaminating the groundwater [3-6]. The composition of leachates varies greatly and the presence of potentially hazardous high concentrations of heavy metals has been reported [7-10]. The rate and extent to which such metals will be attenuated by leaching through the soil would be affected by the extent to which soluble complexes are formed between the metals and other components of the leachates [11].

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Every element is capable of forming at least a few molecular species. An element may occur just as single molecular species or more molecular species in the environment depending on the environmental conditions. If more species of an element are present, then the different species are competitive in nature i.e., the concentration of one of them may be higher than the concentration of the others. The total concentrations of the element can be used to assess its environmental impact only if it is present in the environment as a single species. However, it is quite difficult to identify individual species and quantify them in the environment. Several heavy metals that may be present in landfill leachates are considered as priority pollutants for ground water resources like Cd [12]. The composition of landfill leachates is dependent on many factors such as the origin, waste composition, climate condition, site hydrology, bacterial activities and duration of generation of wastes [13-17]. In aquatic environment, the metals will exist as free metal ions, inorganic complexes, organic complexes and associated with colloids [18-20]. The solubility and mobility of heavy metals are often controlled by complexation with dissolved organic matter [21-26]. The behavior of metal in polluted ground water due to long term leakage of landfill leachates into the ground water is highly influenced by several factors such as dilution [27, 28] and adsorption on the soil.

The objective of the study is to determine the speciation of some selected heavy metals (Cu, Cd and Zn) in the ash pond leachates from a Thermal Power Plant, with a view to ascertain their impact on the ground waters.

The above mentioned metals have been selected for the study because these metals are of common environmental concern vis-a vis. their ecotoxicology and health hazards to the human beings as well as to aquatic biota. Their speciation is also similar, that is, different chemical forms of these heavy metals are very closely correlated to each other and these metals are more likely to affect the water quality parameter depending on the nature of their chemical forms, distributing patterns order of the stabilities of their complexes and so on. Cadmium is the second member of the group IIb triad (Zn, Cd and Hg) in the periodic classification of elements. The metabolism of cadmium is very closely related to zinc metabolism, metallotheonein binds and transports both cadmium and zinc. Cadmium seems to replace zinc in many vital enzymatic reactants, thus study of both metals together will provide understanding of health hazard to living organisms. The chemistry of cadmium is homologous to that of zinc in both the properties of the element and its compound.

Copper is widely distributed in nature in the free state and is sorbed rapidly to sediments, resulting in high residue levels. In the control soil Cd, Cu, Pb and Zn were bounded mostly to the residual phase. Copper was significantly associated with the organic fraction and Cd with the exchangeable fraction, where as Pb and Zn were relatively abundant in the oxide and carbonate fractions [29].

After ignition of the huge amount coal at 1250°C volatile matter escapes to the environment leaving about 2500 tons coal ash/day in which fly ash is collected by electrostatic precipitator (ESP) and then it is piped out to the slurry pond in suspension in water. The metal contents of incinerated ash have been shown to vary widely due to wide variation in the materials incinerated metals contents also differ between flyash and bottom ash. It was found that generally Cd and Cu were higher, but Cr, Ni, Pb and Zn were lower in the fly ash than in the bottom ash from incinerator[30], results of Hjelmar [31], however showed Cd, Pb, Ni and Zn to be higher and Cu and Cr lower in fly ash. It has also been found that from the coal contribution of 3100 x 10^6 metric tons per year emits 4.7 x 10^3 metric tons of copper[32]. The study will aim to carry out the seasonal variations of monsoon, pre-monsoon, post monsoon and the winter season.

Materials & Methods

Badarpur Thermal Power Station(BTPS) is a coal fired power plant having 5 generation units of capacity 3 x 95 mw and 2 x 210 mw, which was selected as the study area. It has the installed capacity of 720 mw. This plant consumes 7500 tons of bituminous coal per day. It was the first central sector power plant conceived in India, in 1965. The coal for the plant is derived from far away(The Jharia coal fields). Being an old plant, BTPS has little automation. Its performance is deteriorating due to various reasons like, poor coal quality, aging, poor quality and quantity of cooling water etc. Just behind this power plant, the ash ponds are situated. The effluents of this power plant are carried through a channel and mix up in the river (Yamuna) waters.

For physico-chemical characterization and speciation of heavy metals of the leachates and ground waters, the samples were collected from the following sites.

(i) The soil from the outlet of the ash pond (Exhausted) at the depth of 3ft.
(ii) The sluicing water from the running ash pond.
(iii) Ground water(tube well) 5km away from the ash pond(Two different places)
(iv) Ground water(tube well) 10km away from the ash pond(Two different places)

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Laboratory Leachate

Leachates were collected from the fabricated lysimeter (Perspex sheet-length 8", width 8" and height 8"). The soil collected from the outlet ash pond was taken in the lysimeter. Sluicing water collected from the sites was added slowly drop by drop to the lysimeter from the aspirator bottle for a period of 3 to 4 hours. It took nearby 8 to 10hrs for all the water to percolate through the sample soil. The laboratory prepared leachate samples were preserved (by freezing) just after collection to stop microbial activities [33, 34]. The sample preparation procedures were worked out by following APHA 2005. After collection, the samples (Leachate) were immediately acidified with conc. HNO_3 upto pH 3. Then, the samples were stored for speciation analysis.

For speciation studies, the procedures were followed as per the schemes of Laxen and Harrison [35], Campanella et al. [36] and Christensen and Lun [37]. In these procedures calcium saturated cation exchange resin chelex-100 was used to determine the fractions of free metal ions. Total metal concentrations were determined by flame atomic absorption spectrometric method using a Philips PU9200X instrument after pre-concentrating the samples through standard procedures [38, 39]. The speciation of the above mentioned heavy metals was carried out in a resin (Chelex-100) column with a short leachate retention time retaining metal bound as "Labile complexes", followed by a batch with a high amount of resin and a long equilibration time to retain found as "Slowly labile complexes". Metal remaining in solution is characterized as "Stable complexes". For speciation studies the batch column batch method was used. It was also followed from the method given by APHA 2005. The laboratory leachates were subjected to the same speciation investigations as outlined above. The general theory behind the exchange resin method has been discussed in 1948 by Schubert [40] and has been applied in 1983 by Sanders [41] and in 1998 by Banerjee and Pani [1]. Total concentration of metals in the solution before passing through the resin columns (Chelax 100) was taken as initial concentration(INI). The concentration of the metals in the solution after passing through the resin column for 24 hours was taken as equilibrium concentration(EQM). The concentration of metals in the solution immediately, after passing through the resin column was taken as effluent concentrations(EFF). Then it could be calculated as:

Free + Labile complex (C+F) = (Initial concentration — Effluent concentration)/Initial concentration x 100

Slowly labile complex (CS1) = (Effluent concentration — Equilibrium concentration)/ Initial concentration x 100 Stable complex (CS) = 100 — [(C + F) + (CS1)]

For the determination of inorganic non-metallic constituents which have a bearing on speciation like pH, alkalinity, DO, COD, SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^- etc. the standard methods was followed [38, 39, 42-44].

Results and Discussion

From the experimental results, it is found that the total concentrations of the heavy metals and their different species vary seasonally considerably. The initial concentrations of the metals Cd, Cu and Zn has been found maximum Pre-monsoon period and minimum in the monsoon season. It may be due to the dilution factor(rain water), the initial concentration of metals found less in monsoon period. The free ions plus labile complex and slowly labile complex ions in the leachates are maximum in the winter period and minimum in the pre-monsoon period. However, the stable complex ions are maximum in the pre-monsoon and monsoon period. It is also found that at different pH levels which are prevalent in different seasons (pre-monsoon, monsoon, post-monsoon and winter), the leachability of different heavy metals Cd, Cu and Zn also varies. The speciation of the metals and the important chemical parameters which have an influence on speciation of metals in the leachates are given in Table 1 and 1a, respectively. The order of leaching of metal ions in different forms is shown in Fig. 1, 1a & 1b.

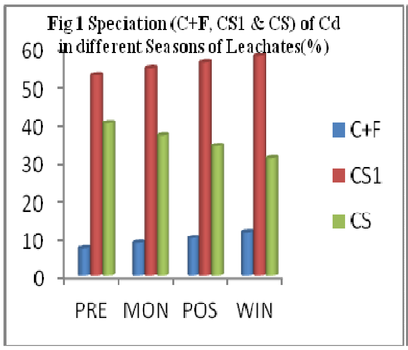
Table 1. The concentration of metals and their different chemical forms(speciation) of leachates in different seasons

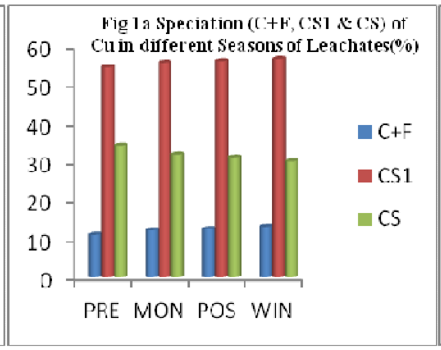
Cadmium(Cd)	INI (ppm)	EQM (ppm)	EFF (ppm)	C+F(%)	CS1(%)	CS(%)
PRE	21.34	8.56	19.82	7.1	52.8	40.1
MON	19.52	7.20	17.86	8.5	54.6	36.9
POS	20.72	7.05	18.68	9.8	56.1	34.1
WIN	19.91	6.15	17.64	11.4	57.7	30.9
Copper(Cu)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	26.48	9.08	23.54	11.1	54.6	34.3
MON	25.57	8.15	22.42	12.3	55.8	31.9
POS	26.10	8.14	22.81	12.6	56.2	31.2

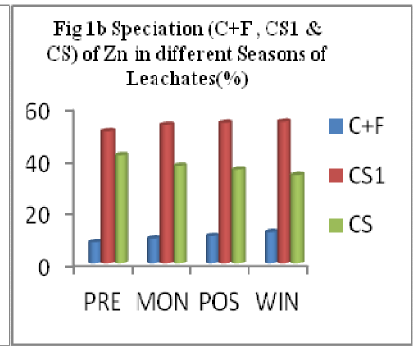
WIN	25.26	7.57	21.90	13.2	56.7	30.1
Zinc(Zn)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	40.22	16.72	37.08	7.8	50.6	41.6
MON	38.65	14.48	35.05	9.3	53.2	37.5
POS	38.28	13.73	34.37	10.2	53.9	35.9
WIN	36.83	12.44	32.48	11.8	54.4	33.8

Table 1a. Various chemical parameters of leachates in different seasons

	pH	TDS (ppm)	AlK (ppm)	DO (ppm)	COD (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	PO_4^{3-} (ppm)	NO_3^- (ppm)
PRE	5.21	542.72	436	0.34	106	226.90	49.12	6.84	8.65
MON	5.92	628.21	382	0.73	158	248.92	52.82	5.12	10.73
POS	6.07	605.84	398	0.62	131	269.08	64.48	5.71	9.92
WIN	6.32	615.24	409	0.42	112	288.12	71.14	4.46	9.30







At the following pH values which correspond to the above mentioned four seasons, the order of leachability of metal ions such as Zn, Cd and Cu particularly the chemical forms of C+F and CS1 in the leachates is:

PRE : pH 5.21 : Zn > Cu > Cd : 226.90 Cl^-
MON : pH 5.92 : Zn > Cu > Cd : 248.92 Cl^-
POS : pH 6.07 : Cu > Cd > Zn : 269.08 Cl^-
WIN : pH 6.32 : Cu > Cd > Zn : 288.12 Cl^-

The lower the pH value, the higher is the proportion of free ions in the solution. The pH of the water controls the toxicity value of the heavy metals. In the present study it is found that the free metal ions plus their labile complex concentrations are more than the stable complexes in the water body. The effluents from the power plant may impart higher toxicity to the leachates, which in turn may affect the ground water.

At the lower pH value, large amount of heavy metals solubilise into the water body which may be the reason for increasing the metal concentrations in leachates and ground water. In the acidic soil, the leaching of metal ions of Zn, Cu, Cd are the most favorable cations. From the experiment, it is found that the leachate is acidic.

If a leachate reaches the water table, it mixes and moves with the ground water. The attenuation mechanisms may be relevant but dilution and disposition have an important bearing on the extent of ground water pollution. Landfill leachates often contain high concentrations of toxic heavy metals [1]. Their presence, even in small amounts can have deleterious consequences to living organisms.

The adsorption of metal cations in the soil mainly depends on the pH, inorganic and organic ligands available in the soil. At pH 5.21, Zn is the most favorable leaching ion in comparison to Cd and Cu ions. As the pH value increases, Zn is the least favorable and Cu is the most favorable leaching ion. In the leachate, the concentration percentage of free ions plus the labile complex ions of Cu, Cd and Zn are found higher in the winter and less in the pre-monsoon season. In these cases the concentration of chloride ions is also found higher in winter and less in monsoon. Generally, chloride complexes of heavy metal are highly mobile. Therefore chlorides could be the very important factor in the distribution and seasonal variation of heavy metals. As the pH value increases, the chloride complexes are more prominent.

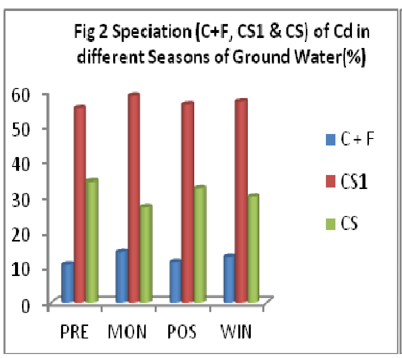
The speciation of the above mention metal ions and the important physico-chemical parameters which have a bearing on the speciation of heavy metals on the ground water are given in Table 2 and 2a, respectively. The distribution pattern of the metal ions in different chemical forms (C + F, CS1 and CS) is shown in Fig. 2, 2a and 2b.

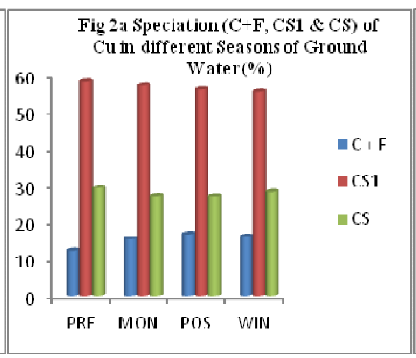
Table 2. The concentration of metals and their different chemical forms(speciation) on ground water in different seasons: Sample 1: 5 km away from the ash pond

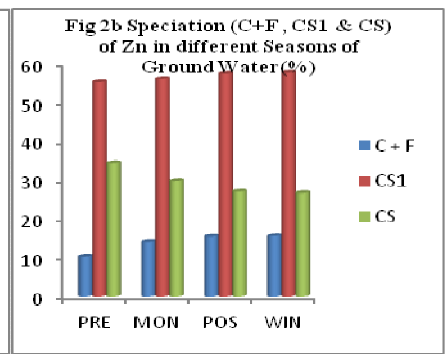
Cadmium(Cd)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	16.24	5.54	14.51	10.6	55.2	34.2
MON	15.71	4.25	13.48	14.2	58.7	27.1
POS	14.98	4.86	13.28	11.3	56.2	32.5
WIN	14.34	4.31	12.50	12.8	57.1	30.1
Copper(Cu)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	19.82	5.82	17.40	12.2	58.4	29.4
MON	18.74	5.09	15.83	15.5	57.3	27.2
POS	17.25	4.66	14.36	16.7	56.2	27.1
WIN	15.66	4.42	13.13	16.1	55.6	28.3
Zinc(Zn)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	35.16	12.09	31.50	10.4	55.2	34.4
MON	33.43	9.97	28.72	14.1	56.1	29.8
POS	32.37	8.77	27.35	15.5	57.4	27.1
WIN	29.78	7.95	25.13	15.6	57.7	26.7

Table 2a. Various chemical parameters of ground water in different seasons: Sample 1 away from the ash pond

	pH	TDS (ppm)	AlK (ppm)	DO (ppm)	COD (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	PO_4^{3-} (ppm)	NO_3^- (ppm)
PRE	7.28	287.81	386	1.24	171	40.82	46.99	5.19	9.13
MON	7.11	324.76	352	0.93	226	40.62	36.38	4.82	9.19
POS	7.64	347.91	371	0.82	211	57.29	44.06	4.48	9.67
WIN	8.02	311.61	363	0.41	198	49.78	42.21	3.69	9.52







The following pH and chloride(Cl^-) values of sample no.1 which are very closely related to the distribution and the concentration of different chemical forms of Cu, Cd and Zn metals in ground water with respect to seasonal variation are analyzed as:

PRE : pH 7.28 : Cu > Cd > Zn : 40.82 Cl^-
MON : pH 7.11 : Cu > Cd > Zn : 40.62 Cl^-
POS : pH 7.64 : Cu > Zn > Cd : 57.29 Cl^-
WIN : pH 8.02 : Cu > Zn > Cd : 49.78 Cl^-

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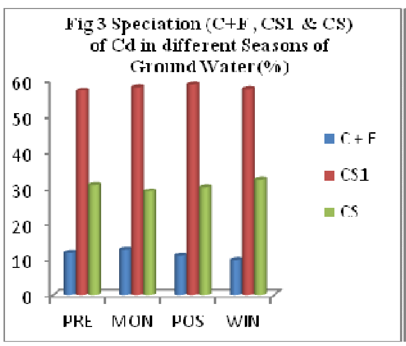
As the pH values moving from acidic to basic range based on experiments (Table 2a), the concentration of free ions plus labile complex and slowly labile complex ions of metals Cu and Cd are becoming more prominent than that of Zn ions. It is observed that chlorides are very selective agents in their interaction with the metals Zn and Cd. As the chloride concentrations increase, the speciation of Zn increases. Chloro-zinc metal complexes can increase the residence time in the water body. But at low concentration of Cl^- ions, zinc does not actively form chloro-complex. It may be the reason for lower concentration of zinc in the pre-monsoon and monsoon and higher concentration in winter season.
The different chemical forms of the metals Cu, Cd and Zn in the ground water with correspond to the different seasons are given in Table 3. The various chemical parameters of ground water in different seasons which directly affect the speciation of the above mentioned metals, are given in Table 3a. The distribution trend of the different chemical forms are shown in Fig. 3, 3a and 3b.

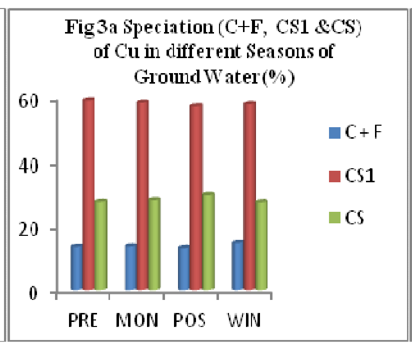
Table 3. The concentration of metals and their different chemical forms(speciation) of ground water in different seasons: Sample-2: 5 km away from the ash pond

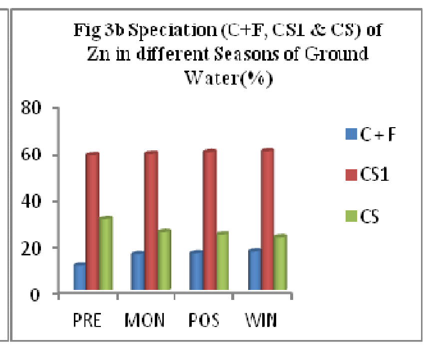
Cadmium(Cd)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	15.84	4.87	13.95	11.9	57.3	30.8
MON	14.63	4.25	12.77	12.7	58.2	29.1
POS	14.21	4.29	12.66	10.9	58.9	30.2
WIN	13.76	4.45	12.41	9.8	57.8	32.4
Copper(Cu)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	17.78	4.89	15.42	13.3	59.2	27.5
MON	17.44	4.89	15.10	13.4	58.5	28.1
POS	16.51	4.90	14.38	12.9	57.4	29.7
WIN	15.92	4.36	13.61	14.5	58.1	27.4
Zinc(Zn)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	34.22	10.50	30.52	10.8	58.5	30.7
MON	33.41	8.41	28.16	15.7	59.1	25.2
POS	28.14	6.77	23.60	16.1	59.8	24.1
WIN	27.53	6.31	22.88	16.9	60.2	22.9

Table 3a. Various chemical parameters of ground water in different seasons: Sample 2 away from the ash pond

	pH	TDS (ppm)	AlK (ppm)	DO (ppm)	COD (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	PO_4^{3-} (ppm)	NO_3^- (ppm)
PRE	7.44	263.98	360	0.95	196	54.71	15.92	2.84	3.25
MON	8.03	317.56	315	0.76	285	61.26	20.77	1.62	3.31
POS	8.27	293.50	346	0.46	232	74.09	27.74	2.08	3.92
WIN	7.92	276.43	328	0.98	267	42.27	36.61	1.21	3.64







At the following pH and Cl^- values which correspond to the speciations of the three selected heavy metals with respect to four seasons are analysed. The increasing order of different chemical forms are as:

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PRE	:	pH 7.44 :	Cu > Cd > Zn	:	54.71	Cl^-
MON	:	pH 8.03:	Zn > Cu > Cd	:	61.26	Cl^-
POS	:	pH 8.27 :	Zn > Cu > Cd	:	74.09	Cl^-
WIN	:	pH 6.92 :	Zn > Cu > Cd	:	42.27	Cl^-

In the sample no. 2, it was found that the speciation of metal Zn is very prominent where both pH and Cl^- have the high values. The metal Zn has the similar trend of seasonal variation as that of the metal Cu. But the metal Cd differs from Zn as it has lower C + F value than that of the Zn in winter season. It may be due to the fact that cadmium may interact with SO_4^{2-} ions to form cadmium sulphide which is precipitated in lower pH value.

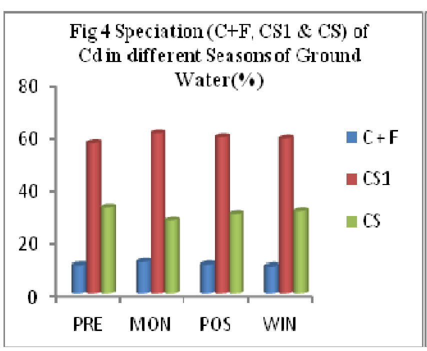
The effect and order of seasonal variation on the speciations of three environmentally important metals and the different chemical parameters which influence the speciation of metals on the ground water are given in Table 4 and 4a respectively. The order of speciation of these metals is shown in Fig. 4, 4a and 4b.

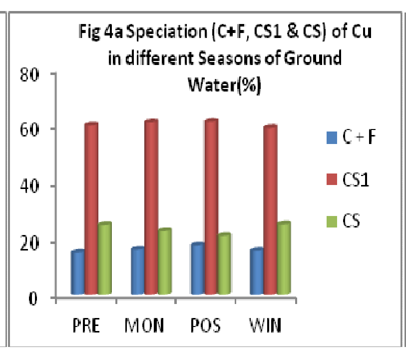
Table 4. The concentration of metals and their different chemical forms(speciation) of ground water in different seasons: Sample-3: 10 km away from the ash pond

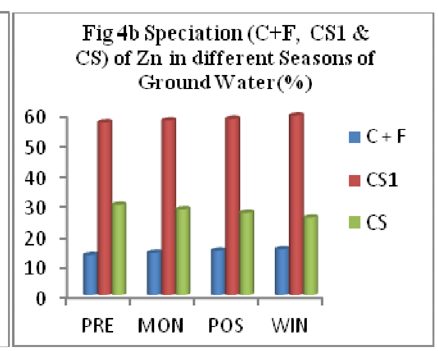
Cadmium(Cd)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	15.89	5.15	14.22	10.5	57.1	32.4
MON	14.24	3.91	12.57	11.7	60.8	27.5
POS	14.12	4.22	12.59	10.8	59.3	29.9
WIN	13.45	4.17	12.08	10.2	58.8	31.0
Copper(Cu)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	17.82	4.40	15.11	15.2	60.1	24.7
MON	17.41	3.92	14.57	16.3	61.2	22.5
POS	16.20	3.37	13.32	17.8	61.4	20.8
WIN	15.28	3.80	12.85	15.9	59.2	24.9
Zinc(Zn)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	27.19	8.08	23.63	13.1	57.2	29.7
MON	25.34	7.15	21.82	13.9	57.9	28.2
POS	23.86	6.45	20.38	14.6	58.4	27.0
WIN	22.42	5.69	19.03	15.1	59.5	25.4

Table 4a. Various chemical parameters of ground water in different seasons: Sample 3 away from the ash pond

	pH	TDS (ppm)	AlK (ppm)	DO (ppm)	COD (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	PO_4^{3-} (ppm)	NO_3^- (ppm)
PRE	7.23	258.31	290	1.91	136	58.01	54.63	5.47	4.98
MON	7.92	332.56	237	2.52	202	91.68	38.74	4.09	6.20
POS	7.41	317.97	254	2.13	187	84.03	49.96	4.92	5.71
WIN	7.72	289.71	285	2.04	163	62.13	45.53	4.49	5.35







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The impact and influence of pH and Cl^{-} values on the speciation of three metals such as Cu, Cd and Zn are found from the experiment in the following order as:

PRE	:	pH 7.23 :	Cu > Zn > Cd	:	58.01	Cl^{-}
MON	:	pH 7.92 :	Cu > Zn > Cd	:	91.68	Cl^{-}
POS	:	pH 7.41 :	Cu > Zn > Cd	:	84.03	Cl^{-}
WIN	:	pH 7.72 :	Cu > Zn > Cd	:	62.13	Cl^{-}

In the sample no. 3, it was found that Cu is the most prominent free ions plus labile complex and slowly labile complex ions at moderate pH and Cl^{-} values. Copper forms complexes with bases like nitrate, sulphate and chloride within the pH range of 7 to 8.5. It was also found that in this sample, nitrate and sulphate both have higher concentrations in comparison to the other previous sample no.1 and 2. It may be the reason for higher C + F and CS1 concentration percentage of Cu metal than those of Zn and Cd. Cu has the greater value in monsoon and post-monsoon seasons as in these two seasons the sulphate and nitrate have the higher concentrations. Therefore, the nitrate, sulphate and chloride may have the greater influence in the distribution of different chemical forms of copper.

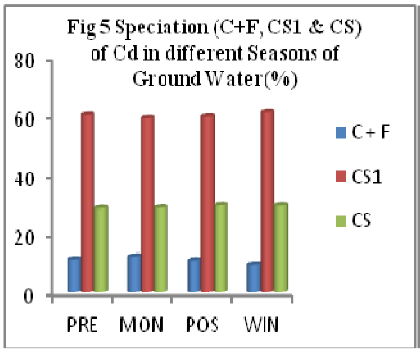
Table 5 and 5a show the different chemical forms of metals and the various chemical parameters of ground water in different seasons respectively. The distribution trend of different chemical forms of metals on the ground water are shown in Fig. 5, 5a and 5b.

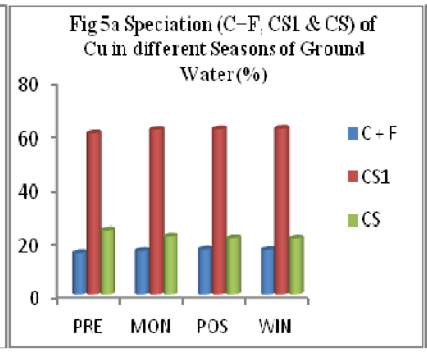
Table 5. The concentrations of metals and their different chemical forms(speciation) of ground water in different seasons: Sample-4: 10 km away from the ash pond

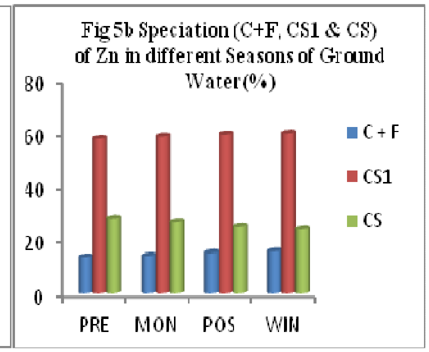
Cadmium(Cd)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	13.53	3.85	12.01	11.2	60.3	28.5
MON	12.72	3.65	11.17	12.2	59.1	28.7
POS	11.26	3.32	10.04	10.8	59.7	29.5
WIN	10.91	3.20	9.88	9.4	61.2	29.4
Copper(Cu)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	16.65	4.03	14.07	15.5	60.3	24.2
MON	16.14	3.53	13.49	16.4	61.7	21.9
POS	15.49	3.28	12.87	16.9	61.9	21.2
WIN	14.87	3.08	12.39	16.7	62.2	21.1
Zinc(Zn)	**INI (ppm)**	**EQM (ppm)**	**EFF (ppm)**	**C+F(%)**	**CS1(%)**	**CS(%)**
PRE	26.68	7.52	23.02	13.7	58.1	28.2
MON	23.92	6.43	20.52	14.2	58.9	26.9
POS	22.41	5.60	18.98	15.3	59.7	25.0
WIN	20.37	4.89	17.13	15.9	60.1	24.0

Table 5a. Various chemical parameters of ground water in different seasons: Sample 4 away from the ash pond

	pH	TDS (ppm)	AlK (ppm)	DO (ppm)	COD (ppm)	Cl^{-} (ppm)	SO_4^{2-} (ppm)	PO_4^{3-} (ppm)	NO_3^{-} (ppm)
PRE	7.32	251.13	282	1.21	127	52.12	43.47	4.71	5.23
MON	7.43	298.62	248	1.83	191	83.86	41.35	3.92	6.15
POS	7.42	282.97	261	1.43	167	69.03	48.21	4.53	5.98
WIN	7.31	262.17	274	1.12	152	62.31	58.43	4.21	5.37







The impact and influence of pH and Cl^- values on the speciations of three metals such as Cu, Cd and Zn are found from the experiment in the following order as:

PRE	:	pH 7.32 :	Cu > Zn > Cd	:	52.12 Cl^-
MON	:	pH 7.43:	Cu > Zn > Cd	:	83.86 Cl^-
POS	:	pH 7.42 :	Cu > Zn > Cd	:	69.03 Cl^-
WIN	:	pH 7.31 :	Cu > Zn > Cd	:	62.31 Cl^-

The sample no. 4 has a similar trend as that of the sample no.3 with all respects of seasonal variation, percentage of metal speciation and the findings of concentration of various physico-chemical parameters of ground water. In this case the metal speciation trend of all seasons was found as Cu>Zn>Cd which was also the same in the case of sample no. 3.

Conclusion

From the experimental results it is found that at lower pH and Cl^- values Zn is the most favourable leaching metal ion. As the pH values go on increasing, the leaching order also changes in the following way.

pH and Cl^- values in increasing order →

Zn > Cu > Cd

Increasing order of leaching →

In the similar way, Cu is the most prominent metal in the form of free ions plus labile complex and slowly labile complex on the ground water. The ground water around the area about 10 km away form the ash pond was found to be basic in nature. The order of C + F and CS1 forms of metals are found as

Cu > Zn > Cd

The free ions plus labile complex and slowly labile complex ions in leachates as well as ground water which are very important in view of environmental pollution have the seasonal variation in the following order:

Cd, Zn and Cu	:	C + F	WIN > POST > MON > PRE
		CS1	WIN > POST > MON > PRE
		CS	PRE > MON > POS > WIN

From the experimental results, it was also found that pH, Cl^-, SO_4^{2-}, NO^{3-} etc. have very important influence over the distribution of different forms of metals and seasonal variation of these three heavy metals.

From the above details it can be said that the ash pond leachates through leaching processes, affect the ground water to a large extent. The leachates therefore have a definite pollution potential for the ground water bodies.

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