Electrochemical attributes and availability of nutrients/toxic elements, and heavy metals in soil of chowki, Rajandgaon Chhattisgarh

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Abstract
Electrochemical properties of soils are very important for the understanding of the physico-chemical phenomena which affect soil toxicity, fertility and the availability of nutrients for plants and ground water which indirectly infiltrates in the ecological cycle. This paper highlights the electrochemical properties of tropical soils in Rajnandgaon, the behavior and the availability of Some toxic elements, nutrients and heavy metals especially for soils with predominant variable charge minerals in Ambagarh Chowki Chhattisgarh where already heavy toxicity of Arsenic in drinking water had been reported.

Keywords: Electric charge, adsorption, model, ionic exchange, speciation

INTRODUCTION

Recent revision of the Maximum Contaminant Level (MCL) for arsenic in drinking water from 50 to 10 Ag/L by the Environmental Protection Agency (EPA) will impact over 4000 US utilities . Of the EPA identified treatment options, adsorption onto solid media is the most attractive for the small utilities (serving populations of less than 3301), which comprise over 92% of the utilities affected .The Toxicity Characteristic Leaching Procedure (TCLP) is used to assess the leaching potential of arsenic from ABSRs. Currently most ABSRs pass the TCLP and are considered safe for disposal in non-hazardous, mixed solid waste (MSW) landfills. However, recent research has shown that the TCLP significantly underestimates the leaching potential of arsenic residuals under landfill conditions , so the potential for arsenic mobilization from landfilled ABSRs presents an obvious environmental concern. In a landfill, many biotic and abiotic factors may influence the leaching of arsenic from the ABSRs and there has been scant research evaluating the relative significance of the various factors. Among the abiotic factors, pH, NOM and competitive anions like phosphate, bicarbonate, sulfate and silicate are potentially important.

The assessment of arsenic bioavailability in soils and its effects on organisms is a crucial issue in ecotoxicology and environmental management. Because the relationships between soil concentrations and their subsequent effects differ according to exposure duration (among other factors), it is suggested that the bioavailability and the fluxes entering an organism are more relevant than the internal concentrations to explain metal toxicity . In addition, research showed likewise that the rate of uptake, not the internal concentration itself, is a better indicator to quantify bioavailability. One way to estimate the uptake rate is to measure concentrations or body burdens as a function of time in an organism exposed to a contaminated soil. Compartment models were developed to study accumulation and elimination kinetics and can be applied to evaluate pollutant fluxes within the tissues of organisms.

Electrochemical properties of soils are very important for the understanding of the physico-chemical phenomena which affect the availability of nutrients for plants, and, therefore, soil fertility. Defined as the capacity of the soil to supply crops with essential elements, soil fertility is a very complex matter because it is the result of the combination of various processes that occur in the soil and dependent upon several soil attributes such as, texture, structure, content and type of clay minerals, content and type of organic matter (OM), nature and transformations of the parent material, for example. Nutrient availability or bioavailability is closely connected to soil fertility. Bioavailability is affected by different features and soil characteristics such as dense or compact layers, nutrient diffusion, and oxygenated roots and so on. Bioavailability of essential elements can also be defined in mechanistic terms (Sposito, 1989): the element is bioavailable if it is in a chemical form that the plant is able to absorb promptly, and if absorbed, it affects the life cycle of the plant. In the view of Soil Chemistry, bioavailability of an element is determined by competition among plant roots, soil solution and solid phases of soil. The electrochemical properties of the solid phase influence directly the behavior of soil elements, especially in both soil solution composition and in the bioavailability of these elements.   In certain soils, like those with predominant constant charge minerals, the two properties most related to the control of movement and to the immobilization of nutrient elements, are the specific surface area (SSA) and surface charge density. These properties altogether define the cation exchange capacity (CEC).

In these soils, which present the majority of their charges as permanent, the CEC and the percentage of base saturation (V%) are the most frequent parameters to evaluate soil fertility. These two parameters vary with other soil properties, such as pH and water holding capacity, and in this way, when used in a combination, they allow good inferences on the soil capacity to supply nutrients to plants. On the other hand, in soils which present predominant variable charge minerals, the properties most directly related to nutrient availability should include the kind of the exposed surface of clay minerals, altogether with the specific surface area and the

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surface charge density. The value of CEC, V% and the properties that vary with them, are not, in general, good enough to make a sound interpretation of the bioavailability of the nutrients, that is, of soil fertility. The main reactions which affect the availability of soil nutrients are the losses either by volatilization or leaching, precipitation and adsorption. Few elements are volatile, and the majority does not reach enough concentrate ns in soil solutions to cause their precipitation. Therefore, reactions related to nutrient availability are the losses by leaching and adsorption, which are directly influenced by electrochemical soil properties.

This paper stress on imposition of such objective of relating the electrochemical properties of soils with the availability of nutrients for plants, especially for soils with predominant variable charge minerals, whose importance is emphasized in the humid tropics. The state of art in this field is discussed in a tentative to outline the perspectives for future studies related to soil electrochemical properties and their influence in the availability of nutrients, toxic elements and heavy metals in the soil plant system

The studied area lies between 20°70' to 22° 29' N latitudes and 81°29'to 88°29' E longitude. The physiography is directly related with the different landforms terrain under broad physiographic classification. The area falls under Chhattisgarh plane of peninsular India. Depending upon the variations in physiographic position and topography of the area, present investigation reveals that the soils are narrow to very deep, taxonomically classified as typic Chromuters, Andic Ustocrepts and typic Ustorthents, belonging to Hyperthermic family.

Soil samples and rock samples were collected from surface and outcrops of representative parts. These soils samples were passed through 2-mm plastic sieve using an agate mortar and pestle to ensure that trace metal contamination did not originate from the grinding process. These soil samples were weighed and digested in a hot oven using modified EPA method 3052 (USEPA 1995). Quality assurance samples (a blank, a duplicate, spike and a standard reference material (SRM)NIST, SRM-1648 for Urban Dust sample) were included for every 20 samples in the digestion following a quality assurance plan (Chen, 1997). Arsenic concentrations in the digestates were analyzed on a Chemito 201 AAS with hydride generation and a Zeeman background correction using EPA SW 846 method 7060 A (USEPA, 1995). The total mapped area was approximately 500 sq kms.

Study involving 248 minor stations was fixed in a manner to provide a representative picture of the contamination levels of soil and to undergo assessment of various other effects including vegetation study and health risks to the large population residing in the area. Sampling stations were spread between 20°30' N to 22°0 N and 80°30' E to 81°15 E. Over all sampling and subsequent analysis of various stations in the area led the sampling zone to be demarcated into three broad zones according to of the following geological-geographical features:

Zone-A: The Mineralized zone considered as maximum contaminated zone the Chowki Block.
Zone-B: Moderately contaminated and mineralized zone which includes Dongargaon and parts of Rajnandgaon block.
Zone-C: The unmineralised or less contaminated zone, which includes Mohla and Manpur blocks.

The results show that the soil Arsenic level generally is higher on the topside. Further, it showed a fluctuating level with depth and ultimately decreasing. Some of the arsenic trend in highly contaminated sites of mineralized zone A like Kaurikasa is shown in Table 7. It is believed that the geology of the area may be held responsible for such a higher level of contamination. This is later on supported by a high adsorbing nature of clay content of the soil, which holds this arsenic, acting as a sink while the mobilisation through the Shivnath river acts as a mobilising medium for spread in the nearby areas. The reported results correlate with the reported groundwater results (Pandey et al 2002) in the same region. In Kaurikasa, soils have higher clay content than other areas, which is expected to facilitate greater arsenic retention during runoff. The presence of significant amounts of carbonate in these soils, 30–64% $CaCO_3$ would also help retain trace elements and hence such soils are expected to show greater accumulation of anthropogenically added trace elements such as arsenic. The Iron Oxide rich weathering products occuring in the mining and geochemically active areas as this one are known to be strong adsorbents for arsenic.This is also supported by a rich clay, Aluminium and Manganese content which enhance the adsorption activity . This is evidenced by the physical properties and Chemical constitution of this area which supports this lithology.These observations find support from a appreciable correlation of Soil Arsenic with Clay and Iron , i.e. 0.66 and 0.54 respectively.

Previous Studies involving geologic origin of arsenic at the present location(Pandey et al 2002) and the available geological data (Sarkar, 1983) showed that there exists a geological anomaly in this part of central India. The formations of this arsenic contaminated area belong to Lower to Middle Proterozoic age. The country rocks comprise phyllitic shales and haematitic quartzites, which is a part of the Lower Proterozoic age formations popularly called as the Bailadila group. This group consists of banded haematite/magnetite quartzites (BHQ) to exploit which one iron ore mine is situated at Dalli-Rajhara about 25 km. east of Kaurikasa. The western part of the district show extensive volcanism and the rocks of Nandgaon group consist of lower Bijli Rhyolites and Pitepani volcanics. The emplacement of Dongargarh granites, intrusion of meta-dolerite dykes and quartz veins followed this volcanic phase. The arsenic contaminated area, which forms the eastern periphery of the Dongargarh granite batholiths, consists of metabasalt and metarhyolites. The area consists of shearing parallel to N-S (north-south) and NW-SE (north west-south east) and a low-grade metamorphism. A sporadic presence of arsenopyrites has been found in the highly sheared metamorphosed contact zones between the metabasalts and metarhyolites, which are auriferous, and uraniferous at certain locations. The origin of arsenic in this area is clearly geologic, affected by the Nandgaon orogeny. Being an under developed region inhabited by the poor indigenous people the use of pesticides or fertilizers is very limited thus it cannot account for high levels of arsenic in soil of the studied location.

This study compared the distribution of arsenic in soils within various blocks of Rajnandgaon. In general, arsenic concentrations in Chauki and particularly in Kauriakasa were higher than rest of the studied sampling areas. Arsenic concentrations varied significantly with Geological background and land-use. Soil arsenic concentrations in these areas showed significant correlation with natural soil properties (clay content and total Fe). Knowledge of classical pedology can be employed to predict arsenic distribution in these areas. Land-use categories can serve as good indicators of arsenic distribution in these areas. Still more research is needed to better understand the temporal variation of arsenic in different

compartments in all these areas so that better decisions can be made about land application of waste and remediation of possibly contaminated soils.

Table 1. Mean soil arsenic concentration in mg kg^{-1} in the three different zones

Sampling Zone		As (mg kg^{-1})	Range (mg kg^{-1})
Mineralised Zone	(Zone A)	1817.77	More than 500
Semi mineralised Zone	(Zone B)	114.23	200-400
Normal Zone	(Zone C)	13.47	Below 5

Table 2. Summary statistics for soil arsenic concentration in 4 major blocks (all concentrations in mg kg^{-1})

Sampling area	AM[a]	Median	GM[b]	GSD[b]	CL(95.0%)[c]
SW1	2970.29	702.48	542.90	3730.82	1500.59
SW2	114.42	28.56	32.54	121.47	53.65
SW3	87.92	2.98	37.73	227.19	189.93
SW4	6.00	5.00	8.06	6.56	16.29

[a]AM, arithmetic Mean. [b]GM, geometric mean; GSD, geometric standard deviation. [c]CL, confidence Level

Table 3. Combined statistical analysis of the arsenic affected blocks in the Rajnandgaon district.

Statistical parameters	SW1	SW2	SW3	SW4
Mean	88.12	216.08	25.93	6.00
Standard Error	32.96	131.34	4.63	0.57
Median	60.95	38.95	24.61	2.23
Standard Deviation	80.73	371.48	13.10	0.12
Sample Variance	6517.77	137995.67	171.73	6.11
Kurtosis	5.29	4.00	3.27	1.40
Skewness	2.25	2.08	1.53	-0.58
Range	219.00	1040.05	42.01	47.63
Minimum	30.95	9.45	12.22	12.32
Maximum	249.95	1049.50	54.23	59.95
Sum	528.70	1728.65	207.47	269.33
Count	83.00	83.00	83.00	83.00

Table 4. Statistical Parameters of soil Arsenic and other soil parameters in the contaminated zone

Statistical parameters	PH	TDS	COND.	ALKALINITY*	Cl-	SULPHATES	As
Mean	7.72	102.78	0.16	1.64	107.97	348.42	91.45
Standard Error	0.16	22.23	0.03	0.27	31.44	91.81	25.42
Median	7.65	96.00	0.14	1.67	88.24	297.50	64.45
Mode	7.38	na	na	1.67	na	na	62.95
Standard Deviation	0.51	66.68	0.10	0.87	99.43	290.32	80.39
Sample Variance	0.26	4446.69	0.01	0.75	9886.16	84287.12	6463.17
Kurtosis	-1.55	2.39	3.11	0.67	3.87	0.01	1.13
Skewness	-0.11	1.21	1.38	-0.19	1.75	0.97	1.57
Range	1.45	233.00	0.37	3.08	346.13	840.00	228.00
Minimum	6.90	15.00	0.03	0.00	4.26	40.00	21.95
Maximum	8.35	248.00	0.40	3.08	350.39	880.00	249.95
Sum	77.15	925.00	1.63	16.43	1079.66	3484.17	914.50
Count	400	400	400	400	400	400	400
Confidence Level(95.0%)	0.37	51.26	0.07	0.62	71.13	207.68	57.51

Table 5. Thermodynamic parameter – Electrode potential and Gibb's free energy of the soil water interface in the contaminated zone.

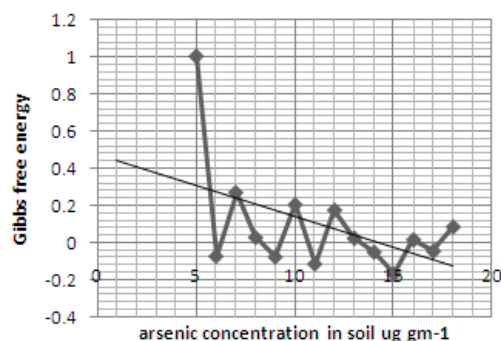| E_0	G_0
5.326×10^{-1}	-1.0278×10^5
5.3×10^{-1}	-1.0228×10^5
5.221×10^{-1}	-1.0075×10^5
5.291×10^{-1}	-1.0211×10^5
5.319×10^{-1}	-1.0265×10^5
5.449×10^{-1}	-1.0516×10^5
5.534×10^{-1}	-1.0678×10^5
5.300×10^{-1}	-1.0228×10^5
5.458×10^{-1}	-1.0532×10^5
5.514×10^{-1}	-1.0640×10^5
5.548×10^{-1}	-1.0706×10^5

Fig 1. Variation of Arsenic concentration in soil and its free energy change

Table 6. Correlation analysis of arsenic (III) with stability constant, and other thermodynamic parameters.

	As(III)	K_c(Na)	E_0(Na)	$-\Delta G_0$(Na)
As(III)	1.00			
K_c(Na)	0.08	1.00		
E_0(Na)	0.12	0.98	1.00	
$-\Delta G_0$(Na)	0.12	0.98	1.00	1.00

Table 7. Calculation of Enrichment Factor values of Arsenic in soils of some selected zones.

Sampling area[A]	Soil mean level	ArsenicEnrichment Factor
Zone A	2970.29	412.54
Zone B	114.42	15.89
Zone B	87.92	12.21
Zone c	6.00	0.83

A Selected places among three demarcated zones
Enrichment calculated against the mean soil As level of ppm (Chen et al 1997)

As retention and release from Fe-hydroxides is controlled by complex pathways of Fe biotransformation. Several studies have observed the reductive dissolution of As-bearing iron hydroxides (McArthur et al., 2001; Delemos et al., 2006; Kocar et al., 2006; Herbel and Fendorf, 2005). However, whether this reductive dissolution promotes or inhibits As sequestration is somewhat controversial. Release (desorption) of As during the onset of reducing conditions and the ensuing reductive dissolution of As-bearing Fe-hydroxides is generally ascribed as dominating the displacement of As from the solid phase (McArthur et al., 2001; Ahmed et al., 2004; Delemos et al., 2006). This hypothesis is often supported by correlations between As and oxalate (solid phase) extractable Fe(III) in contaminated aquifer sediments as well as correlations between Fe(II) and soluble As in well waters (McArthur et al., 2001; Ahmed et al., 2004). However, Kocar et al. (2006) observed enhanced arsenic sequestration upon ferrihydrite reduction to Fe(II). They attributed this to adsorption or incorporation of As into biotransformed solids rather than desorption under reducing conditions. Herbel and Fendorf (2005) demonstrated that Fe(II) and cellular organic matter aid arsenic retention, particularly for As(V). They also observed that arsenic desorption was greatest at the onset of an oxidizing to reducing transition and was promoted by mildly reducing conditions. Tufano and Fendorf (2006) argued that As(III) retention during iron reduction depends on the precipitation of secondary iron phases and during transformation to secondary phases, particularly magnetite, As(III) retention is enhanced. However, conditions that retard secondary mineral formation (more stable iron oxides or limited iron reducing bacterial activity), or prolonged anaerobiosis, will lead to both the dissolution of ferric-hydroxides and release of As(III) to the aqueous phase.

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