Immobilizing Arsenic in Contaminated Soil
Using Humic Mineral Concentrates

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ABSTRACT: Immobilization of heavy metals, especially arsenic, may involve both cationic and anionic forms. Arsenic may occur as both cations and anions. Humic mineral concentrates (HMC), including chemically active functional groups, can form complexes to immobilize both cationic and anionic forms.

   The efficiency of HMC in binding both cations and anions of heavy metals was demonstrated in lab-scale tests. Then, field tests were carried out on a former industrial disposal site destined for construction of commercial/residential structures. Field test results showed efficiencies of immobilization for zinc of 60%, cadmium of 66%, nickel of 72%, lead of 73%, and strontium of 87%. Arsenic immobilization efficiency was 85%.

   The source of initial arsenic cations was AsCl3 and the source of the anion form was NaAsO2. Both were triple valent ions. Arsenic content in soil samples ranged from 2 mg/kg up to 200 mg/kg. Tests showed that the average efficiency of initial cationic arsenic immobilization was 90%, for an initial arsenic concentration in soil of 2 mg/kg and 82% for an initial arsenic concentration of 20 mg/kg. Average efficiency of immobilization of anionic arsenic was 85% for an initial arsenic soil concentration of 2 mg/kg and 76% for an initial arsenic concentration of 20 mg/kg.

INTRODUCTION

   Increased concentrations of arsenic in soils are caused by emissions from industrial activities (metallurgical, power, chemical, etc.), by leaching from landfills or burial sites for a variety of industrial wastes (including processing residues and mineral enrichment wastes), and also by application of mineral fertilizers and pesticides (Zirin and Sadovnikova 1985). Under stable conditions, arsenic is most often found as anion forms in water and soil, but the composition of compounds including cationic forms of arsenic in contaminated soil is not clear.

   Migration of arsenic and other heavy metals in groundwater and into soils is closely connected to alkalinity-acidity and redox conditions, but also is affected significantly by the presence of organic substances in soil. In general, the major sink where polluting substances collect is the sequence of uppermost soil horizons enhanced by humus. These layers constitute a biogeochemical barrier against the migration of chemical elements and substances. Organic compounds in humus bind, in order of priority, Pb, Zn, Cd, Ba, Cr, Cu, Hg and other heavy metals; particularly effective are humic acids (Warshal et al., 1993).

   In contrast to the atmosphere in constant movement, and the dynamic aquatic environment, soil is immobile, and therefore is most vulnerable to pollution. On the one hand, soils lie on pathways for migrating ecotoxicants, and on the other hand, soils work as traps or pollutant accumulators. Resultant concentrations of

contaminants may be harmful and even dangerous for people.

The ecological danger inherent in polluted soils is determined by the exposure of species in a given situation (potentially affected population, severity of exposure, etc.), but soil can serve as a secondary source of pollution of air by microscopic particles of arsenic or arsenic contaminated soil, and of water when arsenic is leached from the soil into receiving waters. Epidemiological risks may be increased by suppression of native soil microorganisms through contact with chemical pollutants, while pathogens carried to a site may survive under the same conditions (Goncharuk and Sidorenko 1986).

HUMIC ACIDS AND ARSENIC – A FEASIBILITY STUDY

Humic acids present as carboxyl, phenolic, carbonyl and other functional groups interact with heavy metals and arsenic in a variety of ways, including: ionic exchange with metal cations; formation of complex heteropolar salts with metal cations; and formation of complexes with anions, including anionic forms of metals. Prior research (Shulgin 2003) demonstrated that sulfate and nitrate anions play a significant role in formation of complexes between metals and humic acids. As a result of such interactions, the concentrations of available metals and the aforementioned anions are reduced significantly.

Arsenic may exist under natural environmental conditions in forms with valence of 5+, 3+, 3-, and 2+, and in the elemental form (Zirin and Sadovnikova 1985). While arsenic in soil tends to be bound and not excessively soluble or mobile, it may be released into the environment under certain conditions. Although not well understood, this mechanism appears to occur under reduced, or anoxic conditions, which cause arsenic to be released into water and to rapidly migrate through groundwater (Jackson 2007). It is well known that in solution in soil porewater, arsenic is most often found as arsenite or arsenate. But the time required for arsenic cations newly released into contaminated soil to be converted into anions through hydrolysis is unknown. The investigation of the interactions of arsenic in both forms with humic acids has great scientific and practical interest.

Examples of practical applications of such interaction include the successful development of an effective technology for remediation of soils contaminated with arsenic, and detoxification of arsenical waste using humic materials (Shulgin et al. 1998; Shulgin et al. 2004). This technology is based on application of humic acid in the form of a Humic Mineral Concentrate (HMC) (Patent 2000). Laboratory tests were performed for preliminary assessment of the interaction of HMC with both cationic and anionic arsenic forms in samples of podsolic, sandy soils with organic content of about 0.4 percent from an industrial site.

In the tests, the soil samples were contaminated by anionic arsenic in $NaAsO_2$ and cationic arsenic in $AsCl_3$. No attempt was made to determine the changes in form of the arsenic during these tests. Standard solutions of these compounds were introduced into soil samples in doses of 2 mg / kg and 20 mg / kg. Anionic arsenic was added also at a concentration of 200 mg / kg. HMC was introduced into the polluted soil samples one week after the samples had been contaminated with arsenic. HMC dosages were 0.5 % and 2 % (dry weight to soil sample dry weight). Determination of the arsenic content in the soil samples was done by nuclear absorption spectrophotometry using a Perkin Elmer model 603 spectrophotometer after the arsenic was leached from the soil samples using an ammonium acetate solution with pH of 4.8. Each determination was repeated

three times, with an average accuracy of 24.2%. This procedure allows extraction of the mobile (water soluble) forms of the arsenic.

Using the same technique, the arsenic level in untreated soil, in a "control sample" was determined to be 0.6 mg/kg. Results for mobile forms of arsenic found in these tests are shown in Table 1.

**TABLE 1. Concentration of As Mobile Forms
in Soil Samples Before Treatment**

Sample	Initial As level (mg/kg)	Arsenic chemical formula	Extractable As content (mg/kg)
Control	—	—	0.6
1	2	$NaAsO_2$	1.93
2	2	$NaAsO_2$	1.99
3	2	$AsCl_3$	1.85
4	2	$AsCl_3$	1.80
5	20	$NaAsO_2$	18.98
6	20	$NaAsO_2$	19.23
7	20	$AsCl_3$	17.90
8	20	$AsCl_3$	17.65
9	200	$NaAsO_2$	190.65
10	200	$NaAsO_2$	190.23

Table 1 shows that arsenic anion forms were adsorbed by soil less strongly than were arsenic cation forms. Most of the added arsenic in both forms was mobile and available for extraction. The results of similar extraction tests on mobile forms of arsenic after treatment with HMC are presented in Table 2.

TABLE 2. Immobilization of Mobile As Forms

by Humic Mineral Concentrate

Test	Arsenic initial level, (mg/kg)	Arsenic chemical formula	Potentially mobile As content in the soil (mg/kg)		Efficiency of fixation (%)
			Before treatment	After treatment	
1	2	$NaAsO_2$	1.93	0.29	85.0
2	2	$NaAsO_2$	1.99	0.27	86.4
3	2	$AsCl_3$	1.85	0.19	89.7
4	2	$AsCl_3$	1.8	0.16	91.1
5	20	$NaAsO_2$	18.98	4.55	76.0
6	20	$NaAsO_2$	19.23	4.26	77.8
7	20	$AsCl_3$	17.9	3.12	82.6
8	20	$AsCl_3$	17.65	3.01	82.9
9	200	$NaAsO_2$	190.65	42.55	77.7
10	200	$NaAsO_2$	190.23	41.36	78.3

The second set of tests showed that the average efficiency of cationic arsenic immobilization was 90% for an initial arsenic concentration in soil of 2 mg/kg and 82% for an initial arsenic concentration of 20 mg/kg. Average efficiency of immobilization of anionic arsenic was 85% for an initial arsenic soil concentration of 2 mg/kg, and 76% for an initial arsenic soil concentration of 20 mg/kg. Average efficiency of immobilization of anionic arsenic was virtually identical to cationic As immobilization for an initial arsenic soil concentration of 200 mg/kg. HMC worked well in these trials, binding cationic arsenic better than anionic arsenic.

One of the main purposes of arsenic immobilization in soil is a reduction or elimination of its toxicity. Immobilized arsenic may be less available for uptake by the root systems of some plants and even unavailable to other plants. To investigate this aspect of the remediation, tests on oats were done to study the impact of arsenic on seed germination and seedling development and to determine arsenic content in the plants. HMC dosage was 0.5 % and 2% for each of two groups of soil samples. Results are presented in Table 3.

**TABLE 3. Impact of As on Seed Germination
Modified by HMC Treatment**

Sample	Arsenic initial level (mg/kg)	Arsenic chemical formula	HMC dose (%)	Seed germination (%)
Control	0.6	—	—	91.0
1	2	$NaAsO_2$	0.50	95.0
2	2	$NaAsO_2$	2.00	96.0
3	2	$AsCl_3$	0.50	98.0
4	2	$AsCl_3$	2.00	97.0
5	20	$NaAsO_2$	0.50	91.0
6	20	$NaAsO_2$	2.00	90.0
7	20	$AsCl_3$	0.50	97.0
8	20	$AsCl_3$	2.00	96.0
9	200	$NaAsO_2$	0.50	86.0
10	200	$NaAsO_2$	2.00	85.0

Under low arsenic levels in the soil (2-20 mg/kg), HMC treated soil samples showed more seed germination than did even the uncontaminated soil (control). A trend was noted, that anionic arsenic is more toxic than cationic arsenic for seeds. For example, for an arsenic initial level of 20 mg/kg, the difference in seed germination between samples containing anionic As and those containing cationic As was 6%. In contrast, no difference was noted in impact between HMC doses of 0.5 % and 2%.

Table 4 contains data on arsenic content in dried oat plants grown on the arsenic-contaminated soil samples treated by HMC. The tests showed that arsenic content in the plants is 1-2% for an initial extractable arsenic concentration of 2-20 mg/kg and 4.8 to 4.98% for an initial concentration of 200 mg/kg. No plant distress or death was detected during the tests.

Table 4. Arsenic Content in Oat Plants

Test	Initial Arsenic level (mg/kg)	Arsenic chemical formula	Extractable As, after treatment (mg/kg)	HMC dose (%)	As content (mg/g)[1]	As in dry plants (%)[2]
1	2	$NaAsO_2$	0.29	0.50	5.8×10^{-3}	2.00
2	2	$NaAsO_2$	0.27	2.00	5.88×10^{-3}	2.17
3	2	$AsCl_3$	0.19	0.50	3.55×10^{-3}	1.87
4	2	$AsCl_3$	0.16	2.00	3.42×10^{-3}	2.14
5	20	$NaAsO_2$	4.55	0.50	1.24×10^{-1}	2.72
6	20	$NaAsO_2$	4.26	2.00	1.21×10^{-1}	2.84
7	20	$AsCl_3$	3.12	0.50	8.42×10^{-2}	2.70
8	20	$AsCl_3$	3.01	2.00	8.28×10^{-2}	2.75
9	200	$NaAsO_2$	42.55	0.50	2.12	4.98
10	200	$NaAsO_2$	41.36	2.00	1.98	4.80

1. Measured on basis of dry plant weight.
2. Measured as percent of extractable arsenic in the soil.

FIELD STUDIES

All the tests listed above showed that there is no significant difference between anionic and cationic arsenic in terms of plant uptake; for practical purposes, the initial As form does not matter. On the basis of these tests, an area of 2 hectares of soil contaminated by heavy metals and arsenic was treated with HMC. Mobile forms of heavy metals and arsenic were isolated from the soil before and after HMC treatment, using an ammonium acetate solution with pH of 4.8. Pollutant concentrations were determined using the aforementioned atomic-absorption method. Results are presented in Table No. 5, on the next page.

The results obtained show that significant fractions of the mobile forms of heavy metals and arsenic were immobilized. Humic Mineral Concentrate showed especially high efficiency in binding strontium (reduction of 7.9 times, or to 12.7 percent of initial concentration), chromium (4.4 times, or to 22.7 percent of initial concentration), lead (3.7 times, or to 26.7 percent of initial concentration), nickel (3.6 times, or to 28 percent of initial concentration) and arsenic (6.8 times, or to 14.7 percent of initial concentration).

CONCLUSIONS

It is possible to draw conclusions based on the tests carried out.

1. Humic acids in the form of Humic Mineral Concentrates work well for immobilization of both anionic and [initially] cationic arsenic. Mechanisms of both ion exchange and formation of complexes operate.

2. The efficiency of arsenic immobilization in the lab scale tests was from 76% up to 91% depending on the initial soil contamination level. The efficiency

**Table 5. Heavy Metal/As Immobilization
with Humic Mineral Concentrate**

Element	Avg. Conc. Before treatment (mg/kg)	Avg. Conc. After treatment (mg/kg)	Efficiency, %
Zn	25.0	10.1	60
Mn	7.7	6.24	19
Sr	45.6	5.78	87
Ni	9.6	2.7	72
Cr	23.7	5.38	77
Cu	4.3	2.46	43
Pb	34.8	9.32	73
As	12	1.76	85
V	8.4	6.18	26
Sb	0.7	0.27	62
Sn	12.2	5.28	57
Cd	0.99	0.34	66
Co	9.3	3.66	61

of arsenic immobilization in the field scale was 85%. Thus, both the lab scale tests and the practical field scale work showed the same result.

3. Through arsenic immobilization, it is possible to reduce the toxic impact of arsenic on seeds and plants. Seed germination was increased and arsenic content in the plants was reduced by treatment with HMC.

4. Typical cationic forms of heavy metals (except chromium, which may exist in both cationic and anionic forms) are bound by HMC differently, but immobilization efficiency looks acceptable for practical application of HMC for contaminated soil detoxification and remediation.

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