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A Quick, Onsite Test for Delineating Arsenic Contaminant Plumes in Soil*

*John E. Thomas,** R. Dean Rhue, and W. H. Reve*

Soil and Water Science Department,
P.O. Box 110290,
University of Florida,
Gainesville, Florida 32611–0290

Dipping vats were used routinely in the southeastern U.S. in the early 1900s to eradicate the cattle fever tick. The legacy is many dip vat sites with arsenic (As)-contaminated soil and ground water. Assessing the extent of these As plumes can be time consuming and expensive. We describe a quicker and less expensive, onsite test for soil As. It is a modification of a commercially available test designed for As in water, taking about 10 min to complete, allowing large plume areas to be delineated in a single day. An As contaminant plume in Alachua County, FL, was delineated using the quick test. Soil samples taken from a large grid encompassing the plume were analyzed in the laboratory for As to confirm the results obtained with the quick test. The comparison showed that the quick test very accurately delineated the outer boundary of the plume as well as zones of higher As concentration within the plume.

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[**] Corresponding Author: Ph. 352-392-1951; FAX: 352-392-3902; email: thomas@ufl.edu

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INTRODUCTION

Arsenic is ubiquitous and can be found in nearly all soils to some degree. Unfortunately, As makes its way into the environment as a result of human activity. Arsenic was used in agriculture for many years, with uses ranging from pesticides to ripening agents. In the early 1900s, As was used extensively in a federally mandated program to eradicate the cattle fever tick from the southeastern United States (Dawson, 1913). Because Florida was an open range state at that time (Akerman, 1976), the most effective method for treating tick-infested cattle was to drive them through large dipping vats containing 1500 to 2000 gal of As solution (Dawson, 1913). By the end of the program, there were over 3000 dip vats in the state of Florida (Wellons, 1992). Each spring the vats were emptied and filled with fresh As solution. The old As solutions were usually dumped on the ground adjacent to the vats where it simply seeped into the ground (Ellenberger and Chapin, 1919). Arsenic at these vat sites has been slowly leaching through the soil and, in some cases, contaminating ground water.

When a dip vat is discovered during an environmental audit, a site assessment is generally required to determine the vertical and horizontal extent to which the As plume has moved. The most common method of assessment involves laying out a grid pattern, usually down gradient from the suspected source, and soil samples taken randomly within the grid at varying depths. The term “blind sampling” is appropriate because the location of the plume in completely unknown. Blind sampling requires considerable resources to be expended in collecting, storing, and analyzing soil samples, many of which may not yield useful information about the contaminant plume. The end result is at least one or two return trips to the site for additional sampling if the plume is to be accurately delineated. This research evaluates a rapid, economical, onsite field test for soil As that can be used to more efficiently delineate soil As contaminant plumes. The results obtained with the quick test were compared with quantitative laboratory analyses in an effort to validate the quick test as an effective means for identifying As-contaminated soil.

EXPERIMENTAL

Field Sampling

The site selected for evaluation was down gradient from a dip vat located within the Payne’s Prairie State Preserve, Alachua County, Florida. A grid on 10-m intervals was laid out starting at the vat and extending down gradient from it. Soil cores were taken at grid intersections using either a 2.5-cm soil probe or 10-cm bucket auger, depending on the depth to be sampled. The entire soil core was not sampled for arsenic analysis. Rather, only those portions of the core consisting of the spodic and/or argillic horizons were selected, because previous experience had shown that these soil horizons account for the bulk of the arsenic retention capacity of sandy soils such as those at this particular vat site. The spodic horizon is characterized by the accumulation of illuvial organic matter, and iron and aluminum oxides (Troeh and Thompson, 1993). The argillic horizon is an illuvial horizon characterized by the accumulation of at least 3 to 8% more clay than the overlying surface horizon. Approximately 1 g of each spodic or argillic sample was immediately taken for the onsite, quick test. The remainder of the sample was taken to the lab, stored at 8°C, and analyzed for total As within 2 weeks of collection.

Although sampling on a grid pattern is not necessary to delineate the arsenic plume using the quick test, it was done in this study in order to identify the location of each sample in order for analytical data and field test data to be compared and to provide sufficient information for subsequent plotting of concentration contours on two- and three-dimensional plots. A more efficient method of delineation would be to simply walk across the site, quick-testing the samples taken from either the spodic or argillic horizons, and placing flags marking the plume boundaries and "hot spots" within the plume. Using this method of plume delineation would save considerable time compared with conventional gridding and blind sampling while providing a much more effective assessment of the plume characteristics while still in the field.

The Arsenic Quick Test

The onsite, quick test for soil As employs the "EM Quant Arsenic Test Kit" (EM Science, Gibbston, NJ) that was designed to test for As in water. The kit comes with zinc dust, an aqueous 30% HCl solution, 100 test strips, and a graduated chart to estimate the concentration of As in the water. The original procedure calls for the addition of 5 mL of water to a 50-mL reaction tube, which is provided with the kit. The modifications for testing soil As follow: Approximately 1 gram of soil, which is measured by volume using a 0.8 cm^3 scoop, is first added to the 50-mL reaction tube. Five milliliters of a solution containing 500 μg P/mL as KH_2PO_4 is then added to the tube. The purpose of the phosphate is to displace soil-bound arsenate (Woolson et al., 1973), enhancing the sensitivity of the test to soil As. Finally, Zn dust and 30% HCl are added, in that order, and the reaction tube is capped.

Arsenic in solution is converted to gaseous arsine. The arsine reacts with the mercuric bromide on the test strip, causing a color change. The test strip goes sequentially through a series of colors, starting with white, then to yellow, to orange, and finally to a dark chocolate brown, depending on the amount of arsine gas generated. Total reaction time is on the order of 10 to 15 min.

Additional modifications may be necessary depending on the type of soil being analyzed. We observed that soil samples taken from spodic horizons, an organic-rich, subsurface horizon, produces a rigid foam that traps the arsine and prevents it from reaching the test strip. Foaming can be completely eliminated by adding a few drops of isopropyl alcohol to the reaction vessel prior to the addition of HCl. Foaming has never been a problem when testing surface soils, which can also be high in organic matter.

Another problem arises when using the quick test on calcareous soils. Calcium carbonate can neutralize the HCl, rendering the test useless. To overcome this problem, the soil is placed in the reaction tube and the acid is added to the soil first, drop by drop, until all the carbonate has been dissolved, as evidenced by the lack of foaming. After the carbonate has been completely dissolved, 5 mL of water are added and the sample treated as described above for noncalcareous soil. Because the solution is likely to be quite acidic following the dissolution of carbonate, the Zn dust is added at the very end, just before capping the tube, in order to prevent loss of arsine. Care must be taken not to overacidify the sample during the removal of carbonate. If the sample is overacidified, the Zn may be consumed too rapidly for effective arsine generation and a false-negative test can result. In cases where the Zn is completely consumed, a fresh sample should be tested, taking care not to overacidify during carbonate removal.

Laboratory Analysis of Arsenic

Soils were digested for As analysis using USEPA. Methods #3051 (USEPA, 1992). Method #3051 is a nitric acid digestion using pressurized Teflon® bombs in a microwave oven. The oven used is a CEM MDS-2000 microwave unit (CEM Corporation, Matthews, N.C.). All reagents were analytical grade.

Arsenic in the digestates was determined by either a cold vapor hydride method, according to the instructions provided with the MHS-10 Hydride System (Perkin-Elmer, 1978), or by graphite furnace as in USEPA. Method SW846-7060 (USEPA., 1992). The instrumentation was a Perkin-Elmer Atomic Absorption Spectrometer (AAS) Model 2380 with either the MHS-10 Hydride System or graphite furnace (Model HGA-400).

Background correction for the graphite furnace utilized a deuterium lamp. This type of correction compensates for smoke; however, it is inadequate for spectral interference. For As analysis by graphite furnace using deuterium lamp background correction, spectral interference from Al occurs (Slavin, 1984). Fortunately, this spectral interference resulted in a linear ($R^2 = 0.996$) increase in the As signal with increasing Al concentration. Therefore, the aluminum concentrations in the soil digests were measured using nitrous oxide flame AAS, and the aluminum interference was mathematically subtracted from the As signal. After correction for aluminum, the As concentration as measured by graphite furnace agreed well with the values obtained by hydride generation, which was free of this particular interference. However, the hydride method was considerably more labor intensive than analysis by graphite furnace, making the latter the preferred method of analysis.

Statistical Analysis and Mapping

Statistical comparison of the quick test and laboratory results was conducted by the Pearson product moment correlation test using "Sigma Stat v.2" software (SPSS, 1995).

The contaminant plume was plotted using "Geo-Eas 1.2.1" (USEPA., 1990) and/or "Surfer v.5" (Golden Software, 1994). Depths to the subsurface horizons were determined by soil probe and measuring tape. Topographical measurements were performed using a Lietz/Sokkisha C3a automatic level.

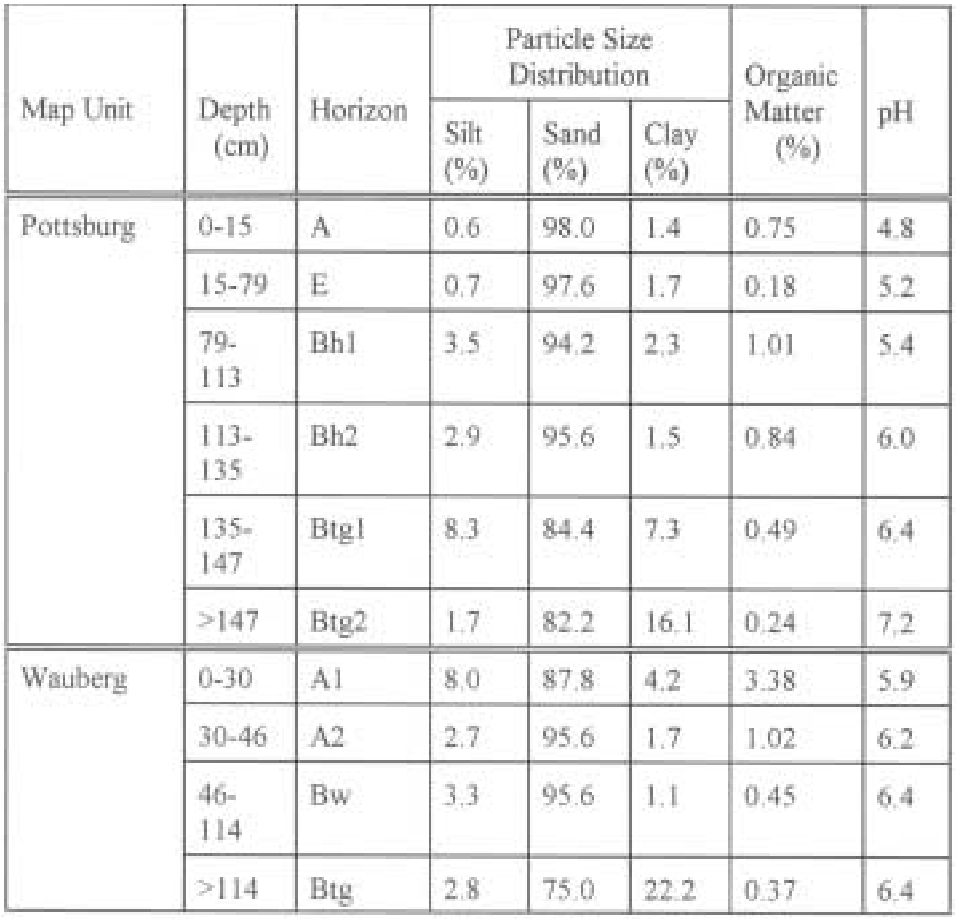
RESULTS AND DISCUSSION

The vat sits in soil that is mapped taxonomically as a Pottsburg sand (taxonomic soil classification: sandy, siliceous, thermic, Grossarenic Haplaquod; Thomas *et al.*, 1985). Table 1 gives a physical description of the actual soil at the vat, which is similar, but not identical, to a typical Pottsburg sand. The prominent subsurface features of the soil at the vat were the spodic horizon, starting at about 79 cm below ground surface (BGS) and the argillic horizon starting at about 135 cm BGS. Experience has shown that spodic and argillic horizons, because of their relatively high clay contents, exhibit sizeable retention capacities for oxyanions such as arsenate. This tendency was used to great advantage in delineating the As plume at this site by concentrating the quick test on samples taken from these two horizons.

About 65 m down gradient from the vat the soil map unit changed to Monteocha loamy sand (taxonomic classification: sandy, siliceous, hyperthermic, Ultic Haplaquod; Thomas *et al.*, 1985). This soil differs from the Pottsburg sand in that the spodic horizon is closer to the surface and an argillic horizon is now within 2 m of the surface. In the transition between Pottsburg and Monteocha, two spodic horizons were actually observed, with a light-colored, sandy layer (E horizon) between them.

Continuing down gradient, the soil map unit changed again to Wauberg sand (taxonomic soil classification: loamy, siliceous, hyperthermic, Arenic Albaqualf; Thomas *et al.*, 1985). At this point, the two spodic horizons had completely disappeared, merging with the surface horizon, and the argillic horizon was less than a meter BGS. The water table also rose along the gradient such that, for the Wauberg sand, the water table may be < 25 cm BGS for 3 to 5 months most years (Thomas *et al.*, 1985). The poor drainage at this site is conducive to the reduction of As(V) to As(III), which is more mobile in the environment than As(V) (Gulens

TABLE 1
Selected Characteristics of Soil within the Pottsburg and Wauberg Map Units Down Gradient from the Dipping Vat



Map Unit	Depth (cm)	Horizon	Particle Size Distribution			Organic Matter (%)	pH
			Silt (%)	Sand (%)	Clay (%)		
Pottsburg	0-15	A	0.6	98.0	1.4	0.75	4.8
	15-79	E	0.7	97.6	1.7	0.18	5.2
	79-113	Bh1	3.5	94.2	2.3	1.01	5.4
	113-135	Bh2	2.9	95.6	1.5	0.84	6.0
	135-147	Btg1	8.3	84.4	7.3	0.49	6.4
	>147	Btg2	1.7	82.2	16.1	0.24	7.2
Wauberg	0-30	A1	8.0	87.8	4.2	3.38	5.9
	30-46	A2	2.7	95.6	1.7	1.02	6.2
	46-114	Bw	3.3	95.6	1.1	0.45	6.4
	>114	Btg	2.8	75.0	22.2	0.37	6.4

and Champ, 1979). A physical description of the actual soil we observed within the Wauberg map unit is given in Table 1. Figure 1 is a simplified schematic of the soil horizons along a transect down gradient and extending over 100 m from the vat.

Figure 2 is a three-dimensional plot showing elevations for the spodic horizon, starting at the vat and grading into the surface horizon of the Wauberg soil. Superimposed on this topographic plot are analytically measured soil As concentrations, showing a "hot spot" about 85 m down gradient from the vat. The As concentration in the surface horizon in the hot spot was 30 +/- 0.9 mg As/kg of soil.

Figure 3 shows the topographic plot for the argillic horizon, starting at the vat and extending down gradient. Also shown on this plot are the As concentration contours for the argillic horizon. The argillic horizon at the far end of the plume contained rather high amounts of clay (Table 1). Most of the As that was associated

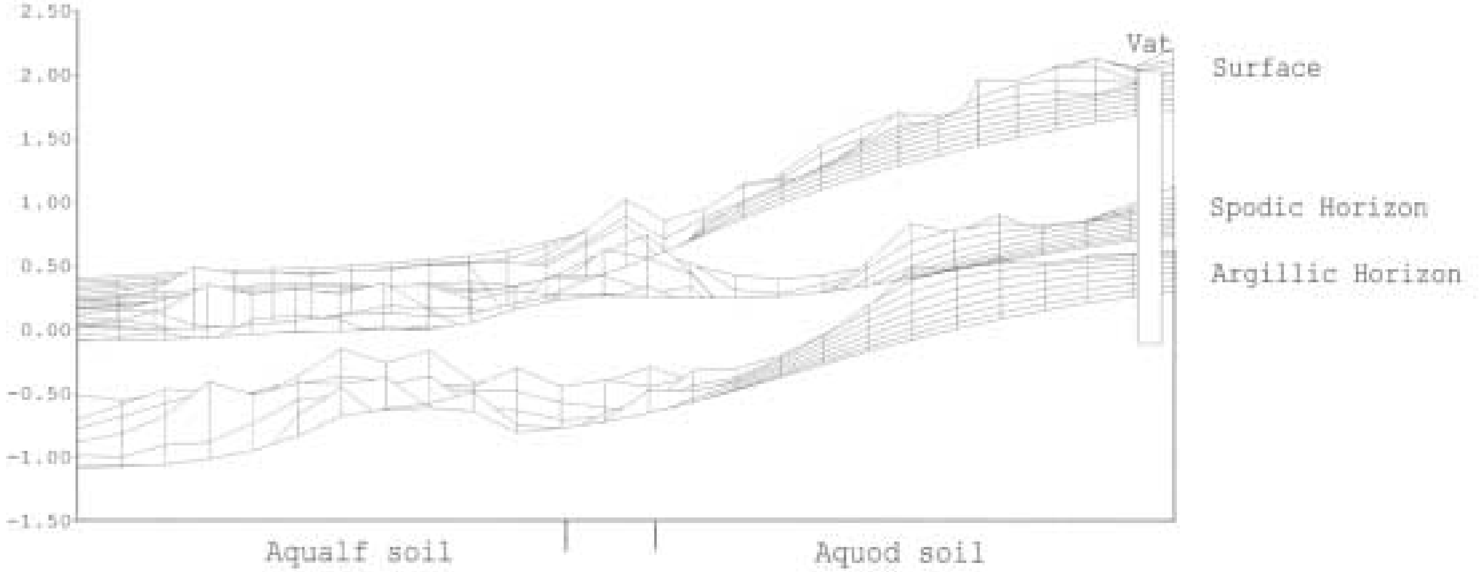


FIGURE 1

Elevations for the surface, spodic, and argillic horizons as a function of distance down gradient from the vat.

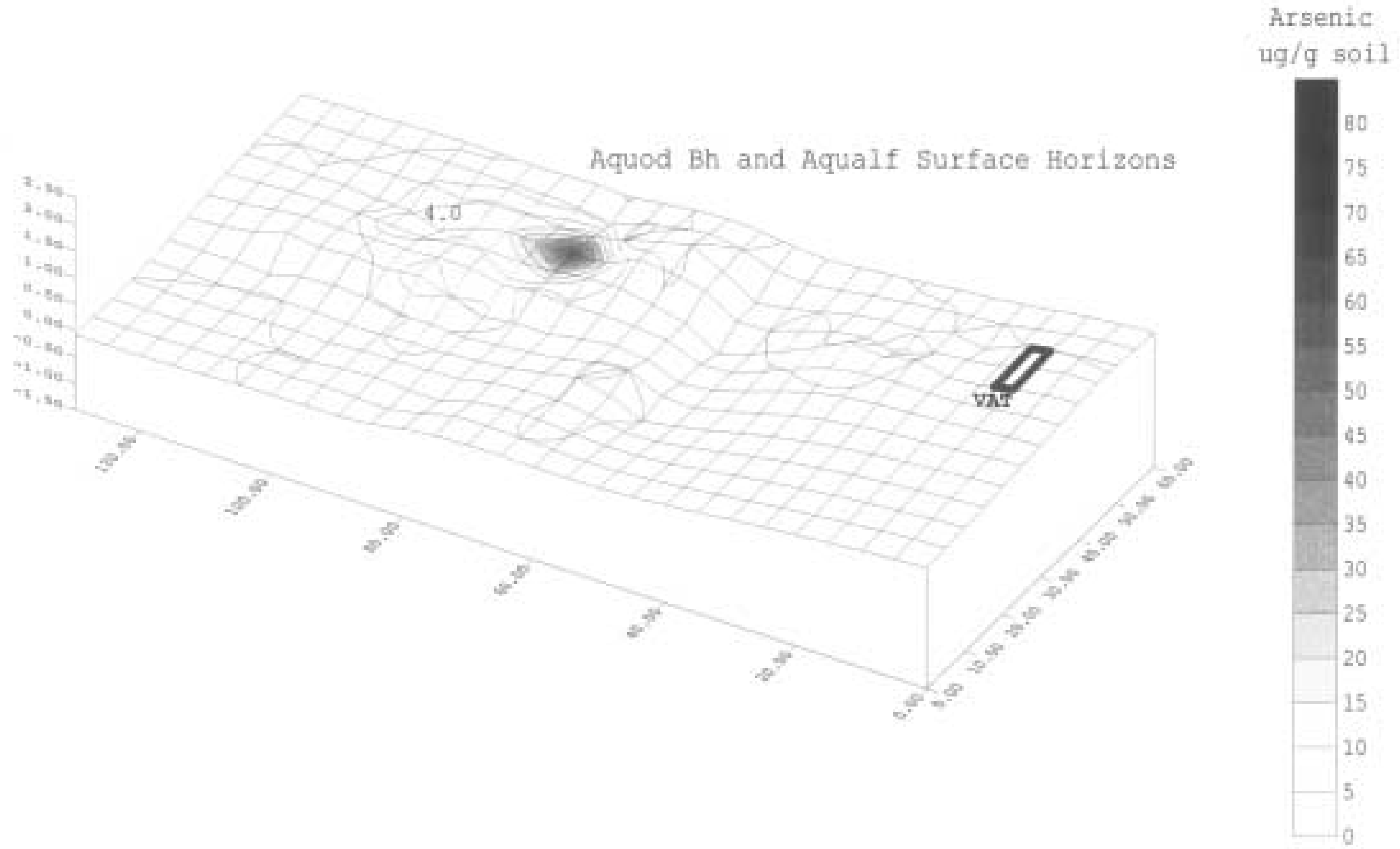


FIGURE 2

Topographic plot of the spodic/surface horizon continuum down gradient from the vat with arsenic concentration contours superimposed. Arsenic concentrations are from laboratory measurements. All distances are in meters.

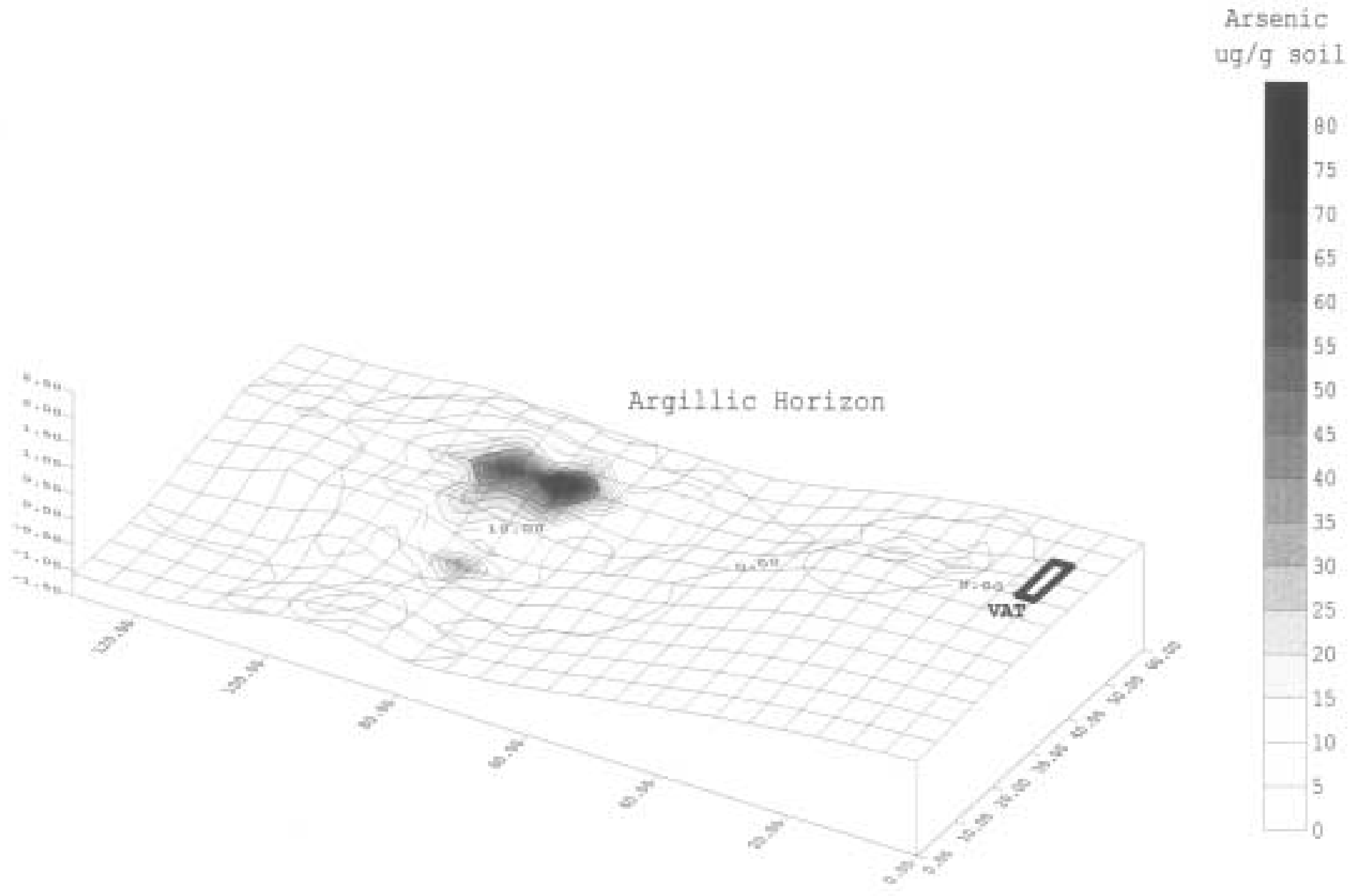


FIGURE 3

Topographic plot of the argillic horizon down gradient from the vat with arsenic concentration contours superimposed. Arsenic concentrations are from laboratory measurements. All distances are in meters.

with this horizon was confined to the upper few centimeters of clay due to its high sorption capacity for arsenic. The As concentration in the upper few centimeters of the argillic horizon within the hot spot was 100 +/- 3 mg/kg of soil.

The color chart provided by EM Science for visually estimating the concentration of As has an upper limit of 3.0 mg As/L, corresponding to a dark, chocolate brown color. This would represent a soil concentration of about 15 mg/kg of soil, provided that the procedure was quantitative in recovering soil As, which probably is not the case. This upper limit of 15 mgAs/kg of soil is the reason for the low correlation factor (R) when the quick test and laboratory results are compared statistically. The Pearson product moment correlation test yields $R = 0.621$ and $R = 0.692$ for the argillic horizon and spodic/surface horizon continuum, respectively. However, this same statistical test yields probability factors (P) of 1.1×10^{-10} and 4.4×10^{-14} for these same sample sets, respectively. Any $P < 0.05$ is regarded as a significant relationship for this statistical test.

Moreover, this relationship does provide a degree of quantitation when we visually compare the quick test results with those from the laboratory analytical measurements. The concentration contours for soil As measured by laboratory analysis and by the quick test for the spodic/surface horizon continuum (Figure 4) and for the argillic horizon (Figure 5) reveal two facts.

First, the quick test underestimated As concentrations within the hot spot, as it should because the quick test has an absolute upper limit of 15 mg/kg of soil that is imposed by the procedure. However, despite this limitation, the quick test did a good job of locating the hot spot that was 80 to 100 m down gradient. The limitation at high soil As concentrations can be eliminated by reducing the amount of soil used, which, in turn, raises the top concentration on the relative scale for the quick test. However, reducing the amount of soil used in the quick test would also increase the degree of sample-to-sample variability, which would have to be taken into consideration.

The second fact is that the quick test effectively delineated soil As along the boundary of the plume. This results from the high sensitivity of this method for detecting As. Possible reasons for the high sensitivity of the quick test in delineating phase boundaries are that (1) the arsine produced is confined to a small volume of headspace in direct contact with the indicator strip, and (2) the low soil-to-solution ratio of 1:5 is used for the quick test. Even small changes in As concentration may be important because they are related to soil topography, soil chemical and physical properties, and the resulting effects of these on water flow through the soil.

The areal extent of the As plume at this vat site represents a very difficult and costly situation from the standpoint of assessment via blind grid sampling. The bulk of the As in the plume occurred over 80 m down gradient from the vat. However, within 40 m of the vat a secondary hot spot with much lower As concentrations was observed. A precursory examination of the site using conventional gridding and blind sampling might have missed the bulk of the contamina-

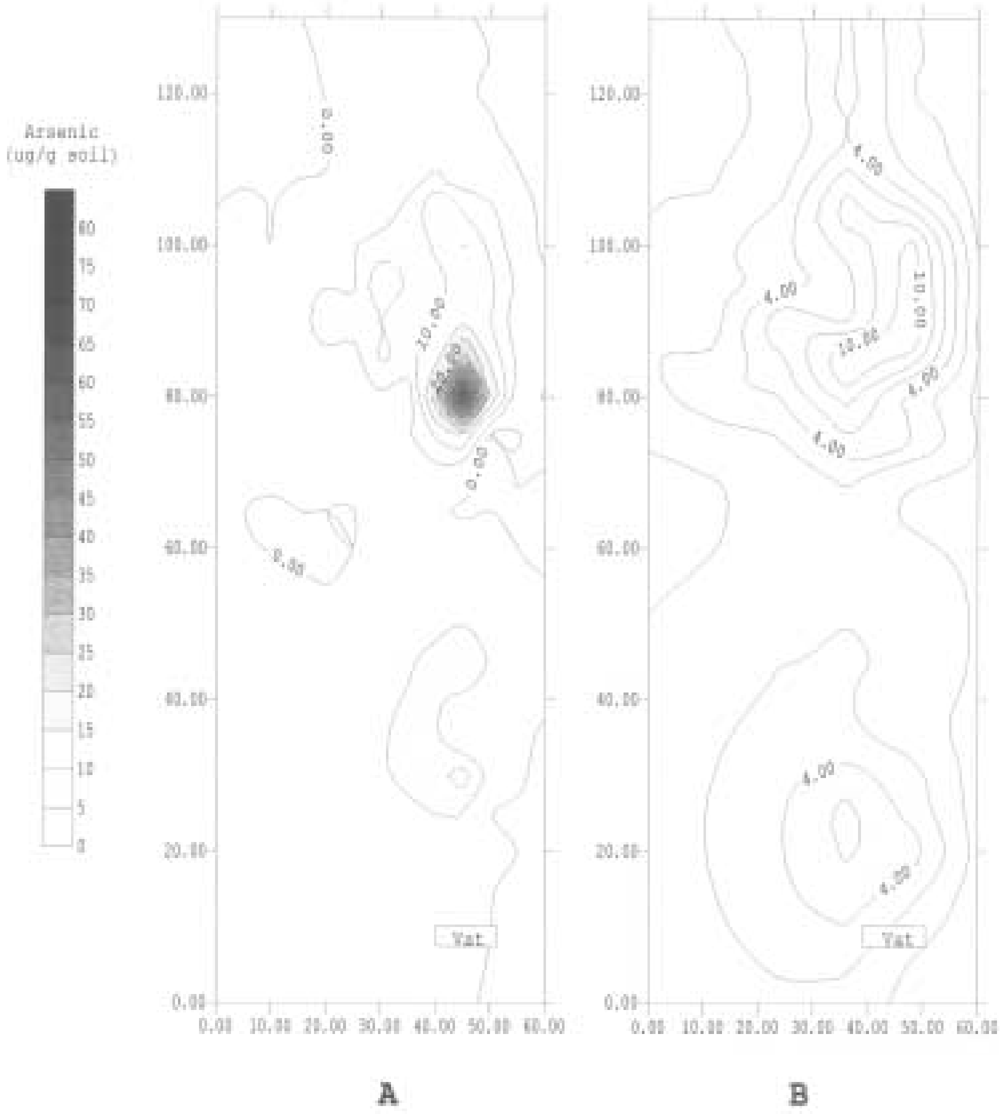


FIGURE 4

Arsenic plume delineation in the spodic/surface horizon continuum using (a) laboratory measurements and (b) results from the quick test. All distances are in meters.

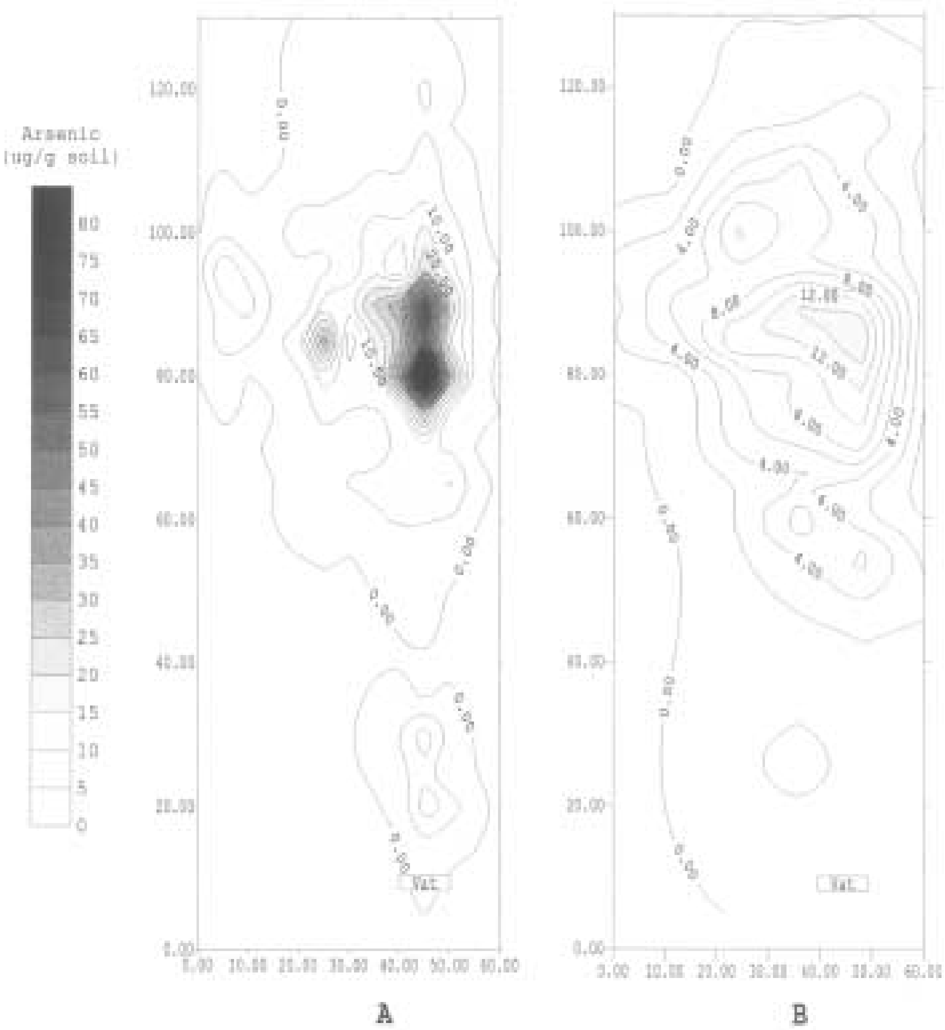


FIGURE 5

Arsenic plume delineation in the argillic horizon using (a) laboratory measurements and (b) results from the quick test. All distances are in meters.

tion lying 80 to 100 m down gradient. However, with the quick test the likelihood of this happening is much less because following a predetermined grid is not necessary, resulting in a much larger land area that can be tested in a given time.

We have used the quick test to rapidly delineate As plumes at vats situated in other soil types with excellent results. The quick test was particularly beneficial at one site where a vat was located in a deep sand less than 100 m from a sink hole. We tested soil samples starting at the vat and moving down gradient toward the sink hole. The quick test did not detect As in any sample, including those taken from a clay layer starting at about 2.5 m BGS. This finding can be explained by the very low As retention capacity of the sand and the fact that an elevated water table commonly occurs at this site, which would have effectively prevented As solution from coming into direct contact with the underlying clay layer. In this case, the As solution appears to have moved laterally into the sink hole, leaving no detectable trace in the soil. Without an onsite quick test for As, considerable expense could have been incurred during the assessment phase only to discover that the site was no longer As contaminated.

CONCLUSIONS

Based on a comparison of the quick test results with analytical measurements, several conclusions can be drawn:

1. The quick test can accurately delineate As contaminant plumes in a rapid and economical manner.
2. Because of its high sensitivity, the quick test is very effective at delineating the outer boundaries of contaminant plumes where the As concentration is low.
3. While the quick test can easily detect small increases in As concentration above background levels, it “saturates” at moderate to high concentrations like those that may be found within the interior of a contaminant plume; however, the quick test can be modified for high As concentration zones by decreasing the amount of soil used.

In general, the As quick test should be a convenient tool for scientists and engineers interested in delineating an As contaminant plume without having to resort to the cumbersome, expensive, and time-consuming process inherent in blind sampling followed by lengthy laboratory analysis.

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