Rapid field screening of soils for heavy metals with spark-induced breakdown spectroscopy

Amy J. R. Hunter, Richard T. Wainer, Lawrence G. Piper, and Steven J. Davis

Spark-induced breakdown spectroscopy (SIBS) is a recently developed atomic-fluorescence-based analytical technique that is analogous to laser-induced breakdown spectroscopy. SIBS, however, uses an electrical plasma generation method on nonconductive samples instead of a focused laser beam. Here we describe the basic characteristics of SIBS and its application to the field-screening analysis of soil, using a standard addition analytical approach. Detection limits of ~25 mg/kg have been seen for lead, chromium, barium, mercury, and cadmium. A variety of soils have been tested, some cocontaminated with organic material and uranium ($^{238}$U). © 2003 Optical Society of America

OCIS codes: 300.2140, 300.6210.

1. Introduction

The remediation community needs field-screening methods to detect the presence of toxic metal contamination in soils. A true multielement screening tool would provide huge time and cost savings. None of the commercial methods currently available for soil screening, however, are capable of performing multielement analysis with adequate sensitivity for all elements of interest. For this reason we have begun to develop a methodology for applying spark-induced breakdown spectroscopy (SIBS) to soil screening. We believe that this technology has considerable potential to address this need.

The two currently available commercial methods accepted by the U.S. Environmental Protection Agency (EPA) for screening soils in the field for metal contamination are x-ray fluorescence (XRF, EPA Method 6200) and an immunoassay technique, which is suitable only for mercury (Hg) detection (EPA Method 4500). XRF is an established technique used to measure elemental composition in many materials, such as metal alloys, painted surfaces, process powders, and soils. Although this method is good for heavier metals such as lead (Pb), it lacks adequate sensitivity for a number of lighter elements such as barium (Ba) and chromium (Cr). Moreover, the detection limits of XRF change with matrix type. Method 6200 gives the interference-free limits (i.e., measured in quartz sand) to be 150 mg/kg for Cr and 20 mg/kg of Pb. Actual repeated field-based detection limits vary substantially with the instrument used and range between 110–900 mg/kg for Cr and 40–100 mg/kg for Pb. Finally, although a number of attempts have been made over the past 10 years to commercialize laser-induced breakdown (LIBS) technology, to date none have been successful.

This paper describes some of our efforts to apply the SIBS technology to screening soils for the presence of metals. Since 1993, SIBS has been under development for use as a monitor for metals in airborne particulate materials. This technique is essentially a marriage between traditional spark spectroscopy and LIBS. The signal detection and spectroscopy of LIBS and SIBS are nearly identical. The key difference is in the spark generation, where LIBS uses a focused laser to cause the dielectric breakdown. SIBS, however, as in atomic fluorescence elemental analysis by spark spectroscopy, uses an electrically generated plasma to process and excite the sample. In classical spark spectroscopy, a conductive sample is used as a cathode, and the spark is generated between this sample and an anode electrode. In SIBS, since the sample is normally nonconductive, the plasma is produced between two rod-shaped electrodes. The sample normally fills at least part of the electrode gap and is processed chiefly by its presence in the atmospheric air plasma. The major benefits of LIBS over SIBS are a better sample vaporization for hard samples such as
metal alloys and the potential for “remote” spark generation or a small (high-resolution) sample volume. The major benefits of SIBS over LIBS are the ruggedness and low cost of the spark-generating hardware and the potential for a high-temperature plasma and strong signal at low cost.

As with a LIBS measurement, the plasma must be allowed to expand and cool before atomic fluorescence is detected so as to minimize the background associated with bremsstrahlung radiation, which is emitted in the early stages of the plasma. The efficiency with which the sample is processed by the plasma is a function of the physical and chemical characteristics of the sample. Various strategies have been developed to make the SIBS output quantitative for different types of samples. The most successful of these is based on standard addition analysis and is explained below.

This paper describes the basics of the SIBS technology as applied to soil analysis. We describe first the basic apparatus needed for the measurements. Then we discuss our methodology for making quantitative measurements of metals in soils. Finally, we present results from studies involving the detection of Pb, Cr, Ba, Hg, and cadmium (Cd) in soils. These results include not only preliminary estimates of achievable sensitivities but also touch on issues such as speciation and potential interferences from other contaminants in the soils being screened.

2. Experimental Apparatus

The apparatus required for performing these analyses has three parts, a sampling head, an excitation system, and a detection system. The excitation system is composed of a power supply coupled to a spark gap. This power supply combines a pulsed high-voltage supply [transformed wall voltage (ignition coil)] in parallel with a capacitor bank. The power is delivered in two steps. A high-voltage (10–40 kV), low-current arc initiates an ion channel between the electrodes (gap usually 5–6 mm). Then, once this channel is open, the charged capacitor bank discharges between the electrodes. This discharge provides most of the energy deposition and, therefore, the majority of the material processing in SIBS. Total energy deposition can be varied from 1 to 5 J with much less than 0.5 J arising from the initiator pulse and has a duration of ~4 μs. The repetition rate can be varied from single pulse to ~10 Hz.

The interface between the soil and the spark gap is shown in Fig. 1. Sparks are made on the surface of the soil by a pair of electrodes angled toward the surface near the soil. An air plasma is generated between the electrodes and incorporates some sample material. Radiation from the plasma is delivered to the detection apparatus with a fiber-optic bundle.

The character of the emission spectrum from the breakdown region depends upon the delay after spark ignition. To best observe the atomic emissions of interest, detection is delayed from the spark ignition and can be up to 100 μs with a 5-J spark. The much shorter typical plasma lifetime of LIBS usually requires a delay of several hundred nanoseconds to 1 μs. This delay simplifies the spectrum. The delay allows the broadband emission from free-electron and ion-electron recombinations to pass, as well as the short-lived ion emissions, minimizing the number of interfering lines sufficiently that a high-resolution spectrometer is not necessary to separate the atomic features of interest. Early studies of SIBS with soils used a short-focal-length spectrometer [Instruments SA (Jobin Yvon)] mated to a linear photodiode array (sometimes known as an optical multichannel analyzer, Princeton Instruments). The spectrometer had a 0.32-m focal length and a 2400 l/mm grating. This provided a spectral dispersion between 0.02 and 0.03 nm/pixel and an overall spectral resolution (FWHM of an isolated atomic line) that varied from 0.15 nm in the ultraviolet to ~0.10 nm in the visible (between 250 and 600 nm). Second-order spectral features are removed from longer-wavelength spectra (>450 nm) with a 420-nm longpass Schott glass filter.

More recently, we have found that the detection system can be simplified further by use of a small card-mounted spectrometer with a CCD detector. These miniature devices (Ocean Optics) are available with approximately 0.15-nm resolution, sufficient in most cases to resolve the spectrum normally observed in soils. More precisely, most spectral features recorded with this system had a half-width of 0.15 to 0.3 nm, whereas the CCD pixel resolution is 0.05 nm. In most cases, the peak height should be just well enough resolved. These more compact spectrometers will probably form the basis of a small and portable field-screening instrument for metals in soils. In both cases, the spectrometers are controlled with a personal computer. A complete diagram of a SIBS-based soil monitoring system is shown in Fig. 2. It should be noted that the elements are not to scale and that the final system could fit easily in a briefcase-style instrument carrying case. Thus the current generation of hardware is totally portable, given a
To meet the challenges associated with any analysis of a soil matrix, a methodology has been developed that will allow application of SIBS to most soils. This method is based upon standard addition. In the method of standard additions, a sample of soil is divided into smaller aliquots of known mass. Then each of these aliquots is spiked with different amounts of the target contaminant. Each aliquot is then analyzed for the contaminant, and a curve of response as a function of spike concentration is constructed from the data. With this curve, the concentration of the initial amount in the sample prior to spiking is determined by division of the ordinate at the abscissa's origin (y intercept) by the slope of the calibration curve (signal level/[added contaminant]). In general a standard addition curve of three to four points is sufficient to quantify most metals in soil.

The value in the standard addition method is that it allows matrix effects to be removed from the analysis. In an ideal world, in which soil matrix variations did not exist, a calibration curve could be made prior to fieldwork for a soil of a fixed composition. Signal-ratio measurements made in the field on samples of this same exact makeup (reference atom concentration is especially critical) could be reliably compared with this calibration curve without performing standard additions. However, soil composition from site to site, and even intrasite, can vary significantly, making the creation of a global calibration curve an unrealistic goal. SIBS with standard addition, on the other hand, can be applied to a wide variety of different soil types, because of its inherent reference to a local baseline composition. These same issues and potential solution apply to LIBS as well. In practice, applying this technique should not be onerous in fieldwork. At any given site usually only a few major soil types are present. Then it may be possible to construct a standard addition curve for each soil type, and individual samples could be quantified with these site-specific standard addition curves.

In the preliminary research, aqueous solutions of metals are added to make spiked subsamples of soil. These samples are dried (all regulatory limits are written as concentration of metals per dry weight). The resulting cakes are broken, and the soil is placed upon a clean, nonconductive surface for analysis. The sampling chamber of the SIBS device is placed on top of the soil, and sparks are generated.

The analysis process involves averaging the signals from approximately 20 successive sparks generated at the soil’s surface. A gate and delay system is used to collect the light. That is, only light extant after a suitable delay, typically 50–80 µs, is measured and averaged. Currently, between each sample, the electrodes are cleaned, first with nitric acid, then with deionized water and methanol. This technique has been observed to prevent carryover from highly doped samples quite effectively. Lesser preparation may suffice.

Currently, no attempt is made to control the amount of material processed in each spark. As a
result, the absolute signal intensity of a given feature varies considerably from one sample to the next. Thus simply plotting the absolute intensity of an analyte line at each concentration generally results in a highly scattered standard addition curve. Good linear correlation can be obtained, however, by normalization of the analyte signal intensities to the intensities of nearby atomic features, such as iron (Fe) or manganese, which are characteristic of the sample matrix. The intensities of these features will not vary with the amount of contaminant added to the aliquot during the standard addition process but will vary only with changes in the quantity of material processed by the spark and with the individual strength of the spark. Therefore the calibration curve is a signal-level ratio versus added contaminant concentration.

An additional requirement for the SIBS analysis of soils is the establishment of the correct analytical line to make the measurement. Since many of the metals of interest have low TCLP limits, this is usually equivalent to locating the most easily excited and brightest emitting feature. However, there are cases in which it is not required or even desirable to use the brightest line. Ba, for example, is a regulated metal with a very high TCLP limit (20× TCLP in this case 2000 mg/kg). Because of the probability of self-absorption and other effects of extremely high concentrations, it is useful to choose a less brightly emitting line for this element.

4. Results

In this publication, results for three major soil types are given as well as data from both the linear photodiode array system and miniature spectrometer system. The three soils are Andover soil (acquired outside our laboratory), and two National Institute of Standards and Technology (NIST) standard reference materials, SRM 2709 (San Joaquin soil) and SRM 2710 (Montana soil). In preliminary research on these samples, we investigated sample preparation procedures including a comparison between pelletized and nonpelletized sample preparatory techniques. It was determined that loose soil was not only simpler to analyze but that the signal levels were much higher than in pelleted samples. Thus all results shown here come from studies of loose soil samples that have had no special treatment other than drying and removal of large stones.

The effort to select the optimum wavelength starts with building a compendium of spectral lines by use of a fairly heavily doped sample. Most of the visible spectrum is mapped out with this sample, with emphasis on the lines expected to be the dominant ones. For example, our survey for Ba lines found nine separate lines (230.42, 233.53, 389.18, 413.07, 455.40, 493.41, 551.91, 553.55, and 577.76 nm) that were clearly visible in the spectrum of Ba-doped Andover soil. Of these, the 230.42-, 233.53-, and 413.07-nm lines are not well separated from background (predominantly Fe lines) and therefore are not ideal. The line at 389.18 nm is too weak for even the relaxed measurement requirements of Ba—i.e., little signal even at 1500 mg Ba/kg soil. The brightest Ba line, at 455.50 nm, appears readily even in unspiked Andover soil (21 mg/kg) and is therefore unlikely to be able to be used to construct a linear calibration curve at the much higher concentrations that are needed to perform standard additions (around the 2000-mg/kg level). Of the rest, the 553.55-nm feature is ideal, as it is moderately strong and has several strong and well-separated Fe lines nearby that can be used for the normalization procedure. Similar evaluations have been performed for Pb, Cr, Hg, and Cd. The analytical lines chosen for these elements are 405.78, 425.43, 546.30, and 508.58 nm, respectively.

Our first example of the application of SIBS to soil analysis involves determining the levels of Pb and Cr in soil. Figure 3 shows spectra between 404 and 409 nm when Andover soil is subjected to spark excitation. Two spectra are shown, one for untreated soil, and one for soil to which 200 mg/kg of Pb has been added in the form of Pb(NO₃)₂. The Pb line at 405.78 nm is clearly quite strong in the spiked sample and notably weaker in the unspiked sample. The other prominent features, whose intensities are essentially the same in both spectra, include Fe lines at 404.58, 406.36, and 407.17 nm and a strontium line at 407.77 nm. These are potential reference lines, and their invariance between the two curves indicates the consistency of the soil makeup between the doped and the undoped samples.

Once obtained, spectral data such as shown in Fig. 3 are converted into quantitative intensities by measuring the peak height of the feature of interest and subtraction of the local baseline. The analyte intensity is then normalized to that of a nearby Fe
line, and this ratio is plotted against added contaminant concentration to construct the standard addition plot. Figure 4 shows such a plot for determining the concentration of Pb in Andover soil. In this plot the 406.36-nm Fe line has been used for normalization. We performed similar analyses for Pb in the two SRMs and also for Cr in all three soil types. The results are shown in Table 1. Table 1 also shows the results of soil analysis on these samples by an independent analytical laboratory and, in addition, the certified values of the SRMs.

The independent laboratory data shown here were analyzed with a normal turnaround time of 2 wk. Their analysis involves digestion of the soil with strong acids, subsequent filtration of the digestate, followed by inductively coupled plasma analysis of the digestate. Depending upon the type of soil, this treatment can be inadequate for the removal of all the analyte from the matrix. When the digestion is incomplete, analyte material is easily lost during the filtration process, leading to results that will be too low. This effect is undoubtedly the reason the Cr results of the SRMs from the independent laboratory are erroneous. On the other hand, the SIBS results compare quite favorably with the certified values. As illustrated in Table 2, our results also show that the sensitivity of SIBS compares favorably with the detection limits achievable by the XRF technique as published in EPA Method 6200.1 To obtain these limits, the XRF researchers had first to dry, grind, and homogenize the samples. Of these steps, only drying is necessary for SIBS analysis.

The performance characteristics for SIBS are defined by the EPA's guidelines (EPA SW-846), including a method detection limit (MDL) of $3.143 \times \sigma$ (where $\sigma$ is standard deviation of replicate samples) and a reliable quantitation limit of $4 \times \text{MDL}$. The detection limits reported in Tables 1 and 2 are detection limits calculated from the accuracy of the curve fit from a single sample analysis. This is dependent on the spectra-to-spectra (i.e., ratio-to-ratio) variation of each spark for each aliquot. Typically, each

---

**Table 1. NIST Certified Values, Laboratory Measurements, and SIBS Values for Pb and Cr**

<table>
<thead>
<tr>
<th>Soil</th>
<th>SIBS Analysis (mg/kg)</th>
<th>Independent Lab Analysis (mg/kg)</th>
<th>NIST Certification (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Cr</td>
<td>Pb</td>
</tr>
<tr>
<td>Andover soil</td>
<td>32 $\pm$ 3$^a$</td>
<td>18 $\pm$ 27</td>
<td>43 $\pm$ 4</td>
</tr>
<tr>
<td>NIST SRM 2709</td>
<td>41 $\pm$ 18</td>
<td>111 $\pm$ 24</td>
<td>$&lt;$4</td>
</tr>
<tr>
<td>San Joaquin soil</td>
<td></td>
<td></td>
<td>18.9 $\pm$ 0.5</td>
</tr>
<tr>
<td>NIST SRM 2710</td>
<td>4700</td>
<td>33 $\pm$ 17</td>
<td>5600 $\pm$ 400$^b$</td>
</tr>
<tr>
<td>Montana soil</td>
<td></td>
<td></td>
<td>5532 $\pm$ 80</td>
</tr>
</tbody>
</table>

$^a$Lower error associated with increased number of averages.

$^b$Higher error results from sample dilution.

$^c$NIST analyzed, but not certified.

---

**Table 2. SIBS and XRF (EPA Method 6200) Detection Limit Comparison**

<table>
<thead>
<tr>
<th>Element</th>
<th>XRF Interference-Free Detection Limits mg/kg$^a$</th>
<th>XRF Field-Based Detection Limits mg/kg</th>
<th>SIBS Detection Limits mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>150</td>
<td>110–900</td>
<td>25</td>
</tr>
<tr>
<td>Pb</td>
<td>20</td>
<td>40–100</td>
<td>25</td>
</tr>
<tr>
<td>Hg</td>
<td>30</td>
<td>Not reported</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>100</td>
<td>Not reported</td>
<td>25</td>
</tr>
</tbody>
</table>

$^a$Interference free” denotes measurements performed in quartz sand (Ref. 1).

$^b$A wide variety of instruments were used to acquire this data; therefore these detection limits are reported as a range (Ref. 1).
doped and undoped aliquot is sparked 60 times (at 1 Hz). Therefore each sample can be analyzed with a three-point standard addition curve in approximately 3 min. The maximum reliable spark rate has not yet been determined, but 3 Hz has also proven to be reliable, cutting analysis time to 1 min. The calculated concentration for the undoped sample is obtained by means of the linear curve fit. The calculated uncertainty represents the uncertainty in the y intercept divided by the slope. Higher precision in the curve fit and lower sample-to-sample deviation MDL can, of course, be obtained with further averaging of acquired spectra and increased number of doped aliquots. The accuracy will eventually be limited by sample-to-sample variation. The first data point in Table 1, for example, is produced from the average of seven replicate sample analyses made in the same manner described above. The uncertainty is the standard deviation of the seven resultant concentrations, showing that the overall accuracy of the technique is significantly better than its precision.

We have also performed standard addition analyses on soils for Ba, Hg, and Cd. The approach is the same for these metals as for Pb. The only difference is the wavelength region of interest. As described above, Ba is interesting in that the strongest line is not ideal. A line that is sufficiently weak enough to be of comparable magnitude to nearby reference lines is required (countering the large Ba concentrations that are necessary to cause a level of environmental concern). A sample spectrum from the Ba analysis in Andover soil is shown in Fig. 5. Detection limits for these elements are between 25 and 35 mg/kg, similar to the Pb and Cr cases. In the case of the Hg analysis, this detection limit is not sensitive enough to establish the proper disposal method for soils and will need to be improved. The most significant source of error in the measurement comes from actual variation in the analyte and doped Hg concentrations in the sample. More careful sample handling, e.g., homogenization by means of sample grinding, is an obvious path to improvement. For the other elements, our detection limits are below the 20× TCLP standard.

We determined all these detection limits with the method of standard additions using aqueous additions and then performing a drying step prior to the SIBS analysis. This method was valuable for establishing proof of principle but was more complex than we would like for field implementation. We therefore developed a dry method for standard addition. This was accomplished by preparation of either a sample of silica sand or an additional soil subsample to make a small amount of highly doped material, with the previously discussed aqueous addition method. We then add small portions of this dried material to our sample aliquots to perform the standard additions.

An example of this approach is to make small quantities with varying high concentrations, such as 400-, 800-, and 1200-mg Hg/kg soil. Portions of 100 mg (small, compared with the analyte soil sample, thus changing the physical properties little) of each of these lots when added to 2-g samples will yield samples spiked to 20, 40, and 60 mg/kg, respectively. The material is dispersed in the unknown samples by means of shaking, and the SIBS analysis is performed. The results for Ba are presented in Fig. 6. We find the sensitivity for detection of Ba and Hg

![Fig. 5. SIBS spectrum of Andover soil near 549 nm with and without the addition of 250-mg Ba/kg.](image)

![Fig. 6. Standard addition curve for Andover soil with the dry-spiking technique. Curve obtained with the 553.55-nm Ba line, normalized to the Fe(I) line at 544.69 nm.](image)
with dry standard additions to be nearly the same as when the reagents were added as solutions.

As previously discussed, SIBS is a technique that measures the total loading of metals in a sample. This should be a natural consequence of the completeness of the plasma processing, but this must be experimentally verified. It is important, therefore, to be certain that the chemical compound in which the contaminant is bound has no effect upon the intensity of the SIBS signal at a given concentration. We have studied this speciation issue with a number of contaminants. The Cd measurement is representative of the rest and is presented here.

Samples of Andover soil were prepared by addition of solutions with varying concentrations of cadmium acetate, cadmium nitrate, and cadmium chloride. The spiked samples had Cd levels of 50-, 100-, and 500-mg Cd/kg for all three compounds. The spectra for the additions of the different compounds at each concentration overlaid each other well. That is, the peak heights associated with all the Cd additions are identical. Moreover, the standard addition plots were identical, i.e., independent of the chemical form of the Cd contaminant. Thus we infer no effect of chemical form on the SIBS analysis. Similar results for water-soluble Hg and Pb compounds have been obtained.

Although there are no compound-specific effects at these relatively low dopant levels, there could be some at higher levels. Compound-specific behavior has been observed in LIBS studies of soils doped near 5% with various compounds of Pb and Ba. At such levels the contaminant forms a significant percentage of the total mass of the sample, and the physical and chemical characteristics of the contaminant appear to become important. At the smaller concentrations used in this study, the dopant makes up only a tiny percentage of the total mass and would therefore be expected to exert a miniscule effect upon the analysis of those samples.

Another area of concern is whether the ability of SIBS to monitor metals in soil is compromised when those soils are contaminated with other commonly encountered substances, such as organics and transuranics. To test the effects of organic contamination on the measurements, a sample of soil that had been previously spiked with Pb to the 225-mg/kg level was subdivided into three portions. Two of these portions were spiked with organic material. After a few measurements, the soil was further contaminated and submitted to additional determinations. The organic spiking procedure involved dissolving a measured amount of vacuum pump oil in trichloroethylene. Measured quantities of this solution were added to weighed soil samples, mixed thoroughly, and allowed to stand overnight.

The analysis was performed with the ratio of the Pb line at 405.78 nm to the Fe line at 406.36 nm as a function of organic contaminant of the soil. As a result of the high volatility of trichloroethylene and the high surface area of the soil, this component was likely completely evaporated before the analysis. Therefore the vacuum-pump oil fraction of the additions was deemed the only remaining organic material. Although we observed that the data had more scatter than in some of our previous runs, the signal ratios were the same within statistical limits at all levels of organic contamination (from 5 to 27 g/kg). Total signal levels were reduced somewhat at the higher levels of organic contamination, but the intensity ratios were not. These results indicate, therefore, that the SIBS technique is equally well suited to soils containing high levels of organic contamination as well as to those that are relatively free of organic contamination.

In addition to the Andover soil contaminated with organics, we also examined whether heavy contamination by 238U would affect the analysis of Andover soil for Ba. Andover soil was doped to the 1000-mg U/kg soil level and then was analyzed for Ba with the standard addition technique. We generated a standard addition curve using additions between 500- and 2500-mg Ba/kg soil with the 553.55-nm line (ratioed to the Fe line at 543.45 nm). These results are shown in Fig. 7. The standard addition curve shown indicates agreement with the laboratory analysis with statistical limits (±300 mg Ba/kg). This apparently large statistical uncertainty is a result of the large standard addition amounts required for measuring Ba at the regulated levels. As uranium (U) has no known emission line near the monitored Ba and Fe lines, we expected no interference from high U doping. In fact, these results are identical to those obtained in soil without U contamination, indicating that the contamination had no deleterious effect on the analysis.

5. Conclusions

The results of these projects indicate that SIBS can identify and quantitate a variety of environmentally interesting metals in soil matrices. Although the
standard addition analysis does represent some investment of time in sample handling, it may be more acceptable to the remediation community for field screening than sending all samples to be analyzed in a laboratory setting. Observed detection limits are \( \approx 25 \text{ mg/kg} \) for all investigated metals. These metals have been investigated in loam (Andover soil), two types of standard reference materials, and, in some cases, sand.

The observed detection limits in most cases overlap the requirements for the field-screening analysis of contaminated soil. For each metal surveyed, the detection limits are sufficient to identify which samples require no treatment prior to disposal and which should be subjected to verification in the laboratory. The one exception to this statement is the analysis of Hg, which is currently insufficiently sensitive. We anticipate being able to increase the sensitivity of our Hg analysis with more careful sample preparation.

This study has been funded by U.S. Department of Energy (DOE) contracts DE-FG02-98ER82643 and DE-FG02-00ER83073 and U.S. EPA contracts 68-D-98-130 and 68-D-00-204.

References