

USE OF A FIELD PORTABLE X-RAY FLUORESCENCE ANALYZER TO DETERMINE THE CONCENTRATION OF LEAD AND OTHER METALS IN SOIL SAMPLES

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Abstract: Field portable methods are often needed in risk characterization, assessment and management to rapidly determine metal concentrations in environmental samples. Examples are for determining: "hot spots" of soil contamination, whether dust wipe lead levels meet housing occupancy standards, and worker respiratory protection levels. For over 30 years portable X-Ray Fluorescence (XRF) analyzers have been available for the *in situ*, non-destructive, measurement of lead in paint. Recent advances made possible their use for analysis of airborne dust filter samples, soil, and dust wipes. Research at the University of Cincinnati with the NITON 700 Series XRF instrument (40 millicurie Cadmium 109 source, L X-Rays) demonstrated its proficiency on air sample filters (NIOSH Method No. 7702, "Lead by Field Portable XRF"; limit of detection 6 µg per sample; working range 17–1,500 µg/m³ air). Research with lead dust wipe samples from housing has also shown promising results. This XRF instrument was used in 1997 in Poland on copper smelter area soil samples with the cooperation of the Wrocław Medical Academy and the Foundation for the Children from the Copper Basin (Legnica). Geometric mean soil lead concentrations were 200 ppm with the portable XRF, 201 ppm with laboratory-based XRF (KeveX) and 190 ppm using atomic absorption (AA). Correlations of field portable XRF and AA results were excellent for samples sieved to less than 125 micrometers with R-squared values of 0.997, 0.957, and 0.976 for lead, copper and zinc respectively. Similarly, correlations were excellent for soil sieved to less than 250 micrometers, where R-squared values were 0.924, 0.973, and 0.937 for lead, copper and zinc, respectively. The field portable XRF instrument appears to be useful for the determination of soil pollution by these metals in industrial regions.

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INTRODUCTION

Exposure to humans to toxic metals can occur through many pathways including through the air, dust, soil and food. The exposure can result from environmental releases of the metals during mining, milling and smelting, from events associated with uses of the metals, such as in the combustion of leaded gasoline, from deterioration of lead-based paints, and from processes designed to recover metals, such as the recycling of batteries, and secondary

smelters. In order to assess the level of exposure it is necessary to have methods which can accurately measure the concentrations of metals in the various media such as air, soil and dust.

Analytical methods which can rapidly provide on-site information on contaminant levels can be very useful in facilitating the making of "real-time" decisions regarding exposure assessment, risk assessment and risk management.

In the U.S. decisions on whether a house is safe for children to occupy are currently based, in part, on the

quantity of lead measured in the dust on the floor and various window locations [9]. After collecting the samples, the process of sending samples to the laboratory, analysis, and receiving the results frequently takes a week or more. In the meantime, the family is either temporarily housed in another location with the costs and inconvenience associated with the relocation, or the children remain exposed if they are living in the housing. A method to determine the lead content of the wipe sample while the inspector was still in the home would greatly speed up this process.

The protection of workers from airborne metal contamination often requires the use of respirators worn by the workers. Whether or not respirators are needed, and the specific requirements of the respirators needed, depends on knowledge of the lead content of the air. Air conditions in some settings frequently change and in new work sites levels are often not known. Current knowledge of air lead levels, for example, would facilitate accurate decisions on whether there was a need to increase respiratory protection or whether respirators are needed at all. Air samples often take several hours to collect, followed by the several days before results are available as for dust wipe samples as mentioned above.

In assessing exposure risk of a child's home environment, making decisions on the suitability of a particular area for a vegetable garden, or the location of a play area, or the level of hazard posed by contaminated house dust, or in recommending what type of medical screening would be appropriate, the rapid availability of information on the level of metal contamination can be useful. Providing site specific recommendations to a family while public health staff are already at the home site can often be more efficient and helpful to the family and others involved.

Paint Lead. For over 30 years XRF instruments for the *in situ* measurement of lead in painted surfaces in housing have been used to help assess the risk of childhood lead poisoning [8]. With these instruments, atoms of lead are excited and their characteristic x-rays are released through fluorescence, as they return to their unexcited state, and are detected by the instrument. During the past several years there has been a marked improvement in the technology of the field portable XRF instruments that have increased the sensitivity of the measurements and made possible their use for measurement of lead in dusts and soils. At the University of Cincinnati research is being conducted to explore the usefulness of field portable XRF for measuring lead in air sample filters, in dust wipes and in soil. The XRF instrument used thus far in these research efforts has been one manufactured by the Niton Corporation (Bedford, Massachusetts). This instrument, model series 700, uses a 40 millicurie Cadmium 109 sealed source and measures the L x-ray. The effective measurement area is 1×2 cm. The XRF instrument is also capable of measuring other metals, including arsenic, copper and zinc. For each reading an uncertainty range is also determined. Metal concentrations measured by XRF were compared with results determined by atomic absorption spectroscopy (AAS)

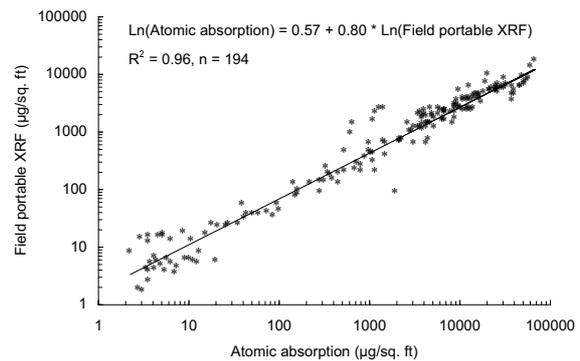


Figure 1. Relationship between dust lead levels measured by field portable XRF and by atomic absorption [12].

Air Samples. Workplace air samples were collected from a bridge lead abatement site, first measured with the field portable XRF analyzer, and then in the laboratory with graphite furnace atomic absorption (GFAA) with hot nitric acid digestion using a modification of NIOSH Method No. 7082 [5]. Each air filter was measured in five locations (top, middle, bottom, left, right) by the XRF instrument to achieve the algorithm that yielded the best correlation with the results by GFAA [2, 3]. The resulting algorithm is:

$2.0 * \text{Middle Reading} + 3.8 * (\text{Top} + \text{Bottom Readings})$
The data were judged by an independent agency to be sufficient for the development of an approved analytical method: U.S. National Institute for Occupational Safety and Health (NIOSH): No. 7702, Lead by Field Portable XRF [6]; estimated limit of detection of 6 micrograms of lead per sample and a working range of 17–1,500 micrograms per m^3 of air [6].

Dust Wipe Samples. Research comparing measurement of lead in dust wipes from floor and window areas of housing by field port x-ray fluorescence and atomic absorption is currently underway. Dust wipe samples were collected in housing containing lead-based paint, some during pre-intervention activities and some in housing that had undergone lead hazard control and was ready for determination of suitability for occupancy. After collection, the dust wipes were folded five times in order to produce a folded area of about 2×4 cm, a size that for which four adjacent readings with the XRF instrument would cover the entire surface of the folded wipe. In initial work [12], a plot of readings by XRF and by the GFAA method described earlier (Fig. 1) shows that the results are strongly correlated. Current U.S. standards for lead in surface dust in housing range from 100 micrograms per square foot for floors to 500 for window sills and 800 for window troughs [9, 10]. The area measured is usually one square foot for floors and somewhat smaller for the window samples. The standard for floor dust lead will probably be lowered substantially in the near future [11]. Field blank results thus far have indicated

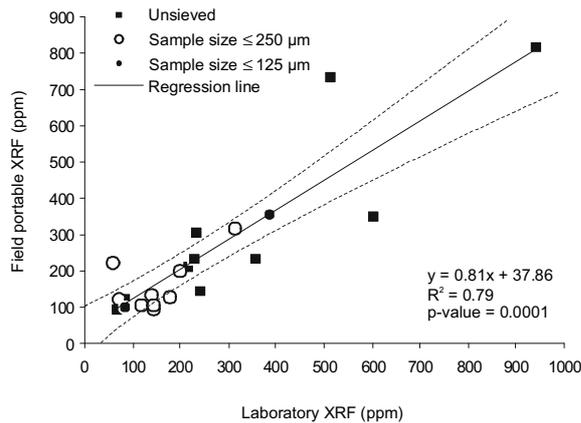


Figure 2. Relationship between soil lead levels analyzed by field portable XRF (analyzed in Poland) and by Laboratory XRF. The dotted lines are the 95% confidence intervals.

average levels of about 13 micrograms of lead by XRF and about 0.3 micrograms by flame AA. Further research is currently underway using different types of wipes and a variety of surfaces. The use of field portable XRF could speed up the process of determining whether the housing was suitable for occupancy. Many housing units currently do not meet occupancy standards when first tested after lead hazard control work. Of 2,217 housing units in an on-going evaluation of effectiveness of lead hazard control intervention strategies, more than one-fourth did not pass the initial testing to determine occupancy (clearance) standards [4]. This housing, then, must be re-cleaned, re-sampled and re-analyzed again until clearance is met before occupancy can occur. The costs associated with these clearance failures, including the costs of finding alternative housing for the occupants during this period, can be substantial.

Soil Samples. Soil samples collected in areas of industrial and residential contamination are generally analyzed using atomic absorption spectrometry laboratory methods. Prior to analysis, the samples are frequently prepared by a sieving

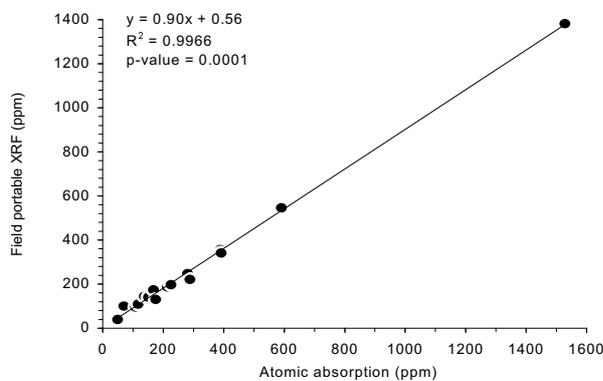


Figure 4. Relationship between soil lead levels analyzed by field portable XRF and by atomic absorption method (particle size $\leq 125\mu\text{m}$) ($n = 16$).

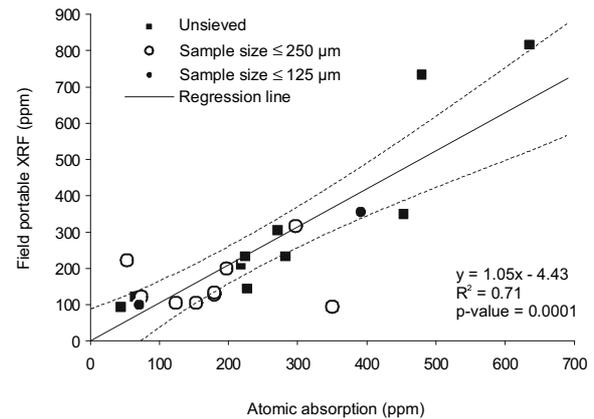


Figure 3. Relationship between soil lead levels analyzed by field portable XRF (analyzed in Poland) and by atomic absorption method. The dotted lines are the 95% confidence intervals.

process followed by an acid digestion step. For example, in a study of soil contamination in a residential community near a former lead smelter [1], soil was sieved to less than 2 mm and less than 250 micrometers followed by digestion in 7N nitric acid. A considerable savings in time and effort would occur if a field method could be developed which did not require laboratory digestion and analysis. This paper represents one of the first published applications of the field portable XRF instruments for the examination of the pollution of soil with lead and other metals in an industrial region.

MATERIALS AND METHODS

The XRF instrument has a sample holder attachment [7] that will permit the analysis of bulk samples of dust and soil. During the summer of 1997 there was an opportunity to perform some testing with the portable XRF in Poland in cooperation with the Foundation for the Children of the Copper Basin (Legnica) and the Wrocław Medical Academy. The timing of the planned sample collection, unfortunately, coincided with the very serious and tragic

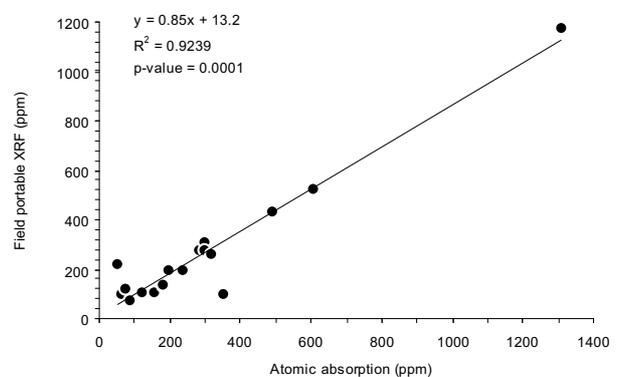


Figure 5. Relationship between soil lead levels analyzed by field portable XRF and by atomic absorption method (particle size $\leq 250\mu\text{m}$) ($n = 18$).

Table 1. Lead determinations in Polish soil samples by three methods (ppm) (n=21)*.

Method	Statistics	Geometric Mean	Median	Range
Field Portable XRF (in Poland)		200	205	92–817
Lab XRF (KeveX)		201	208	61–941
Atomic Absorption		190	216	43–637
Field Portable XRF (UC)		174	186	43–879

*10 samples unsieved, 9 sieved to <250 μm and 2 sieved to <125 μm.

flooding of the Odra (Oder) River area. Thanks to the efforts of the staff of the Foundation for the Children of the Copper Basin and the Wrocław Medical Academy, the project was still able to be completed.

Twenty-one soil samples from the copper smelter regions of Poland (Legnica and Głogów), collected and analyzed by field portable XRF in Poland, were selected for additional analysis at the University of Cincinnati (UC). The uncertainty of the lead analysis in Poland for these samples was less than or equal to plus/minus 15%. About one-half of these samples were measured *in situ* in Poland and the rest were sieved in Poland, most to less than 250 micrometers, prior to analysis, also in Poland. Additional analysis at UC used the following methods:

- Laboratory-based XRF using a KeveX instrument (for lead).
- Atomic absorption using GFAA for arsenic and copper and flame AA for lead and zinc, after hot nitric acid digestion, using a modified version of NIOSH method No. 7082 [5].
- Field portable XRF at UC (for lead, arsenic, zinc and copper).

Of the 21 samples, 10 were received at UC as unsieved samples since they had been measured *in situ* in Poland and were later sieved at the University of Cincinnati to provide two additional subsamples: less than 250 μm and less than 125 μm. Nine of the other samples had previously been sieved to less than 250 μm and were later sieved to less than 125 μm at the University of Cincinnati. The total number of

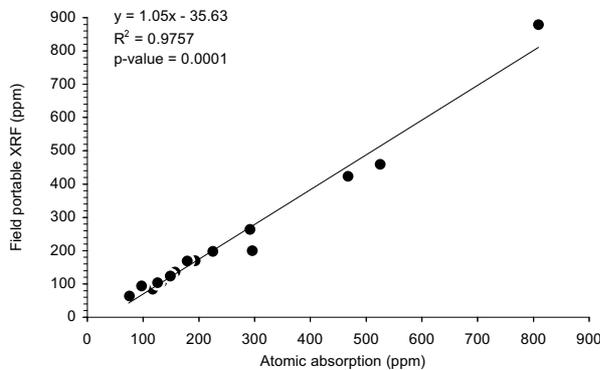


Figure 6. Relationship between soil zinc levels measured by field portable XRF and by atomic absorption method (particle size ≤ 125 μm) (n = 17).

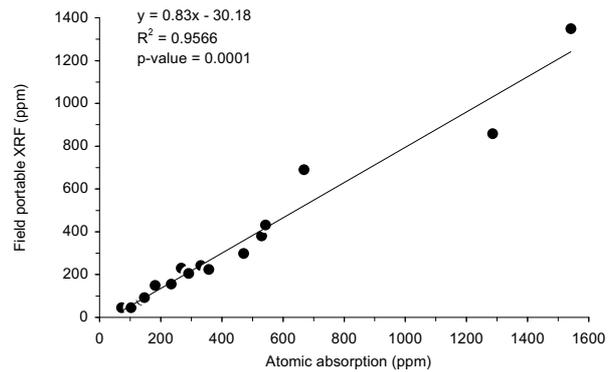


Figure 7. Relationship between soil copper levels analyzed by field portable XRF and by atomic absorption method (particle size ≤ 125 μm) (n = 17).

samples, including sieved fractions, was 49. Where possible, aliquots of the sieved samples were prepared for XRF and AA analysis.

RESULTS

Lead. Comparisons of the results by the field portable XRF in Poland with those at UC by laboratory XRF (Fig. 2), by flame atomic absorption (Fig. 3) and by a field portable XRF (UC) are summarized in Table 1.

The R² values ranged from 0.71–0.86; with the highest involving the comparison of results for field portable XRF, for XRF (UC) and atomic absorption.

The relationship between results using field portable XRF instruments in Poland and at the UC was similar to those previously examined (R² = 0.75). The strongest correlation of lead concentration was found by comparing results of the two laboratory methods: flame AA and laboratory XRF (R² = 0.95).

For a concentration of 300 ppm lead determined by the field portable XRF in Poland, the equivalent value with the laboratory XRF method, as shown by the 95% confidence

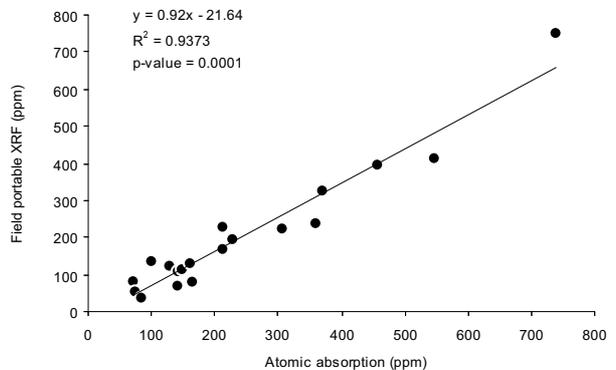


Figure 8. Relationship between soil zinc levels measured by field portable XRF and by atomic absorption method (particle size ≤ 250 μm) (n = 18).

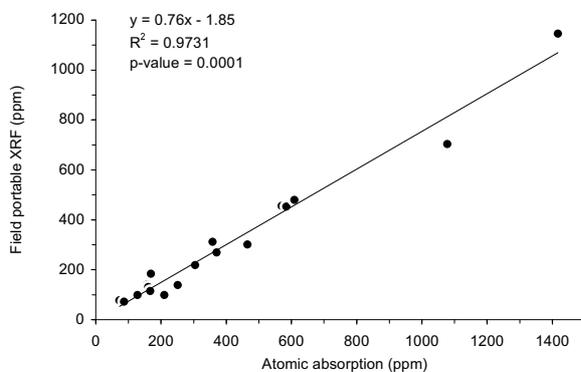
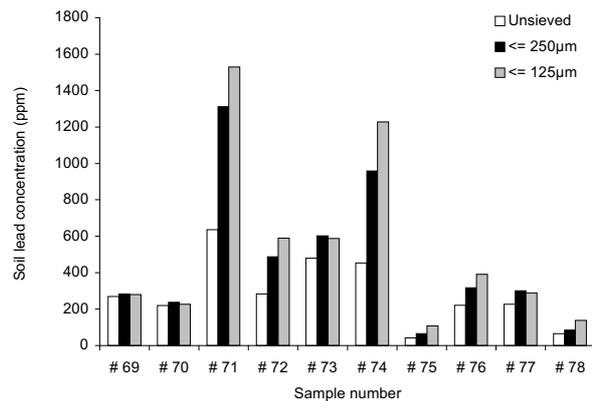
Table 2. Comparison of lead concentrations (ppm) in Polish soil by particle size as determined by AA and Laboratory XRF.

Particle size	Laboratory XRF (n=8)		Atomic absorption (AA) (n=10)	
	Geom. mean	Median	Geom. mean	Median
Total	220	232	224	248
<250 μm	263	272	325	309
<125 μm	298	270	384	340

intervals on Fig. 2, is between 280–380 ppm and the corresponding interval by the AA, from Fig. 3, is 240–360 ppm.

Almost one-half of the 21 field portable XRF readings from Poland were obtained directly from soil on the ground. Although an attempt was made to collect soil which was measured by the portable XRF (a volume of soil with a surface area of 1×2 cm and a depth of about 1 cm), the exact sample of soil deviated somewhat. Thus, the fact that the sample collected for later testing did not coincide exactly with the precise volume of soil measured *in situ* may account for part of the differences between the results using the different procedures. In addition, XRF instruments perform more satisfactorily on samples with a uniform and small particle size. To test this hypothesis, a comparison of results for lead by field portable XRF and AA was made using only the samples sieved to less than or equal to 125 micrometers (Fig. 4). Excellent agreement was reached ($R^2 = 0.997$), virtually the same as that for the samples less than 125 micrometers analyzed by the two laboratory methods ($R^2 = 0.999$). Comparison of field portable XRF and AA lead results from samples sieved to less than or equal to 250 micrometers was also very good, $R^2 = 0.924$ (Fig. 5).

Other Metals. Concentrations of arsenic were found to be below the detection level of the instrument. AA analysis

**Figure 9.** Relationship between soil copper levels analyzed by field portable XRF and by atomic absorption method (particle size $\leq 250 \mu\text{m}$) ($n = 18$).**Figure 10.** Soil lead concentrations by size fraction by atomic absorption method.

of these samples revealed that arsenic concentrations ranged from 3.9 to 30 ppm with a geometric mean of 13 ppm. Zinc and copper concentrations were also determined using the field portable XRF and AA at the UC. When both unsieved and sieved samples as received from Poland were used together, correlations were similar to those for lead, $R^2 = 0.76$ and 0.81 for zinc and copper, respectively. Using only samples sieved to less than or equal to 125 micrometers, correlations improved substantially, $R^2 = 0.98$ and 0.96 for zinc and copper, respectively (Figs 6 and 7, respectively). For samples sieved to less than or equal to 250 micrometers, the R^2 values were 0.94 and 0.97 for zinc and copper, respectively (Figs 8 and 9).

Effect of Particle Size. Lead concentrations of samples in three different particle size categories (total-unsieved, sieved to less than $250 \mu\text{m}$ and sieved to less than $125 \mu\text{m}$) are compared for AA and laboratory XRF in Table 2. For 10 sets of samples, data by AA are available for all three categories. The amount of data for laboratory XRF is somewhat less because of a lack of sufficient sample quantity.

Concentration of lead by particle size for the 10 individual samples analyzed by AA (Fig. 10) indicate a wide range of values with the highest values for the fraction less than 125 micrometers for two samples (#71, 74) in the vicinity of the Legnica smelter.

Lead concentrations were somewhat higher as determined by AA than by laboratory XRF and were higher by both methods for smaller particle sizes, but the differences were not statistically significant. Similarly, copper and zinc levels did not significantly differ by particle size.

DISCUSSION

For more accurate results the soil samples should be sieved prior to analysis, preferably to less than 125 micrometers. In the present study, soil sample sieving occurred in the laboratory, either at the Foundation for Children of the Copper Basin or at the University of Cincinnati. It would be

useful to demonstrate the methods used here with sieving performed in the field at the time of sample collection and before the XRF-analysis.

CONCLUSIONS

A field portable X-ray fluorescence analyzer was demonstrated to be capable of measuring lead and other metals in soil samples collected from the copper region of Poland and thus would be useful in exposure assessment activities. Results from the lead analysis by the field portable XRF used in Poland were compared to results from the same samples analyzed in Cincinnati by a laboratory XRF, atomic absorption, and another model of the same field portable XRF, as was used in Poland. Correlations were excellent for soil sieved to less than 125 micrometers with R^2 values of 0.997, 0.957, and 0.976 for lead, copper and zinc, respectively. For soil sieved to less than or equal to 250 micrometers, R^2 values were 0.924, 0.973 and 0.937 for lead, copper and zinc, respectively. For a soil lead level of 300 ppm measured by the field portable XRF (for samples measured *in situ* and after sieving), the amount measured by a laboratory XRF would be 280–380 ppm and 240–360 by flame atomic absorption. For the samples collected, concentrations of lead, arsenic, copper and zinc did not vary significantly by particle size. The field portable XRF had previously been demonstrated to be capable of measuring the lead in air sample filters and dust wipes.

The potential usefulness for the analysis of other metals should be explored.

Acknowledgments

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Kelsey. The expert assistance of John Pesce in providing training to the first author in the use of the portable XRF for soil analysis is also acknowledged. The results and conclusions reported herein are those of the authors.

Dedication

This paper is dedicated to the memory of the late Professor Paul B. Hammond who was a mentor, scientific inspiration and friend to three of the co-authors (S.C., P.S., S.R.).

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