

## Rapid detection and characterization of surface CO<sub>2</sub> leakage through the real-time measurement of <sup>13</sup>C signatures in CO<sub>2</sub> flux from the ground

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Surface monitoring of CO<sub>2</sub> over geologic sequestration sites will be essential in the monitoring of sequestration projects. Surface monitoring is the only tool that can be used to detect and quantify leakage on the order of 1000 tons/year CO<sub>2</sub>. Near-surface detection and quantification is made complicated by large variations in natural background CO<sub>2</sub> fluxes from biological processes. Carbon isotopes of CO<sub>2</sub> provide an opportunity to distinguish between biogenic CO<sub>2</sub> fluxes from the ground and CO<sub>2</sub> leaking from a sequestration reservoir that has origins in a process giving it a distinct isotopic signature such as natural gas processing. Recent developments in commercially available wavelength scanned cavity ringdown spectroscopy (WS-CRDS) have made it possible to rapidly measure the <sup>13</sup>C and <sup>12</sup>C isotopic composition of CO<sub>2</sub> in a field setting. A portable WS-CRDS has been used to rapidly detect and characterize an intentional leakage of CO<sub>2</sub> from an underground pipeline at the ZERT experimental facility in Bozeman, Montana. Rapid (1 hour) surveys of the 100m x 100m site were collected and the resulting concentration and <sup>13</sup>C isotopic abundance maps permit the identification of specific leakage locations and clearly distinguish petrogenic sources of CO<sub>2</sub> from biogenic sources. The work simulates a survey that could be performed over an area of 100 km<sup>2</sup>, the scale of expected industrial sequestration operations. This provides a powerful tool for surface monitoring, combining the utilities of leak detection, characterization, and source identification with rapid deployment across large spatial scales and high spatial resolutions.

## Soil contamination and health risks associated with former smelting of Pb - Zn ores at Kabwe, Zambia

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Soil sampling was carried in the neighborhood of an old Pb-Zn smelter at Kabwe, Zambia, to discriminate natural concentrations of metals from those caused by dust fallout. Two soil horizons were sampled: contaminated topsoil and reference soil horizon taken at a depth of 80-90 cm that is obviously not affected by dust fallout. It was established that total Cd, Pb, Zn, Cu and Se contents are significantly higher in topsoil relative to subsurface soil over a large part of the explored area. Contents of lead in topsoil are as high as 4%, those of zinc attain a maximum of 6.7%, copper 0.7%, arsenic 0.06% and selenium 0.01%. Sequential extraction of topsoils revealed that most of Cd, Pb, Zn and Mn are present in exchangeable form or bound to carbonates and poorly crystallized ferric oxides regardless of the distance from the smelter. However, a large part of Cu in close neighborhood of the smelter is confined to oxidizable fraction, presumably to sulfides, whereas this metal in outlying parts of the contamination halo occurs in carbonate fraction. The majority of As and Fe were found in residual fraction. A modeling of gastric availability of lead and other metals revealed that the amount of available metals in topsoil increases in the following order: Fe → As → Cu → Mn → Co → Zn → Pb → Cd. This indicates that lead and cadmium pose the greatest environmental hazard when dust particles are swallowed during eating unwashed vegetables or fruits. The amount of metals in soils available for metabolism by plants (plant-available metals) increases as follows: Fe → As → Co → Mn → Cu → Zn → Pb → Cd. The experiments undertaken showed that the addition of phosphate solutions to contaminated soils significantly reduces the amount of plant-available lead and cadmium in polluted soils, while the plant-bioavailability of zinc has not been affected by added phosphate. This work was supported by grant 774 No. 205/08/0321 of the Czech Academy of Sciences.