

## Cr isotopes reveal progress of natural reduction of contaminant Cr(VI) in a groundwater system

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Mass-dependent kinetic isotope fractionation occurs during reduction of Cr(VI) to Cr(III).  $^{53}\text{Cr}/^{52}\text{Cr}$  measurements may provide a quantitative indicator for the extent of reduction, which renders toxic, mobile Cr(VI) immobile and relatively innocuous. Previous studies give fractionation factors for Cr(VI) reduction in the laboratory; now the approach is being developed in field settings. Here we present results from a multi-year study of an urban Cr(VI) plume that is managed with a combination of monitored natural attenuation and injection of reductant.

Two batch reduction experiments with unamended, greenish, reduced site sediments yielded  $\epsilon$  [1000( $\alpha$ -1)] values of 2.5‰ and 3.1‰; these provide an estimate for the isotopic fractionation factor. In several other experiments with reddish oxidized sediment, no reduction occurred. Cr(VI) from a present-day plating bath at the site yielded  $\delta^{53}\text{Cr} = 0.8\text{‰}$ . In groundwater from 16 monitoring wells over a five year period,  $\delta^{53}\text{Cr}$  of Cr(VI) ranged from 1.2‰ to 6.3‰. Assuming  $\delta^{53}\text{Cr} = 0.8\text{‰}$  for the original contaminant and  $\epsilon = 2.8\text{‰}$  for reduction, and neglecting dispersion/mixing, extents of reduction calculated with a Rayleigh model range from 12% to 86%, with a clear spatial pattern. Groundwater near the contaminant source and in the high-Cr(VI) core of the plume shows less reduction than more distal groundwater. This suggests that the reducing capacity of matrix materials is diminished in the plume core. The average temporal trend in  $\delta^{53}\text{Cr}$  is weakly positive, with erratic variation in a few wells. The isotope data and longer-term concentration trends are both consistent with slow natural attenuation of Cr(VI) occurring mostly within the fringes of the plume.

While temporal and spatial trends in  $\delta^{53}\text{Cr}$  are very informative qualitatively, accurate and precise quantitative determinations of the extent of reduction are hampered by incomplete understanding of a few issues: 1) The Rayleigh model yields underestimates of the extent of reduction whenever groundwater dispersion/mixing or diffusive mixing of Cr(VI) occurs. 2) The contaminant source was removed, and its  $\delta^{53}\text{Cr}$  may have differed from that of the present day plating bath. 3) Estimates of  $\epsilon$  from laboratory experiments with disturbed sediment slurries may deviate from actual values.

## Analyzing trace pigments in oligotrophic waters using long pass cell spectrophotometry

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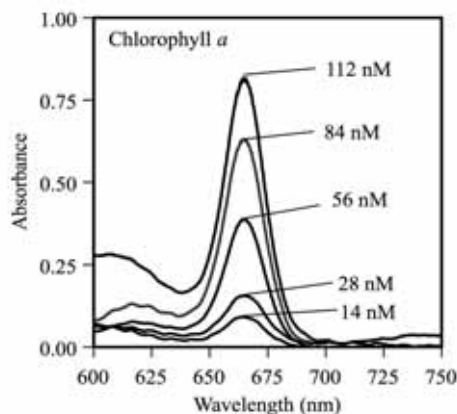
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Photosynthetic pigments such as Chlorophylls and Bacteriochlorophylls are light harnessing molecules produced by photosynthetic organisms. Pigment concentrations in natural waters can be used to track the distribution and size of phototrophic communities. In low productivity environments, large volumes of water have to be filtered to obtain sufficient pigment for spectral analyses. Liquid core waveguide (LCW) cells with long optical pathlengths of 1-5 m have been used to dramatically increase the sensitivity of spectrophotometric chemical analyses [1]. Here, we present a sensitive, portable method of pigment analysis using a LCW (1 m pathlength) coupled to a USB4000 spectrophotometer (Ocean Optics).



In the figure above, we demonstrate the linearity of the method over Chl *a* concentrations of 14 to 112 nmol l<sup>-1</sup>. The detection limit, estimated as 3x the SD of spectral noise between 600-700 nm, is 4 nmol l<sup>-1</sup>, and the RSD at 28 nmol l<sup>-1</sup> Chl *a* is 4%. This method requires less water filtration and improves the detection limit when compared to traditional spectrophotometric analyses. We have applied our method to studies of primary and secondary production in oligotrophic Lake Matano, Indonesia.

[1] Waterbury *et al.* (1997) *Anal. Chim. Acta* **357**, 99-102.