

## Evidence of transport of Composition B colloids/nano-colloids in range soils

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### Abstract

Munition constituents (explosive particles such as Composition B or simply Comp B) distributed heterogeneously at operational range sites from low-order detonations may be the source of contamination of TNT, RDX and HMX to underlying aquifers. Comp B consists of ~59% RDX, 40% TNT and 1% HMX. Mobility of these compounds in soils/groundwater may occur via dissolution of Comp B and/or via transport of Comp B particles/colloids. To determine this, we collected soils from the E horizon of Massachusetts Military Range (MMR) where RDX and TNT contamination was recently observed. Column experiments were conducted where Comp B particles (<2 µm) were applied on top of the MMR-E soil filled column and leached with background solution of 1 mM NaCl. Effluents were collected every hour and separated into two aliquots: 1) <1 µm (or total), 2) dissolved (<2nm) fractions. Each aliquot was analysed with HPLC to quantify TNT, RDX and HMX. Difference between the <1 µm and <2 nm fraction denotes the amount of TNT, RDX and HMX in the colloidal/nano-colloidal fraction.

Results showed that up to ~80% of TNT and between 40-50% of RDX and HMX in the system were transported in colloidal/nano-colloidal (>2 nm -1 µm). While comparing the breakthrough in <1 µm fractions, the breakthrough of RDX was the fastest followed by HMX and then TNT. While comparing breakthrough of dissolved vs colloidal/nano-colloidal fractions, the breakthrough of the colloidal fraction for TNT, RDX and HMX was relatively faster than the dissolved fraction. Using ATR-FTIR spectroscopy we were also able to identify Comp B colloids in column effluents.

Results conclude that: 1) Comp B particles may move as colloids/nano-colloids in soils, 2) Faster breakthrough of RDX and HMX suggests lower binding affinity whereas TNT binds more strongly to the soil matrix regardless of particle size and 3) The faster breakthrough of TNT, RDX and HMX in <1 µm fraction compared to the dissolved fraction suggests that Comp B colloids/particles may move in the subsurface with less retardation compared to dissolved TNT, RDX and HMX.

The results, for the first time, show evidence of colloidal transport of munition constituents in column systems. Transport of Comp B as colloids should thus be considered while studying contaminated field sites such as MMR. Current results will be compared with column experiments in which Comp B will be applied to intact MMR-E columns collected from the same site. Intact columns may contain fractures and macropores likely to enhance the propagation of colloidal phases.

## Precise, accurate measurement of U-Th isotopes in a single solution by ICP-MS

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U-series isotope measurements by ICP-MS commonly utilize separate runs for U and Th, and standard-sample bracketing to determine corrections for mass fractionation and ion counter yield. Here we present an approach where all information necessary to calculate a sample's age (aside from background/baseline levels) is determined while analyzing a single solution containing both U and Th. Such an internally calibrated procedure reduces any bias caused by distinct behavior of samples versus standards (e.g., matrix effects), eliminates drift, and offers simplicity of operation, calculation of preliminary ages in real time, and simplified analysis of errors and their sources. Hellstrom [1] developed a single-solution, internally calibrated technique for an ICP-MS with multiple ion counters (Nu Plasma), but to our knowledge such a technique has not been available previously for an ICP-MS with a single ion counter. We use a Thermo Neptune *Plus* multi-collector ICP-MS with eight movable Faraday cups and a fixed center cup/ion counter equipped with a high abundance-sensitivity filter (RPQ). We use Faraday cups to measure all masses except 230 and 234, which are generally measured on the ion counter with the RPQ detuned (i.e., set 50 volts below the acceleration voltage). Analyses are dynamic, with sequential axial masses of circa 229, 230, 233, 234, and 239. <sup>238</sup>U is maintained in cups throughout the analysis to avoid reflections and is used to normalize signal instabilities related to sample introduction. Each analysis has a three-part structure in which 1) background/baseline levels, 2) sample composition, and 3) peak-tails are sequentially measured. In step 1, multiplier dark noise/Faraday baselines plus background intensities at each mass are determined while aspirating running solution. During sample measurement in step 2, ion counter yields for Th and U are determined using signals of 300-500 kcps for <sup>229</sup>Th and <sup>233</sup>U by measuring <sup>229</sup>Th/<sup>238</sup>U and <sup>233</sup>U/<sup>238</sup>U ratios with the minor masses first on the ion counter and then in cups. Mass bias can be determined using the <sup>233</sup>U/<sup>236</sup>U ratio of the spike, allowing the sample's <sup>238</sup>U/<sup>235</sup>U ratio to be measured. In step 3, we monitor peak-tails at half-mass positions (229.5, 231.5, 234.5) and on mass 237 while aspirating sample solution. Tail measurement requires a distinct cup configuration to maintain 238 in the cups; however, no sample is consumed during automated cup reconfiguration.

We monitor the accuracy of <sup>234</sup>U/<sup>238</sup>U ratios using CRM 145, which gives a weighted mean atom ratio of  $(5.2899 \pm 0.0021) \times 10^{-5}$  (all errors 2 SEM), consistent with published and reference values. The reproducibility of <sup>230</sup>Th/<sup>238</sup>U ratios is monitored using the Schwartzwalder Mine secular-equilibrium standard (SM). We detect no bias in <sup>230</sup>Th/<sup>238</sup>U or <sup>234</sup>U/<sup>238</sup>U ratios measured for SM at beam intensities ranging over a factor of four, consistent with accurate correction for IC yields. Aladdin's cave coral (AC-1), analyzed to check our method on carbonate, yields a mean age of  $124.42 \pm 0.37$  ka, in agreement with published values. We are currently applying the method to corals, speleothems, pedogenic coatings, and tufas.

[1] Hellstrom (2003) *J. Anal. At. Spectrom.* **18**, 1346–1351.