

## Geochemical investigations of the hyporheic zone of the Columbia River, Hanford Site, USA

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The hyporheic zone, where groundwaters and surface waters interact at or near streambeds, is critical habitat for juvenile fish, and for organisms that act as the base of the aquatic food chain. The zone extends beneath the streambed and includes mixtures of surface water and groundwater. Although, in most environments, streams are *gaining* groundwater, they may also be *losing* water to the groundwater environment on a very local scale. The flux of nutrients and contaminants from groundwater to streambeds at any particular point thus may positively or negatively influence threatened or endangered surface water species such as salmon.

At the Hanford Site in southeastern Washington, the free-flowing Columbia River acts as critical salmon spawning habitat. The site also includes large plumes of contaminants, including dissolved uranyl and chromate, that move with aerobic groundwater through riverbed sediments. The river bottom is a cobble bed, with little apparent organic matter or fine sediment. We deployed passive multilevel samplers (MLS) in the riverbed to determine the chemical profile of the hyporheic zone and to estimate the concentrations of contaminants impacting riverbed biota. Stainless steel screens were driven into the riverbed using a jackhammer, and the MLS rods were placed in the uppermost 1.5 m, isolated from surface water by seals at the screen tops.

In the area of a known chromate plume, the samplers were allowed to equilibrate at high and low stage for ca. 24 h, then withdrawn. Hydraulic head measurements indicated the river was gaining at low stage and losing at high. In terms of electrical conductivity, the high and low stage concentration gradients had similar slopes, but conductivities near the river bottom at high and low stages were 125 and 375  $\mu\text{S}$ , respectively; equivalent  $\text{CrO}_4^{2-}$  concentrations were 0 and 100  $\mu\text{g L}^{-1}$ .

In the area of a known uranyl plume, the samplers were placed at varying (0 – 8 m) distances from the riverbank. At intermediate stage and 5 m from the bank, the uranyl concentration was relatively constant with depth, at ca. 100  $\mu\text{g L}^{-1}$ , but at 8 m from the bank, the concentration gradient was steeper, from 100 to 250  $\mu\text{g L}^{-1}$  at 1 m beneath the river bottom.

Our results indicate that the hyporheic zone in this cobble-bed river presents variable and significant concentrations of contaminants to riverbed biota.

## Shunga Event – Was it a case of Palaeoproterozoic mass extinction?

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The most significant accumulation of organic material (OM) and oil generation in the Proterozoic took place at c. 2000 Ma in the aftermath of the c. 2400-2060 Ma global perturbation of the carbon reservoir recorded in the isotopic composition of sedimentary carbonates and oxygenation of the terrestrial atmosphere. Occurrences of 2000 Ma-old, matured OM have been documented in northern America, Greenland, Africa and Fennoscandian Shield. In the Fennoscandian Shield, OM occurs in thick volcano-sedimentary successions with an estimated total carbon reserve of  $>10 \times 10^{11}$  tonnes. The OM occurs in the form of a mineraloid, locally termed shungite (SH), which is a black, non-crystalline, glassy material with a strong lustre and contains  $>98$  wt.% C.

The SH-bearing rocks were accumulated within continental rift settings, in non-euxinic lagoonal and lacustrine environments developed on the rifted margins of the Archaean craton. The occurrences of SH-bearing rocks represent a combination of a petrified oil field, and petrified organosiliceous diapirs and oil spills. These are exemplified by three types of deposit: (i) *in situ* stratified, (ii) migrated diapir, and (iii) redeposited clastic.

*In situ* stratified deposits are composed of metamorphosed oil shales (C<50 wt.%), rocks containing autochthonous kerogen residue and allochthonous OM (C = 50-75 wt.%), and migrated bitumen, originally liquid hydrocarbons (C>80 wt.%).

Diapiric deposits form non-stratified, cupola or mushroom-like bodies which are made up of SH rocks containing 35-75 wt.%  $\text{SiO}_2$  and 20-55 wt.% C. These are considered to represent organosiliceous rocks, originally gels or mud. The SH rocks show abundant shrinkage cracks as well as cryptic fluidal textures and brecciation caused by multiple fluidisation processes. The current data are consistent with a diapiric or mud-volcanic origin or a combination of both.

Occurrences of clastic SH are hosted by lacustrine volcanoclastic greywackes deposited from turbiditic flow. SH occurs in rocks as clasts of lustrous SH ranging in size from <1 mm to 20 cm. The SH clasts are considered to represent redeposited, oxidised oil derived from oil spills.

Such unprecedented accumulation of OM might have been caused by a mass-extinction of old biological communities which were not adaptive towards oxygenation of the terrestrial atmosphere in the aftermath of the Palaeoproterozoic positive isotopic excursion of  $^{13}\text{C}/^{12}\text{C}$ .