Fluxes of pore waters which transport metals and nutrients to the German Wadden Sea

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Advective flow of sea water through shallow (5-10 cm) permeable sediments is driven by ocean waves and currents. Deeper advective flow (to at least 4 m) is driven by multiple forces including hydraulic gradient, wave and tidal pumping, buoyancy, and storms. These deep advective flows release fluids enriched in metals, nutrients, and carbon to coastal waters. We have studied the biogeochemistry and trace metal dynamics associated with advective flow of pore water in the backbarrier area of Spiekeroog Island, NW Germany. During low tide sandy tidal flats stand next to deeply incised tidal channels. In the water column of the tidal channels, radium isotopes, silica, alkalinity, and manganese concentrations show a tidal cyclicity, with maximum concentrations during low tide. Average concentrations in pore waters of the sandy tidal flats show consistent values of ^{224}Ra (9.7±2.4) and ^{228}Ra (5.1±1.8) (n=16) regardless of depth or location. This is not true for the other components. Silica shows a range of 200-900 μM, alkalinity varies from 3-50 mM, and Mn from 2 to 190 μM. Here we estimate the ^{224}Ra and ^{228}Ra budgets for the tidal channels and use the rather well-constrained pore water concentrations of ^{224}Ra and ^{228}Ra to estimate the amount of pore water required to support the measured radium inventories. The results indicate that 1-3% of the water in the tidal channels is pore water that entered the surface water during the last 3 tidal cycles. The pore water, added primarily during falling tide, causes the strong enrichments of radium, silica, and alkalinity measured in the tidal creeks. Based on the radium balance, we can estimate the fluxes of silica, alkalinity, manganese, and other metals due to pore water exchange with the tidal creeks. These fluxes are substantial. As the tide rises most of the enrichments are exported to the North Sea.

The ozonolysis of β-caryophyllene

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Ozonolysis experiments were performed in a 570-liter spherical glass reactor at 295 K and 730 Torr. Initial mixing ratios were 100-2000 ppb for O_3 and 90-1050 ppb for β-caryophyllene in synthetic air. Reactants and gas-phase products (CO, CO_2, HCHO and HCOOH) were measured by *in situ* FTIR spectroscopy. Particulate products were sampled on Teflon filters, extracted with methanol and analyzed by LC-MS-MS-TOF. A variety of hydroxyketone-, diketone-, acid- and diacid-type products was identified [1, 2]. The residual FTIR spectra indicate the formation of an internal secondary ozonide (SOZ) of β-caryophyllene [2].

Using cyclohexane (10-100 ppm) as OH-radical scavenger and by monitoring the yield of cyclohexanone by PTR-MS, an OH-yield of (8.2±0.7) % was determined for the ozonolysis of the more reactive internal double bond (DB), and (12.8±0.4) % of the first-generation products.

The aerosol yield has been studied by SMPS, and ranged between 5 and 24 %, depending on the aerosol mass. The yield increased upon addition of H_2O or HCOOH, and decreased in the presence of HCHO. From experiments in the presence of HCOOH it was concluded that at least 60% of the formed Criegee Intermediate (CI) are collisionally stabilized.
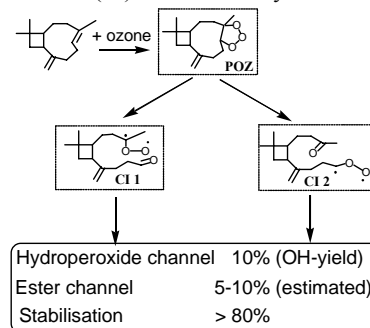
Figure 1: A condensed mechanism is displayed in Fig. 1, indicating the fate of the CIs. The reaction mechanisms is discussed and compared with the results from a theoretical study [3].

[1] Kanawati *et al.* (2008) *Rapid Commun. Mass Spectrom.* **22**, 165-186. [2] Winterhalter *et al.* (2008), *PCCP*, submitted. [3] Nguyen *et al.* (2008), *PCCP,* submitted.