Divergent behaviors in global geochemical cycling of bromine and chlorine

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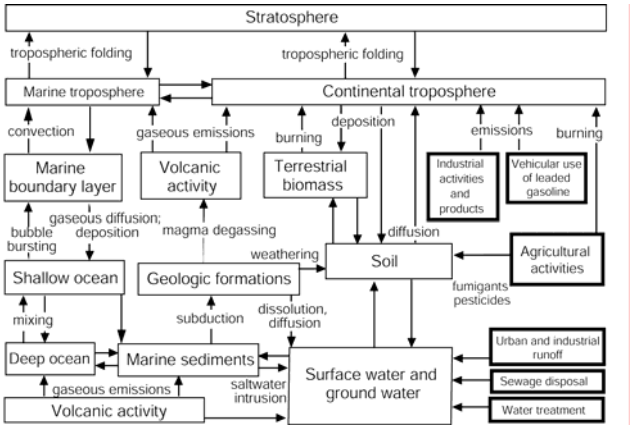
Global geochemical cycles of bromine (Br) and chlorine (Cl) largely parallel one another. Oceanic emissions dominate the atmospheric fluxes of both halogens, augmented by terrestrial biogenic sources and volcanic emissions. Wet and dry deposition and biological uptake transfer the halogens to soil and vegetation. Ultimately, the halogens return to their marine origins via surface runoff or are carried into the subsurface with groundwater.

Cl/Br ratios are widely used as natural tracers of groundwater history due to generally conservative behavior in this environment. In other parts of their geochemical cycles, however, multiple physical and chemical processes lead to differing rates of transformation and transport and subsequent fractionation of Cl/Br ratios. These include bursting bubbles at the ocean surface, partitioning between gas and particulate phases in the atmosphere, partitioning between organic and inorganic atmospheric compounds, photodissociation, aerosol acidification, precipitation scavenging, sorption onto organic and inorganic surfaces, plant uptake, and precipitation of salts from brines. A conceptual box model lays the groundwork for assessing past, present and future variations in Cl/Br ratios in global environmental compartments.

Figure 1: Chlorine and bromine geochemical cycles. (Only major compartments and transfer paths are shown. Bold boxes indicate anthropogenic activities.)



Formation waters are connate, meteoric, saline and their Cl / Br disclose tagging by brine-spray on land

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Shallow cycling groundwaters, are (a) of recent ages; (b) isotopicaly light (meteoric), and (c) tagged by airborne sea-spray (Cl/Br around 300 and no Ca-chloride).

In contrast, formation waters are (a) fossil (high He-4, Ar-40); (b) also meteoric, i.e. recharged by rain; and (c) tagged by airborne brine-spray, with Cl/Br of 80 to 220, and significant Ca-chloride concentrations.

Formation waters, encountered in adjacent drill holes, often reveal different compositions, indicating entrapment within hydraulically isolated rock- compartments, i.e. these are connate groundwaters.

The formation water hosting rocks are commonly of a marginal marine facies, whereas the isotopic composition of the water phase indicates on-land meteoric origin, and the composition discloses formation in intensive evaporitic environments. These boundary conditions lead to the working hypothesis that formation waters were formed on paleo-flatlands in the following stages: (a) sea transgression and sedimentation of marine rocks; (b) sea regression, exposing a low-land covered by sabkhas and lagoons, and subjected to rain, and the latter infiltrated to the exposed low rock landscape, flushed the originally contained interstitial water, and replaced it with meteoric brine-tagged groundwater; (c) upon the following sea invasion new rocks were sedimented, confining the former rocks with their contained on-land formed saline groundwaters. A multitude of such stages, as well as facies variations, formed the isolated rock-compartments that host the connate formation waters.

The presented geological-hydrological findings open a wide scope of studies of the halogens and their isotopes in marine and terrestrial aqueous systems, e.g.: (a) patterns of sea-spray tagged shallow groundwaters at different distances from the oceans; (b) patterns of a variety of evaporitic precipitates and residual brines; to be studied at different locations; (c) a variety of formation waters of different properties, from various locations and of different depths and ages.

The obtained isotopic data will serve to identify the origin of formation waters at different study areas and to check the above presented working hypothesis.