The reduction of hexavalent uranium to tetravalent uranium has a significant impact on the fate of the radionuclide in the environment. This is because the reduced species are typically insoluble and thus immobile. While U(IV) oxide (UO$_2$) was long thought to be a major product of this reduction, it has become clear in recent years that other U(IV) species are also important in field and laboratory settings.

We evaluated U(IV) speciation at two field locations and identified non-crystalline U(IV) as the dominant species in the reduced regions of the soil. Despite the fact that U(IV) was coordinated to phosphate in both cases, the U(IV) species are likely distinct. In one case, a uranium-impacted wetland, U(IV) was associated with inorganic aggregates containing Al, Si and Fe [1]. In the other, a bioremediated aquifer, U(IV) was associated with mackinawite (FeS) and microbial biofilms [2]. Additionally, we probed laboratory systems to evaluate the mechanism of formation of non-crystalline U(IV). When chemogenic or biogenic minerals reduce U(VI) in the absence of phosphate, UO$_2$ is the dominant product formed [3]. In purely biotic systems, we found that non-crystalline U(IV) was preferentially associated with extracellular polymeric substances (EPS) whereas UO$_2$ was produced when EPS was absent.

Based on this compilation of field and laboratory results, we provide insight into how uranium reduction can result in the formation of non-crystalline U(IV) in biotic and abiotic systems. We can discriminate between the two mechanisms using $^{238}$U/$^{235}$U isotope fractionation and propose that the biotic and abiotic forms of non-crystalline U(IV) may differ in structure and in reactivity.