

# Abiotic reduction mechanism of As(V) by fulvic acid in the absence of light and the effect of Fe(III)

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## Abstract

In this paper, the mechanism of the redox cycling of arsenic under dark conditions was studied to help explain the high prevalence of As(III) in groundwater where no photochemical redox cycling is expected to occur. Most research has focused on the photochemical oxidation and reduction of metals and metal ions with dark redox cycling not given as much attention. A full understanding of the geochemical cycle and speciation of arsenic makes it equally important to study reduction of As(V) to As(III) under dark conditions.

The reduction of As(V) by FA in the absence of light is hypothesised to occur via complexation, which can be greatly enhanced by the presence of iron. Fe(III) is envisaged to play two roles:

- It facilitates binding of arsenate by FA through intermetallic bridging which results in the reduction of As(V) to the intermediate As(IV).
- It can be reduced by FA to Fe(II) which then can reduce As(IV) to As(III). The reduction of As(V) is felt to occur in two one-electron steps, where the As(IV) is reduced by Fe(II).

In solutions with no added Fe(III), binding of the negative arsenate by the negative FA occurs through inter-metallic bridging by cationic metals inherent in the FA. Competition from H<sup>+</sup> ions for the binding sites on FA at lower pH results in the diminished reduction.

**Keywords:** abiotic reduction, mechanism, As(V), fulvic acid, Fe(III)