Attenuation and Source Zone Depletion of Boron from Coal Combustion Residuals in Groundwater

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ABSTRACT

Boron is an important constituent of CCR leachate. It is ubiquitous and may be found in concentrations exceeding prevailing standards in leachate-impacted groundwater. Because boron generally sorbs weakly to most geologic media, a boron plume often moves passively with groundwater transport, with the dominant attenuation mechanisms being dispersion and dilution. Despite this, boron impacts to groundwater have been observed to attenuate rapidly. For unlined CCR impoundments, this observed attenuation may begin as soon as the ponds are taken out of service and prior to any remedial activities. This likely reflects depletion of the finite amount of mobile boron remaining in the impounded CCR material. In evaluating and ranking the effectiveness of remedies such as excavation or capping, most groundwater models consider CCR material to be an inexhaustible source of contaminants. This may be adequate for constituents with more limited mobility, but this assumption significantly over-estimates the impact of boron on groundwater quality over time. Here, modeling methods for source zone depletion are reviewed. Results are compared to case studies of rapidly attenuating boron groundwater impacts.

INTRODUCTION

Even though boron is not yet an Appendix IV constituent in the Federal CCR rule, it is an Appendix IV constituent in many states. Boron frequently occurs in groundwater at sites with former and active CCR landfills and impoundments, often above State regulatory criteria. Therefore, boron may drive remedial actions or trigger other sampling requirements. Since boron is relatively inert in groundwater, numerical groundwater transport models are relatively simple, conservative and therefore well suited to assess and rank potential remedies.

Boron is naturally abundant in present day seawater, with a typical marine concentration of approximately 4.5 mg/L. Consequently, boron is abundant in most natural brines, and appears in evaporite deposits as the mineral borax (historically mined in dry lakebeds in the western United States and used as an ingredient in detergents). Boron is also naturally abundant in coals; in a USGS compilation of domestic coals, boron had a median concentration of 35.7 mg/kg with some coals in excess of 300 mg/L (EPRI, 2020). We speculate that Paleozoic Illinois Basin coals may have higher boron content because of their marine affiliation, but this distinction is not made in the EPRI publication. When burned, boron in coal is concentrated in coal combustion residuals (CCRs). Fly ash tends to have higher boron concentrations than bottom ash, with typical fly ash values in the range of 100-1000 mg/kg This abundant CCR boron is highly leachable and experiences little retardation by aquifer solids, making born a common indicator of early release of CCR leachate to groundwater.

BORON ATTENUATION

In comparison to the recalcitrant groundwater plumes of more reactive species, many boron plumes attenuate rapidly. In some cases this attenuation may begin as soon as the responsible ash pond is removed from service and may have a comparable or greater apparent effect than active groundwater remediation. This seems to be particularly the case for coarse grained alluvial aquifers adjacent to rivers (e.g., Figure 1).

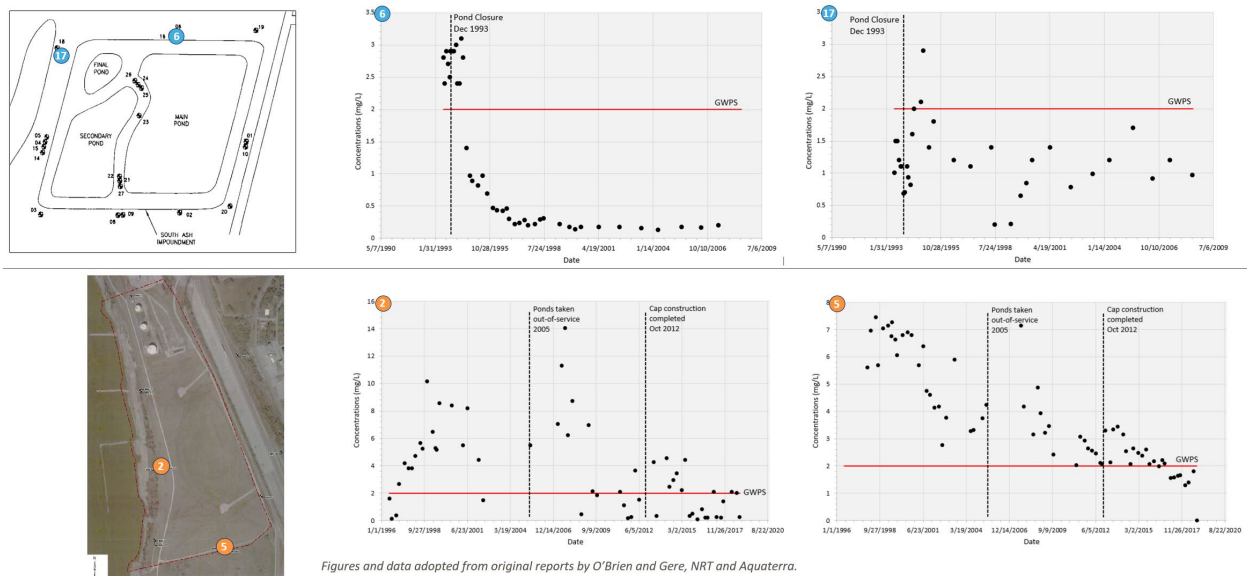*Figures and data adopted from original reports by O'Brien and Gere, NRT and Aquaterra.*

Figure 1: Two examples of rapid boron attenuation in groundwater following pond closure (confidential locations).

RANKING EFFECTIVENESS OF REMEDIES

Combined groundwater flow and contaminant transport models are often used to rank the effectiveness of post-closure remedies such as capping, removal, and hydraulic

control. Groundwater flow is usually simulated using MODFLOW (standard modeling code from United States Geological Survey); contaminant transport models are built on this using program such as MT3DMS (e.g., Zheng, 2012). The model is calibrated to historical concentration and head data; the remedy is applied to the present day in the simulation, and then the model is run forward into the future to create a forecast. The metric analyzed is usually the time required to reach a key regulatory criterion at a simulated point of compliance. The standard output is then a series of predictive concentration trends at the point of compliance, ranked by the time required to achieve compliance (Figure 2).
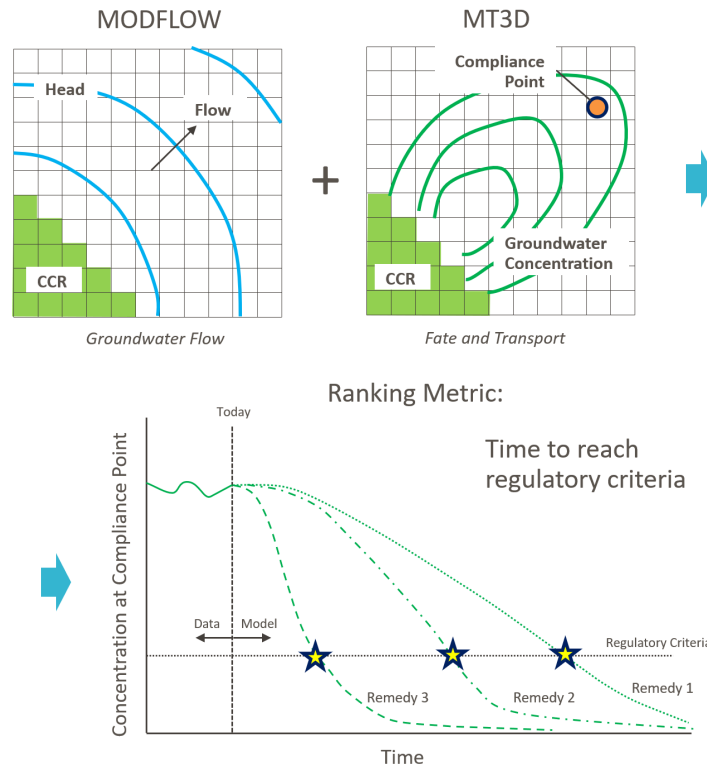

Figure 2: Ranking Remedial Strategies with Modeling

This metric-focused modeling approach has proven very useful for high level analysis but may obscure the larger picture of the planned remedy. It can be advantageous to accompany this analysis with modeled animations of plume growth, attenuation, and remediation. For purposes of illustration, we present such an example for a hypothetical model of boron plume remediation (Figure 3).
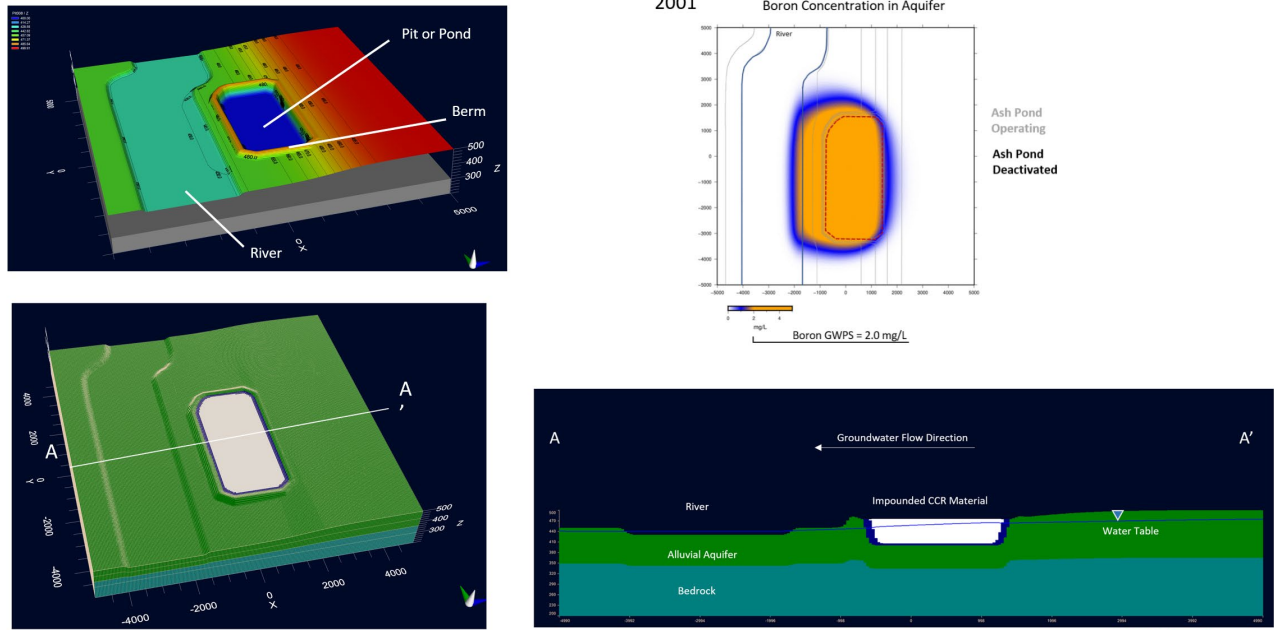
Figure 3: Visuals for illustrating remediation strategy, hypothetical scenario (static images)

One typical strategy often employed in this modeling is to treat the CCR material somewhat independently from the rest of the aquifer. In this approach, the CCR material may be a hydraulic component of the aquifer in MODFLOW but is treated as a flux boundary condition in MT3DMS: contaminant loading from the CCR to the aquifer is calculated a function of vertical infiltration through the CCR material and concentration of the constituent measured in site leachate or estimated from databases of leachate concentrations. This directly facilitates the ranking of capping remedies, as the infiltration rate through various cap designs can be reliably calculated. However, this effectively treats the CCR as an inexhaustible source of the constituent. For some non-reactive constituents like boron, it is likely that the CCR will become depleted over time; more so for sites with CCR situated below the water table enabling significant lateral flow through the CCR material. Including such a depleting CCR boron source to the model adds another dimension, as the parameters controlling boron transport must be assigned to both the aquifer and CCR material.

BORON TRANPORT IN CCR

Most groundwater transport modeling is performed by assuming a linear equilibrium partitioning between water and aquifer solids by sorption. This is parameterized primarily via the partition coefficient (Kd). For a given amount of mass in the system, the partition coefficient defines the equilibrium concentrations in the aqueous and solid phases (mobile vs. immobile domains). With the typical linear approximation, sorption capacity of the aquifer solids is not limited by the mass of the constituent already sorbed, and transfer between domains is instantaneous. These are major assumptions

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to be sure. While more sophisticated treatments are available, this approximation has been a reliable workhorse for including the effects of retardation during contaminant migration for many situations.

The chemical behavior of the constituent is of primary importance for sorption, but the composition of aquifer solids and groundwater chemistry are also very important. The organic carbon content of aquifer solids is often one of the most important controls of sorption for organic compounds, such that the partition coefficient is usually given as the product of the organic carbon content of the aquifer solids and a chemical specific water/organic carbon partition coefficient. This organic carbon methodology is reliable for clastic soils and sedimentary rock containing variable amounts of organic matter but can be somewhat rootless in igneous/metamorphic bedrock aquifers where sorption is more a function of inorganic minerology. The type of solid organic carbon can also be a factor. For example, Grathwohl (1990) found that increased diagenetic alteration ("coalification") of woody organic matter increased the organic carbon partition coefficient for chlorinated solvents by up to three orders of magnitude (Figure 4).
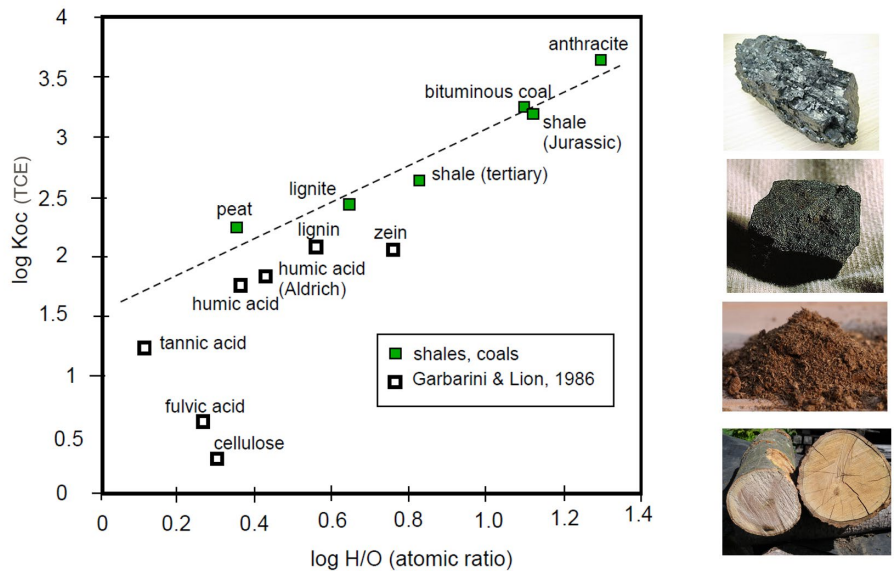

Figure 4: Effect of diagenetic alteration of woody organic matter on organic carbon partition coefficient of chlorinated solvents. After Grathwohl (1990).

It is unclear if the same would apply for more inert CCR-derived metals, but this does further underscore the point that the natural aquifer properties are at least as important as the chemical properties of the constituent.

There are numerous published values for measured boron partition coefficients in natural aquifers (e.g., EPRI 2005; 2020). From these compilations, linear partition coefficients of Kd = 0.1 – 1.0 L/kg are typical for natural aquifers. Note that there are a number of literature values given Langmuir Isotherm parameters for boron instead of linear partition coefficients. Langmuir Isotherms allow for decreased sorption at higher concentrations as the solid media becomes saturated.

From other compilations of data from CCR sites, typical CCR contact and pore water boron concentrations are on the order of 10 mg/L (EPRI, 2020). From the same compilations, typical dry bulk boron content of CCR materials is on the order of 100 mg/kg. Using a first order fugacity partitioning calculation (e.g., MacKay and Paterson, 1982) and some assumed physical properties for an aquifer composed of CCR material (porosity = 30%, bulk density = 1.6. kg/L, 100% water saturation), this suggests a partition coefficient (Kd) on the order of 10 L/kg. This is higher than those measured for natural aquifers, although not more than an order of magnitude so. However, there are two important caveats: this is assuming equilibrium partitioning with no saturation effects, and (more importantly) not all of the boron in the bulk CCR material may be accessible for dissolution. If not all of the boron in the bulk CCR material may be accessible for dissolution, a Kd value lower than 10 L/kg is likely more appropriate. This is the motivation for a closer look at the occurrence of boron in CCRs.

ORIGIN OF BORON IN CCR

Boron occurs in CCR as both a solid-solution in the glass phase (borosilicate glass), or as a surface coating of polyborate on CCR granules (EPRI, 1998). Note that CCR materials may have some unusual modes of porosity such as micron-sized hollow glassy spherules that are normally not encountered in natural aquifers (Figure 5).

Solid solution in glass phase, or as borosilicate glass

Surface coating of B_2O_3 or polyborate   (EPRI 1998)

CCR materials can have some unusual modes of porosity not often found in natural materials

Scanning Electron Micrograph of Typical Coal Fly Ash Particles. From Tishmack, J.K. and P.E. Burns, 2004

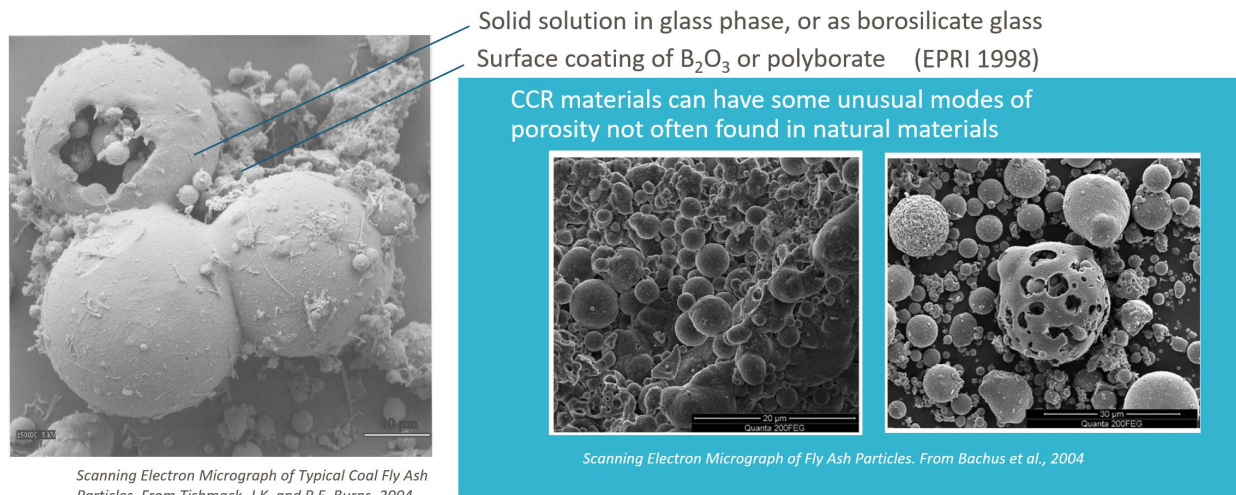*Scanning Electron Micrograph of Fly Ash Particles. From Bachus et al., 2004*

Figure 5: Boron occurrence and unusual modes of porosity in CCR

A laboratory study from James et al. (1982) found for a range of US CCRs, only between 5 and 65% of bulk solid boron was leachable. From examples in EPRI (2005 and references therein), the majority of mobile boron is typically removed in the very earliest parts of leaching experiments: in one example, 90% of all recovered boron was removed in the first two pore volume flushes. This suggests that the source of most available boron is the easily washed polyborate surface coatings, while the solid solution glass phase boron remains immobile. Further evidence of this can be found from inspection of the various EPRI compilations referenced above. The highest

concentrations of CCR-derived boron are found in porewater from dry-managed fly ash (Figure 6).
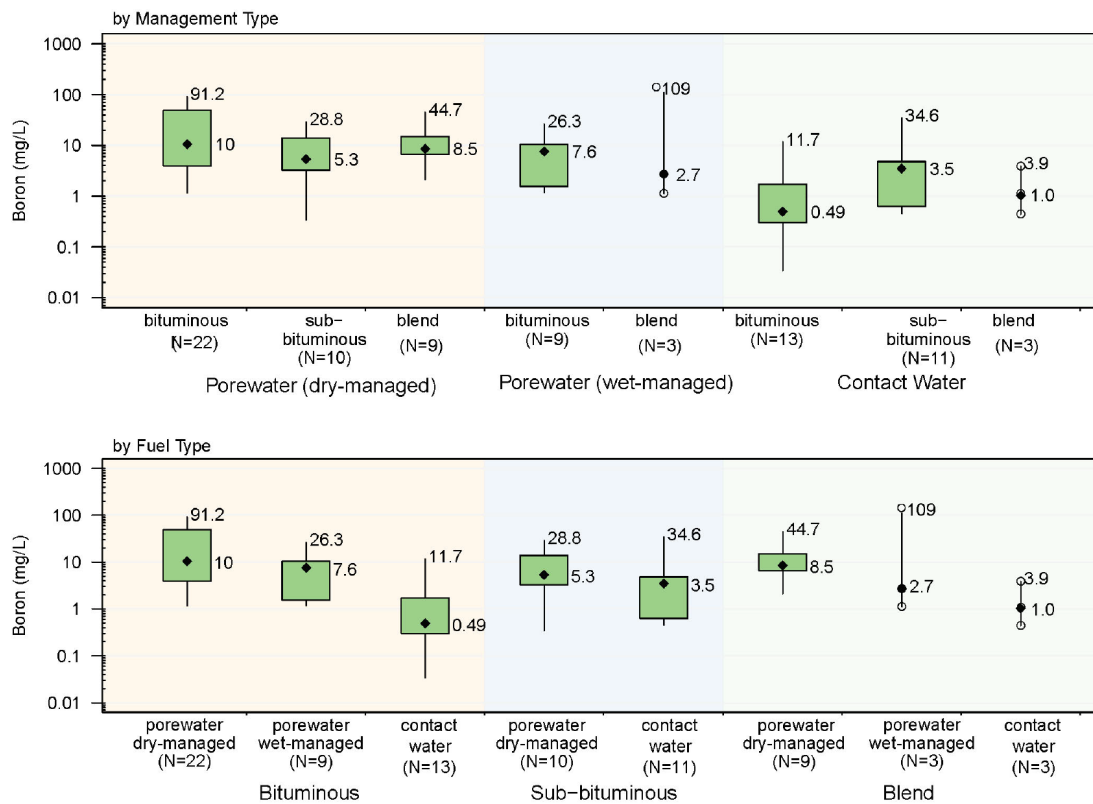

Figure 6: CCR-derived aqueous boron concentrations; from EPRI 2020.

For wet-handled CCRs, some of this available boron may be washed off by sluice water during transport to the impoundment, potentially making wet-handled CCR a less potent source of boron in leachate. Conceptually, this also helps explain the rapid attenuation of some boron plumes following pond closure. Once the pond stops receiving new CCR, the only source of additional boron to the aquifer is the available boron for dissolution from the existing CCR. Based on some of the above referenced experiments, this boron may be substantially depleted after a few volumes of pore water have been exchanged. More appropriate site-specific Kd values for the CCR material may be obtained through leaching experiments.

Since there is likely no rate-limiting diffusive processes taking place in the washing of grain coatings by water flowing through the CCR material, such a weakly sorbed depleting source can be readily represented by standard MT3DMS modeling. However, care must be taken to assure that the mass of boron in the solid phase is realistically high. It should also be noted that this is not necessarily a good approximation for the source zone depletion of other chemical species which may be entering leachate by diffusion from the CCR solid matrix.

CONCLUSIONS

It has been observed that CCR derived boron in groundwater may attenuate rapidly once impoundments are removed from active service, sometimes with more apparent effectively than active groundwater remediation programs. Numerical groundwater flow and transport modeling is often used to forecast the effectiveness of such remedies. For a variety of reasons, the CCR is often modeled as a separate entity than the natural aquifer. Modeling this requires that typical aquifer transport properties (most notably the partition coefficient; Kd) be assigned to both the natural aquifer and CCR. More appropriate site-specific Kd values for the CCR material may be obtained through leaching experiments. Examination of boron partition coefficient leads to an examination of the occurrence of boron in CCR. Boron found in CCR leachate likely began as a polyborate coating on glassy CCR granules. This coating may be easily washed off, which is inferred to be the primary mechanism for CCR source zone depletion in boron and helps to explain rapid pre-remedy attenuation of some plumes. Such source zone depletion can be readily modeled with programs such as MT3DMS, together with appropriate site-specific Kd values.

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