Dioxin degradation and metal biovolatilization at a former wood treating site

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Introduction

A large scale contamination assessment of a former wood treating site was completed on behalf of Alberta Environment and Parks in 2015. Previous field work in the early 1990s provided reliable analytical results for a metal and chlorophenols 'hot spot' where sludge from the wood treating process was burned as a waste management practice from 1967 until 1970. Dioxins were analyzed infrequently but were present in soil at high concentrations in later investigations until a comprehensive investigation was undertaken in 2015 to delineate the extent of contamination with dioxins, chlorophenols, hydrocarbons and metals. The hypothesis at the start of the 2015 investigation was that dioxins and metals would be the main contaminants at the Site, and that chlorophenols and diesel would be largely biodegraded since the Site closed in 1970.

The 2015 results clearly show that dioxins, chlorophenols and metals are the main contaminants at the Site, but that significant natural attenuation of all contaminants has occurred. These results are attributed to reductive dechlorination of dioxins and chlorophenols, and biovolatilization of metals.

Materials and Methods

The field sampling program targeted shallow soil contamination that was identified during previous investigations. The field work was completed in two major phases with Phase 1 covering the entire 16 hectare (approximately 40 acres) property, and then Phase 2 to delineate the 'hot spot' near the mill building. This investigative approach was designed to minimize the potential for cross-contamination and to ensure that the full spatial extent of soil contamination could be properly delineated in two phases of work.

Field work locations were tracked using a tablet computer with a georeferenced overlay showing historical air photographs. This allowed field staff to select sampling locations relative to the historic configuration of the Site buildings. Final sampling locations were professionally surveyed. All spatial data was incorporated into a GIS database to manage and present the data generated for the project.

Soil samples were collected using direct push sampling technology to depths of either 0.6 m or 1.5 m depth. The soil cores were collected in dedicated plastic sleeves and capped for later logging and sub-sampling for chemical analyses. The direct push soil sampling technology was selected as the best approach to efficiently collect soil samples while minimizing the potential for cross-contamination.

Groundwater samples were collected from standard 50 mm diameter PVC monitoring wells according to industry standard protocols. The wells were developed prior to sampling using Waterra inertial lift pumps, and samples were collected using either a peristaltic pump, Waterra, or disposable PVC bailers as appropriate depending on the sampling parameter and the monitoring well completion details.

Soil and groundwater samples were analyzed according to standard methods for parameters such as metals, hydrocarbons, chlorophenols, dioxins and general water chemistry. The dioxin analyses were completed by SGS AXYS Analytical Services Inc. in Sydney, British Columbia, using HRGC-GCMS (EPA Method 1613B). Dioxin bioassays for soil samples (EPA Method 4435) were completed by Xenobiotic Detection Systems (XDS) in Durham, North Carolina. Axys completed almost all of the HR-GC/MS dioxin analyses at the Site since 2003, and XDS completed dioxin bioassay analyses in 2009 and 2015.

Results and Discussion

The recent investigation shows a reduction in the spatial extent and peak concentrations of all contaminants and these results are considered indicative of natural biological activity.

The analytical results from the various investigations show a significant reduction in total dioxin mass, dioxin-TEQ and a change in the congener profile toward less chlorinated dioxins. The dioxin-TEQ half life estimated based on 369 soil analyses since 2003 (223 by HR-GC/MS and 146 bioassays) is approximately four years. The half-life for dioxin contamination derived for this Site is consistent with values presented in the literature for reductive dechlorination of dioxins [1,2]. The shift toward less chlorinated dioxins is apparent in the HR-GC/MS data, and these results are also consistent with the dioxin-TEQ values derived from the bioassay method.

The chlorophenol contamination has also continued to biodegrade along with the diesel fuel that was used as the carrier for pentachlorophenol (PCP). The PCP half life in soil is approximately two years (289 samples from 1990-1993, and 353 samples from 2009-2015). The highest PCP concentrations were found at ground surface which is consistent with the interpretation that anaerobic processes have reductively dechlorinated dioxins and chlorophenols.

Chromium, copper and arsenic were used as the wood preservative CCA prior to 1967 when the site switched to PCP. The molar ratio of these metals is fixed in CCA [3], but soil metals results from 1990 showed mostly arsenic contamination. Arsenic was never used at the Site except as CCA, and copper and chromium would have been initially present in the contaminated soil at concentrations reflecting the molar ratio in CCA. Subsequent sampling has shown that the metals concentrations in soil have decreased since 1990, and this decrease cannot be attributed to groundwater transport or changes in soil analytical methods.

The potential impact of groundwater transport on the soil and groundwater concentrations since 1970 was evaluated using a mass balance limiting case. This evaluation showed that based on the mass of metals initially present in the soil, and the groundwater flux through the contaminated zone, the noted decrease in soil metals concentrations cannot be attributed to groundwater contaminant transport. The initial mass present in the soil is relatively high, and the potential mass that could be removed by groundwater transport is far too low to account for the noted change in the soil metal concentrations. The groundwater flow velocity estimated for the Site is 10 m/year.

Another potential factor regarding the interpretation of the decreased contaminant concentrations is changes in soil analytical methods since the first investigations in the early 1990s. The earliest reports in the 1990s regarding metals and chlorophenols analyses in soil did not reference the specific analytical methods used, but the analytical methods are similar to current methods, and the results are considered comparable. For example, the measured concentrations of copper and chromium in 2015 are very similar to the concentrations reported in the early 1990s. Metals concentrations measured in 2015 using a total acid digestion (EPA Method 3052) confirm that the concentrations measured using the standard metals digestion (EPA Method 3050) are representative of the total metals concentrations in soil.

The decrease in the arsenic concentrations and the lack of chromium and copper contamination is attributed to biovolatilization which has been a known biogeochemical process for arsenic for over 100 years [4]. The arsenic half life based on 276 samples analyzed in 1990-1993, and 384 samples from 2009-2015 is approximately eight years. In the early 1990s, approximately 25 years after CCA was used at the site, 89% of the chromium and >95% of the copper was no longer measured in the soil when evaluated against the peak arsenic concentrations and the fixed molar ratio of metals initially present in CCA. Subsequent soil metals analyses confirms that the copper and chromium concentrations in soil are now largely at background levels.

The combination of persistent organic pollutant degradation and metals biovolatilization seen at this Site is not unprecedented as arsenic biovolatilization in the presence of DDT has been documented [5], and more recently the addition of biochar has promoted organochlorine degradation at a similar site [6].

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References

1. Adriaens, P., et al., (1995) *Bioavailability and Transformation of Highly Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Anaerobic Soils and Sediments*, Environmental Science and Technology, v. 29, 2252-2260.
2. Bunge, M., et al., (2003) *Reductive dechlorination of chlorinated dioxins by an anaerobic bacterium*, Nature, 357-360.
3. Nico, P.S., et al., (2004) *Chemical Structure of Arsenic and Chromium in CCA-Treated Wood: Implications of Environmental Weathering*, Environmental Science and Technology, 5253-5260.
4. Mestrot, A., et al., (2013) *Biovolatilisation: a poorly studied pathway of the arsenic biogeochemical cycle,* Environmental Science Processes & Impacts, 1639-1651.
5. Edvantoro, B.B., et al., (2004) *Microbial formation of volatile arsenic in cattle dip soils contaminated with arsenic and DDT*, Applied Soil Ecology, 207-217.
6. Gregory, S.J., et al., (2015), *Biochar in Co-Contaminated Soil Manipulates Arsenic Solubility and Microbiological Community Structure, and Promotes Organochlorine Degradation,* PLoS ONE 10(4): e0125393. doi:10.1371/journal.pone.0125393