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What do Total and Dissolved Metal Concentrations in Groundwater Samples Really Tell Us?

Part 2: Groundwater Colloidal Transport, Well Construction and Sampling Artefacts, and Concluding Thoughts

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INTRODUCTION

PART 2:

- Part 1 Recap
- Groundwater Colloidal Transport: How significant is the mobile particle issue?
- Monitoring Well Construction and Sampling Artefacts: What can we get when we sample and how can we improve?
- Concluding Thoughts

Part 1 Recap

Contemplated Policy – ESRD

Wallace (2012)

Analysis of Metals in Groundwater

- The project was initiated in response to a need identified by departmental staff involved with contaminated sites
- The purpose is to identify a consistent, science-based approach for measuring mobile metals in groundwater
  - Methodology will also apply to other areas (eg. EPEA approvals, GoA provincial monitoring network)
- Recommended analysis is for:
  - Total metals where a domestic use aquifer (DUA) may be impacted **Unfiltered, Field Acidified**
  - Dissolved metals in fine-grained media **Filtered 0.45 µm filter, Field Acidified**
- Stakeholder consultation is ongoing
- Implementation planned for January 1, 2013

Part 1 Discussion

1. There is a good understanding of what the relevant forms (chemical species) of the metal will be.

2. Analytical methods exist that can accurately quantify total metals as well as relevant species concentrations

3. Toxicological data exists that allows us to assess the (relative) bioavailability and toxicity of all forms.

Groundwater Colloidal Transport

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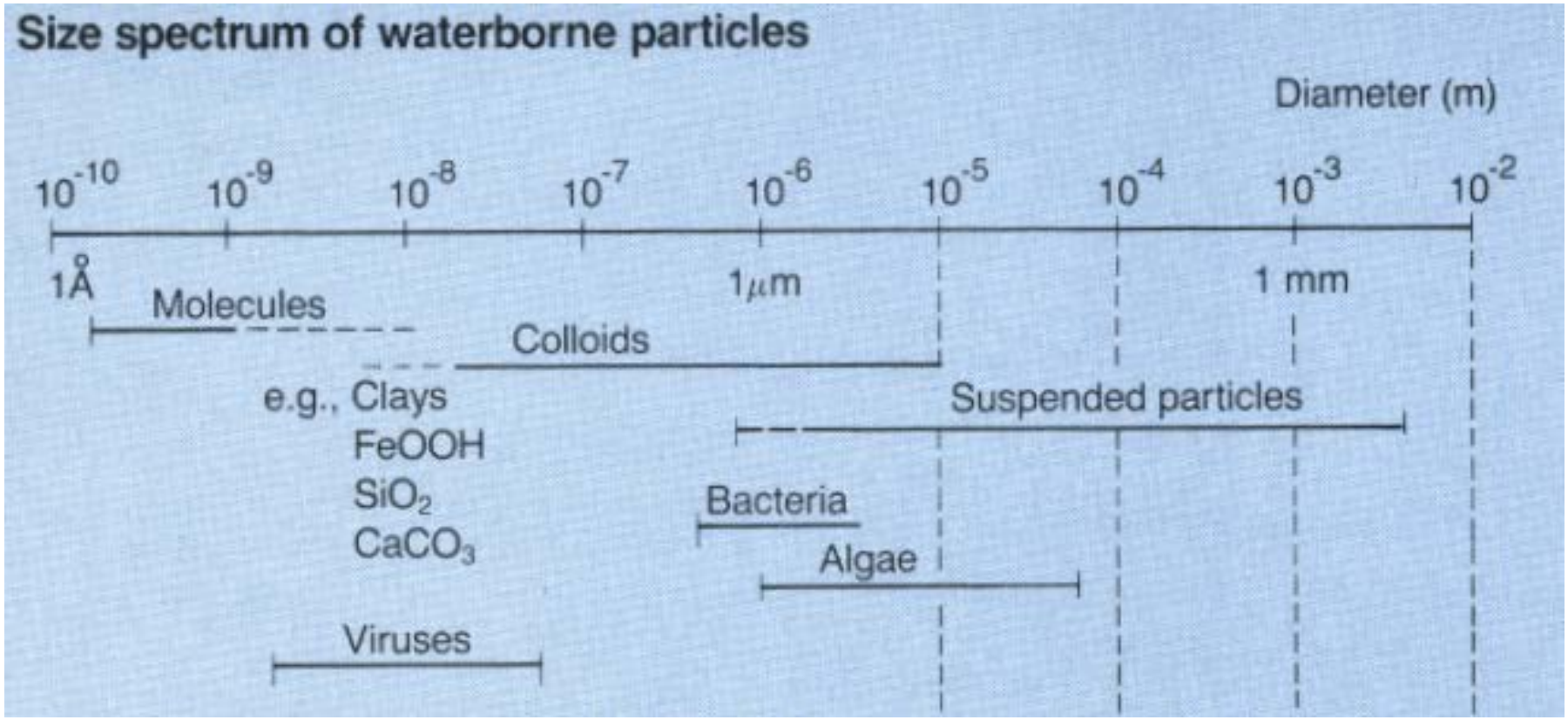
What is behind the contemplated policy?

- Concern that colloid and colloid-facilitated contaminant transport are possible within Domestic Use Aquifers (DUAs), and so groundwater samples should not be filtered.
- Issue goes back to 1980s with publishing of papers on colloids and other particulate matter obtained with then-traditional sampling methods such bailers (see Nielsen & Nielsen 2006), and colloid-facilitated transport of radionuclides (e.g. review by McCarthy & Zachara 1989).
- USA dealt with issue by mandating collection of unfiltered samples and low-flow or no-purge sampling.
- Let’s take a closer look at how significant the issue is …

First, a few words about colloids



McCarthy & Zachara (1989), citing Stumm (1977)

What are colloids?

- Remain dispersed due to thermal (Brownian) motion.
- Usually defined as approx. 0.001 to 1 µm, some consider to range up to 10 µm.
- Include (McCarthy & McKay 2004):
  - mineral precipitates (e.g. oxyhydroxides, carbonates, silicates) and coatings
  - rock and mineral fragments and coatings
  - biocolloids (viruses, bacteria, protozoans)
  - micro-emulsions of non-aqueous phase liquids
  - natural organic matter and coatings

Colloids are ubiquitous, but what is the evidence for mobility?

- Most studies simply identified colloids in groundwater samples without considering their mobility, or inferred transport without using colloid tracers, or used laboratory columns (e.g. Puls & Powell 1992).
- Most early field studies of biocolloids (see Ryan & Elimelech 1996).
- Radionuclide transport including Mn, Co, U in 1980s (see McCarthy & Zachara 1989, McCarthy & McKay 2004, Serco 2011) **… but there remain issues as to how significant colloid mobility is (Serco 2011) and radionuclides toxic at lower concentrations than non-radioactive isotopes**

Evidence for mobility?

- Metals transport with leachate from landfills in 1990s and 2000s (see Serco 2011).
- Metals transport from acid mine drainage, lead smelters (see Kretzschmar & Schafer 2005).
- Colloids tend not to advance ahead of the chemical or physical perturbations that caused their mobilization (Ryan & Elimelech 1996, Ryan et al. 1999).

- **So far, not much field evidence of widespread mobility, even in coarser grained formations**

Conditions when colloids clearly mobile?

- **Karst aquifers** (see McCarthy & McKay 2004).
- **Fractured bedrock**, but there are uncertainties as to how significant the issue is (see Serco 2011).
- **Fractured fine-grained till** (see McCarthy & McKay 2004 re latex microsphere and bacteriophage colloid tracer tests in glacial till).
- **Fractures, root and worm holes** (see Cey et al. 2010 re dye and fluorescent microspheres 0.5 – 4.9 µm tracers in silt loams).

Well Construction and Sampling Artefacts

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Sampling Considerations

Critical evaluation of the occurrence, composition, nature and abundance of subsurface colloids requires testing and validation of sampling methodologies that correctly sample mobile material in groundwater so that suspended colloidal particles are included and immobile particles are excluded.

(McCarthy & Zachara 1989)

Are we any further ahead 20+ years later?

Particulates in groundwater samples from monitoring wells

- Trying to measure mobile particulates that could enter a water supply well or be transported to a surface water body.

- Depending on sampling method, especially with Alberta use of bailers & inertial foot-valves, can get ...
  - fines from matrix grinding and formation perturbation during drilling
  - fines from drilling muds if used
  - formation fines from over-pumping
  - bentonite from poor well construction
  - colloids created by changes in O_2, CO_2, pH, Eh

What can we do to improve?

- **Well Design and Construction:**
  - Install monitoring wells with same design as drinking water wells **… best technical approach to get "representative" sample, but clearly impractical**
  - Follow principles of water supply well design to optimize slot sizes and sand pack design (see Nielsen & Schalla 2006 and ASTM Standard) **… options limited, particularly for fine-grained formations**

- **Well Development:**
  - important, but limited by well construction **… do not over-develop, over-pump**

More improvements

- **Well Purging and Sampling**
  - Use bailers and inertial foot-valve pumps gently to minimize disturbance
  - Low-flow and no-purge sampling **… best option? but at higher cost**
- **Filtration**
  - Filter pore size 1 – 10 µm includes potentially mobile colloids and exclude larger non-mobile fraction (Nielsen & Nielsen 2006)
  - **not common industry practice, but may be considered in future?**

Filtration allowed by some USA states

- Metals filtration allowed in some USA states (e.g. Connecticut 2012, Florida 1994, Ohio 2003) **if**:
  - Monitoring wells properly designed, installed, developed according to guidelines
  - Low flow sampling recommended or mandatory
  - Field parameters stabilized (temperature, pH, conductivity)
  - Sample turbidity > 5 NTU and likely to contain non-mobile particles (e.g. clay-rich)
  - Allowed filter pore sizes 1 µm (Florida), 5 µm (Ohio), or unspecified (Connecticut)

Concluding Thoughts

Concluding Thoughts

- Requiring total metals analysis where a DUA may be impacted: Will we necessarily obtain meaningful and scientifically-defensible data using this approach?

- Interim, somewhat arbitrary approach to assessing risks to receptors that will require refinement.

More Thoughts

- Approach will require better understanding of:
  - metal behaviour in groundwater flow systems
  - sampling methodologies that minimise collection of well construction and sampling artefacts; and
  - possible exceptions to the generalized approach such as “macroporous” soils

- Will tend to provide over-estimates of mobile, bioavailable metals in non-filtered samples due to both lab and current Alberta sampling methodologies.

More Thoughts

- Contemplated policy anticipated to result in:
  - more analyses of both total and filtered samples where a DUA may be impacted
  - re-evaluation of sampling methods and increased need for ESRD to release guidelines for conducting ESA work
  - more effort in classifying formations as DUAs or non-DUAs at contaminated sites

- More research coming on speciation-specific toxicity and analysis of metals and more research needed on significance of colloidal transport of metals.

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Thank You, Questions?

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