

Chemical Limitations of Groundwater Treatment

Effective ways of analyzing groundwater, and how to determine if chemistry can be used to purify it.

Yellow Quill's Roberta Neapetung climbing into a "treated" water reservoir for yearly clean-up before a new biological-RO treatment system was implemented.

By Dr. Hans Peterson

Often groundwater sources are analyzed with the main objective of compliance to guidelines. This is great if you want to comply with guidelines, but if you want to produce safe drinking water a different approach is required. There are many compounds in groundwater that are not included in guidelines, but they present problems either in the treatment plant or in the distribution system.

Therefore, analysis of raw groundwater sources need to include compounds that are of concern for health (typically in guidelines), aesthetic (mostly in guidelines) as well as bacterial energy and nutrient sources (rarely in guidelines at levels where they can cause problems). Some physical/chemical conditions, such as redox (reduction-oxidation) potential should also be determined. To give you an idea of what to determine have a look at the raw water quality of the George Gordon, Pasqua and Yellow Quill First Nations below.

Raw water chemical composition

Groundwater from 100 m depth is used by Yellow Quill, while Gordon and Pasqua First Nations obtain their water from 200 m depth. The depth where the water is collected is important as shallower depths (100 m) are considerably colder (5-6°C) than deeper (200 m) water intakes (9-10°C). The colder the water, the more challenging it is to treat with most processes both for pre-treatment and actual reverse osmosis (RO) treatment.

A series of compounds were well below guideline levels for all raw water sources, including aluminum, copper lead, selenium and zinc. For the water sources discussed here only one health guideline, arsenic, was exceeded in the raw water. Yet all of these raw water sources can be regarded as undrinkable without excessive treatment.

The alkalinity levels are very high, ranging from 380 mg/L at Pasqua to 470 mg/L at George Gordon. Ammonium

levels are also quite high ranging from 1.3 to 4.7 mg/L (as ammonium-N). The arsenic levels are also well above Canada's current guideline of 0.010 mg/L ranging from Yellow Quill's 0.017 mg/L through Pasqua's 0.036 to Gordon's 0.072 mg/L. Barium is a compound of concern for RO treatment, but all the different groundwater supplies were quite low in this element (0.007-0.009 mg/L). Boron levels were well below the 5 mg/L guideline value at 0.34 to 0.76 mg/L.

The calcium levels were high – ranging from Pasqua's 130 mg/L to Yellow Quill's 270 mg/L and Gordon's 360 mg/L. Magnesium levels follow a similar trend at 48 mg/L at Pasqua, 100 mg/L at Yellow Quill and 170 mg/L at Gordon's. Magnesium levels were below the guideline level of 200 mg/L with a low of 48 at Pasqua, and intermediate 100 at Yellow Quill and a high of 170 at Gordon's. The ratio between calcium and magnesium was similar, ranging from 2.1 to 2.7. As calcium and

magnesium constitute the main part of water hardness, a similar trend is shown for this component with Pasqua at 523, Yellow Quill at 1086, and Gordon's at 1599 mg/L. All groundwater sources were above the recommended European Union limit for calcium (100 mg/L) and Yellow Quill and Gordon's were above the Saskatchewan guideline for hardness (800 mg/L). All the groundwater sources must however, be classified as extremely hard.

Raw water chemical composition of George Gordon's, Pasqua's and Yellow Quill's ground water sources (bolded and italicized, compounds that bacteria can use as either energy or nutrient sources) with guideline values indicated.

The chloride levels were all below the 250 mg/L guideline ranging from 46 to 72 mg/L. There is no guideline for dissolved organic carbon (DOC), but it is expected that to comply with future guidelines for chlorinated disinfection, by-products (trihalomethanes and haloacetic acids) levels as low as 2 mg/L may need to be achieved and removal of DOC will be required for many raw water sources. To meet the current Canadian Drinking Water Quality Guideline for trihalomethanes (0.1 mg/L), DOC levels below 5 mg/L are required. Both Pasqua and George Gordon are around 5 mg/L with Yellow Quill being double that at 11mg/L. If there is ammonium in the water, the relationship between organic carbon and disinfection by-products follow a different path. Fluoride levels need to be below 1.5 mg/L and all raw water sources were below this level (0.18-0.46 mg/L). This is a key element in some raw water sources and RO is an effective way of decreasing its level.

The iron levels were substantially above the Canadian guideline of 0.3 mg/L with Gordon's at 1.41 through to Pasqua's at 2.41 and Yellow Quill's at 8.49 mg/L. Manganese levels were close to three times above the guideline at Pasqua (0.13 mg/L), five times at Yellow Quill (0.25 mg/L), and 32 times (1.59 mg/L) above the guideline at Gordon's. These groundwater sources are anaerobic and as a result the nitrate levels were all below detection (less than 0.04 mg/L). Phosphate-phosphorus, an essential bacterial nutrient, ranged in concentration from 0.06 mg/L at Gordon's through Pasqua's 0.15 mg/L to Yellow Quill's 0.23 mg/L. In anaerobic groundwater sources the redox potential

will be low and it was always less than -100 mV. This anaerobic water is extremely hard on redox probes and not many determinations can be carried out until the probes malfunction.

Silicon levels were relatively high and almost identical for the different raw water sources hovering around 12 mg/L for all of them. Silicon is an important component for RO membrane treatment. Sodium levels were below the guideline of 200 mg/L at Gordon's, but at Pasqua they were twice the guideline (420 mg/L) and at Yellow Quill the level was just above the guideline (230 mg/L).

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The sulphate levels were all well above the guideline level of 500 mg/L ranging from 850 mg/L at Pasqua through 1100 at Yellow Quill and 1300 mg/L at Gordon's. Without sulphate removal all these water sources would be distinctly "laxative." The total dissolved solids (TDS) were well above guidelines for all water sources (hovering around four times above the Canadian guideline). To make some ground water sources in Saskatchewan comply with "guidelines" the Saskatchewan guideline for TDS has been increased to 1,500 mg/L. The World Health Organization classifies TDS levels above 500 mg/L as high, between 900-1,200 mg/L as poor and greater than 1,200 mg/L as unacceptable.

If the water was allowed to absorb oxygen from air the particle levels generated from mainly iron oxidation translated into a turbidity of 17 NTUs at Gordon's through to 37 at Pasqua and 102 at Yellow Quill. This is equal to particle levels of more than 400,000/mL in the 2 to 40 micro-m size range at Yellow Quill.

The chemical brew

A community contemplating constructing new water treatment processes or improving on existing processes need to take into consideration the entire extent of how chemistry can impact the actual treatment processes, life expectancy of equipment, as well as distribution of the

treated water. It has been too common to simply pick a couple of chemicals, say iron and manganese, and ignore everything else. But, let's use iron and manganese as an example as so many water treatment plants have been constructed with the primary objective of removing these two compounds.

First, iron and manganese both have aesthetic guidelines associated with them. For iron it is 0.3 mg/L and for manganese it is 0.050 mg/L. From a regulatory perspective the concerns with these two metals are taste, odour, and staining issues. But, these two

elements are excellent sources of energy for bacteria and can also be used to generate bacterial slimes that will foul RO membranes or cause problems in the distribution system. But, for now let's just deal with the regulatory perspective.

Let us assume that we are going to use manganese greensand fed with potassium permanganate to treat the three water sources above. This is an old treatment technique and the chemistry behind the process has been resolved. Potassium permanganate oxidizes the iron and the manganese, which results in the precipitation of the compounds in the manganese filters. The precipitates are then removed from the filters by backwashing around once per day and the process is then repeated. There are variations of this, such as intermittent potassium permanganate feed or replacing potassium permanganate with chlorine, but the principles remain similar.

In theory, 1.06 parts of potassium permanganate is required to oxidize one part of iron, and 1.92 parts are required for manganese oxidation. Therefore you may think that this is fairly simple: add up the potassium permanganate requirements (or demand) for iron and manganese and we have the dose level required. Well, let's do that for the three water sources above.

The potassium permanganate demand for iron and manganese were: Gordon's 4.5 mg/L, Pasqua 2.8 mg/L and



For the raw water at George Gordon, the actual potassium permanganate demand is higher, at least 10 mg/L – five times greater than any additions carried out in the treatment process. Potassium permanganate’s pink colour (which is unreacted potassium permanganate) only shows up at 15 mg/L.

Yellow Quill 9.5 mg/L. The engineered “solution” to all of these treatment plants was originally to use manganese greensand. At George Gordon three different engineering companies applied various forms of this treatment over a 15-year period. Yet the potassium permanganate dose at George Gordon was never recommended to be higher than 2 mg/L. When SDWF got involved with Gordon’s, we rapidly showed that what the engineers had tried to do was simply chemically impossible. Even with an incredibly dedicated operator, doing the chemically impossible is simply not possible!

Pasqua also used manganese greensand, and this treatment was even recommended for Yellow Quill First Nation until SDWF showed that it had no hope of working. Once a pilot was established at Yellow Quill, it did not take long to show that indeed this treatment did not work at realistic potassium permanganate levels.

These points all assumed there was only iron and manganese in the water. But, looking at real raw water samples, we get a totally different picture. There are many compounds in the above water that also have potassium permanganate demands, including reduced arsenic, hydrogen sulphide, and organic material. For the raw water at George Gordon, the actual potassium permanganate demand is higher, at least 10 mg/L – five times greater than any additions carried out in the treatment process.

Yet plant after water treatment plant has been designed and built without consideration even for the basic chemistry reactions between iron, manganese and potassium permanganate. Indian and Northern

Affairs Canada (INAC) is hanging its hat on “engineering stamps.” To be worth something, these engineering stamps need to be coupled with scientific facts. It is doubly unfortunate that the truth behind drinking water quality in many communities have been covered up by inadequate testing leaving both the federal government (Health Canada) and provincial governments with a lot of room for improvement.

The first thing federal and provincial inspectors should do is to examine treated water reservoirs in rural communities. A foot of black sludge at the bottom of a treated water reservoir simply means that a large part of the treatment process is actually happening outside of the water filters. This can be the result of incomplete flocculation or oxidation, resulting in further flocculation and oxidation in the reservoirs. The presence of bottom sludge is a real concern when treated reservoir levels are low, as this can result in spikes of really turbid water, which can be loaded with disease-causing microorganisms. At Yellow Quill (before it received an integrated biological and RO membrane treatment plant), particle counts in the distribution at times exceeded 40,000 per mL, when acceptable drinking water particle levels should be below 100 per mL.

Highly turbid water can pass as “safe to drink” if only free and total chlorine, E. coli and total coliforms are measured – you just have to add lots of chlorine. Slime layers in the distribution system and sludge deposits in the treated water reservoirs call for a re-evaluation of how Health Canada is carrying out its testing on reserves across the country.

The SDWF has pointed out flaws in testing and how to assess rural water

since its inception 10 years ago. We have seen improvements after Walkerton and North Battleford, but improvements have mainly centered around larger and better monitored chlorine additions with less work focusing on the need for better water treatment technologies to combat challenges treating poor quality water sources. Native Canada and INAC have done an excellent job improving operator training and certification. But, it really doesn’t matter how well the operators are trained if they are forced to use tea strainers when, at a minimum, they should be using coffee filters.

There are some exceptions to the above, and INAC’s efforts at Yellow Quill, Gordon’s and Pasqua, have led the way to gain a better understanding of the challenges communities are facing and what is required to resolve those challenges. Yearly removals of treated water reservoir sludge layers have become a thing of the past. In February 2004, after the reservoir cleanup at Yellow Quill, we tossed a quarter into each treated water reservoir; even at full reservoir levels (3.3 to 3.6 m) they can be seen as clearly today as when they were tossed in four years ago. This is what the federal government should be doing – helping in the search for real solutions, rather than sticking Band-Aids over the symptoms or attempting to download the responsibility and subsequent liability. www.safewater.org



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