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Performance of reverse osmosis and manganese greensand plants in removing naturally occurring substances in drinking water

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ABSTRACT

The Water Security Agency has a legislative authority to regulate water treatment systems and enforce standards with respect to drinking water quality in the Province of Saskatchewan. A number of communities in Saskatchewan which depend on groundwater as a source for drinking water have reported high levels of naturally occurring substances, such as arsenic, uranium and selenium, in their raw water. These communities continue to upgrade their systems by installing new or retrofitting with treatment units, such as reverse osmosis (RO) and manganese greensand (MGS) filters to reduce the levels of naturally occurring substances in finished water. In order to assess the treatment performance of these systems, a study was initiated to collect samples from 20 communities across Saskatchewan and analyse naturally occurring substances in raw and finished water. The study focused on the removal efficiency and the effect of parameters such as sulfate, total dissolved solids, and hardness on the removal efficiency. The paper includes discussion on the results and analysis of sampling/research studies conducted to assess the performance of treatment systems. Results showed that RO plants are effective in removing uranium and MGS are effective in removing arsenic from drinking water.

Key words | arsenic, drinking water, manganese greensand, reverse osmosis, treatment, uranium

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INTRODUCTION

In the Province of Saskatchewan, Canada, the quality of drinking water, the conditions of systems that produce it and the protection of source water is one of the top priorities and continues to be an important public health and environmental goal. As such, ensuring safe drinking water is a shared responsibility among a number of provincial agencies and the Water Security Agency (WSA) is a lead agency in implementing the Safe Drinking Water Strategy in the province. Nearly 50 per cent of the people who live in Saskatchewan depend on groundwater as a source for drinking water and the remaining population use surface water as a source. The Guidelines for Canadian Drinking Water Quality (Health Canada 2012) are used in Canada as the definitive measure of science-based safety criteria for drinking water. Saskatchewan has adopted these guidelines as legally enforceable standards.

Drinking water health and toxicity parameters include a range of naturally occurring substances (arsenic, barium, boron, lead, nitrate, selenium, uranium, etc.), and other substances such as trihalomethanes, which may be produced during chlorine-based disinfection processes. These substances represent a small potential for adverse health effects over longer time periods. While the safety gains associated with eliminating microbial threats far outweighs any possible adverse health risks associated with disinfection by-products, it is important to monitor and to ensure they remain within safe levels. Nearly 10 to 15 per cent of communities in Saskatchewan who depend on groundwater as a source of drinking

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water have reported increased levels of naturally occurring substances, such as arsenic and uranium, in their raw water.

Arsenic, a potential carcinogenic element is present in natural water systems as a result of both natural and anthropogenic activities. The natural weathering processes contribute approximately 40,000 tons of arsenic to the global environment annually, while twice this amount is being released by human activities (Paige *et al.* 1996). Arsenic concentrations are generally higher in groundwater due to increased contact levels with these arsenic-containing deposits. Arsenic can, however, find its way into water sources through industrial and agricultural processes. There are both organic and inorganic forms of arsenic that exist in water sources, but inorganic arsenic is the most likely to exist in concentrations high enough to cause concern for drinking water quality (Thirunavukkarasu *et al.* 2001). The health effects of arsenic have been widely studied in humans, most notably in Taiwan. The health effects of arsenic in humans vary depending on the compound and form. The maximum acceptable concentration (MAC) for arsenic in drinking water is 10 μg/L in Canada and it was established based on the incidence of internal (lung, bladder, and liver) cancers in humans, through the calculation of a lifetime unit risk (Health Canada 2006).

Arsenic can be effectively treated in municipal-scale treatment facilities through a number of well-documented methods, which typically include both a pretreatment step and a final polishing step (Health Canada 2006). Several studies have demonstrated that arsenic removal can be achieved by various technologies, such as coagulation/filtration, lime softening, activated alumina, ion exchange, reverse osmosis (RO), and manganese greensand filtration (Viraraghavan *et al.* 1994; US EPA 2000); in particular, coagulation with ferric salts was found to be the most effective method in the case of large-scale water utilities (Cheng *et al.* 1994; Scott *et al.* 1995). Fixed bed and filtration treatment systems are becoming increasingly popular for arsenic removal in small-scale treatment systems because of their simplicity, ease of operation and handling, regeneration capacity and sludge-free operation.

In manganese greensand (MGS) filtration treatment systems that are suitable for small-scale communities, groundwater containing arsenite (As III) is oxidized to arsenate (As V) by the addition of an oxidant such as $KMnO_4$ solution and subsequently arsenate is removed in MGS filtration systems. The MGS filtration system is initially used to remove iron and manganese from the water, but the iron that has been adsorbed onto the greensand filter is capable of removing arsenic from the water. Arsenic removal efficiency is based on the amount of iron present in the source water and studies showed that iron to arsenic ratio played an important role in removing arsenic in MGS filtration systems (Subramanian *et al.* 1997; Viraraghavan *et al.* 1999).

Iron oxides, oxyhydroxides and hydroxides (all are called 'iron oxides') play an important role in a variety of industrial applications, including pigments for the paint industry, catalysts for industrial synthesis and raw materials for the iron and steel industry (Cornell & Schwertmann 1996). Studies showed that adsorption and filtration treatment systems using iron oxide-coated media are effective in removing arsenic to a level below the arsenic guideline (Joshi & Chaudhuri 1996; Driehaus *et al.* 1998; Thirunavukkarasu *et al.* 2003), and are suitable technologies for small-scale water treatment utilities.

Uranium is a naturally occurring element that can be present in water supplies. In Saskatchewan, uranium in groundwater typically occurs as a result of leaching of the element from soils and rocks. The interim MAC for uranium in drinking water in Canada is 20 μg/L (Health Canada 2001). Regarding treatment, laboratory studies and pilot plant tests have shown that conventional anion exchange resins are capable of removing uranium from drinking water supplies to concentrations as low as 1 μg/L (Clifford & Zhang 1994). Favre-Re'guillon *et al.* (2008) demonstrated that nanofiltration membranes are capable of removing uranium to a level lower than the World Health Organization guideline for uranium. The purpose of this study is to evaluate the performance of MGS and RO treatment plants in removing naturally occurring substances from raw water of the communities located in Saskatchewan, Canada. This paper also outlines some of the water management activities undertaken by the WSA to implement the drinking water standards and manage drinking water in the province.

SAMPLING, RESULTS AND DISCUSSION

The WSA has water quality standard and monitoring guidelines for the province's drinking water quality and all 673 communities in Saskatchewan are required to monitor and achieve the physical, chemical, health and toxicity, and biological standards as specified in the operating permits issued to the communities. Table 1 shows the details of compliance with sample submission requirements and testing compliance for health and toxicity parameters during the 2011–12, 2010–11, and 2009–10 fiscal years based on routine samples submitted by WSA regulated communities in Saskatchewan. The decrease in sample submissions in 2011–12 is the result of decreased monitoring by some smaller existing waterworks to determine compliance with the health and toxicity standards that took effect in December 2010. WSA has and will continue to follow up on a quarterly basis with waterworks owners who have not submitted the required samples as a means to help ensure compliance with monitoring and drinking water quality standards.

In 2011–12, there were 100 of 673 human consumptive waterworks that exceeded at least one health and toxicity related chemical standard, resulting in a total of 128 exceedences. When exceedences for health and toxicity parameters, such as arsenic or uranium, were encountered and would represent a short-term health risk, waterworks owners were advised of the results and Precautionary Drinking Water Advisories were issued for the affected water supplies. Forty-six arsenic exceedences occurred in 23 human consumptive systems. Additional arsenic testing was conducted by 10 human consumptive systems. Sixty uranium exceedences occurred in 26 human consumptive systems. Additional uranium testing was conducted by eight human consumptive systems. Table 2 provides a list of the parameters and number of excursions at all WSA regulated waterworks.

Table 1 | Health and toxicity sample submission and parameter result compliance 2011–12, 2010–11 and 2009–10[a]

Fiscal year	Health and toxicity sample submission compliance rate (%)	Parameter standards compliance rate (%)
2011–12	75	80
2010–11	89	84
2009–10	86	88

[a] Health and toxicity parameters include: aluminum, arsenic, barium, boron, cadmium, chromium, copper, iron, lead, manganese, selenium, uranium and zinc.

A study was designed to evaluate the performance of MGS and RO treatment plants, and in this study raw and treated water samples from 20 groundwater communities in Saskatchewan were collected and analysed for naturally occurring substances. During the summer of 2012, samples were collected from 10 MGS and RO plants, respectively, and analysed at the Saskatchewan Centre for Disease Control (Provincial) Laboratory. Figures 1 and 2 show the results of samples collected from MGS filtration plants of 10 communities; the arsenic concentration in the raw water of these communities varies from 4 to 38 μg/L. Arsenic removal efficiency of these plants ranged between 70 and 94 per cent and the highest removal efficiency was achieved in the MGS plant of the community Kelliher. The results showed that all the plants removed arsenic to a level well below the drinking water guideline of 10 μg/L. The raw water uranium levels in these communities ranged between 1 and 14.3 μg/L and the results showed that the performance of MGS plants was poor in removing uranium from raw water. Selenium was not detected in the raw water of all these plants. High levels of iron and manganese were detected in most of the raw water of these communities and all the MGS plants removed iron and manganese well below the guideline.

Figures 3 and 4 show the results of samples collected from RO plants of 10 communities; raw water uranium levels of these communities ranged between 1 and 43 μg/L and from the treated water results it was observed that

Table 2 | Health and toxicity parameter specific excursion totals for WSA regulated waterworks during 2011–12 and 2010–11

Parameter	Number of excursions in 2011–12	Number of excursions in 2010–11
Arsenic	46	55
Barium	0	1
Copper	2	0
Nitrate	0	0
Lead	3	2
Selenium	3	8
Uranium	60	62

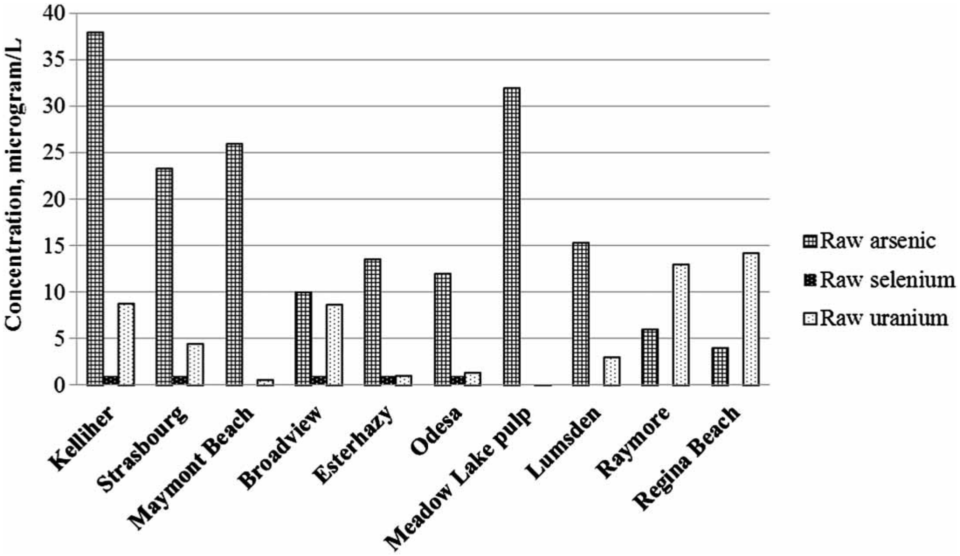

Figure 1 | MGS plants: levels of naturally occuring substances in raw water.

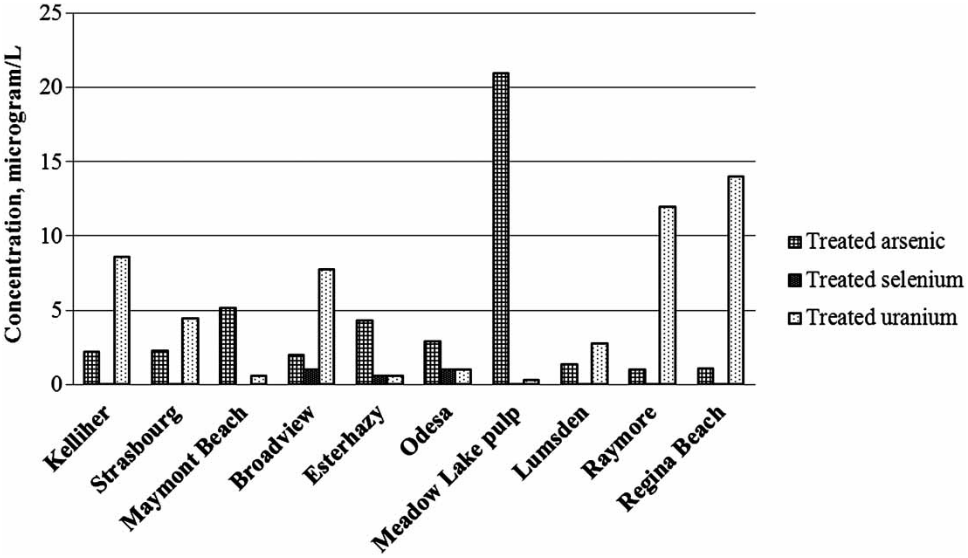

Figure 2 | MGS plants: levels of naturally occuring substances in treated water.

more than 99 per cent uranium was removed by these RO plants. However, the results showed that RO plants are not effective in removing arsenic from the raw water of some communities. There may be many reasons why RO plants could not remove arsenic, perhaps because of the molecular weight cut off (MWCO) of the membrane (used to describe the pore size: the smaller the MWCO the tighter the membrane size), but in this study it was observed that the presence of sulfate, total dissolved solids (TDS) and hardness in water (Figures 5 and 6) affects or inhibits arsenic removal. In the case of communities such as Arlington Beach, Balcarres, and Foam Lake, the TDS, hardness and sulfate levels in raw water are high and that may be the reason for the poor performance of RO plants in these communities in removing arsenic. Raw water TDS, hardness and sulfate levels in communities of

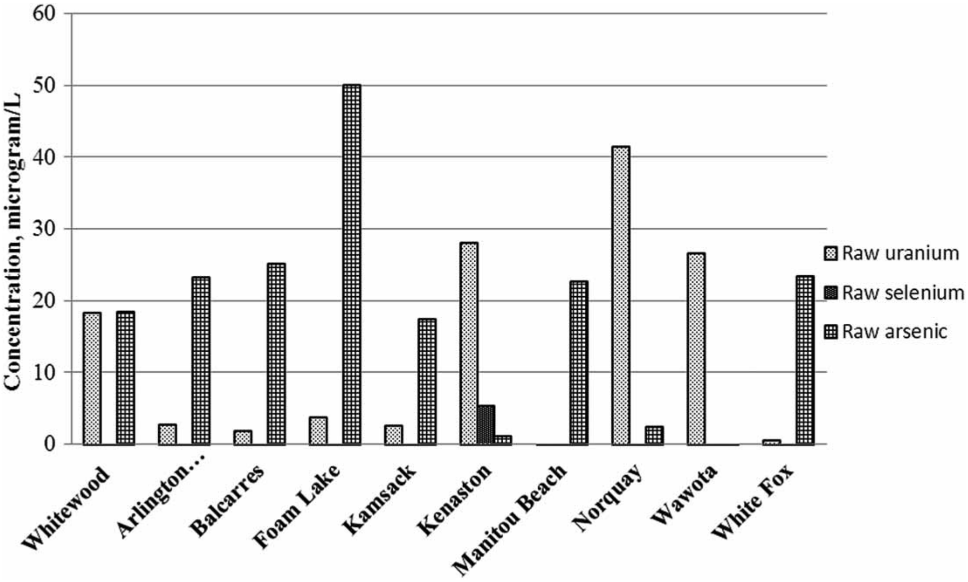

Figure 3 | RO plants: levels of naturally occuring substances in raw water.

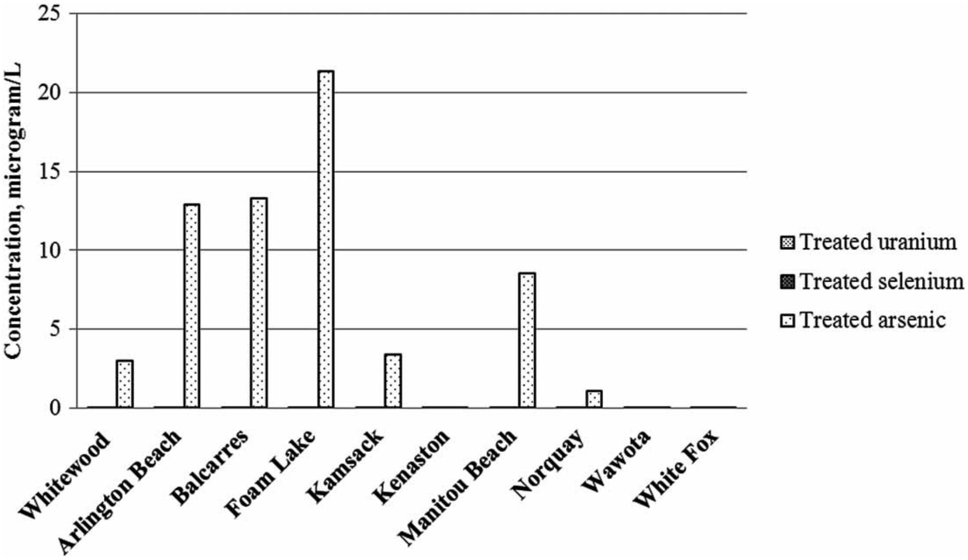

Figure 4 | RO plants: levels of naturally occuring substances in treated water.

White Fox and Kamsack are low and the results showed that RO plants of these communities removed arsenic to well below the drinking water guideline. The community of Kenaston has two wells, well 1 has high uranium (30 μg/L) and the other has none, water from well 1 goes to the RO plant and the water from well 2 is treated in the MGS plant and finally the treated water from both RO and MGS plants is blended (uranium level less than the guideline in blended water) and distributed to the community. Selenium was also detected (5.3 μg/L) in raw water from well 1 and was removed by the RO plant. The results also showed that both RO and MGS plants removed iron and manganese (Figure 7) to levels below the drinking water guideline.

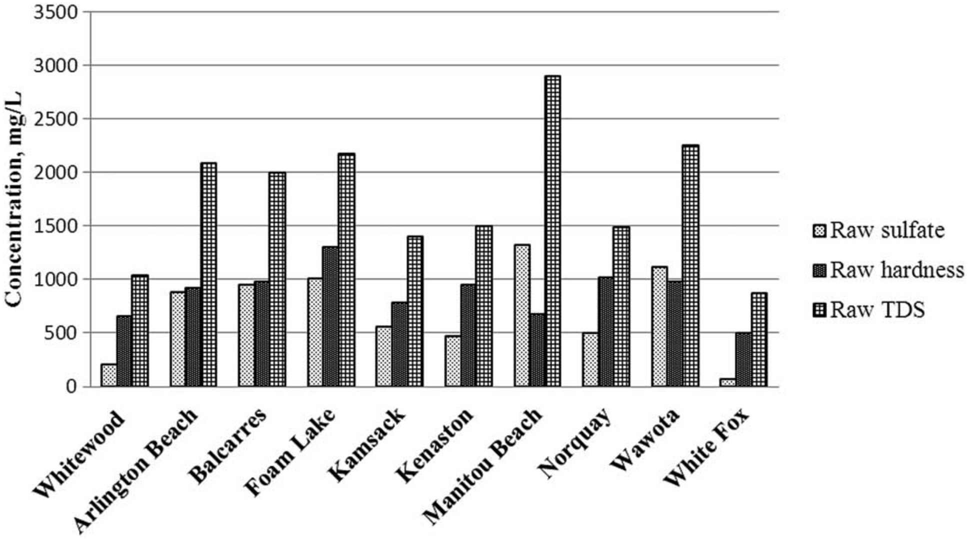

Figure 5 | RO plants: levels of sulfate, hardness and TDS in raw water.

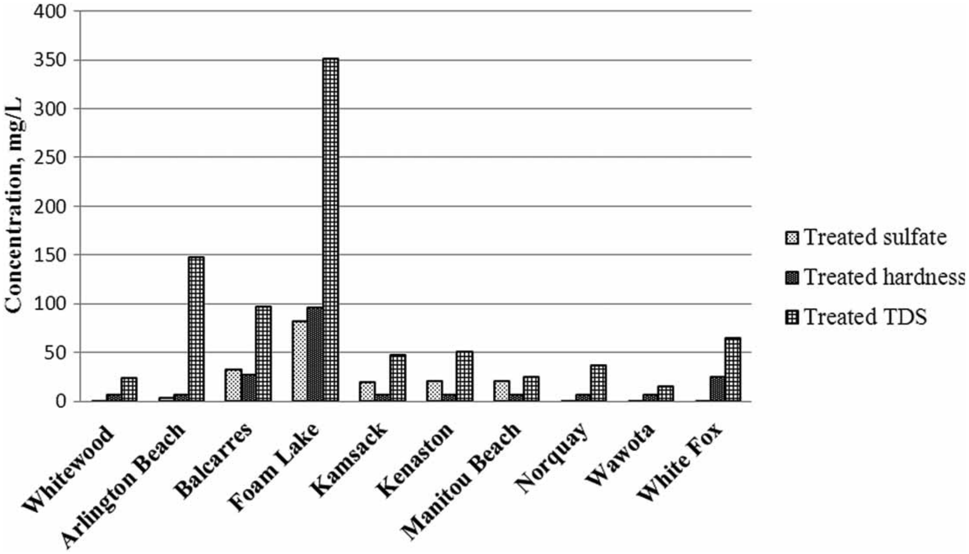

Figure 6 | RO plants: levels of sulfate, hardness and TDS in treated water.

TREATMENT STRATEGIES AND COST ECONOMICS

Communities in Saskatchewan also adopt different treatment strategies and/or multiple treatment systems to meet the drinking water guideline and reduce the cost of treatment. The raw water from the well of community Wapella (population close to 500) has a uranium level higher than the MAC, the community has a MGS filtration system and recently (2012) the community has upgraded the existing system by adding an ion-exchange (IE) resin treatment system. A portion of treated water from the MGS filtration system is further treated in the IE system, and the final blended water from both MGS and IE plants has a uranium level lower than the guideline of 20 μg/L. The total upgrade cost of the system including addition of some distribution system infrastructure is close to Can$1 million. The source

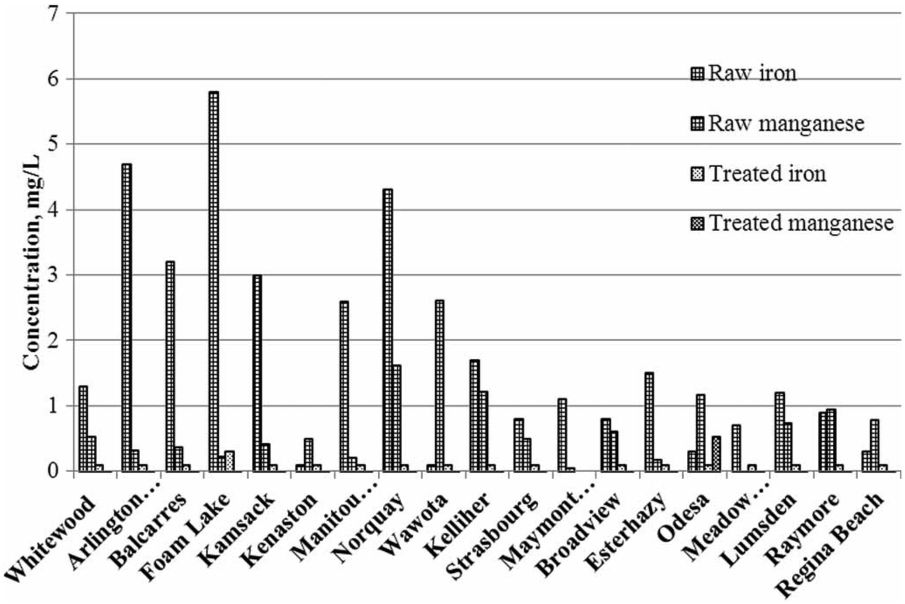

Figure 7 | Iron and manganese levels in water.

water for Grenfell was from both surface and groundwater and the existing system (MGS filtration plant) could not meet the treated water turbidity guideline; the town came up with an alternative source, i.e. two new groundwater wells; however, sampling results showed that the uranium levels in these wells are high and the community built a RO plant in 2012 to remove uranium from raw groundwater. The total upgrade cost including wells, distribution system and pumps is $1.8 million.

A group of University of Regina engineering students developed cost equations that can be used by owners of Saskatchewan water supplies with high naturally occurring arsenic levels. Ten arsenic-affected Saskatchewan water supplies were considered in this study. Three different filter media (AdEdge, MGS and Media G2) that are capable of removing arsenic levels to below that of the arsenic standard were used in this study, and based on available raw water quality data, cost analysis was conducted and cost equations developed.

AdEdge AD26 Series Systems are stand-alone systems designed specifically for well head use. The system utilizes a dry granular form of manganese dioxide, which is an NSF 61 certified solid phase oxidation mineral media. Through co-precipitation and filtration, the system effectively removes iron, manganese and sulfide, as well as arsenic if it coexists with high levels of iron in water. The removal efficiency of the system as claimed by the manufacturer is greater than 90 per cent; however, it should be noted that this removal efficiency relies on an iron to arsenic ratio of at least 30:1. Additionally, the operating range for pH is 6.5 to 9.0 and water outside this range may require additional pre-treatment to ensure the effectiveness of AD26 media.

The AD26 treatment process often includes using chlorine as an oxidizer. Chlorine is injected into the water as a pre-treatment and oxidizes As(III) to As(V) and Fe^{+2} to Fe^{+3}. The water is then filtered through the media where ferric arsenate is able to form on the surface of the catalytically active media. Backwashing, a process which effectively removes oxidized precipitated iron, manganese and arsenic from the media bed, is necessary to maintain this system's efficiency. This process typically required backwashing one to three times per week, and a percentage of the backwash water can be re-filtered through the system. In Kannata Valley, a Saskatchewan community that recently implemented an AdEdge AD26 system, backwash water is collected, stored and left to settle in an underground storage tank. After settling, up to 90 per cent of the supernatant from this backwash water has been sent back through the system for treatment. Air wash is also typically implemented in the systems and occurs before the backwash cycle is initiated. This process allows captured precipitated material to be dislodged from the filter media and allows for a shorter overall backwash cycle.

GreendsandPlus by Inversand Company is an advanced filter media system used to remove soluble arsenic, manganese, iron, radium and hydrogen sulfide that are found in municipal or industrial groundwater. GreensandPlus is a purple charcoal filter media, which is similar to the original MGS media. Both media have the same effective size, uniformity coefficient, density, weight, capacity, and backwash and pressure drop curve. They also use manganese dioxide as their substrate media. The difference is found in the core of the media; the GreensandPlus core is made of silica sand, which allows the manganese dioxide to coat the surface and act as a catalyst in the oxidation-reduction reaction of iron and manganese.

The ideal parameters for the system include a pH range of 6.8–7.2, iron concentration of 3 mg/L and a manganese concentration of 0.3 mg/L. GreensandPlus can withstand water with low silica, total dissolved solids and total hardness without any degradation and is effective at high temperatures and higher differential pressures allowing for longer run times. The GreensandPlus media system is operated using a catalytic oxidation process, which involves pre-injecting an oxidant, such as chlorine or potassium permanganate, directly into the raw water source. The oxidant should be fed at least 10–20 seconds upstream of the filter. This will oxidize the iron in order to convert arsenite to arsenate and is removed in the filter. GreensandPlus has an approximate life expectancy of 10–15 years. This ensures that the annualized costs of the media and system are relatively low compared with other treatment systems (Inversand 2013).

Media G2, a filter media developed by ADI International Inc., is made up of a material called diatomite. This material is effectively the skeleton of diatoms, and is used often in filtration for treatment of groundwater. It resembles sand, and the basic particles are obtained from ancient dried sea beds. This media works in a similar way to granular ferric hydroxide (GFH). Media G2 is capable of removing both arsenate and arsenite between a pH of 5.5 and 7.5, but is not affected by high levels of iron. Regeneration of Media G2 is possible up to four or five times before replacement, and regeneration is dependent on specific pH levels and arsenic levels in raw water. Media G2 can be placed in any existing pressure filters, which can simplify the retrofitting process for many communities, as well as potentially decreasing retrofitting costs (ADI 2011).

The design flow that was used to develop the cost equations was based on the maximum daily flow and fire flow demand. The filter or vessel dimensions and media volume are based on the design flow, empty bed contact

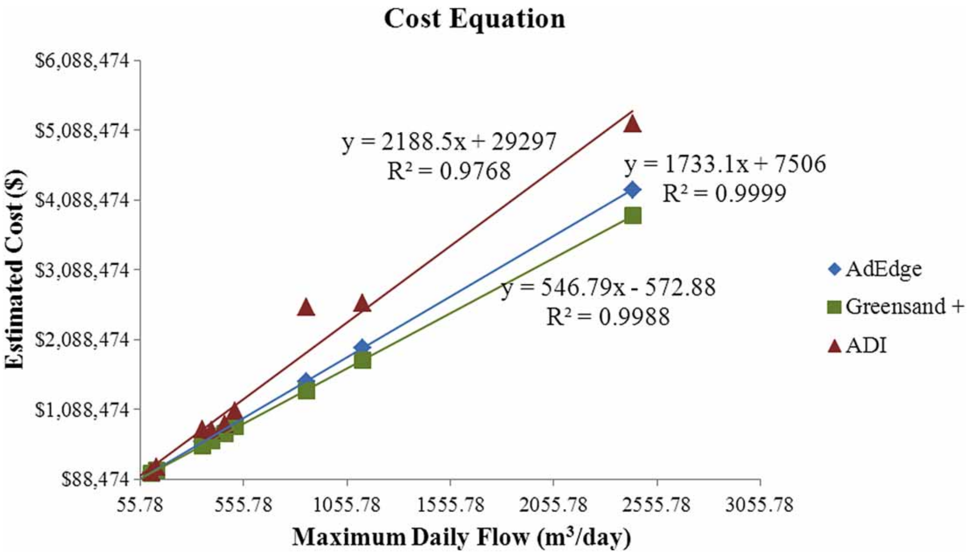

Figure 8 | Cost equations for three media for different flow requirements.

time (EBCT), surface loading rate (SLR), media height (Lcritical), and an expansion coefficient value (E). The values for EBCT, SLR and Lcritical provided by respective media companies were used in developing the cost equation. The cost analysis conducted for each media and system considered both capital and operating costs. The capital cost was determined based on media, volume, type of vessel and quantity, construction and auxiliary cost. The operational cost requirements are based on media replacement, chemical costs, etc. The cost of chemicals includes the cost of $KMnO_4$ and chlorine; the demand of $KMnO_4$ includes the concentrations of iron and manganese in the raw groundwater and chlorine demand is based on residual chlorine levels in the distribution system. The auxiliary cost includes cost for engineering and management, additional pumps, pipes and valves, and monitoring equipment.

The cost equation (Figure 8) for each media for different flow requirements was developed and adjusted with inflation as per Kawamura & McGivney (2008). A Microsoft Excel based user interface with a cost template (Table 3) was also developed based on the cost equations, which was useful for the communities to determine approximate treatment cost and select the appropriate filter media to remove arsenic from drinking water. The cost analysis showed that in communities with a design flow below 500 m^3/day, the cost of the GreensandPlus system is lower compared with other systems; however there may be other factors that may influence selection more than cost. For example, if pre-treatment is necessary, the cost and additional treatment system may make another treatment choice more desirable. In communities with design flow more than 500 m^3/day, the cost of Media G2 system is lower; however, the costs of GreensandPlus and AD26 system are still comparable and once again other factors including site-specific conditions and system footprint may influence the selection of an appropriate treatment system.

Table 3 | User interface cost template

Community info	**AdEdge or Greensand or ADI**	
Name	EBCT (min)	××
Source water	SLR (m/min)	××
Treatment goals	Lcritical (m)	××
System parameters	Media volume (m^3)	##
Population served	Area required (m^2)	##
Average daily flow (m^3/day)	No. of required vessels	
Fire flow (m^3/day)	16"	##
Design flow (m^3/day)	21"	##
Existing pre-treatment	26"	##
Existing disinfection	**System costs**	
Existing facility sq ft	Media	##
Water analysis	*Pressure tank*	
pH	16"	##
Total As (ug/L)	21"	##
Treated As (ug/L)	26"	##
Iron (mg/L)	Auxiliary equipment	##
Manganese (mg/L)	New construction	##
	Media lifetime cost	##
	Annualized replacement	##
	Total estimated cost	##

CONCLUSION

Study results showed that MGS filtration plants are capable of reducing arsenic levels in finished water to a level below the arsenic drinking water guideline and RO plants are effective in removing uranium to less than 1 μg/L in finished water. Results also showed that MGS plants are not effective in removing uranium from drinking water. RO plants are not effective in removing arsenic from raw water of some communities and this may be due to the presence of high levels of sulfate, TDS and hardness in raw water that affects or inhibits arsenic removal. Communities in Saskatchewan, Canada adopt different treatment strategies and/or multiple treatment systems to reduce arsenic and/or uranium in treated water. The cost equations and user friendly interface model developed in this study are useful to arsenic-affected water supplies in Saskatchewan as a 'decision making tool' and help the communities in selecting appropriate filter media to remove arsenic from drinking water.

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