

## Arsenic Removal for Drinking Water Production in Rural Nicaraguan Communities

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**Arsenic Removal for Drinking Water  
Production in Rural Nicaraguan  
Communities**



# **Arsenic Removal for Drinking Water Production in Rural Nicaraguan Communities**

## **Proefschrift**

ter verkrijging van de graad van doctor  
aan de Technische Universiteit Delft,  
op gezag van de Rector Magnificus prof. dr. ir. T. H. J. J. van der Hagen;  
voorzitter van het College voor Promoties,  
in het openbaar te verdedigen op  
dinsdag, 16 juli 2019 om 12.30 uur

door

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Al pueblo de Nicaragua

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# 1. Introduction

## 1.1. Arsenic in groundwater

Among the natural contaminants that can be found in water sources, arsenic (As) is the most carcinogenic (Smith et al., 1992; Smith et al., 2000). The World Health Organization (WHO, 2001) has recommended in their drinking water guidelines that As levels should not exceed 10 µg/L. In natural groundwater (pH 6.5–8.5) arsenic can be found as a neutral ion as As(III) (reducing conditions) and as a negatively charged ion as As(V) (oxidizing conditions) (Welch and Stollenwerk, 2003). Depending on the pH As(V) exists mainly as the monovalent  $\text{H}_2\text{AsO}_4^-$  specie (pH < 6.9), and for a higher pH, the divalent  $\text{HAsO}_4^{2-}$  specie is dominant (Welch and Stollenwerk, 2003). On the other hand, under reducing conditions and for a pH < 9.2,  $\text{H}_3\text{AsO}_3^0$  is the dominant As(III) specie (Welch and Stollenwerk, 2003). As is a common element on earth (Smith et al., 1992); nevertheless, its abundance and concentration in rocks and soils is not directly related to its distribution or concentration in groundwater (Ravenscroft et al., 2009). This is because specific geochemical mobilization processes are needed to dissolve As from its solid source into groundwater (Smedley and Kinniburgh, 2002). In the case of natural contamination, four mobilization mechanisms are of special interest: reductive dissolution, alkali desorption, sulphide oxidation and geothermal arsenic mobilization (G. Webster and Nordstrom, 2003; Plummer et al., 2004; Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). These mobilization mechanisms are frequently correlated with specific chemical conditions in groundwater sources (Ravenscroft et al., 2009). Reductive dissolution is often reported in anoxic and strongly reducing aquifers; under this condition As-bearing minerals (e.g. iron oxides) tend to dissolve into water (Bhattacharya et al., 1997; Nickson et al., 2000). In aquifers where reductive dissolution occurs, with a near-neutral pH, the uncharged As(III) is the dominant specie in water. The waters in these aquifers are generally also characterized by high iron (Fe) and bicarbonate ( $\text{HCO}_3^-$ ) concentrations and low levels of oxidized compounds such as sulphate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ). Reductive dissolution has been identified in Asian countries such as Bangladesh, India (Nickson et al., 2000) and Nepal (Gurung et al., 2005). In aerobic and oxidizing aquifers alkali

desorption is often mentioned to explain the As enrichment in this groundwater type (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). In these kinds of aquifers, which are also characterized by low iron and manganese (Mn) concentrations and high levels of  $\text{HCO}_3^-$ , charged As(V) are the dominant species. It is also possible to find high concentrations of oxidized compounds (e.g.,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) in these aquifers (Ravenscroft et al., 2009). Alkali desorption has been proposed, for example, to explain As contamination in the Chaco–Pampean Plains in Argentina (Bhattacharya et al., 2006; Smedley and Kinniburgh, 2002). Sulphide oxidation is commonly reported in mining areas and occurs where sulphide minerals ( $\text{FeS}_2$  and  $\text{FeAsS}$ ) are exposed to oxygenated or nitrate-rich water (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). Here, As enrichment of water occurs due to the dissolution of sulphide minerals and the subsequent desorption of their As content into the groundwater. Arsenic is mainly found as As(V) in aquifers where sulphide oxidation occurs. These aquifers are also characterized by their low pH and high concentration of  $\text{SO}_4^{2-}$  (Ravenscroft et al., 2009). Ghana and Thailand have been listed by Smedley and Kinniburgh (Smedley and Kinniburgh, 2002) as regions where As contamination occurs due to sulphide oxidation. Geothermal arsenic dissolution is often associated with waters with high temperature and high  $\text{Cl}^-$  concentrations (Welch et al., 1988; Wilkie and Hering, 1998). In geothermal fluids, As (III) is the dominant species (M. Ballantyne and N. Moore, 1988). Nevertheless, as geothermal water mixes with oxygenated water from shallow aquifers, it is oxidized to As(V) (Wilkie and Hering, 1998). Therefore As-rich drinking water sources due to geothermal influences tend to be dominated by As(V) (Smedley and Kinniburgh, 2002; Wilkie and Hering, 1998). Furthermore geothermal As-rich waters are usually associated with other trace elements of health concern such as Ba, B, Li and Cr. (G. Webster and Nordstrom, 2003). Geothermally influenced As-water has been reported, among others, in Rio Grande Valley, Colorado, and New Mexico, USA (Bexfield and Plummer, 2003). The impact of geothermal As in drinking water sources (surface and groundwater) have also been reported throughout Latin America both in urban and rural areas (Hurtado-Jiménez and Gardea-Torresdey, 2006; López et al., 2012).

## 1.2. Geothermal arsenic in drinking water sources in Latin America

In Los Altos de Jalisco, Mexico, As concentrations up to 263 µg/l and temperatures ranging from 22 to 45°C have been reported in the drinking water sources (Hurtado-Jiménez and Gardea-Torresdey, 2006). While in Bajío Guanajuatense, Mexico, also a good correlation has been found between temperature and As concentration. In this area the highest temperature reported in a water supply well was 50°C and its corresponding As concentration was around 50 µg/l (Rodríguez et al., 2015). In El Tatio, Chile, geothermal waters (As concentrations up to 27,000 µg/l) feed the Rio Lao (with average As concentrations of 1,400 µg/l), which is the only water source for the population (420,000 habitants) of the region of northern Chile (López et al., 2012; Romero et al., 2003). In Nicaragua, the geothermally influenced arsenic was initially reported in Xolotlán Lake (10 to 30 µg/L) and in Tipitapa's hot springs (up to 200 µg/L) (Lacayo et al., 1992). Later Longley (2010) reported drinking water sources influenced by the geothermal fields of the Telica volcano, and used by rural communities located in the western part of Nicaragua. The arsenic concentration in this area ranged between 50 to 900 µg/l and the average temperature was 34°C.

As-rich waters have been found in 14 out of the 20 Latin America countries and it is estimated that around 14 million of people are consuming As-rich water exceeding 10 µg/L (Bundschuh et al., 2012). Nowadays, Argentina has the largest population (4 million of inhabitants) affected by the consumption of water with high As concentrations (Bundschuh et al., 2012; McClintock et al., 2012; Villaamil Lepori, 2015). In 1999 it was estimated that in Mexico 2 million inhabitants were exposed to As concentration ranging from 30 to 1200 µg/L (Bundschuh et al., 2008; Cebrian et al., 1994). Currently it is estimated that 1.8 million people are exposed to As-rich water sources in Chile (Sancha and O'Ryan, 2008) and in 2004 it was estimated that, 56,000 people, living in rural communities in Nicaragua, were exposed to As-rich water (Barragne, 2004).

However, there is little information about the health effects of the As-rich water consumption in these countries (McClintock et al., 2012). In Latin America the As poisoning can be traced back to 7,000 years ago, to the indigenous population in northern Chile (Arriaza et al., 2010). Nevertheless, the health effects of As-rich water consumption, in a living population, was documented for the first time in the

beginning of the 20<sup>th</sup> century in Chaco Pampean, Argentina (Goyenechea, 1917). Since then several studies have reported As-rich water and the effects on the health of the population located on the Chaco-Pampean Plains and in the Cuyo regions of the Andes (Carrera and Cirelli, 2005; McClintock et al., 2012; Nicolli et al., 1989; Silvina Guber et al., 2009; Smedley and Kinniburgh, 2002). In 1962 the first cases of As poisoning were reported in Antofagasta (Chile), where, for more than a decade, half a million people consumed water with As concentrations of about 800 µg/l (Bundschuh et al., 2008). In Central America the first documented case of As poisoning was reported in 1996 (Gomez, 2002).

### **1.3. Low pressure nanofiltration**

Among the As removal technologies that have been suggested for developing countries (precipitation, adsorption and membrane filtration) (Jiang, 2001; Kabir and Chowdhury, 2017), membrane filtration is a promising alternative option for rural areas. As removal technologies such as adsorption and precipitation processes are not always suitable to produce drinking water with As concentrations below 10 µg/L (Kabir and Chowdhury, 2017). Furthermore, both As removal processes are pH dependent and could be influenced by co-occurring ions (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004). While the As removal efficiency of membrane technology (reverse osmosis (RO) and nanofiltration (NF) could be less sensitive to pH or water composition (Ng et al., 2004; Sato et al., 2002) and high As rejection efficiencies (>90%) have been reported (J. Waypa et al., 1997; Jiang, 2001; Ng et al., 2004; Padilla and Saitua, 2010). The lower operational pressure of NF, compared with RO (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004; Padilla and Saitua, 2010; Saitúa et al., 2005), makes NF systems the most attractive option for As removal in rural areas in developing countries. Scientific literature related to the use of NF systems to remove As from geothermally influenced waters is scarce. For example the influence of co-occurring ions on the rejection of As(V) during NF filtration of high temperature water has not been studied previously. Furthermore, studies regarding the NF application for As removal in natural geothermally influenced waters have not been reported earlier, while demonstration of such a

system is crucial towards further development and maturing of this technology for rural application.

#### **1.4. Research questions and methods**

Nicaragua's concern about the presence of As in groundwater, and its influence on human health, was first recognized in 1996 (Gomez, 2002). The geothermal influence on the As contamination in drinking water sources of rural communities have been reported in several reports (CARE, 2002; González, 2004; Longley, 2010; PIDMA-UNI, 2001). However, the majority of recent information (2010–2015) on arsenic contamination can only be found as non-peer reviewed reports and dispersed raw data held by various organizations within the country. Furthermore, in spite of the awareness of the presence of arsenic and efforts of universities and NGOs, so far there is not much practical experience with the use of arsenic removal systems. Therefore, the aims of this research were to gather the available information related to arsenic in Nicaragua and to enhance understanding of As(V) removal during NF membrane filtration of geothermally influenced water. These findings were subsequently used to develop an effective and affordable NF treatment system, eventually driven by Human or Solar power, for the arsenic removal in rural communities and small towns in Nicaragua.

The specific research objectives were as follows:

1. What is the current state of information and knowledge on arsenic occurrence and mobilisation mechanisms in Nicaragua?
2. How the interaction of As(V) with co-anions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) influence the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species during NF membrane filtration of high-temperature waters (up to  $50^\circ\text{C}$ )?
3. In which degree the concentration of  $\text{Cl}^-$  and membrane properties (MWCO and zeta potential) influence the rejection of As(V) during NF of high-temperature waters?
4. To what extent flux and temperature affect the As (V) rejection performance of a low-pressure NF pilot plant during filtration of natural, geothermally influenced groundwater in Nicaragua?

To answer these questions the research was done in three parts. The first part consisted of a literature review, as well as the compilation of information from different institutions and sources. The second stage consisted of experimental research conducted at the Waterlab of TU Delft. To complete the last part of this research a NF pilot plant was built and operated in a Nicaraguan rural community exposed to As-rich drinking water sources due to geothermal influences.

### 1.5. Outline of the thesis

In **Chapter 2** an overview is given of arsenic occurrence and mobilisation mechanisms in Nicaragua, based on studies related to arsenic contamination of groundwater, processed during the past two decades. **Chapter 3** describes the possible role of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species (at pH 6, 7 and 8) during NF membrane filtration of a multi - component solution at high-temperature (25-50°C). Chapter 4 focuses on the effect of co-ions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) and increasing  $\text{Cl}^-$  concentrations on the rejection of As(V) during NF filtration of water at high temperatures. This chapter also study in which extent the pore size expansion and zeta potential of the membrane are affected by high temperature, and how this change in membrane properties affect the As(V) rejection. **Chapter 5** presents the effects of flux (16, 23 & 30 L/m<sup>2</sup>h) and temperature (31,35 & 43°C) on the rejection of As(V) during NF of natural geothermally influenced groundwater in Nicaragua. Finally, the general conclusions and recommendations for future research are given in **Chapter 6**

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## **2. Arsenic contamination of rural community wells in Nicaragua: a review of two decades of experience**

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### **Abstract**

Several surveys have been conducted in Nicaragua between 1996 and 2015 confirming the presence of high levels of arsenic ( $> 10 \mu\text{g/L}$ ). In this paper, these peer-reviewed ( $n=2$ ) and non-peer reviewed sources ( $n=14$ ) have been combined to provide an extensive overview of the arsenic contamination of drinking water sources in Nicaragua. So far, arsenic contamination has been detected in over 80 rural communities located in 34 municipalities of the country and arsenic poisoning has been identified in at least six of those communities. The source of arsenic contamination in Nicaragua is probably volcanic in origin, both from volcanic rocks and geothermal fluids which are distributed across the country. Arsenic may have directly entered into the groundwater by geothermally-influenced water bodies, or indirectly by reductive dissolution or alkali desorption, depending on the local geochemical conditions.

### **2.1. Introduction**

In Latin America (from Argentina to Mexico) As occurrence has been reported in 14 out of 20 countries and it is estimated that around 14 million people regularly ingest water with As concentrations exceeding  $10 \mu\text{g/L}$  (Bundschuh et al., 2008; Bundschuh et al., 2012). The first documented case of natural As-contaminated water, including the impact on human health, was reported in the beginning of the 20<sup>th</sup> century in Argentina (Bundschuh et al., 2008; Bundschuh et al., 2012; Goyenechea, 1917). With an estimated number of inhabitants of 4 million (around 9% of the total population) consuming As-contaminated water (Villaamil Lepori<sup>1</sup>, 2015), Argentina is nowadays considered to have the largest population affected by the consumption of

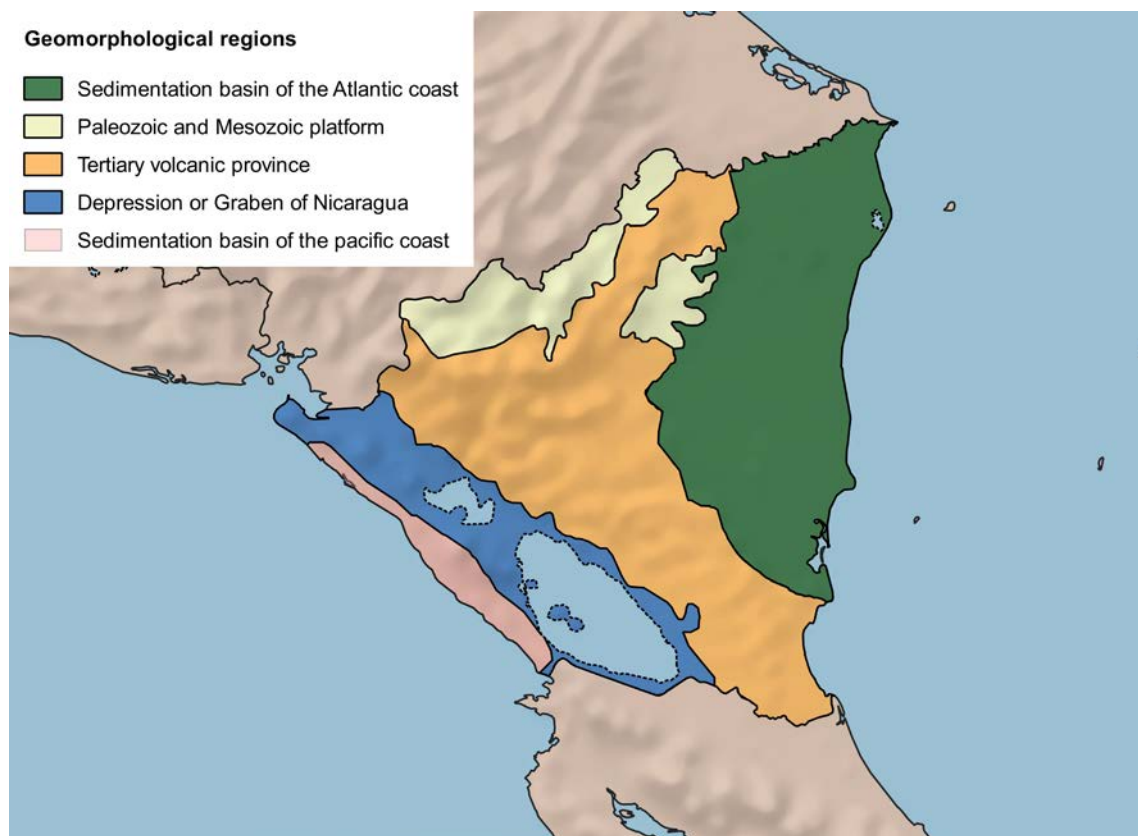
water with high concentrations of As in Latin America (Bundschuh et al., 2012). Between 1950 and 1970 water sources in Mexico and Chile were identified as being contaminated with As (Bundschuh et al., 2008; Bundschuh et al., 2012). During the last two decades, cases of As contamination have been reported in various countries in Central America (Bundschuh et al., 2008; Bundschuh et al., 2012).

In Nicaragua, the first documented case of arsenic poisoning was reported in 1996 in a rural community located in the northern part of the country (Gomez, 2002). Since then, several assessments confirmed the presence of high levels of arsenic in drinking water sources located in different geological environments (Altamirano Espinoza and Bundschuh, 2008; Barragne, 2004; CARE, 2002; CISTA, 2012; ENACAL et al., 2005; González et al., 1997; INAA, 1996; L. Morales et al., 2008; OPS/OMS and Nuevas-Esperanzas, 2011; OPS/OMS and UNICEF, 2005; PIDMA-UNI, 2001; PIDMA-UNI and UNICEF, 2002; PIDMA-UNI and USAID, 2001). The source of arsenic contamination in Nicaragua is probably volcanic in origin, both from volcanic rocks and geothermal fluids which are distributed across the country (Altamirano Espinoza and Bundschuh, 2008; Bundschuh et al., 2012; González et al., 1997; L. Morales et al., 2008; OPS/OMS and Nuevas-Esperanzas, 2011). In Nicaragua, the provisional guideline of the World Health Organization (WHO, 2001) has been adopted as national guideline (10 µg/L).

Nicaragua is situated on the isthmus of Central America, with both Caribbean and Pacific coasts. The Central American volcanic front extends from Mexico to Costa Rica and is formed by subduction of the Cocos Plate beneath the Caribbean Plate. Nicaragua forms part of the Chortis Block, one of the major structural units which make up the Caribbean Plate (Weinberg, 1992). Most Central American volcanoes occur along a volcanic front that trends parallel to the strike of the subducting Cocos Plate (Carr et al., 2003). Three major volcanic events have occurred in Nicaragua since middle Tertiary time, from shield volcanism which produced ignimbrites in the Highlands, though basaltic and andesitic magmas along the Pacific coast, to arc volcanism which created the modern volcanic chain (Ehrenborg, 1996). Nicaragua is composed of five geomorphologic regions (Figure 2.1). These are: (1) the Paleozoic and Mesozoic platform, with the oldest rock formations of the country; (2) the Tertiary volcanic region (central area); (3) The Central Depression or graben, a new geologic area in which Quaternary volcanism is concentrated; (4) the sedimentary basin of the

Atlantic coast; and (5) the sedimentary basin of the Pacific coast which consists of Tertiary marine sediments, partly overlain by Quaternary deposits (Hodgson, 1998; McBirney and Williams, 1965).

The majority of recent knowledge (2010 - 2015) on arsenic contamination in Nicaragua cannot be found in international publications, but as non-peer reviewed reports and dispersed raw data held by particular organizations within the country (e.g., Nuevas Esperanzas, CISTA – UNAN LEON). Therefore, the objective of this paper is to present an overview of the current state of knowledge of arsenic occurrence and mobilization mechanisms in Nicaragua, based on existing literature, as well as the interpretation of unpublished research reports and data files. These studies related to arsenic contamination of groundwater processed during the past two decades have been obtained from Nicaraguan research organizations, government institutes and non-governmental organizations.



**Figure 2.1** Map of Nicaragua showing the geological settings of the country (Hodgson, 1998)

## **2.2. Methods**

### **2.2.1 Data collection and mapping of As occurrence**

This study is based on a review of research literature related to As contamination of water in Nicaragua produced between 1996 and 2015, including two peer-reviewed paper and 14 non-peer reviewed reports. Most of the non-peer reviewed reports were published in Spanish.

Table 2.1 shows a list of the peer reviewed and non-peer reviewed reports, and data files obtained from different organizations in Nicaragua. Additionally,

Table 2.1 shows a classification of the studies based on their geologic settings and their research areas. The research areas correspond to municipalities grouped according to their geographic proximity. The data extracted from the studies mentioned in

Table 2.1 were used for the preparation of maps showing municipalities and water supply points affected by As contamination. Of the total number of samples cited, 40% were georeferenced.

**Table 2.1** Overview of published and unpublished reports related to arsenic occurrence in Nicaragua produced from 1996 to 2015.

Reference of Study	Type of research literature	Number of Water Supply Points Tested (*)	Number of Water Supply Points Exceeding The National Norm (10 µg/L)	Percentage of Water Supply Points Exceeding The National guideline (10 µg/L)	Maximum As concentration (µg/L)	Geological settings	Research Area
INAA. (1996)	Non-peer reviewed reports	25	11	44%	289 µg/L	Tertiary Volcanic-region	Alluvial aquifer of the Sebaco valley and surrounding areas
GONZALE Z.M. et al. (1997)	Non-peer reviewed reports	46	12	26%	50 µg/L	Tertiary Volcanic-region	Alluvial aquifer of the Sebaco valley and surrounding areas
PIDMA - UNI. (2001)	Non-peer reviewed reports	20	6	30%	69 µg/L	Tertiary Volcanic-region	Alluvial aquifer of the Sebaco valley and surrounding areas
PIDMA-UNI-USAID (2001)	Non-peer reviewed reports	124	6	5%	23 µg/L	Tertiary volcanic region, Paleozoic and Mesozoic platform & Depression or Graben	Central Region of Nicaragua & North-west region
CARE International al. (2002)	Non-peer reviewed reports	11	2	18%	16 µg/L	Tertiary Volcanic-region	Alluvial aquifer of the Sebaco valley and surrounding areas
PIDMA - UNI. (2002)	Non-peer reviewed reports	106	6	5.7%	88 µg/L	Tertiary Volcanic-region & Depression or Graben	Hydrothermal mineral deposit areas
Barragne-Bigot (2004)	Non-peer reviewed reports	77	22	28.6%	108 µg/L	Tertiary Volcanic-region &	Hydrothermal mineral deposit areas

ENACAL. (2005)	Non-peer reviewed reports	44	41	93%	1,200 µg/L	Depression or Graben  Tertiary volcanic region	Central region of Nicaragua
L. Morales et al.	Peer reviewed reports	12	3	25%	115.00 µg/L	Tertiary Volcanic- region & Depression or Graben	Hydrothermal mineral deposit areas
González, R.M. (2004)	Non-peer reviewed reports	11	2	18%	10 µg/L	Tertiary Volcanic- region	Alluvial aquifer of the Sebaco valley and surrounding areas
PAHO/WH O/UNICEF. (2005 )	Non-peer reviewed reports	1488	50	3%	161 µg/L	Tertiary Volcanic- region , Paleozoic and Mesozoic platform Depression or Graben	Alluvial aquifer of Sebaco valley and surrounding areas Central region of Nicaragua & North-west region Hydrothermal mineral deposit areas
Altamirano E.M. et al (2009)	Peer reviewed reports	57	24	42%	122 µg/L	Tertiary Volcanic- region	Alluvial aquifer of the Sebaco valley and surrounding areas
Longley, A.J. (2010)	Non-peer reviewed reports	59	20	34%	235 µg/L	Depression or Graben	North-west region
OPS - OMS/Nicar agua - Nuevas Esperanza s. (2011)	Non-peer reviewed reports	183	45	25%	325 µg/L	Depression or Graben	North-west region
CISTA UNAN LEON (2012)	Non-peer reviewed reports	141	13	9%	57 µg/l	Depression or Graben	North-west region

Longley, A.J. (2015).	Raw data files	369	95	26%	1,050 µg/L	Tertiary Volcanic-region, Paleozoic and Mesozoic platform & Depression or Graben	Central region of Nicaragua & North-west region
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(\*) Public piped water supplies (urban areas); community water systems; boreholes/tubewells and protected wells.

## 2.2.2 Detailed analysis of four research areas

Four different highly As-affected areas were identified within the existing data sets to provide new insights into arsenic mobilization mechanisms in Nicaragua. These research areas are:

(1) *Alluvial aquifer of the Sebaco valley and surrounding areas*: one of the main alluvial aquifers in the country (Meza, 2004; Plata Berdmar, 1988), located in the Tertiary volcanic province; the surface area of the catchment extends approximately 652.79 km<sup>2</sup>.

(2) *Central region of Nicaragua*: subdivided into two distinct geologic areas: the northern area which belongs to the Paleozoic and Mesozoic platform, and the central northern area belonging to the central geologic province, comprising groups of Tertiary volcanic rocks (Hodgson, 1998; McBirney and Williams, 1965)

(3) *Hydrothermal mineral deposit areas*: parallel to the graben, a series of mineralized geologic structures are found which area associated with gold and arsenic minerals (Barragne, 2004; Estrada, 2003).

(4) *North-western region*: belonging to the depression or graben; a volcanic chain is formed by 19 volcanos (active and inactive) which are part of the Pacific ring of fire (McBirney and Williams, 1965).

## 2.2.3 Pearson correlation of co-occurring compounds

Co-occurrence of As with other physicochemical parameters (e.g. temperature, trace elements, major ions) may provide a better understanding of the As mobilization mechanisms. The Pearson correlation coefficient ( $r$ ) was determined, which is a measure of the linear relationship between two quantitative aleatory variables (Currell and Dowman, 2009), with absolute values oscillating between 0 and 1. The closer  $r$  is to 1, the stronger the correlation (Currell and Dowman, 2009). To determine the level of significance of the calculated correlation, the  $p$  value was calculated. When the  $p$  value was below 0.001, the correlation was considered to be meaningful.

## **2.3. Results**

### **2.3.1 Occurrence of arsenic in Nicaragua**

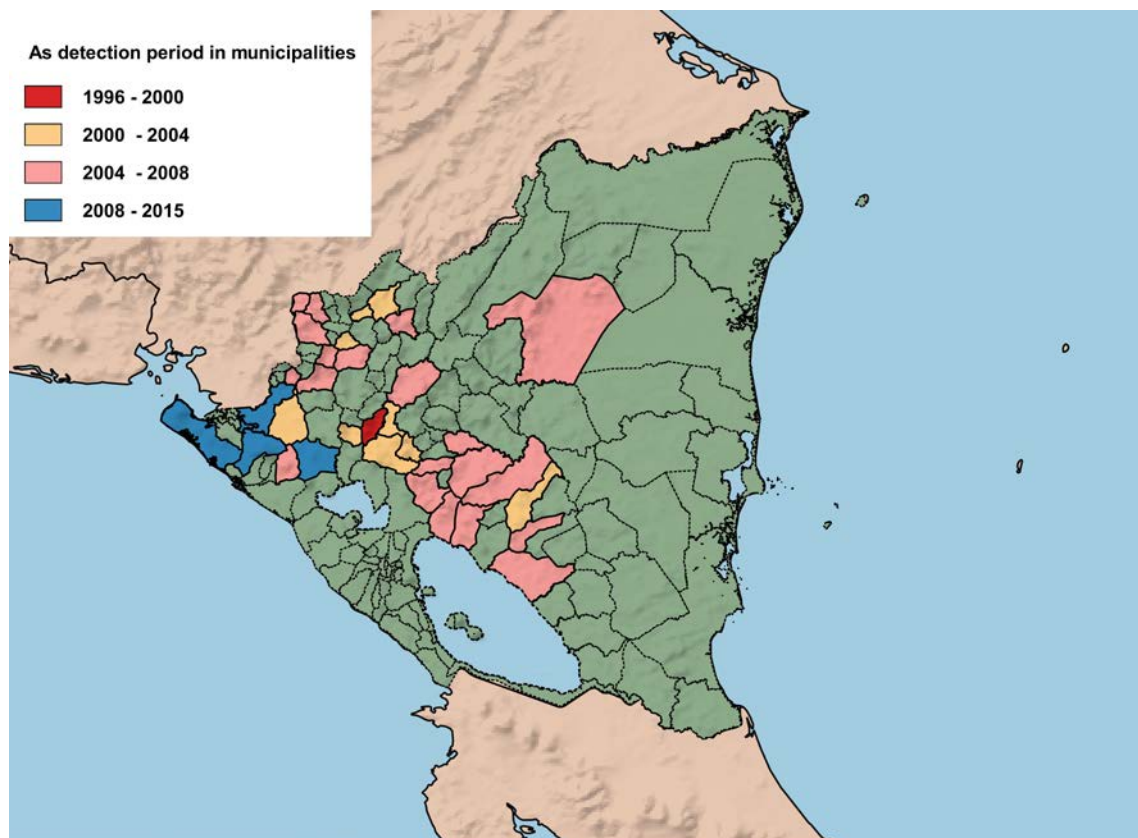
#### **History of reported arsenic contamination**

In Nicaragua, the presence of As in water bodies was reported for the first time in surface water (a lake of volcanic origin) in the early 1990s (Lacayo et al., 1992). This study observed As contamination (ranging between 10 to 30 µg/L) in Xolotlán Lake and Tipitapa's hot springs ( $\approx$  200 µg/L). Concern in Nicaragua about the presence of As in groundwater, the principal source of potable water for rural and urban populations, and its influence on human health, started in 1996. In that year, the first documented case of As poisoning was reported in a rural community (El Zapote) in the north of the country. From 1994 to 1996, this community was supplied by a well that extracted water from the alluvial aquifer of the Sebaco Valley, with an As concentration of 1,320 µg/L (Gomez, 2002).

The Zapote incident led to the beginning of research related to As contamination in Nicaraguan groundwater resources. New studies, conducted between 1996 to 2015, resulted in the discovery of more As-contaminated drinking water sources exceeding 10 µg/L in scattered rural communities distributed in 34 municipalities (Altamirano Espinoza and Bundschuh, 2008; Barragne, 2004; Bundschuh et al., 2008; Bundschuh et al., 2012; CARE, 2002; CISTA, 2012; Estrada, 2003; González et al., 1997; INAA, 1996; Longley, 2010; Longley, 2015; OPS/OMS and UNICEF, 2005; PIDMA-UNI, 2001; PIDMA-UNI and UNICEF, 2002; PIDMA-UNI and USAID, 2001) (Figure 2.2). As concentrations exceeding the national guideline in water samples taken from public piped supply systems in the main urban areas have not been reported.

While most of the research over the last two decades has focused on identifying water sources contaminated by As, several studies have also related the presence of As in drinking water to As poisoning of rural communities based on dermatologic and epidemiologic studies (Gomez, 2002; OPS/OMS and Nuevas-Esperanzas, 2011) as well as the use of biomarkers (OPS/OMS and Nuevas-Esperanzas, 2011). These

studies considered the impact of historic as well as current As exposure and concluded that As poisoning was responsible for a wide range of skin and pulmonary diseases in at least six rural communities.



**Figure 2.2** Nicaraguan municipalities containing at least one drinking water source with an arsenic concentration exceeding the 10 µg/L, classified by the year in which arsenic was first detected (Altamirano Espinoza and Bundschuh, 2008; Barragne, 2004; Bundschuh et al., 2008; Bundschuh et al., 2012; CARE, 2002; CISTA, 2012; Estrada, 2003; González et al., 1997; Longley, 2010; Longley, 2015; OPS/OMS and Nuevas-Esperanzas, 2011; PIDMA-UNI, 2001; PIDMA-UNI and UNICEF, 2002; PIDMA-UNI and USAID, 2001).

### Distribution of exposed rural communities

This study has identified the presence of high arsenic concentrations in the drinking water sources of more than 80 rural communities (Figure 2.3). These rural communities are distributed over 34 municipalities, belonging to the Central and Pacific regions of the country. In 23 of these affected communities it was estimated that around 5,000 inhabitants were exposed to high As concentrations in drinking water sources (Bundschuh et al., 2012; ENACAL et al., 2005; Gomez, 2002; OPS/OMS and Nuevas-Esperanzas, 2011). In 2004 it was estimated that approximately 56,000 people were ingesting water contaminated by As (Barragne, 2004). Most of those people lived in scattered, small rural communities or were semi-

concentrated in municipal and small towns (Barragne, 2004). In urban and rural areas, when potential water sources are found to be contaminated by arsenic, the corresponding authorities proceed to close such sources and look for alternative ones. In some cases, despite of the fact that the authorities have prohibited the consumption of water of the wells affected by As, the population still uses them because of the lack of alternative water sources. In one case, in Telica, a “dual water” system was devised which provides warm, As-contaminated water to two communities with a combined population of approximately 900 for non-potable use, while a second distribution system provides potable water from an uncontaminated spring source 4 Km away. The spring source was insufficient to meet the total domestic demand but is sufficient to meet drinking water needs (Nuevas-Esperanzas, 2013).

Throughout Latin America several As removal technologies have been assessed (Cardoso S et al., 2010; Hoyos et al., 2013; Litter et al., 2010). In Nicaragua the experiences with arsenic removal systems is scarce. Few arsenic mitigation programs have been carried out. In 2009, the Minister of Health and OPS gave 39 Kanchan filters to the community of Muy Muy after discovering arsenic concentrations of up to 30 to 40  $\mu\text{g/L}$ . Half of the community had stopped using the filter within the first eight months. Because of a lack of funding, the project was stopped after one year (Admiraal et al., 2015). In 2012, a Kanchan filter pilot project was conducted by the NGO Nuevas Esperanzas in a community located in the municipality of Telica. Eight Kanchan filters were given to this community, but after six months the filters already had a very poor removal and the pilot project was stopped (Admiraal et al., 2015).

In the alluvial aquifer of the Sebaco Valley and surrounding areas, 54 (31.6%) out of 170 investigated drinking water sources contained As concentrations ranging from 10 to 289  $\mu\text{g/L}$  (Altamirano Espinoza and Bundschuh, 2008; CARE, 2002; González et al., 1997; González, 2004; INAA, 1996; PIDMA-UNI, 2001). The contaminated water sources are distributed over 19 rural communities.

In the central region of Nicaragua, 42 rural communities have been found to be affected by the presence of high concentrations of As in drinking water sources. In this area, 95 (16.3%) out of 583 drinking water sources tested exceeded the

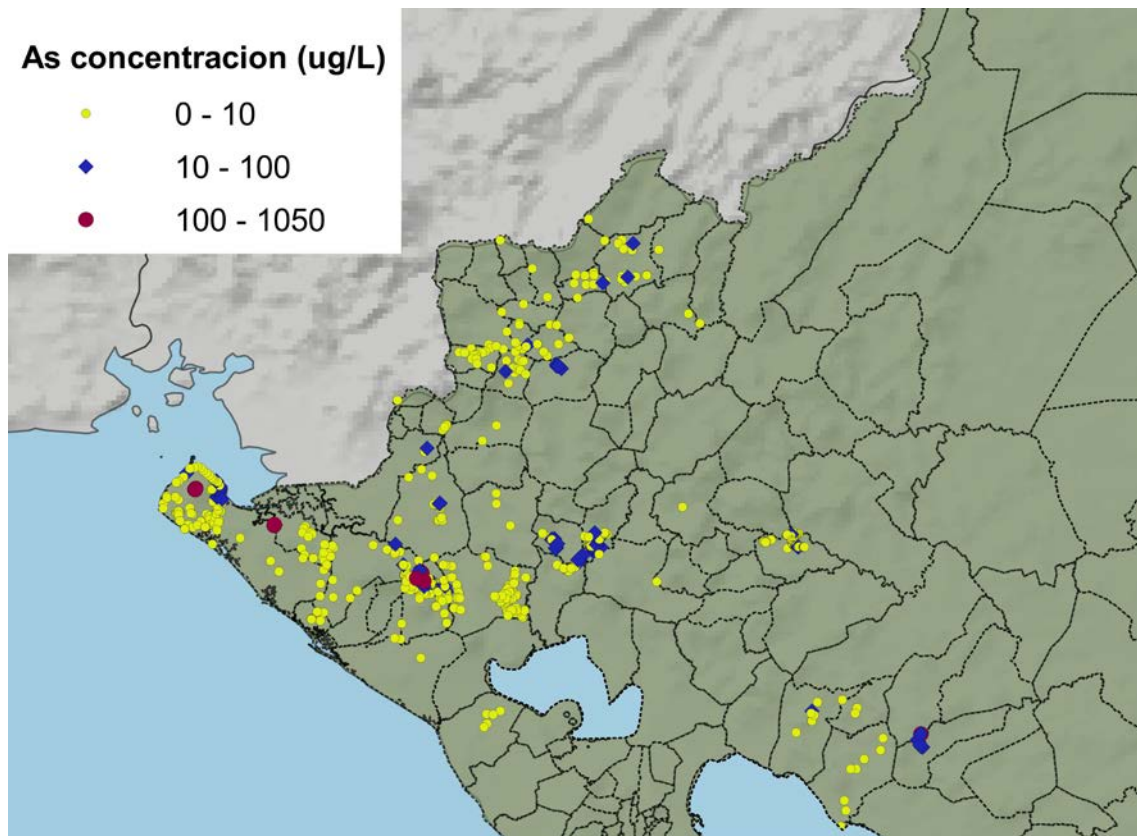
provisional guideline of the World Health Organization (ranging between 11 µg/L to 1,196 µg/L) (ENACAL et al., 2005; OPS/OMS and UNICEF, 2005; PIDMA-UNI and USAID, 2001).

In the hydrothermal mineral deposit area 270 drinking water sources have been analyzed. Of these sampling points, 36 (13.3%) were reported to have an As concentration ranging between 11 and 161 µg/L (Barragne, 2004; L. Morales et al., 2008). The affected water sources are located in nine rural communities within the study area.

Studies conducted more recently in the north-western region resulted in the identification of around 20 rural communities with As contaminated drinking water sources, exceeding the national regulatory limit (CISTA, 2012; Longley, 2010; Longley, 2015; OPS/OMS and Nuevas-Esperanzas, 2011). From a total of 510 sampled water sources, 108 (21%) contained As concentrations higher than 10 µg/L. The arsenic concentration in the samples ranged from 10 µg/L to 1,050 µg/L.

The studies referenced have mainly focused on the rural areas belonging to the Central and Pacific region of the country. To date, no arsenic contamination studies have been carried out in the Atlantic coast region.





**Figure 2.4** Measured arsenic concentrations across in Nicaragua – This map was based on 40 % of the total samples (Altamirano Espinoza and Bundschuh, 2008; Barragne, 2004; CISTA, 2012; Estrada, 2003; L. Morales et al., 2008; Longley, 2015; PIDMA-UNI and USAID, 2001).

### 2.3.2 Detailed analysis of four arsenic-affected areas

#### **Alluvial aquifer of the Sebaco Valley and surrounding areas**

Several reports (CARE, 2002; González, 2004; PIDMA-UNI, 2001) mentioned water sources with relatively high temperatures (ranging between 30.5°C to 32.7°C where the average temperature of other sources was around 27°C) and As contamination on the western half of the Sebaco valley (Table 2.2). These relatively high temperatures were interpreted to be caused by geothermal influence (CARE, 2002). The existence of a residual hydrothermal influence on the western half of the Sebaco valley, has been reported previously (Plata Berdmar, 1988). In this area the water reaches temperatures of up to 35°C, which has been related to the occurrence of saline water and elevated silicate (SiO<sub>2</sub>) concentrations, found in the same part of the aquifer (Plata Berdmar, 1988) .

The study conducted by Altamirano Espinoza and Bundschuh (2008) focuses on the southwestern part of Sebaco valley (El Zapote area), which is located in the contact zone between the alluvial valley with Tertiary volcanic rocks. This area is far from the residual hydrothermal focus (Plata Berdmar, 1988), and the water temperatures are equal to or below 28°C. This investigation states that the dissolution of minerals from the extensive hydrothermally altered Tertiary volcanic rocks aid As release into groundwater by reductive dissolution or alkali desorption (Altamirano Espinoza and Bundschuh, 2008). Similar As contamination processes have been identified in the municipality of Mixco in Guatemala (Bundschuh et al., 2012; Cardoso S et al., 2010). From the data (Table 2.2) obtained from Altamirano Espinoza and Bundschuh (2008) a high (positive) and significant correlation ( $r = 0.88$ ,  $\rho < 0.001$ ) has been observed between As and potassium ( $K^+$ ) concentration, which could be a consequence of hydrolysis of K-feldspar (Kouras et al., 2007). No other high correlation between As and other physicochemical parameters (e.g. pH, EC, TDS and major ions) have been found.

**Table 2.2** Water matrix composition for some communities located in alluvial aquifer of the Sebaco Valley and surrounding areas

Parameter	Unit	Altamirano	González, R.M.	PIDMA-UNI
		Espinoza and Bundschuh (2008)	(2004)	(2001).
		Range	Range	Range
As	µg/L	0 - 122	2 - 11	1 - 69
Turbidity	NTU	0.15 - 203	0.24 - 26	NM
pH	-	6.3 - 8.3	6.4 - 7.4	6.5 - 7.7
Conductivity	µs/cm	121 - 764	386 - 1148	159 - 1291
Temperature	°C	23 - 28	26 - 32	25 - 31
Eh	mV	166 - 636	NM	NM
Ca <sup>2+</sup>	mg/L	10 - 115	38 - 99	NM
Mg <sup>2+</sup>	mg/L	3 - 19	6 - 22	NM
Na <sup>+</sup>	mg/L	8 - 96	3 - 189	NM
K <sup>+</sup>	mg/L	0.5 - 18	1 - 5	NM
Cl <sup>-</sup>	mg/L	4 - 26	7 - 141	NM
NO <sub>3</sub> <sup>-</sup>	mg/L	0 - 32	1.5 - 20	NM

SO <sub>4</sub> <sup>2-</sup>	mg/L	1 - 24	10 - 184	NM
HCO <sub>3</sub> <sup>-</sup>	mg/L	57 - 435	120 - 509	NM
Si	mg/L	31 - 98	34 - 94	NM
Fe	mg/L	0.02 - 14	0.04 - 1.4	NM
F	mg/L	0.1 - 0.6	0.2 - 0.9	0.1 - 0.9
B	mg/L	NM	0.09 - 0.25	NM

NM = Not measured

### Central region of Nicaragua

Among the studies conducted in the central region of Nicaragua, only PIDMA-UNI and USAID (2001) have included water quality parameters that can be used to elucidate the mechanism of arsenic mobilization. In the area studied by PIDMA-UNI and USAID (2001) the As-contaminated water sources have been characterized by temperatures between 23°C to 30°C with a pH that varied from slightly acid to alkaline (6.3~11.2). Oxidized species such as SO<sub>4</sub><sup>2-</sup> (0.2~180 mg/L) and NO<sub>3</sub><sup>-</sup> (0.2 ~14 mg/L) were present in low and medium concentrations. Another feature of the water quality is the low levels of Fe (0.04 ~ 1 mg/L) and Mn (<1 mg/L). The HCO<sub>3</sub><sup>-</sup> concentration varied from 63 mg/L to 370 mg/L. With the available data it was not possible to find a correlation (Pearson) between arsenic and other physicochemical parameters. However, based on the characteristics of the drinking water sources (both oxic and anoxic waters), mentioned above, it seems that reductive dissolution and alkali desorption could play a role in the As mobilization mechanism in this area.

### Hydrothermal mineral deposit areas

Barragne (2004) has pointed out two areas of interest, each with a different As mobilization mechanism. The first area corresponds to drinking water sources belonging to the municipality of Santa Rosa del Peñon (western region of Nicaragua). In this area the water sources have a relatively high temperature (up to 32.2°C) and commonly As concentrations (ranging between 11 to 95 µg/L) exceed maximum allowable levels (10 µg/L) with pH ranging between 6.2 to 8, and Eh values ranging between +40 ~ +260 mV. The authors proposed that the dominant As species was the oxidized form of arsenate (As(V)). The high As concentrations and the relatively high temperature found in the water sources of Santa Rosa del Peñon have been

attributed to the influence of geothermal fluids (Barragne, 2004). Geothermally influenced As-water has been reported along the Pacific region of Latin America (López et al., 2012) The second area, mentioned by Barragne (2004), is located in the municipality of La Libertad (southeast region). The maximum temperature in the As-contaminated water sources (ranging between 10 and 110 µg/L) did not exceed 28.7°C. The pH varied from 6.8 to 7.5, and the Eh values were between +89 to +188 mV. The dominant species in the area was the reduced form of arsenite (As(III)). This underlines that it is likely that reductive dissolution plays an important role in the As contamination in the area of La Libertad. Reductive dissolution as an As mobilization mechanisms have been identified in Asian countries such as Bangladesh, India (Nickson et al., 2000) and Nepal (Gurung et al., 2005).

L. Morales et al. (2008) studied groundwater sources in the municipality of San Juan de Limay (northwestern region). The pH varied from neutral (7) to alkaline (10.3) and the As-contamination ranging between 10 to 115 µg/L. The dominant As species in the tested wells was As(V). This study suggested that the volcanic ash layer could be the main source of As contamination in this area. This research noted that the wells with higher As concentration also have higher pH values. The relationship between high pH and high As concentration has also been observed in earlier research conducted in La Pampa, Argentina (Smedley et al., 2002). L. Morales et al. (2008) proposed that dissolution of carbonate and dissolution of silicates in volcanic glass may explain the mentioned relationship.

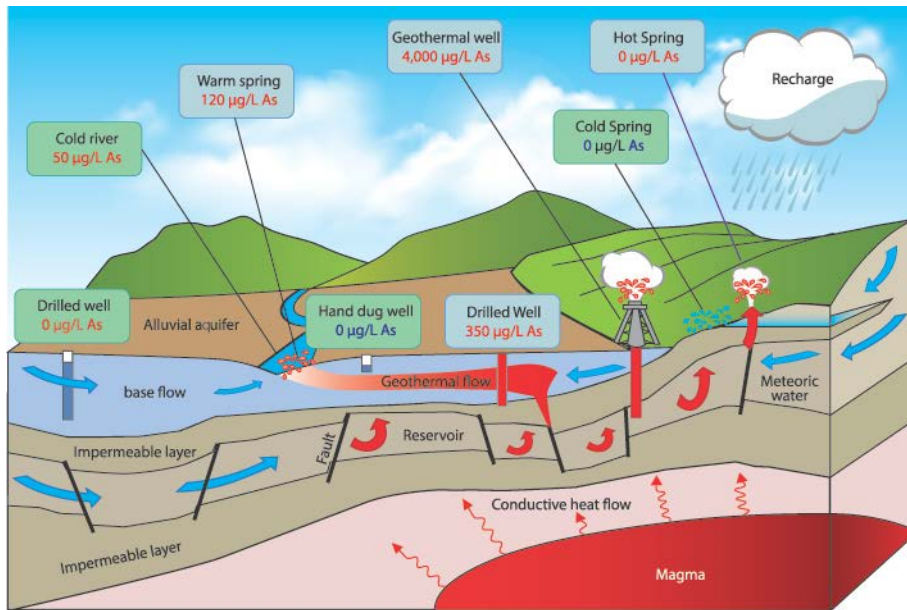
### **North-west region**

The authors(OPS/OMS and Nuevas-Esperanzas, 2011) who conducted the research in the Municipality of Telica have identified two distinctive study areas with different potential As mobilization mechanisms. In the first area, the authors have suggested that the reductive dissolution As mobilization mechanism influences arsenic contamination in this region. The average temperature in this area was 29°C, and the As concentration varied between 10 to 50 µg/l. For the second area, however, the shallow alluvial aquifer is influenced by the hot fluids associated with active geothermal fields located in the volcanic chain of “Los Maribios” (OPS/OMS and Nuevas-Esperanzas, 2011) (Figure 2.5). The drinking water sources in this area tend

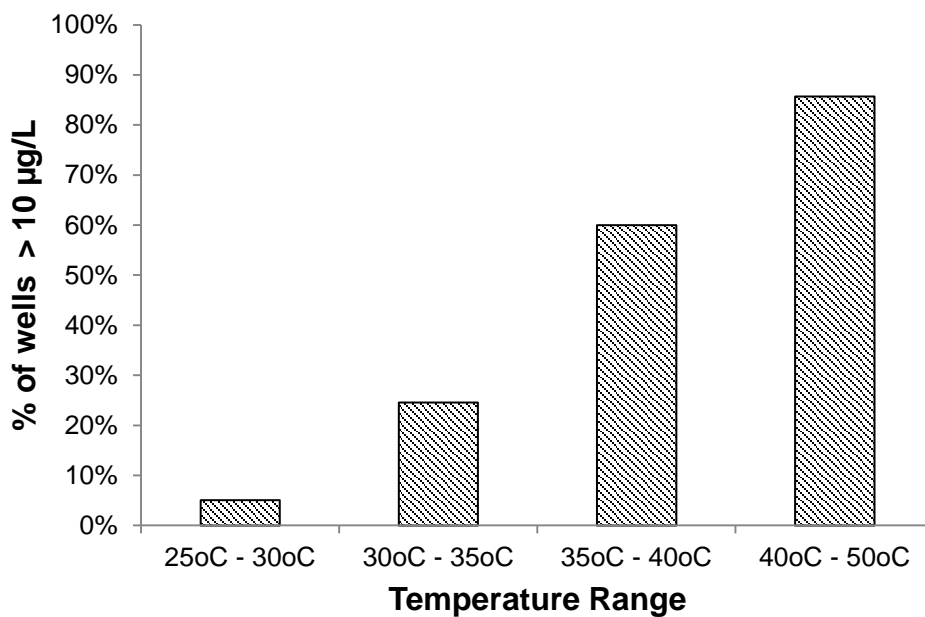
to be dominated by high temperature (average of 33.8°C), and elevated As concentrations, above 50 µg/l (up to 325 µg/l). This explanation is aligned with other As-contaminated geothermal waters found throughout Latin American, which have been related with the active geothermal fields associated with the volcanic chain of the Pacific Ring of Fire (Lopez et al., 2012). For example the influences of geothermal arsenic in drinking water sources have also been recognized in Los Altos de Jalisco, Mexico (Hurtado-Jiménez and Gardea-Torresdey, 2008). In this area the drinking water is mainly extracted from aquifers located in the Transmexican Volcanic Belt. The temperature varies from 22.2 to 45.2°C and the As concentration varies from 0.5 to 263 µg/l. The mentioned study also found that the higher the temperature is the higher the As concentration in the aquifers. A similar trend can be observed in Telica, where the percentage of As-contaminated wells (above 10 µg/L) (Figure 2.6) and the As concentration increases as temperature increases. Table 2.3 presents a summary of the water composition for some of the rural communities located in Telica.

**Table 2.3** Water matrix composition for some communities located in Telica (OPS/OMS and Nuevas-Esperanzas, 2011).

Parameter	Units	Range
As	µg/L	0 – 325
Temperature	°C	30 – 49
Ca <sup>2+</sup>	mg/L	37 – 118
Mg <sup>2+</sup>	mg/L	21367.0
Na <sup>+</sup>	mg/L	28 – 320
K <sup>+</sup>	mg/L	3 – 26
Cl <sup>-</sup>	mg/L	26 – 252
SO <sub>4</sub> <sup>2-</sup>	mg/L	25 – 369
HCO <sub>3</sub> <sup>-</sup>	mg/L	58 – 494



**Figure 2.5** Representation of As geothermal influence in Telica municipality (OPS/OMS and Nuevas-Esperanzas, 2011).



**Figure 2.6** Percentage of As – contaminated wells in the municipality of Telica for different ranges of temperature (OPS/OMS and Nuevas-Esperanzas, 2011).

The raw data provided by CISTA (2012) (Table 2.4) show that As-contaminated drinking water sources have a pH ranging from neutral to alkaline (7 to 8.2) and  $\text{HCO}_3^-$  concentrations varying from 50mg/L to 600mg/L. Furthermore, these waters are characterized by the low content of Fe (< 0.1 mg/L) and Mn (<0.15 mg/L). On the

other hand, oxidized species such as  $\text{SO}_4^{2-}$  (0.6 mg/L to 90mg/L) and  $\text{NO}_3^-$  (1.5 mg/L to 400 mg/L) are present, although it is likely that the high content of  $\text{NO}_3^-$  is caused by anthropogenic influences (e.g. agriculture). Temperature, Eh, and dissolved oxygen concentration measurements were missing in the CISTA-UNAN report (CISTA, 2012). From the data obtained from the mentioned study a positive, high, and moderate correlation was found between As and some trace elements such as Se ( $r=0.46$ ,  $\rho < 0.001$ ), Mo ( $r=0.48$ ,  $\rho < 0.001$ ), B ( $r=0.59$ ,  $\rho < 0.001$ ) and V ( $r=0.82$ ,  $\rho < 0.001$ ). Altogether this water type suggests As mobilization through alkali desorption (Bhattacharya et al., 2006; N. Robertson, 1989; Smedley and Kinniburgh, 2002). However, the co-occurrence of As with V (Vanadium) and the other trace elements reported by CISTA-UNAN (CISTA, 2012) has also been observed by (Smedley and Kinniburgh, 2002) in arid oxidizing environments like The Chaco-Pampean Plain of Central Argentina.

**Table 2.4** Summary of the water matrix composition provided by (CISTA, 2012)

Parameter	Units	Range
As	$\mu\text{g/L}$	0.3 - 57
TDS	mg/L	2 - 612
Conductivity	$\mu\text{S/cm}$	127 - 1225
pH		7 – 8.2
$\text{Na}^+$	mg/L	5 - 57
$\text{Ca}^{2+}$	mg/L	4 - 85
$\text{Mg}^{2+}$	mg/L	0 - 39
$\text{HCO}_3^-$	mg/L	49 - 615
$\text{SO}_4^{2-}$	mg/L	0.6 - 90
$\text{Cl}^-$	mg/L	5 - 148
$\text{NO}_3^-$	mg/L	1.5 - 400
Fe	mg/L	~ 0.1
Mn	mg/L	~ 0.15
B	$\mu\text{g/L}$	0 - 330
V	$\mu\text{g/L}$	1 - 240
Se	$\mu\text{g/L}$	0.7 - 2.1

Mo	µg/L	0.02 - 20
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## **2.4. Conclusion**

Natural As contamination in groundwater, exceeding the provisional guideline of the World Health Organization of 10 µg/L, has been detected in drinking water sources in more than 80 rural communities distributed in 34 municipalities in Nicaragua between 1996 until 2015. It is likely that more contaminated drinking water sources will be detected with the increase in monitoring campaigns, since As monitoring has so far only been conducted in 23.5% of municipalities.

The source of arsenic contamination in Nicaragua is probably of volcanic origin, both from volcanic rocks and geothermal fluids, resulting in widespread occurrence across the country. As may enter into the groundwater directly, from geothermally influenced water bodies, or indirectly, by reductive dissolution or alkali desorption, depending on local geochemical conditions.

In order to understand the full extent of As contamination in Nicaragua and to be able to reliably map As distribution, a more extensive sampling campaign is recommended. A good understanding of regional arsenic mobilization mechanisms will aid in the selection of appropriate technologies for arsenic removal or alternative mitigation strategies.

## **2.5. Acknowledgements**

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### 3. As(V) rejection by NF membranes using high temperature sources for drinking water production

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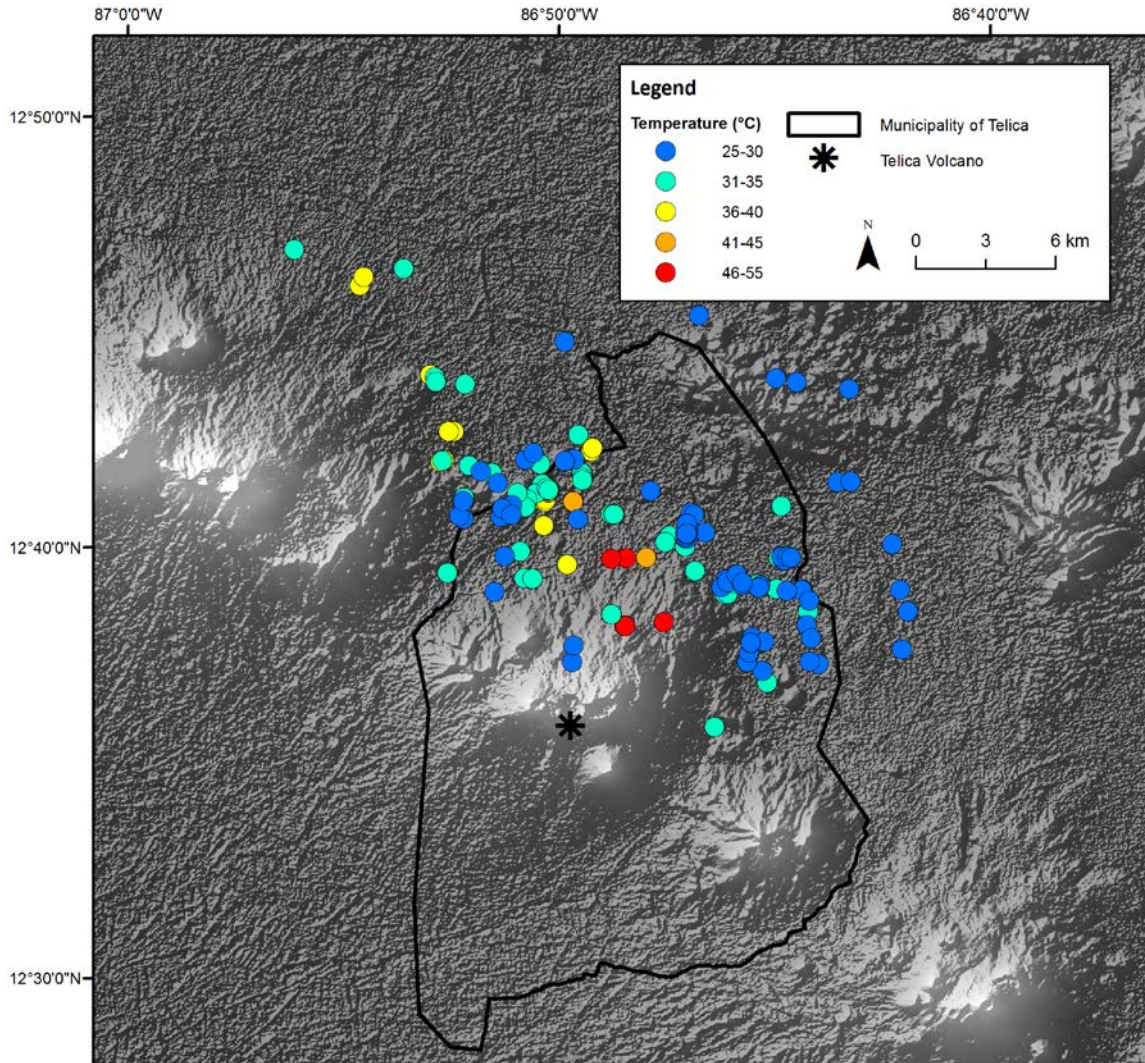
#### Abstract

In Nicaragua, a Central American country, geothermally influenced waters are frequently found to be contaminated with arsenic (as As(V)). This study investigated the effect of high-temperatures (25-50°C), as found in geothermally influenced source waters, on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species (at pH 6,7 and 8) during NF membrane filtration of a multi-component solution containing  $\text{Cl}^-$  and  $\text{HCO}_3^-$ . In this multi-component solution, As(V) rejection was found to be enhanced at higher temperatures, which was in contrast to the previous assumption that temperature increase would have a negative effect on As(V) rejection. Previous studies were conducted with deionized waters, where pore size expansion and decreased viscosity drove As(V) rejection; however, in the presence of other anions such as those utilized in this study, As(V) rejection was promoted at higher temperatures. The enhancement of As(V) rejection at high temperature was associated with the presence of  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , which are considerably more permeable than both As(V) species. An additional advantage of the higher temperature was the lower feed pressure (down to 1.5 bar) needed to operate these NF membranes, compared to colder waters. The lower energy consumption in combination with the improvement in As(V) rejection at higher temperatures shows the potential application of this technology for efficient treatment of As(V) contaminated, geothermally influenced waters for decentralised, rural drinking water production, in As-affected countries such Nicaragua.

### **3.1. Introduction**

Geothermal systems are known to be a source of arsenic (As) contamination since geothermal fluids are responsible for transporting As and heavy metals, contaminating both surface water and groundwater (Webster and Nordstrom, 2003). These geothermally influenced waters may have high As concentrations in combination with high temperatures (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). The contamination of water sources by geothermal As has been reported around the world in locations such as Waikato River in New Zealand (McLaren and Kim, 1995) and Eastern Sierra Nevada in the USA (Wilkie and Hering, 1998).

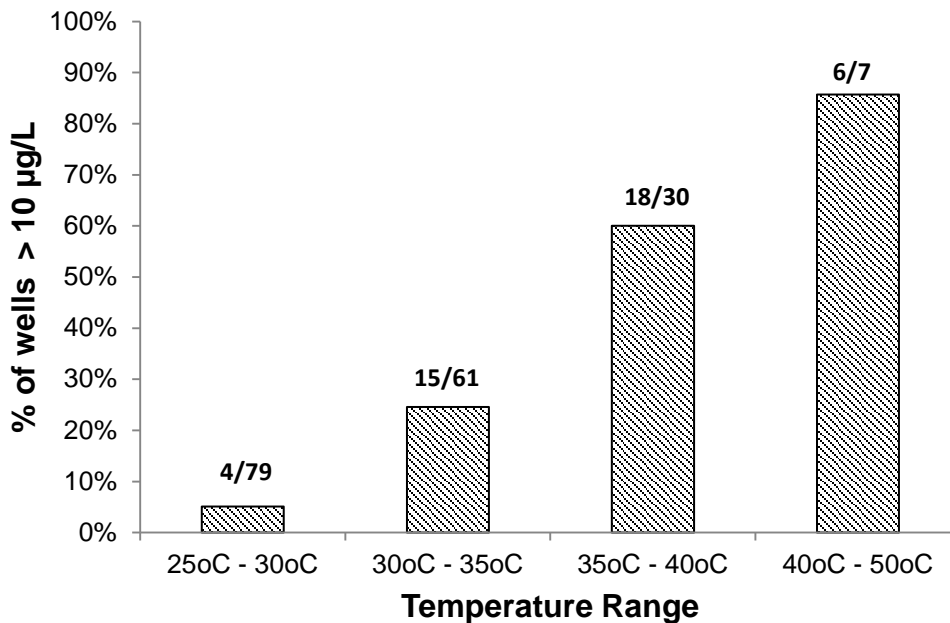
In Latin America, geothermal As has been recognized mainly in the Pacific region and is usually associated with the active volcanism (Lopez et al., 2012) of the Pacific Ring of Fire. Geothermally influenced waters often present elevated temperatures (above the background) (Ravenscroft, Brammer, and Richards, 2009). In Nicaragua, a Central American country, drinking water sources with high temperatures and high As concentration has been identified in scattered rural communities in the municipality of Telica (Figure 3.1 and Figure 3.2) (OPS/OMS and Nuevas-Esperanzas, 2011), located in the Pacific region of the country where Quaternary volcanism is concentrated (Mcbirney and Williams, 1965) .



**Figure 3.1** Temperature of groundwater sources in the rural communities of Telica municipality. Adapted from OPS - OMS/Nicaragua - Nuevas Esperanzas (OPS/OMS and Nuevas-Esperanzas, 2011).

The shallow alluvial aquifer of this area is influenced by the hot fluids associated with active geothermal fields located in the volcanic chain of “Los Maribios.” Consequently, the water source tends to be dominated by high temperature (up to 50°C; Figure 3.2) and high levels of As concentrations (>350 µg/L) (OPS/OMS and Nuevas-Esperanzas, 2011). The range of concentrations of the major anions and cations is as follows: Ca<sup>2+</sup> (40 to 77 mg/L), Mg<sup>2+</sup> (9 to 58 mg/L) , Na<sup>+</sup> (100 to 320 mg/L), K<sup>+</sup> (6 to 26 mg/L), HCO<sub>3</sub><sup>-</sup> (240 TO 495 mg/L), SO<sub>4</sub><sup>2-</sup> (25 to 340 mg/L) and Cl<sup>-</sup> (146 to 250 mg/L) (OPS/OMS and Nuevas-Esperanzas, 2011). Figure 3.2 provides an overview of the percentage of wells with As concentrations >10µg/L (WHO, 2001), illustrating the correlation between As contamination and elevated temperatures in

these geothermally influenced sources. Although As-safe wells with colder water are available in the surroundings of these rural communities, it is found that due to practical (e.g., walking distance) and social (e.g., private wells) factors, approximately one thousand people have been drinking water contaminated with As for the past two decades (OPS/OMS and Nuevas-Esperanzas, 2011).



**Figure 3.2** depicts the percentage of As contaminated wells > 10 µg/L (WHO guideline) per temperature cohort. Adapted from OPS - OMS/Nicaragua - Nuevas Esperanzas (OPS/OMS and Nuevas-Esperanzas, 2011).

The As speciation in natural groundwater (pH 6.5–8.5) is mainly determined by redox potential (Eh) and pH (Smedley and Kinniburgh, 2002), leading either to As(III) or As(V) in the water. As(V) is a charged ion and is commonly found under oxidizing conditions. For a pH lower than 6.9, As(V) exists mainly as the monovalent  $\text{H}_2\text{AsO}_4^-$  species, and for a higher pH, the divalent  $\text{HAsO}_4^{2-}$  species is dominant (Smedley and Kinniburgh, 2002). On the other hand, As(III) is predominantly found under reducing conditions and as an uncharged ion when the pH is below 9.2 (Smedley and Kinniburgh, 2002). In geothermal fluids, the dominant species of As is the reduced form As(III). However, as geothermal water ascends to the surface and mixes with oxygenated water from shallow aquifers, it is oxidized to As(V) (Wilkie and Hering, 1998). Therefore, arsenic-contaminated drinking water sources in geothermally influenced waters are dominated by As(V) (Smedley and Kinniburgh, 2002; Van Halem et al., 2009).

For rural Nicaraguan communities exposed to geothermally influenced As contaminated drinking water sources, an As removal technology has to meet guidelines specific to resource-limited environments, such as restrictions regarding availability of electricity, spare parts and knowledgeable operators. To overcome the unavailability of electricity, this research paper examines the feasibility of treating hot waters (with a temperature similar to those found in geothermally influenced waters ~ 50°C) with a low pressure nanofiltration (NF) membrane, aiming to rely on the naturally available elevation in these volcanic areas for membrane pressure. Due to pore expansion and decreased viscosity, the high water temperature will be favorable for low-pressure operation; however, this might have a negative effect on the rejection of As(V) (Figoli et al., 2010). Polyamide negatively-charge NF systems have consistently demonstrated a high efficiency for the removal of As(V) from water with ambient temperatures (Harisha et al., 2010; Urase et al., 1998; Vrijenhoek and Waypa, 2000), and it is known from industrial applications that NF is capable of treating water at temperatures up to 65°C (Mänttari et al., 2002). The influence of high temperatures has been identified as responsible for the deterioration of the NF rejection for different solutes such as trace organic contaminants (TrOCs) (Dang et al., 2014), Cl<sup>-</sup> (Ben Amar et al., 2009) and As (Figoli et al., 2010). Scientific literature related to the use of NF membranes to remove As from high temperature waters is scarce. Figoli et al. (Figoli et al., 2010) worked with temperatures ranging from 15°C to 40°C, using distilled water spiked with As(V) (100 µg/L) and two types of membranes (NF90 and N30F). When temperature increased from 15°C to 40°C, the rejection efficiency diminished by 2.3% for NF90 and 11% for N30F membranes. This study attributes the decline in As(V) rejection as a consequence of the increase in the diffusive transport of As(V) across the membrane. Nevertheless, the mentioned research did not consider the influence of co-occurring ions. Furthermore, the influence of co-occurring ions on the rejection of As(V) species during nanofiltration have only been studied at 25°C. These earlier works (Nguyen et al., 2009; Vrijenhoek and Waypa, 2000) conducted at 25°C reported that in a multi-component solution (containing Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>), the rejection of As(V) species could be enhanced or decreased by the presence of co-occurring anions. Nevertheless, the influence of co-occurring ions on the rejection of As(V) during NF filtration of high temperature water has not been previously studied. With our research, we intend to fill this knowledge gap. Therefore, the objective of this study was to demonstrate the effect of high temperature (up to

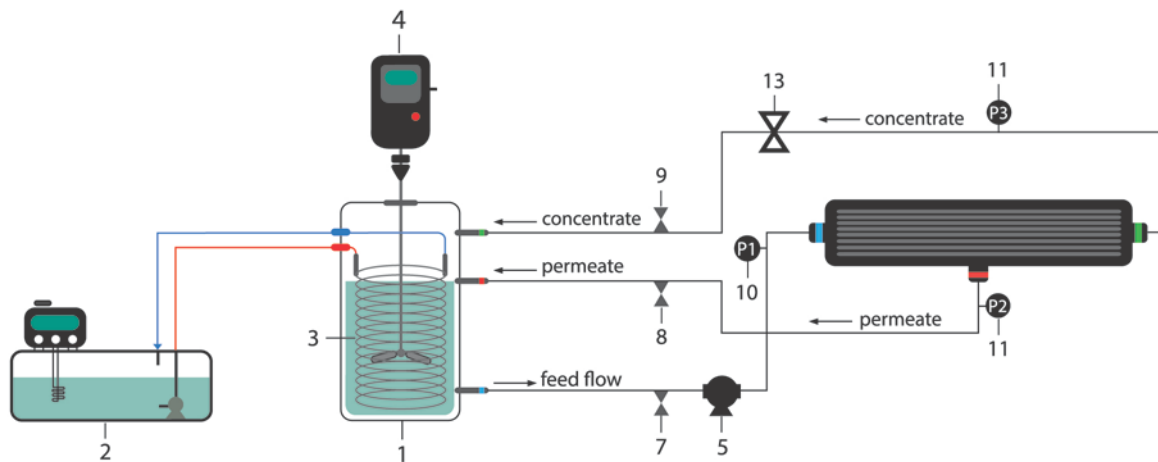
50°C) waters on NF membrane filtration with regard to transmembrane pressure, pore size (molecular weight cut-off), rejection of major anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) and, specifically, the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species (at pH 6,7 and 8) during NF membrane filtration of a multi-component solution containing  $\text{Cl}^-$  and  $\text{HCO}_3^-$ . The research consisted of experimental research with a flat-sheet cross-flow module in order to identify proof-of-principle for future pilot-scale research in rural Nicaragua. With consideration of the intended implementation setting, membranes were operated at a lower recovery of 10%, as this would generate a concentrate flow with sufficiently low As content that could be used by local villagers for daily activities such as washing and bathing.

## **3.2. Material and methods**

### **3.2.1 Experimental set-up**

The experiments were conducted using a flat-sheet cross-flow module, as illustrated in Figure 3.3. The experimental setup was operated as a closed circuit system with a feed water tank containing 50 L of solution. To avoid heat exchange with the environment, the feed tank was wrapped with heat insulation material (Aluminum Foil Air Bubble Heat Insulation Sheet). Prior to the start of the experiments, overhead stirrers (Heidolph RZR 2020, Heidolph Instruments GmbH & Co, Germany) were utilized for a period of 4 h to guarantee the homogeneity of the solution. During this time, the solution was heated to the desired temperature (25°C or 50°C). The temperature of the solution was controlled by a recirculating thermostatic bath (TC 16, Tamson Instruments B.V, NL), which was connected to a heat exchanger (coil) submerged in the solution. After this stage, the feed water was pumped, using a rotary (vane positive) displacement pump (Fluid-o-Tech s.r.l., Italy), from the tank into stainless steel plates containing the NF membrane. The active area of the rectangular flat sheet NF membrane inside the metallic plates was 0.25 m<sup>2</sup>. The solution was filtered through the membrane for two hours to achieve stabilization of the rejection and to reach thermal equilibrium between the solution and flat-sheet cross-flow module. At the end of the preliminary filtration cycle, the rejection

experiments began. The pressure in the feed, permeate, and concentrate line was monitored with a pressure gauge (En 837-1, Econosto, NL). Sampling of the feed, permeate, and concentrate was performed at both the middle and the end of each filtration cycle.



**Figure 3.3** Schematic representation of experimental setup. 1. Feed water tank, 2. Thermostatic bath, 3. Heat exchanger, 4. Overhead stirrer, 5. Pump, 6. Membrane module, 7. Sampling point - feed water, 8. Sampling point - permeate, 9. Sampling point - concentrate, 10. Pressure gauge – feed, 11. Pressure gauge – permeate, 12. Pressure gauge – concentrate, 13. Concentrate valve.

### 3.2.2 NF membranes and solutions

Two commercially available NF polyamide membranes were used. The specifications given by the respective manufacturers indicate that Dow NF270 (DOW FILMTEC™) has a molecular weight cut-off (MWCO) ranging between 200 and 400 Da and a recommended maximum operating temperature of 45°C. Nevertheless, due to the relatively short duration of the experiment, we decided to exceed the maximum recommended temperature. The second membrane from Alfa Laval NF (Alfa Laval) has a MWCO of 300 Da and a maximum operating temperature of 55°C. In general, polyamide membranes are negatively charged for the tested pH range (between 6 and 8) (Bellona and Drewes, 2005; Boussu et al., 2006; Childress and Elimelech, 2000; Nguyen et al., 2009).

A standard stock solution of 1g/L of As(V) was prepared using  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich) dissolved in deionized water and acidified (pH 3) using 1.6 M HCl (Sigma-Aldrich). The solution, used in all As(V) rejection experiments, was kept in an aluminum foil-covered glass container and refrigerated ( $5^\circ\text{C} - 8^\circ\text{C}$ ). The individual salt rejection experiments were carried out with monovalent (NaCl; VWR Chemical) and divalent ( $\text{Na}_2\text{SO}_4$ ; Sigma-Aldrich) salts. To obtain the desired As(V) concentration of 300  $\mu\text{g/L}$  (0.004 mM  $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$ ), the stock solution was diluted in demineralized water. To ensure the buffering capacity of the water matrix,  $\text{NaHCO}_3$  (Sigma-Aldrich) was dosed. According to the requirements of the experiments, 1.6 M HCl (Sigma-Aldrich) or 0.1 M NaOH (Sigma-Aldrich) was employed for pH adjustment.

### **3.2.3 Effect of temperature on MWCO**

The determination of MWCO for Dow NF270 and Alfa Laval membranes was carried out at  $25^\circ\text{C}$  and  $50^\circ\text{C}$ . The solution used for the determination of MWCO was prepared using ethylene glycol (62 g/mol) and different polyethylene glycols (PEGs) with molecular weights ranging from 200 to 1000 g/mol (Sigma-Aldrich). The experiments were performed at constant flux ( $30 \text{ L/m}^2\text{h}$ ) and a recovery of 15%. Samples of the feed permeate and concentrate were taken every 3 h. MWCO was measured by filtering the ethylene glycol /PEGs mixture and measuring the rejection with HPLC-GPC (Shimadzu) with RI-detection.

### **3.2.4 Transmembrane pressure (TMP) and temperature using demineralized water as feed solution**

The relation between transmembrane pressure (TMP) and temperature ( $25^\circ\text{C}$  and  $50^\circ\text{C}$ ) was determined for Dow NF270 and Alfa Laval. Demineralized water was used as feed solution. The experiments were conducted at constant flux ( $40 \text{ L/m}^2\text{h}$ ) (a cross-flow velocity of 0.15 m/s) and a recovery of 10%.

### 3.2.5 NF rejection experiments

Table 3.1 provides an overview of the experimental settings, membranes tested, and the water composition used for the NF rejection experiments. The rejection experiments were conducted at constant flux (40 L/m<sup>2</sup>h) (a cross-flow velocity of 0.15 m/s) and a recovery of 10%. All experiments were performed in duplicate and executed at both 25°C or 50°C.

**Table 3.1** Overview of NF rejection experiments

Experimental settings	pH	NF tested	Water matrix composition
Rejection of Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup>	6	Dow NF270 and Alfa Laval	Demineralized water + 1 mM NaCl / 1 mM Na <sub>2</sub> SO <sub>4</sub>
Rejection of monovalent H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> and divalent HAsO <sub>4</sub> <sup>2-</sup> species from buffered water	6,7 & 8	Dow NF270 and Alfa Laval	Demineralized water + 0.004 mM (300 µg/L) H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> / HAsO <sub>4</sub> <sup>2-</sup> + 1 mM NaHCO <sub>3</sub> + HCl /NaOH

### 3.2.6 Rejection of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

Single solutions of monovalent (NaCl) and divalent (Na<sub>2</sub>SO<sub>4</sub>) salts were used to determine the individual rejection of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The ionic strengths of the solutions were 1mM for NaCl and 3mM for Na<sub>2</sub>SO<sub>4</sub>. Dow NF270 and Alfa Laval were used for these experiments.

### 3.2.7 Rejection of monovalent H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and divalent HAsO<sub>4</sub><sup>2-</sup> species in the presence of NaHCO<sub>3</sub>

Rejection of H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> was evaluated by maintaining constant temperature (25°C or 50°C) and varying the pH (pH 8, 7 and 6) of the feed water. Samples were collected over 5 h of operation for each evaluated pH value. For each temperature, a series of three 5 h runs was executed, with the starting solution

adjusted to pH 8 (0.1 M NaOH) and then corrected to pH 7 and pH 6 in the 2<sup>nd</sup> and 3<sup>rd</sup> run using HCl (1.62 M). Dow NF270 and Alfa Laval NF were used for these experiments.

### 3.2.8 Analysis of samples

Temperature, pH, and electrical conductivity of the feed water were measured using a multimeter (WTW GmbH, Germany). For the single solute rejection experiments of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, conductivity measurements of the feed and permeate were used to determine the rejection of both anions. The conductivity of the samples of the experiments carried out at 50°C was automatically converted into an equivalent conductivity at 25°C. For the rejection experiments of H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>/HAsO<sub>4</sub><sup>2-</sup>, the concentrations of HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> were determined using titrimetric (702 SM Titrino, Metrohm) and ion chromatography analysis (IC - 883 Basic/Plus, Metrohm), respectively.

For the analysis of As(V), the samples from the feed, permeate, and concentrate were acidified using 1.7 ml of HNO<sub>3</sub> (22%) per 330 ml of sample. The concentration of As(V) in the samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS Thermo – XSERIES II, Thermo Fisher Scientific). The method is equivalent to NEN-EN-ISO 172941-2 and can be applied to drinking, surface, process and groundwater.

## 3.3. Result and discussion

### 3.3.1 Effect of temperature on MWCO

Figure 3.4 summarizes the effect of temperature increase on MWCO for Dow NF270 and Alfa Laval. An increase of 39% (from 231 Da to 322 Da) and 20% (from 217 Da to 260 Da) in MWCO was observed for Dow NF270 and Alfa Laval NF, respectively, as a result of temperature increase (from 25°C to 50°C). The larger increase in

MWCO was found for Dow NF270 compared to Alfa Laval NF. The suggestion that pore size of the NF membranes is larger at 50°C agrees with earlier findings that for mono-component solutions, rejection is lower at higher temperatures.

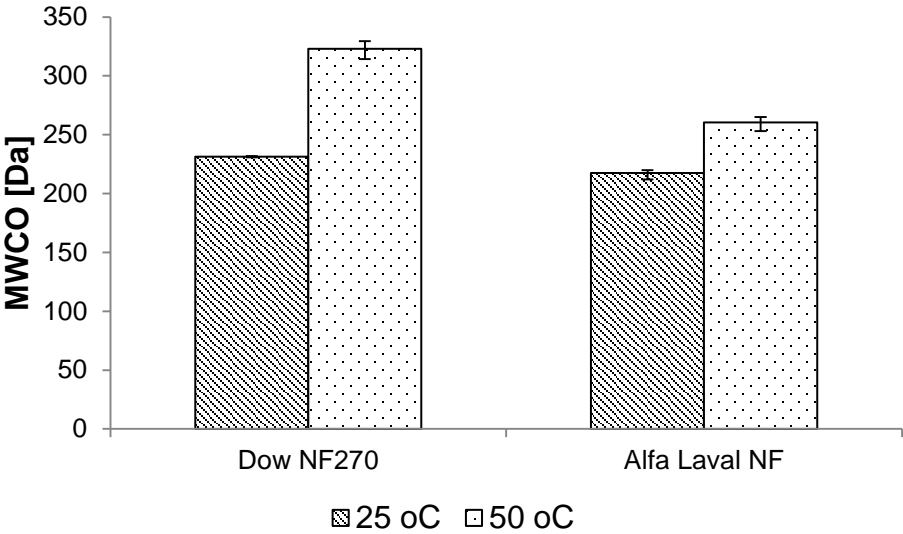
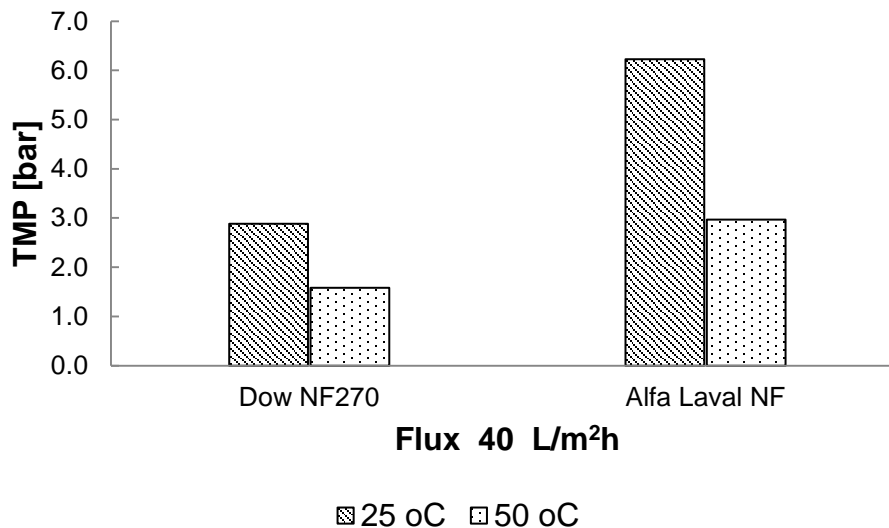


Figure 3.4 Variation of the MWCO with temperature (25°C and 50°C) for Dow NF270 and Alfa Laval NF.

**3.3.2 Transmembrane pressure (TMP) and temperature using demineralized water as feed solution**

The relation between temperature (25°C and 50°C) and TMP is depicted in Figure 3.5 for a constant flux of 40 L/m<sup>2</sup>h. Temperature and pressure had an inverse relationship, i.e. an increase in temperature resulted in a lower transmembrane pressure. For both membranes, the transmembrane pressure at 50°C was approximately 50% of the transmembrane pressure at 25°C. For both temperatures, Dow NF270 needed lower transmembrane pressures than Alfa Laval NF to produce the same flux. The low operating pressure required by Dow NF270 at 50°C (15 mwc) in combination with the elevated topography found in Nicaragua's volcanic region may make it feasible to operate the system without a pump (i.e. gravity-fed NF system).

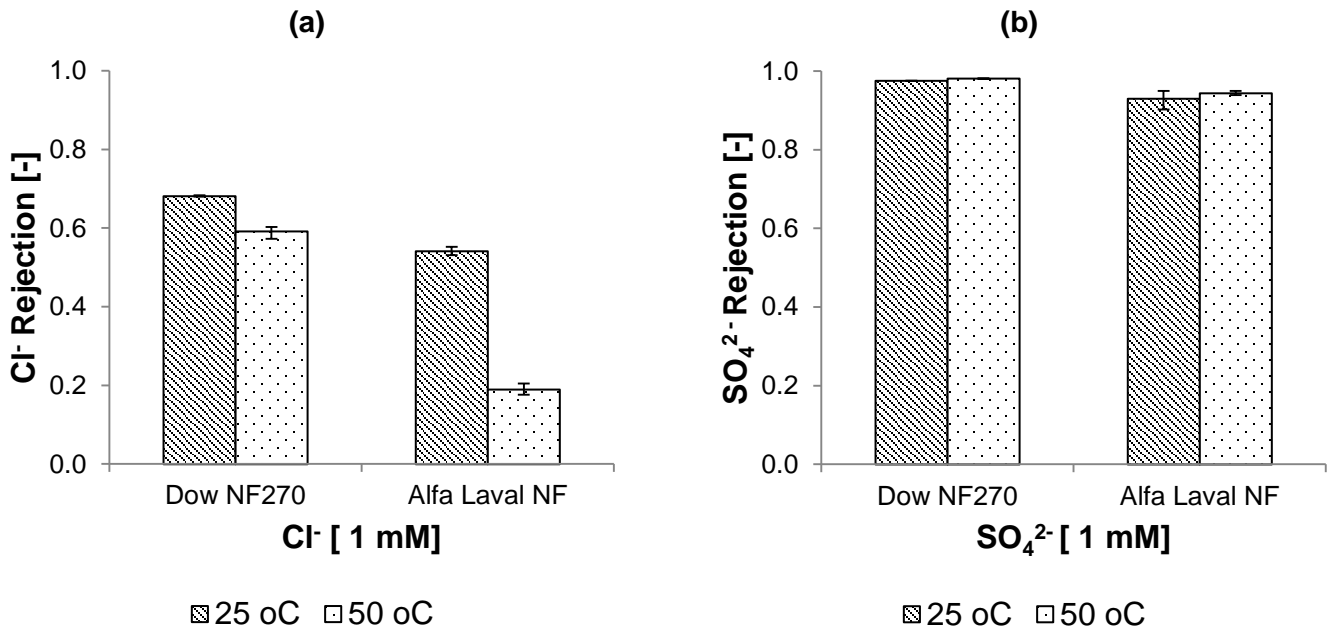


**Figure 3.5** TMP in bar evaluated as a function of a constant flux (40 L/m<sup>2</sup>h) and different temperatures (25°C and 50°C). Demineralized water was used as feed solution.

For both membranes, the reduction in transmembrane pressure could be associated to both the decrease in water viscosity and the expansion of the effective pore diameter due to increased temperature. The difference between the two tested membranes could be associated with their different physical properties (i.e., pore size, thickness, tortuosity).

### 3.3.3 Rejection of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

Figure 3.6 depicts the single solute rejection of Cl<sup>-</sup> (left) and SO<sub>4</sub><sup>2-</sup> (right) at 25°C and 50°C. The rejection of Cl<sup>-</sup> (monovalent ion) was lower compared to SO<sub>4</sub><sup>2-</sup> (divalent ion) at both temperatures. This order in rejection was valid for both NF membranes and is in line with expectations for negatively charged NF membranes (Peeters et al., 1998). A considerable decrease in rejection was noted for the monovalent anion (Cl<sup>-</sup>) as a consequence of the temperature increase (26% for Dow NF270 and 68% for Alfa Laval NF). On the other hand, the rejection of the divalent anion (SO<sub>4</sub><sup>2-</sup>) was found to be less sensitive to temperature changes.



**Figure 3.6** Individual rejection of (a) monovalent anion ( $\text{Cl}^-$ ) and (b) divalent anion ( $\text{SO}_4^{2-}$ ) evaluated as a function of temperature (25°C and 50°C) at constant flux (40 L/m<sup>2</sup>h).

With the temperature increase (from 25°C to 50°C), the reduction of  $\text{Cl}^-$  rejection can be ascribed to changes in its thermodynamic and physical properties (e.g., increase in diffusivity, decreases in hydration free energy and hydrated radius) as well as to the diminishing size exclusion mechanism due to thermal expansion of the pore (Sharma et al., 2003). As a consequence, there was an increase in the diffusive transport of  $\text{Cl}^-$  across the membrane layer resulting from increased temperature (Brandhuber and Amy, 2001; J. Waypa et al., 1997). This effect was more significant for  $\text{Cl}^-$  compared to  $\text{SO}_4^{2-}$  because of its higher diffusivity, lower charge, lower hydrated radius and lower hydration free energy (Nightingale, 1959; Tansel, 2012), offering an explanation for the large decrease of the  $\text{Cl}^-$  rejection and the unaffected rejection of  $\text{SO}_4^{2-}$ .

A lower rejection of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  was observed for Alfa Laval NF when compared with the rejection for DOW NF270, while the average pore size (at 25°C and 50°C) of Alfa Laval NF is smaller than DOW NF270. This could imply that aside from the size exclusion, the membrane charge and membrane material had a significant effect on the rejection, particularly for monovalent ions ( $\text{Cl}^-$ ).

Nguyen et al. (Nguyen et al., 2009) tested As(V) concentration ranging from 20 to 100 µg/L, reporting an improvement in the rejection of  $\text{H}_2\text{AsO}_4^-$  (3 to 6 %) and  $\text{HAsO}_4^{2-}$

(1% to 3%) when using deionized water + 10 mM NaCl as a background solution compared to the rejection values obtained when only deionized water was used. The same study noted a decrease in the rejection of  $\text{H}_2\text{AsO}_4^-$  (1% to 1.7%) and  $\text{HAsO}_4^{2-}$  (< 0.6%) when deionized water + 10 mM  $\text{Na}_2\text{SO}_4$  was used as a bulk solution compared to the rejection values obtained when only deionized water was used. Vrijenhoek and Waypa (Vrijenhoek and Waypa, 2000) compared the effect of two background solutions on the rejection of a wide range of divalent arsenate concentrations (from 10 to 1000  $\mu\text{g/L}$ ). The first solution contained deionized water + 1mM  $\text{NaHCO}_3$ , and the second contained deionized water + 10 mM NaCl + 1mM  $\text{NaHCO}_3$ . In both cases, the rejection of  $\text{HAsO}_4^{2-}$  increased as a function of its concentration in the bulk solution. In general, a higher rejection was achieved during filtration of the solution containing NaCl and  $\text{NaHCO}_3$ . This phenomenon has been ascribed to the relative “mobility or permeability” of the ions present in the bulk solution (Hodgson, 1970;Vrijenhoek and Waypa, 2000). The so-called “mobility or permeability” of the ion could be defined by the thermodynamic and physical properties (e.g., charge, diffusivity, hydrated radius and hydration free energy). For example, anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  (e.g., with smaller hydrated radius and smaller hydration free energy) compared to  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  are considered more permeable (Binder and Zschörnig, 2002;Linde and Jönsson, 1995;Nightingale, 1959;Saitua et al., 2011;Stumm and Morgan, 2009;Tansel, 2012). The rejection of the more mobile anions is lower (e.g.,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ), and, because of the electro-neutrality that needs to be maintained in the feed solution, the rejection of the less permeable anions tends to be enhanced. In other words, the As(V) species tend to increase in the presence of  $\text{Cl}^-$  and  $\text{HCO}_3^-$ .

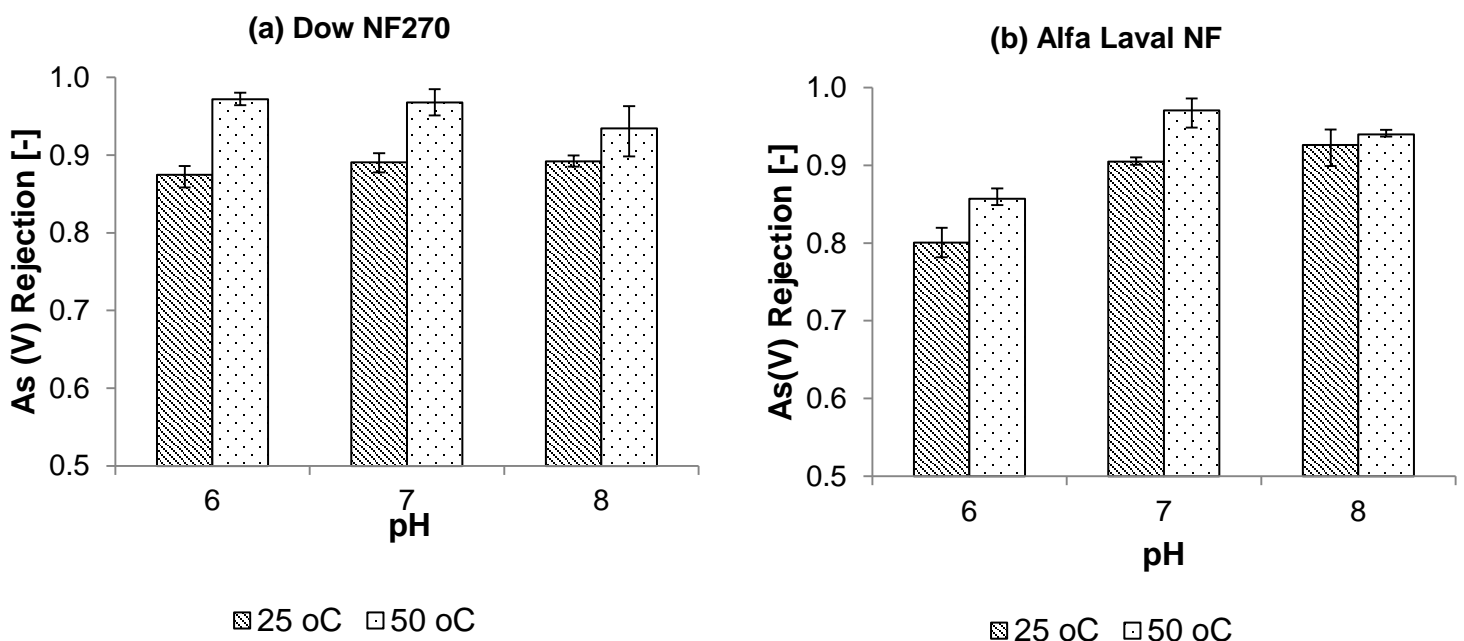
### **3.3.4 Rejection of monovalent $\text{H}_2\text{AsO}_4^-$ and divalent $\text{HAsO}_4^{2-}$ species in presence of $\text{NaHCO}_3$**

Figure 3.7(a) shows that at 25°C, the order of rejection of As(V) in the presence of  $\text{NaHCO}_3$  for Dow NF270 was  $\text{H}_2\text{AsO}_4^-$  (pH 6) <  $\text{HAsO}_4^{2-}$  (pH 7 & 8), although there was only a slight difference (2%). At 50°C, this rejection order was reversed, and the rejection of monovalent As(V) was equal or greater than that of the divalent As(V) at pH 7 and pH 8 ( $\text{H}_2\text{AsO}_4^- \geq \text{HAsO}_4^{2-}$ ). However, the hierarchy in rejection of As(V)

species for Alfa Laval NF was  $\text{H}_2\text{AsO}_4^-$  (pH 6) <  $\text{HAsO}_4^{2-}$  (pH 7 & 8) for both temperatures (Figure 3.7(b)), i.e. divalent As(V) was better rejected than monovalent As(V). The degree of rejection for both As(V) species was higher at 50°C than the rejection obtained at 25°C for both membranes tested. Dow NF270 showed a rejection up to 0.97 and 0.93 for mono and divalent As(V), respectively, at 50°C. At the same temperature, Alfa Laval presented a rejection of 0.86 for monovalent and 0.97 and 0.94 for divalent As(V).

At 25°C, the As concentration in the permeate of both membranes tested exceeded the WHO regulatory limit of arsenic in drinking water (10 µg/L). The As concentration in the permeate for Dow NF270 is close to 35 µg/L for the evaluated pH values, whereas the concentration in the permeate of Alfa Laval NF was around 57, 27 and 21 µg/L for pH 6, 7 and 8 respectively.

At 50°C, the permeate quality is improved. Furthermore, for some of the evaluated pH values, the As concentration in the permeate was reduced to less than 10 µg/L for Dow NF270 (pH 6 and pH 7) and Alfa Laval NF (pH 7). Our results suggest that there is a restriction related with the maximum As(V) concentration that can be treated with NF, where NF systems seem most appropriate at As(V) concentrations below 300 µg/L.



**Figure 3.7** Rejection efficiency of  $\text{H}_2\text{AsO}_4^-$  (pH 6) and  $\text{HAsO}_4^{2-}$  (pH 7 & pH 8) as a function of a constant temperature (25°C or 50°C). For (a) Dow NF270 and (b) Alfa Laval NF.

An improvement in rejection of  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  was achieved as the result of an increase in temperature. One would not expect this result based on the observed  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  rejection at higher temperatures, where a lower and an equal rejection were observed for these mono and divalent ions, respectively. Furthermore, previous work (Figoli et al., 2010) executed in deionized water showed a decline in the rejection of As(V) as a result of increased temperature. The difference between the cited research and our findings could be explained by the presence of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  (used as a pH and ionic strength buffer in our study), which may have played a considerable role in the improvement of As(V) rejection. Earlier studies (Nguyen et al., 2009; Vrijenhoek and Waypa, 2000) conducted at 25°C have shown that in a multi-component solution, the rejection of  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  during nanofiltration could be influenced by the presence of co-occurring anions. Our results suggest that this phenomenon was temperature dependent, supporting the rejection of As(V) at higher temperatures. Anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  with an equal or lower valence, higher diffusivity, smaller hydrated radius and lower hydrated free energy are generally more permeable than  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  (Nightingale, 1959; Padilla and Saitua, 2010; Vrijenhoek and Waypa, 2000). As temperature increases, the permeability or mobility of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  also increases. In addition, due to friction forces originating during nanofiltration,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  (with lower hydration free energy) decrease their hydrated radius (Tansel, 2012). Because of the inverse relationship between the hydration free energy with temperature, the hydrated radius of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  decrease as the temperature increases. This characteristic in combination with the enlargement of the pore size and the increase in the mass transfer across the membrane due to the temperature effect enhanced the permeation of  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ; correspondingly, the rejection of the less permeable As(V) species increases because of electro-neutrality that needs to be maintained in the bulk solution. Therefore,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  permeation had a beneficial effect on the rejection of As(V) species, and this effect was enhanced as temperature increased. In natural waters, other anions will also interact with As(V) and thus may affect the rejection efficiency of the membranes. This study is a first step towards

understanding As(V) rejection at higher temperatures, but further research will be required to elucidate the mechanism of As(V) rejection in the complex, natural water quality matrices in Nicaraguan geothermal waters.

### **3.4. Conclusions**

At 50°C, the transmembrane pressure required to operate the NF membranes was on average 50% lower than at 25°C. This can be explained by the decreased viscosity of the water and the expansion of membrane pores (MWCO) at higher temperatures. The operational pressure for Dow NF270 at 50°C was 1.5 bar (15 mwc), making it suitable for the use of natural elevation in volcanic areas, therefore not requiring electricity for operation. Depending on the pH tested, the As(V) concentration in the permeate was either slightly below (9 µg/L) or above (21 µg/L) the WHO regulatory limit in drinking water (10 µg/L), which indicates that there are restrictions related with the maximum As(V) concentration to be treated with NF.

It was found that at the higher temperature the rejection of both monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species increased. This finding differs from previous work where the As(V) rejection from deionized water showed a decline as a consequence of temperature increase. The presence of more permeable anions,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , may have been responsible for enhanced As(V) rejection. The interaction between ions (as will also be present in natural waters in Nicaragua) apparently counteracts the effect of increased pore size, resulting in enhanced As(V) rejection at higher temperatures.

### **3.5. Acknowledgements**

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#### **4. The effect of co-ions ( $\text{Cl}^-$ and $\text{HCO}_3^-$ ) and increasing $\text{Cl}^-$ concentrations on the rejection of As(V) in high temperature water (25°C and 50°C) using nanofiltration membranes.**

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This chapter will be submitted for publication

##### **Abstract**

The presented study assessed the effect of co-ions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  As(V) species during NF membrane filtration of high-temperature water (25°C and 50°C). Filtration experiments were conducted using a flat-sheet cross-flow module. Two different batches (NF-A and NF-B) of one type, commercially available polyamide membrane, were used. The rejection of As(V) differed from one batch to another. On the one hand, for NF-A, as  $\text{Cl}^-$  concentration increased a higher As(V) rejection (up to 6%) was achieved at 50°C, compared with the rejection obtained at 25°C. On the other hand, this effect was not observed for NF-B, whose rejection of As(V) was similar at 25°C and 50°C.

The enhancement of As(V) rejection with NF-A at higher temperatures was not attributed to variation in the charge of the membrane (the zeta potential was constant), but to the enlargement of the pore size (MWCO increased) and as a result the increase of the mass transfer of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  across the membrane. Apparently, only a threshold concentration of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  passing through the membrane was necessary to enhance the  $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$  rejection at 50°C. This could be understood considering that As(V) (0.004 mM) was present in low concentrations compared with  $\text{Cl}^-$  (0.8 to 11 mM) and  $\text{HCO}_3^-$  (0.11 to 1mM).

##### **4.1. Introduction**

Polyamide Nanofiltration (NF) membranes have shown a high removal of arsenate (As(V)) from water within a wide range of temperatures (10°C to 50°C) (Gonzalez et al., 2019; Harisha et al., 2010; J. Waypa et al., 1997; Uruse et al., 1998; Vrijenhoek and Waypa, 2000). Under oxidizing conditions As(V) can be found as monovalent

( $\text{H}_2\text{AsO}_4^-$ ) and divalent ( $\text{HAsO}_4^{2-}$ ) anions (Smedley and Kinniburgh, 2002), while, during filtration of natural groundwater (pH 6.5–8.5), a polyamide NF membrane has a negatively charged surface (Nguyen et al., 2009). Therefore, both charge exclusion and size exclusion are important mechanisms in the ions' rejection (Bowen et al., 1997). In a charged membrane, the rejection efficiency is also affected by the charge and concentration of the co-ions, i.e., ions with the same charge as the membrane, as well as the counter-ions, i.e., ions with the opposite charge as the charge of the membrane (Peeters et al., 1998).

Sharma and Chellam (2006) have reported an increasing negative charge density for two NF membranes as a result of temperature increase (from 6 to 42°C), during filtration of an electrolyte solution containing NaCl. This effect was attributed to the adsorption of the co-ions on the membranes. Additionally, the weakening of the size exclusion effect with temperature increase has been reported by several researchers (Brandhuber and Amy, 2001; Dang et al., 2014; Figoli et al., 2010), with, as a consequence, a reduction of the rejection of the target compounds. However, Gonzalez et al. (2019) have recently reported an increase in rejection of  $\text{H}_2\text{AsO}_4^-$  (6% to 10%) and  $\text{HAsO}_4^{2-}$  (1% to 4%), when filtering a solution containing a low concentration of  $\text{Cl}^-$  (0 to 0.6 mM) and  $\text{HCO}_3^-$  (0.3 to 1mM), as temperature increased from 25°C to 50°C. This study was unable to fully explain why at higher temperatures As(V) rejection increased, as it did not consider the effect of high concentrations of  $\text{Cl}^-$  during filtration of high temperature water, while measuring the charge of the NF membranes. Especially at high concentrations of co-ions, the effect on the membrane's zeta potential would become apparent. Therefore, the objective of this study was to determine the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species during nanofiltration of high temperature water as a function of temperature and the concentration of  $\text{Cl}^-$ .

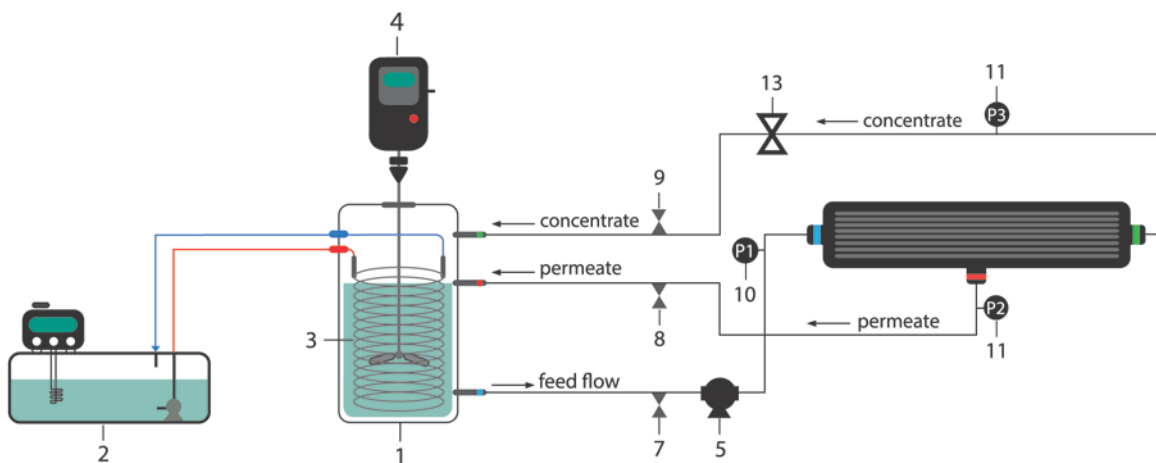
## 4.2. Materials and methods

### 4.2.1 NF membranes and solutions

Two different batches (NF-A and NF-B) of a negatively charged, commercially available polyamide membrane, Dow NF270 (DOW FILMTEC™), were used. Salt solutions were prepared using NaCl, NaHCO<sub>3</sub> and Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O analytical grade, supplied by Sigma-Aldrich.

### 4.2.2 Experimental set-up

Experiments were conducted using a flat-sheet cross-flow module and operated as a closed circuit system, as illustrated in Figure 4.1. The active area of the flat sheet membrane was 0.25m<sup>2</sup>. The experimental setup was operated as a closed circuit system. The set up and the NF filtration experiments were described in detail in Gonzalez et al.(2019).



**Figure 4.1** Schematic representation of experimental set up. 1. Feed water tank, 2. Thermostatic bath, 3. Heat exchanger, 4. Overhead stirrer, 5. Pump, 6. Cross flow membrane module, 7. Sampling point feed water, 8. Sampling point permeate, 9. Sampling point concentrate, 10. Pressure gauge – feed, 11. Pressure gauge – permeate, 12. Pressure gauge – concentrate, 13. Concentrate valve.

### 4.2.3 Effect of temperature on streaming potential measurement

The effect of temperature on the membranes' zeta potential was determined for membrane NF-A by the streaming potential method using an electrokinetic analyzer with operating temperature of 20°C to 40°C (SurPASS, Anton Paar, Graz, Austria) and an adjustable gap cell. It was measured in tangential mode and the charge was measured at the membrane surface (Shang et al., 2014a; Shang et al., 2014b). The experiment was conducted at 25°C (room temperature) and 40°C (maximum operation temperature of the electrokinetic analyzer). In order to measure the streaming potential at 40°C, the electrolyte was placed in a water bath, and the temperature in the adjustable gap cell was monitored using a thermometer, installed next to the cell. The zeta potential was then calculated by the instrument using the Helmholtz-Smoluchowski equation (Christoforou et al., 1985; Werner et al., 1998):

$$\zeta = \frac{dl/dp \times \eta}{(\epsilon \times \epsilon_0)} \times L/A \quad (1)$$

where,  $dl/dp$  is the measured streaming current coefficient;  $L$  is the length of membrane sheet in the adjustable gap cell;  $A$  is the cross-sectional area of the adjustable gap (channel width \* gap height);  $\eta$  and  $\epsilon \times \epsilon_0$  are the viscosity and dielectric coefficient of the electrolyte solution (0.89 mPa.s and 78.36 (-), respectively, at 25°C; and 0.64 mPa.s and 72.82 (-) respectively at 40°C).

Two types of electrolytes (NaCl and NaHCO<sub>3</sub>) were used for the streaming potential measurements, as shown in Table 4.1. The electrolyte solutions all had the same ionic strength of 3 mM and the cell was thoroughly flushed prior to the measurements. The pH of the electrolyte solutions, ranging from 6 to 8, was adjusted with 0.1 mM NaOH.

**Table 4.1** Background electrolyte solutions for zeta potential measurements

No.	Type of electrolyte	Ionic strength, mM	Temperature in the cell, °C	pH of electrolyte solution	Measured pH
1	NaCl	3	25	6	6.1 ± 0.1
2	NaCl	3	25	8	7.7 ± 0.1
3	NaHCO <sub>3</sub>	3	25	8.5 *	8.5 ± 0.1 *
4	NaCl	3	40	6	6.3 ± 0.1

5	NaCl	3	40	8	7.7 ± 0.1
6	NaHCO <sub>3</sub>	3	40	8.5 *	8.5 ± 0.1 *

\* The pH of electrolyte solution as prepared.

#### 4.2.4 Effect of temperature on MWCO

The molecular weight cut offs (MWCO) for NF-A and NF-B were determined at 25°C and 50°C. The solution, used for the determination of MWCO, was prepared using ethylene glycol (62 g/mol) and different polyethylene glycols (PEGs) with molecular weights ranging from 200 to 1000 g/mol (Sigma-Aldrich). The experiments were performed at constant flux (30 L/m<sup>2</sup>h) and a recovery of 15%. MWCO was measured by filtering the ethylene glycol /PEGs mixture and measuring the rejection with HPLC-GPC (Shimadzu) with RI-detection.

#### 4.2.5 NF rejection experiments

Table 4.2 gives an overview of the experimental settings and the water composition used for the NF rejection experiments. The rejection experiments were conducted at constant flux (40 L/m<sup>2</sup>h) and a recovery of 10%. All experiments were performed in duplicate and were executed at 25°C and 50°C. Both NF batches (NF-A and NF-B) were tested.

**Table 4.2** Overview of NF rejection experiments

Experimental Settings	pH	Water Matrix Composition
Rejection of monovalent H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> species in the presence of NaHCO <sub>3</sub> and NaCl	6	Demineralized water + 0.004 mM H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> + 1 mM NaHCO <sub>3</sub> + NaCl (0.8 to 11 mM)
Rejection of divalent HAsO <sub>4</sub> <sup>2-</sup> species the presence of NaHCO <sub>3</sub> and NaCl	8	Demineralized water + 0.004 mM HAsO <sub>4</sub> <sup>2-</sup> + 1 mM NaHCO <sub>3</sub> + NaCl (0 to 10 mM) + NaOH

The effect of  $\text{Cl}^-$  concentration on NF rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  in the presence of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  was studied by keeping the pH=6 constant and while varying the  $\text{Cl}^-$  concentration for each filtration cycle (1.5 h). A fresh solution was prepared (0.004 mM  $\text{H}_2\text{AsO}_4^-$  + 1 mM  $\text{HCO}_3^-$ ) for each experiment. The initial pH of the mixture (around pH 8) was decreased to pH 6 using HCl (1.62 M). For batch NF-A the  $\text{Cl}^-$  concentration was 0.8, 1, 2, 5, 8, and 11 mM. For batch NF-B the  $\text{Cl}^-$  concentration was 1, 2, and 6 mM. During the experiment testing pH 6 at 50°C, an increase in pH was observed probably due to stripping of  $\text{CO}_2$ . Therefore, HCl was continually added to keep the pH constant.

The effect of  $\text{Cl}^-$  concentration on NF rejection of divalent  $\text{HAsO}_4^{2-}$  in the presence of  $\text{HCO}_3^-$  was studied by keeping the pH=8 constant while varying the  $\text{Cl}^-$  concentration for each filtration cycle (1.5 h). At the beginning of the experiment, NaOH (0.1 M) was dosed to the feed water solution to adjust the pH to 8. The  $\text{Cl}^-$  concentrations evaluated in these conditions for batch NF-A were 0, 0.3, 1, 4, 7 and 10 mM and for batch NF-B were 0, 1 and 5 mM .

#### **4.2.6 Analysis of samples**

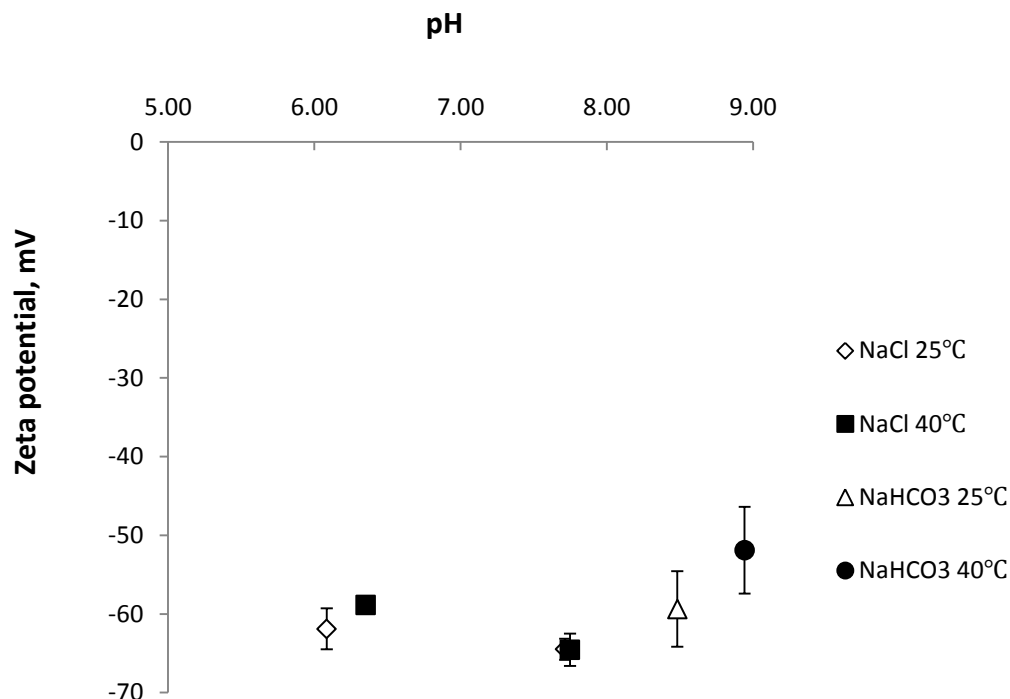
The As concentration in the samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS PlasmaQuant MS , Analytik Jena AG). The concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  were determined using titrimetric (702 SM Titrino, Metrohm) and ion chromatography analysis (IC - 883 Basic/Plus, Metrohm), respectively. Temperature and pH of the samples were measured using a multimeter (WTW GmbH, Germany).

## 4.3. Results and discussion

### 4.3.1 Effect of temperature on Zeta potential

Figure 4.2 depicts the Zeta potential (mV) of NF-A as a function of pH and temperature for a constant concentration (3 mM) of NaCl and NaHCO<sub>3</sub>. For all the evaluated conditions the surface charge of the membrane remained negative. As pH increased (from 6.0 to 7.8) there was a slight increase (~ 6 %) in the negative charge of NF-A for the electrolyte solution contained NaCl, while at higher pHs the charge decreased again. This pH effect is well known and has been well documented by other researchers (Kim et al., 2006; Luo and Wan, 2013; Nguyen et al., 2009; Urase et al., 1998).

At pH 6.0-6.3, the negative charge of the membrane slightly decreased (5%) when the temperature increased from 25°C to 40°C. However, at pH 7.8 there was no change in zeta potential observed as a result of temperature increase. At pH 8.4-8.9 there was a clear differentiation between the two temperatures, with a higher negative surface charge at 25°C, but, considering the large error bar and the overlap between the samples for the electrolyte solution containing NaHCO<sub>3</sub>, the decrease in zeta potential as a consequence of temperature increase was within the accuracy of the measurement.



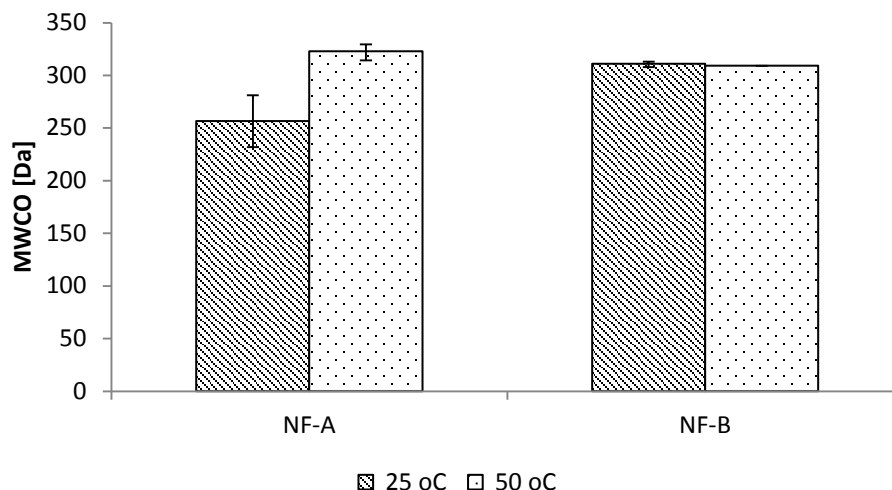
**Figure 4.2** Zeta potential of the NF-A membrane

It is therefore concluded that the increase in negative charge for NF membranes as a result of temperature increase, as reported by Sharma and Chellam (2006), was not measured for the tested membrane. This could be related with the difference in chemical composition and surface modification of the membranes (Sharma and Chellam, 2006). On the basis of the obtained results it can be concluded that variation in pH was more important parameter than the variation in temperature.

#### 4.3.2 Effect of temperature on MWCO

Figure 4.3 depicts the effect of temperature increase on MWCO for batches NF-A and NF-B. An increase of 25% in MWCO (from 256 Da to 323 Da) was observed for NF-A, which is in agreement with earlier studies and could be attributed to the thermal expansion of the polyamide layer (Ben Amar et al., 2007; Dang et al., 2014; Sharma et al., 2003). However, no increase in MWCO (from 311 to 309) was observed for NF-B. At 25°C the MWCO of NF-B (311 Da) was larger than NF-A (256

Da), but as temperature increased to 50°C the MWCO of NF-A (323 Da) became larger than NF-B (311).



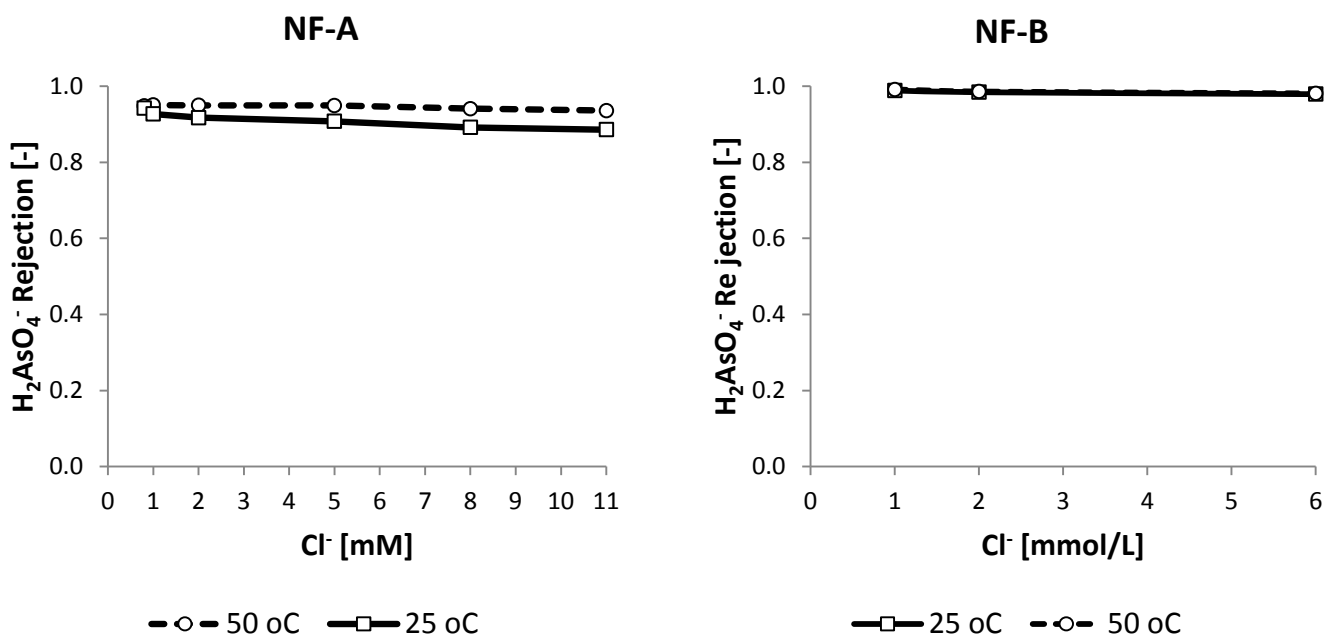
**Figure 4.3** Variation of the MWCO with temperature (25°C and 50°C) for NF-A and NF-B.

A reduction of the size exclusion mechanism of the membrane could be the consequence of an increase in the MWCO, as observed by Dang et al.(2014), who reported that when the feed water temperature increased from 20°C to 40°C the pore size of its membrane increased by 12% and produced a drop in the rejection of trace organic contaminants.

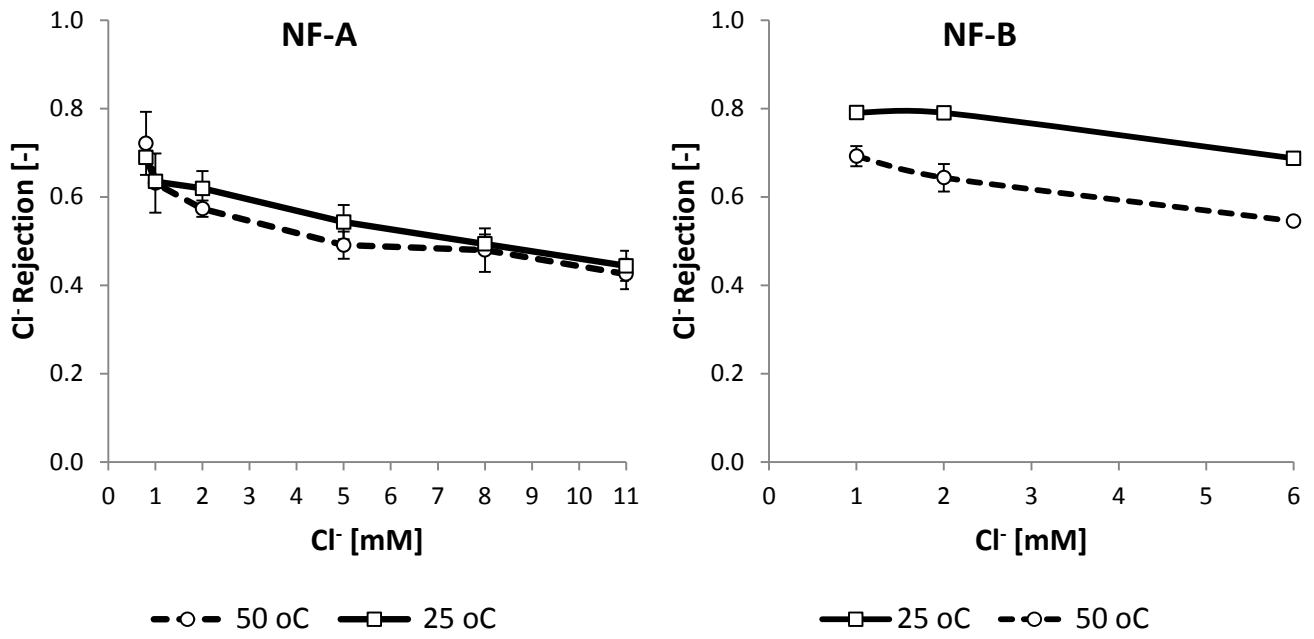
#### 4.3.3 Rejection of monovalent $\text{H}_2\text{AsO}_4^-$ and divalent $\text{HAsO}_4^{2-}$ species in presence of $\text{NaHCO}_3$ and $\text{NaCl}$

Figure 4.4 (a) shows the results for  $\text{H}_2\text{AsO}_4^-$  rejection at an increasing  $\text{Cl}^-$  concentration for both NF-A and NF-B. For NF-A, as  $\text{Cl}^-$  concentration increased (from 1 to 11 mM) a higher rejection (up to 6%) was achieved at 50°C (0.94) compared with the rejection obtained at 25°C (0.88). At 50°C, the  $\text{H}_2\text{AsO}_4^-$  rejection could be considered steady after 0.8 mM  $\text{Cl}^-$ . On the other hand at 25°C the  $\text{H}_2\text{AsO}_4^-$  rejection decreased from 0.94 to 0.88. The improvement of As(V) rejection due to

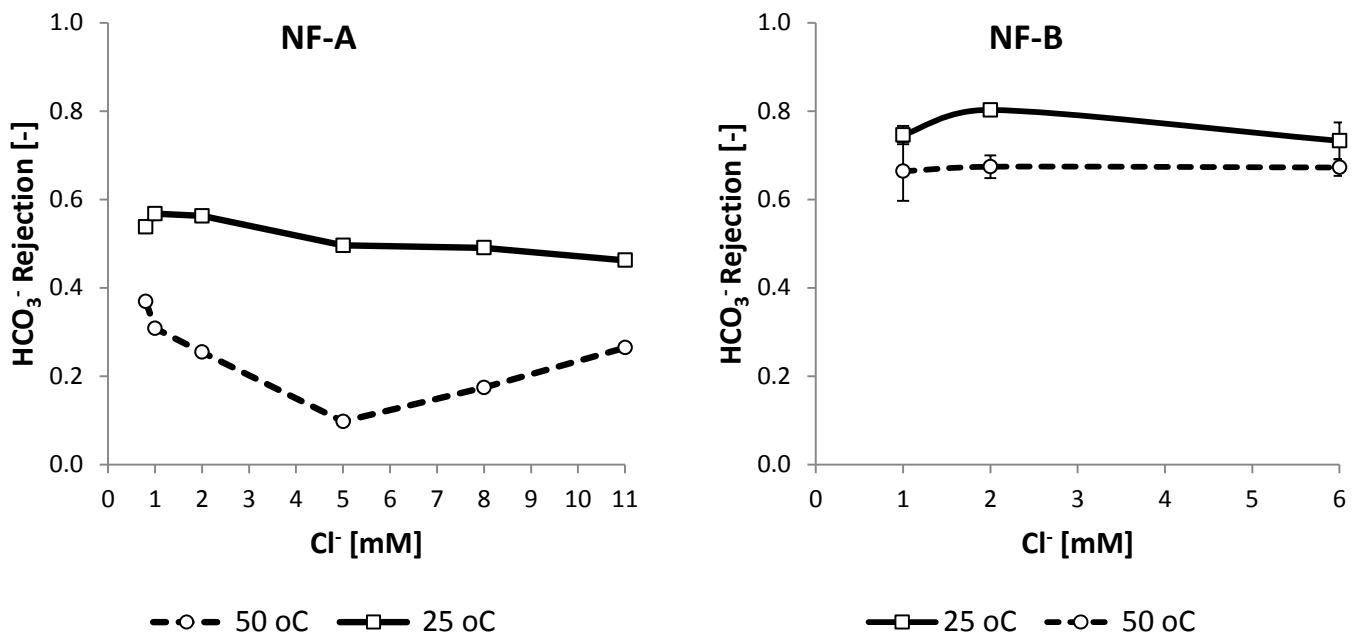
temperature increase implied that the permeate concentration was reduced from approximately 30  $\mu\text{g/L}$  (at 25°C) to 15  $\mu\text{g/L}$  (at 50°C). At 25°C, NF-B showed similar  $\text{H}_2\text{AsO}_4^-$  rejection ( $\sim 0.99$ ) when increasing the temperature to 50°C. For both membranes a slight reduction in  $\text{H}_2\text{AsO}_4^-$  rejection was observed at increasing  $\text{Cl}^-$  concentrations. The rejection of  $\text{H}_2\text{AsO}_4^-$  for both NF batches (NF-A and NF-B) was higher than the rejection of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  (Figure 4.4 (b) and (c)). When comparing the overall  $\text{Cl}^-$  and  $\text{HCO}_3^-$  rejection between NF-A and NF-B, a better rejection of both ions was observed for NF-B (Figure 4.4 b & c). For NF-B, the difference in  $\text{Cl}^-$  rejection between the two temperatures ( $\sim 10$  to 15%) was clearly larger than for NF-A ( $\sim 1$  to 6%), whereas the opposite was the case for  $\text{HCO}_3^-$  rejection (i.e.,  $\sim 17$  to 50% for NF-A and  $\sim 6$  to 13% for NF-B). In NF-A,  $\text{HCO}_3^-$  rejection was apparently strongly affected by the temperature increase.



[a]  $\text{H}_2\text{AsO}_4^-$



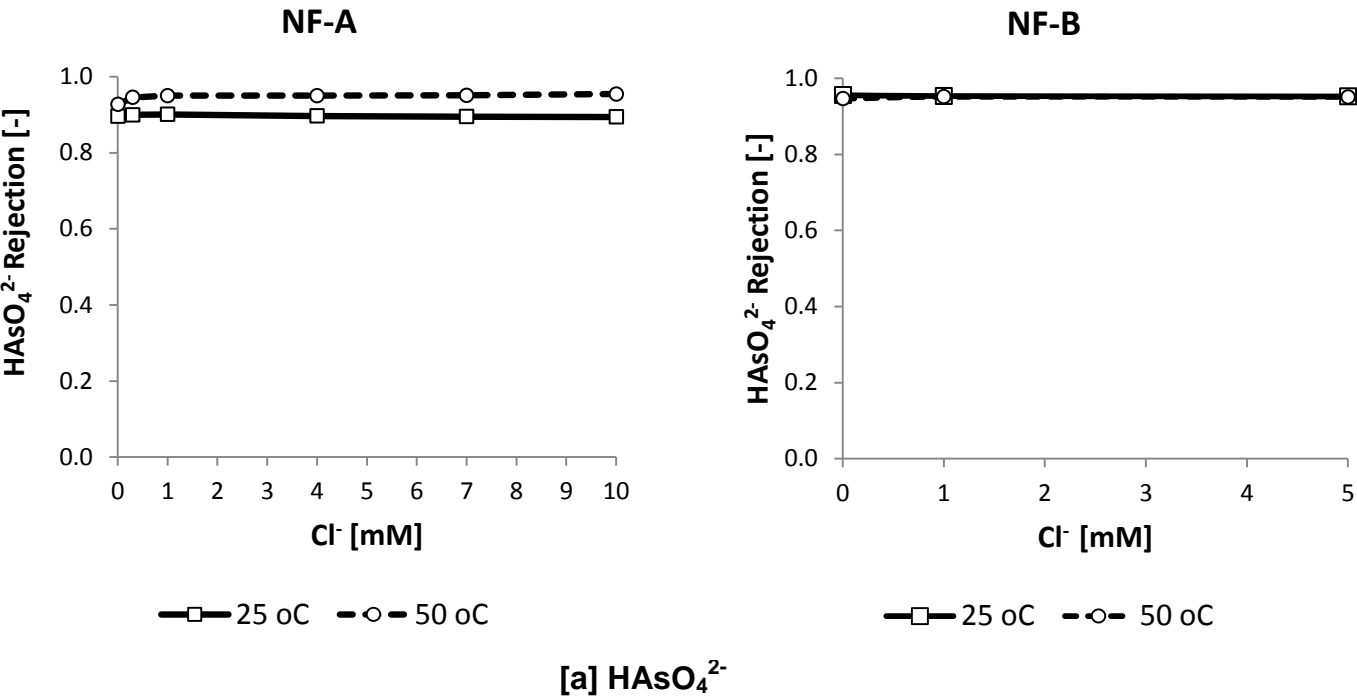
**[b] Cl<sup>-</sup>**

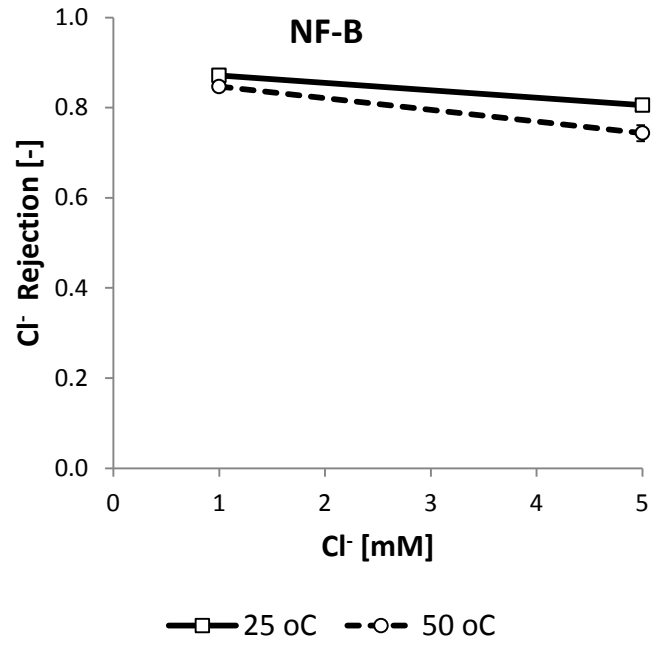
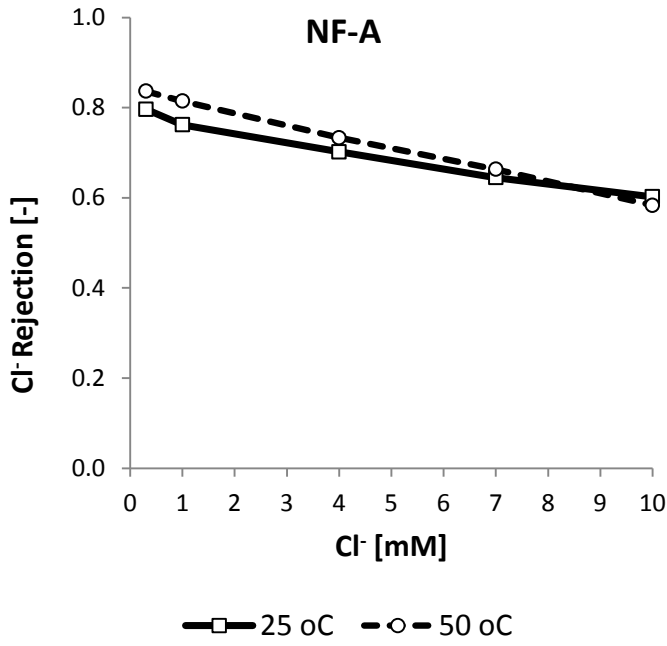


**[c] HCO<sub>3</sub><sup>-</sup>**

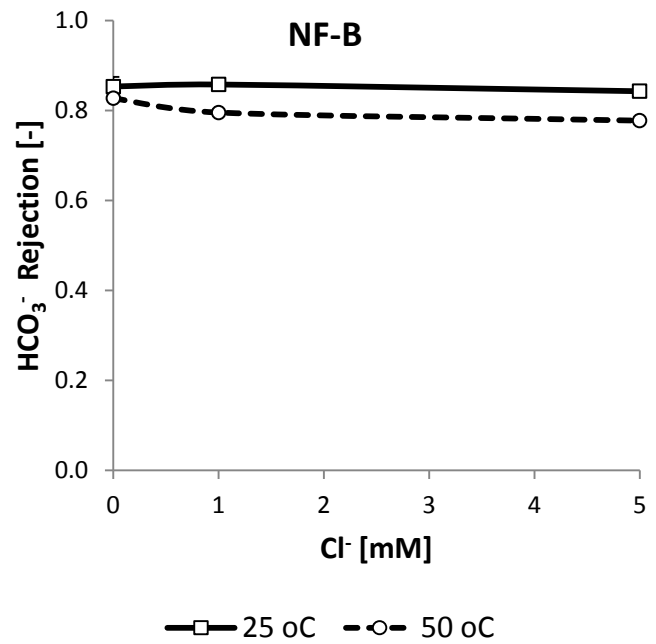
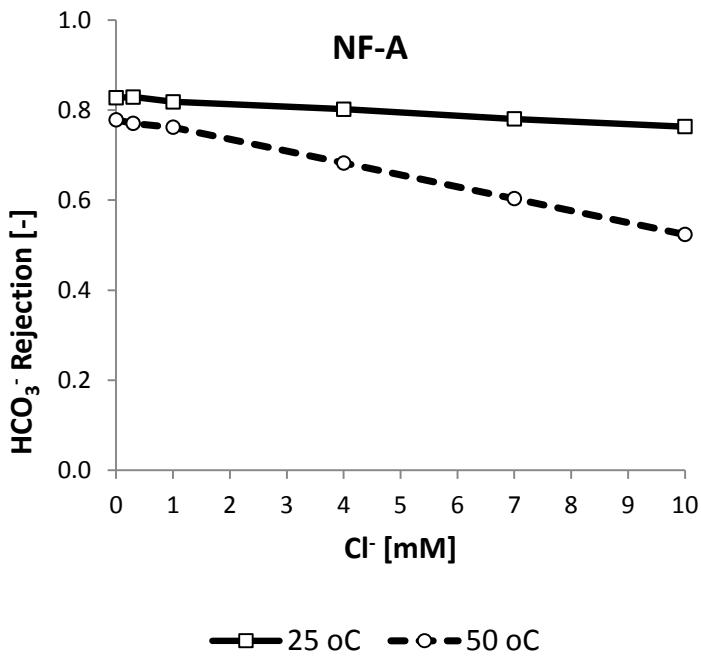
**Figure 4.4** Rejection of (a) H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> (0.004 mM) (b) Cl<sup>-</sup> and (c) HCO<sub>3</sub><sup>-</sup> as a function of a constant temperature (25°C or 50°C), HCO<sub>3</sub><sup>-</sup> (0.3 mM to 0.11 mM) and variable Cl<sup>-</sup> concentration. Experiment at pH=6.

The rejection experiments with varying  $\text{Cl}^-$  concentrations at  $25^\circ\text{C}$  and  $50^\circ\text{C}$  were repeated for divalent  $\text{HAsO}_4^{2-}$ , as depicted in Figure 4.5 (a). For NF-A, as  $\text{Cl}^-$  concentration increased (from 0 to 10mM), a higher  $\text{HAsO}_4^{2-}$  rejection (up to 6%) was achieved at  $50^\circ\text{C}$  (0.95) compared with the rejection obtained at  $25^\circ\text{C}$  (0.89). The concentration in the permeate reduced from  $\sim 30 \mu\text{g/L}$  to  $\sim 15 \mu\text{g/L}$  at  $25^\circ\text{C}$  and  $50^\circ\text{C}$ , respectively. The rejection of  $\text{HAsO}_4^{2-}$  for both NF batches (NF-A and NF-B) was higher than the rejection of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  (Figure 4.5 (b) and (c)). This rejection order, or the permeability (Hodgson, 1970), of the ions could be related with the order of their charge and hydration free energy ( $\text{HAsO}_4^{2-} > \text{Cl}^- / \text{HCO}_3^-$ ) (Saitua et al., 2011; Tansel, 2012).  $\text{HCO}_3^-$  rejection in NF-A is, alike to the experiments with monovalent  $\text{H}_2\text{AsO}_4^-$ , strongly affected by an increase in temperature. However, as depicted in Figure 4.5 5 (c), the decrease in rejected is related to the  $\text{Cl}^-$  concentration. This direct relationship was not observed in monovalent  $\text{H}_2\text{AsO}_4^-$  experiments, for membrane NF-B.





[b] Cl<sup>-</sup>



[c] HCO<sub>3</sub><sup>-</sup>

Figure 4.5 Rejection of (a) HAsO<sub>4</sub><sup>2-</sup> (0.004 mM), (b) Cl<sup>-</sup> and (c) HCO<sub>3</sub><sup>-</sup> rejection as a function of a constant temperature (25°C or 50°C), constant HCO<sub>3</sub><sup>-</sup> (1 mM) and variable Cl<sup>-</sup> concentration (mM) experiment at pH=8.

#### 4.4. Overall discussion

The rejection of both monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species increased with approximately 6% in membrane NF-A when the temperature was raised from 25°C to 50°C. This increase of rejection might be limited but the effect on the arsenic concentration in the permeate is important for the produced water quality : The permeate concentration decreased with the increase of the temperature to 50°C with 50%(from 30 to 15µg/L). This observation cannot be attributed to change in the zeta potential of NF-A, because it rather decreased than increased at higher temperature (see

Figure 4.2). Therefore, the possible explanation for improved As(V) rejection at higher temperatures must be related to the rejection of  $\text{Cl}^-$  and  $\text{HCO}_3^-$ , which are the more permeable ions in the solution. Previous research at 25°C show that if the rejection of single ions (for instance  $\text{HCO}_3^- / \text{Cl}^-$  and  $\text{H}_2\text{AsO}_4^-$ ) is compared with mixtures, the rejection of a well rejected ion ( $\text{H}_2\text{AsO}_4^-$ ) is improved in the mixture and the rejection of the ion with the lower rejection (e.g.  $\text{HCO}_3^- / \text{Cl}^-$ ) is decreased in the mixture (Nguyen et al., 2009; Vrijenhoek and Waypa, 2000). The mechanism behind this phenomenon is electro-neutrality: the  $\text{Na}^+$  ion (counter – ion) that passes the membrane will “choose” in the mixture for an ion with a low rejection rather than the ion with a high rejection. For NF-A, this mechanism is indirectly related to temperature, as the MWCO experiments have shown NF-A pores to expand due to a temperature increase to 50°C. Consequently, more permeable ions will pass the membrane, positively affecting the rejection of As(V). Apparently (see Figure 4.4 (a) and Figure 4.5 (a)), only a threshold concentration of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  passing through the membrane was necessary to enhance the  $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$  rejection at 50°C (e.g. after 0.8 mM  $\text{Cl}^-$ , the  $\text{H}_2\text{AsO}_4^-$  rejection could be considered steady). Once this required concentration (of  $\text{HCO}_3^-$  and  $\text{Cl}^-$ ) had passed through the membrane, the  $\text{H}_2\text{AsO}_4^-$  rejection stabilized. This could be understood considering that As(V) (0.004 mM) was present in low concentrations compared with  $\text{Cl}^-$ .(0.8 to 11 mM).For NF-B a change in the pore size with temperature was not observed and the decrease in  $\text{HCO}_3^-$  rejection was not so pronounced as it was for NF-A. Therefore, for NF-B, there was no change in  $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$  rejection due to temperature increase.

As ionic concentration increased a reduction of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  rejection was observed for both NF-A and NF-B. This is commonly observed in negatively charged membranes when the ionic strength of the solution increases (Paugam et al., 2004) and could be related to diffuse double layer theory (Hunter, 1981). As ionic strength increases, the diffuse double layer is compressed, resulting in a larger concentration of negative ions close to the surface. Consequently, the rejection of anions decreases. The inverse relation between ionic strength and rejection for a negatively charged membrane has also been described for different electrolyte solutions at 25°C in earlier studies (Nyström et al., 1995; Paugam et al., 2004; Wang et al., 1997).

In summary the increase in temperature trigger a sequences of processes which could be beneficial for the rejection of As(V). The concentration of co-ions in the membrane is associated with its rejection (i.e. the higher the concentration of the co-ions in the membrane, the lower their rejection) (Peeters et al., 1998). This concentration depends on the charge and concentration of the co-ions and counterions, present in the solution, and the charge of the membrane (Peeters et al., 1998). Based on the results obtained for the zeta potential, we can assume that there was not any change in the charge of the membrane. Therefore, the concentration of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and As(V) (co-ions) in the membrane phase should be similar for both temperature (25°C and 50°C) for the same tested conditions.  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and As(V) distributed in the membrane phase are transported across the membrane layer as a result of convection, diffusion and electric field gradient (Bowen and Mukhtar, 1996). As temperature increases the weakening of the size exclusion and the increase of the diffusion transport (Brandhuber and Amy, 2001; J. Waypa et al., 1997) favors the mass transport of the less permeable anions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ), and, as a consequence of the principle of electro neutrality, As(V) is better retained in the bulk solution at higher temperatures, as here observed in membrane NF-A.

#### **4.5. Conclusions**

In this study, the effect of  $\text{Cl}^-$  concentration on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species during NF membrane filtration of high-temperature water (25°C and 50°C) containing  $\text{HCO}_3^-$  was investigated. The enhancement of As(V) as effect of temperature increase (from 25°C to 50°C) observed for all the evaluated  $\text{Cl}^-$  concentrations was not attributed to change in the zeta potential of the

membrane at higher temperatures, but was related to the presence  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , which are considerably more permeable than both As(V) species. The enlargement of the pore size and the increase of the mass transfer across the membrane due to temperature effect seems to be essential to improve the rejection of  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . Apparently, only a threshold concentration of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  passing through the membrane was necessary to enhance the  $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$  rejection at  $50^\circ\text{C}$ . This could be understood considering that As(V) (0.004 mM) was present in low concentrations compared with  $\text{Cl}^-$  (0.8 to 11 mM) and  $\text{HCO}_3^-$  (0.11 to 1mM).

#### 4.6. Acknowledgements

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## 5. Arsenic removal from geothermal influenced groundwater with low pressure NF pilot plant for drinking water production in Nicaraguan rural communities

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### Abstract

This research evaluated the effect of different fluxes (16, 23 & 30 L/m<sup>2</sup>h) and temperatures (31,35 & 43°C) on the rejection of As(V) during nanofiltration (NF) of natural geothermal influenced groundwater in Nicaragua. A NF pilot plant powered by solar panels was built and operated in rural community Telica, exposed to As-rich drinking water sources due to geothermal influences. The results showed that even at high temperatures it is possible to obtain high rejection of As(V) (0.87 ~ 0.9) during NF filtration (recovery 10%; flux 16 L/m<sup>2</sup>h) of geothermal influenced groundwater, with the additional advantage of requiring low operating pressures (1.2 bar~12mwc). The permeate concentration (~ 5 µg/L) complied with the WHO guideline for drinking water and the concentrate (~ 55 µg/L) could be used by local villagers for daily activities (e.g., laundry and bathing). For all investigated fluxes and temperatures the order of rejection of As(V) (as HAsO<sub>4</sub><sup>2-</sup>), compared with the other anions, could be interpreted on the basis of its charge, hydrated radius and hydration free energy. At lower temperatures (31 and 35°C) permeate quality improved slightly (~ 3 µg/L), but although an increased temperature had a negative effect on the As rejection, As concentrations in the permeate never exceeded 5 µg/L, while the required TMP dropped - depending on the flux - with 0.5 to 1bar. This decrease in required pressure might be of huge benefit in deserted, rural locations where electricity is scarce, as with an overhead tank of 10-15 m a gravity-fed NF system would be feasible.

## 5.1. Introduction

Arsenic (As) rich drinking water sources have been identified in Nicaraguan rural communities in a geothermally active area near the volcanic chain of “Los Maribios” (Longley, 2010). Hot, As-rich fluids flow from a geothermal zone mixed with the groundwater in the shallow alluvial aquifer causing locally variable well contamination (OPS/OMS and Nuevas-Esperanzas, 2011). The groundwater in this region has a temperature higher than 30°C with some sources that can exceed 40°C (Longley, 2010; OPS/OMS and Nuevas-Esperanzas, 2011). As-rich drinking water sources in geothermal influenced waters is likely to be dominated by charged As(V) species (Smedley and Kinniburgh, 2002).

Several arsenic removal technologies for drinking water production have been proposed for developing countries ,i.e. precipitation, adsorption and membrane filtration (Jiang, 2001; Kabir and Chowdhury, 2017). Although adsorption technologies have shown high efficiencies (90 to 100%) in As removal for drinking water production (Kabir and Chowdhury, 2017), precipitation processes (e.g. through alum or iron coagulation) are not always appropriate to produce drinking water with As concentrations below the WHO guideline of 10 µg/L (Kabir and Chowdhury, 2017). Also, precipitation and adsorption processes are pH dependent and could be influenced by co-occurring contaminants (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004). Furthermore, both processes could lead to the production of As-containing wastes (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004). Among the membrane technologies, reverse osmosis (RO) and nanofiltration (NF) show the highest efficiency (90 – 99%) in arsenic removal (J. Waypa et al., 1997; Jiang, 2001; Ng et al., 2004; Padilla and Saitua, 2010). An important advantage of membrane technology is that the efficiency removal of arsenic does not depend on the composition of the water matrix or the pH (Ng et al., 2004; Sato et al., 2002). Furthermore operated at low recovery the waste streams could be used for daily activities (e.g. laundry and bathing). The lower operational pressure of the NF (<10 bar) compared with RO (>20 bar) (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004; Padilla and Saitua, 2010; Saitúa et al., 2005) make NF systems a better choice for arsenic removal in developing countries.

Nanofiltration (NF) systems have shown to have a high efficiency (above 90%) for As(V) removal, demonstrated in experimental research at bench scale (J. Waypa et al., 1997; Padilla and Saitua, 2010; Saitúa et al., 2005) and at on-site pilot plants (Oh et al., 2000; Saitua et al., 2011). These experiments have been conducted in a range of temperatures between 10°C to 30°C and with operating pressures ranging from 2 to 7 bar. As the temperature of the water source increases, a lower energy consumption is required during nanofiltration. This feature can be of great advantage in rural areas where there is no reliable energy supply system, but where the As-rich water sources have high temperatures.

The rejection efficiency of NF mainly relies on two mechanisms: size exclusion and Donnan exclusion. Size exclusion depends on the ratio between the ion size and the pore radius of the membrane, i.e. ions with a size larger than the pore size are more likely to be rejected by the membrane. On the other hand, the Donnan exclusion refers to the reciprocal action between the surface charge of the membrane and the charge of the ions present in the bulk solution (Bowen et al., 1997). In a negatively charged membrane, the Donnan exclusion mechanism determines the distribution of the co-ions (anions; same charge as the membrane) between the bulk and the membrane phase. Moreover, the concentration of the co-ions in the membrane usually shows a direct relationship with its rejection, i.e. the higher the concentration of the co-ions in the membrane, the lower their rejection (Peeters et al., 1998). The concentration of co-ions in the membrane phase depends on variables such as the valence and concentration of the co-ions and counter-ions (cations, different charge as the membrane), present in the solution, and the charge of the membrane (Peeters et al., 1998; Schaep et al., 1998).

Thus, the properties of the bulk solution, such as ionic strength and temperature, influence the permeability of the ions through the NF membrane. Furthermore, thermodynamic and physical properties of the ions namely hydrated radius and hydration free energy (Favre-Réguillon et al., 2008; Tansel, 2012), have been pointed out to play an important role in the rejection of the ions during NF filtration. As the temperature increases (in the bulk solution), a weakening of the size exclusion mechanism occurs due to thermal expansion of the pore (Dang et al., 2014; Gonzalez et al., 2019; Sharma et al., 2003), in addition to an increase in diffusive

transport of the ions across the membrane layer (Brandhuber and Amy, 2001; J. Waypa et al., 1997), potentially leading to a lower As rejection.

Therefore, to determine the effect of the properties of geothermal influenced groundwater on As rejection, the objective of this paper is to investigate the performance of low-pressure NF membranes for various temperatures and fluxes. For this work, a NF pilot plant was built and operated in a Nicaraguan rural community exposed to As-rich drinking water sources due to geothermal influences. The NF pilot plant was operated during 6 to 7 hours per day and was powered by solar panels in order to be able to be operated in remote areas. A low recovery of 10%, was chosen to operate the NF pilot plant, producing a concentrate flow with a relatively low As content that can be used by local villagers for other daily activities (e.g. laundry and bathing.) To the best of our knowledge, pilot studies regarding the NF application for As removal in natural geothermally influenced waters have not been reported earlier.

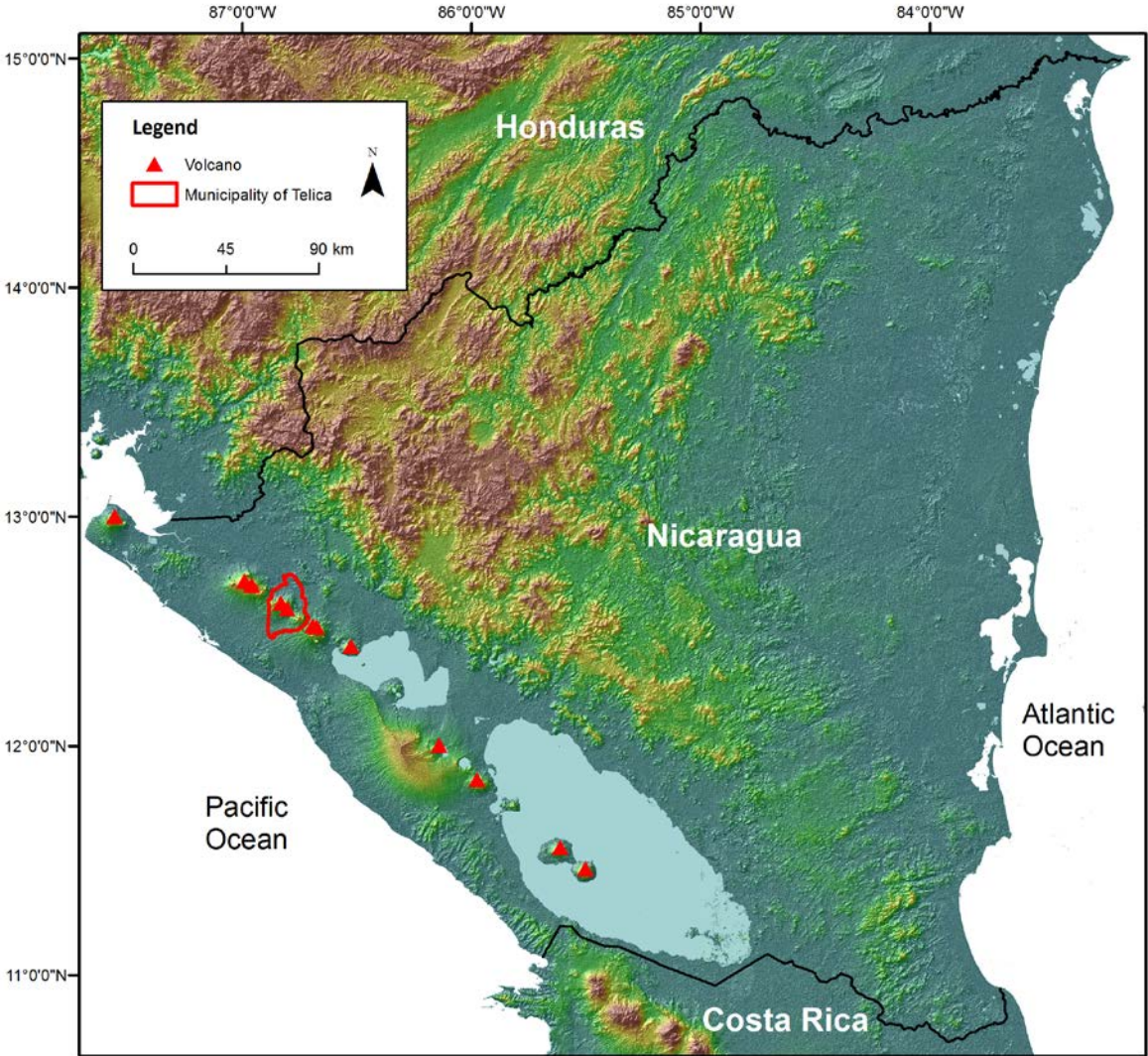
## **5.2. Material and methods**

### **5.2.1 Location**

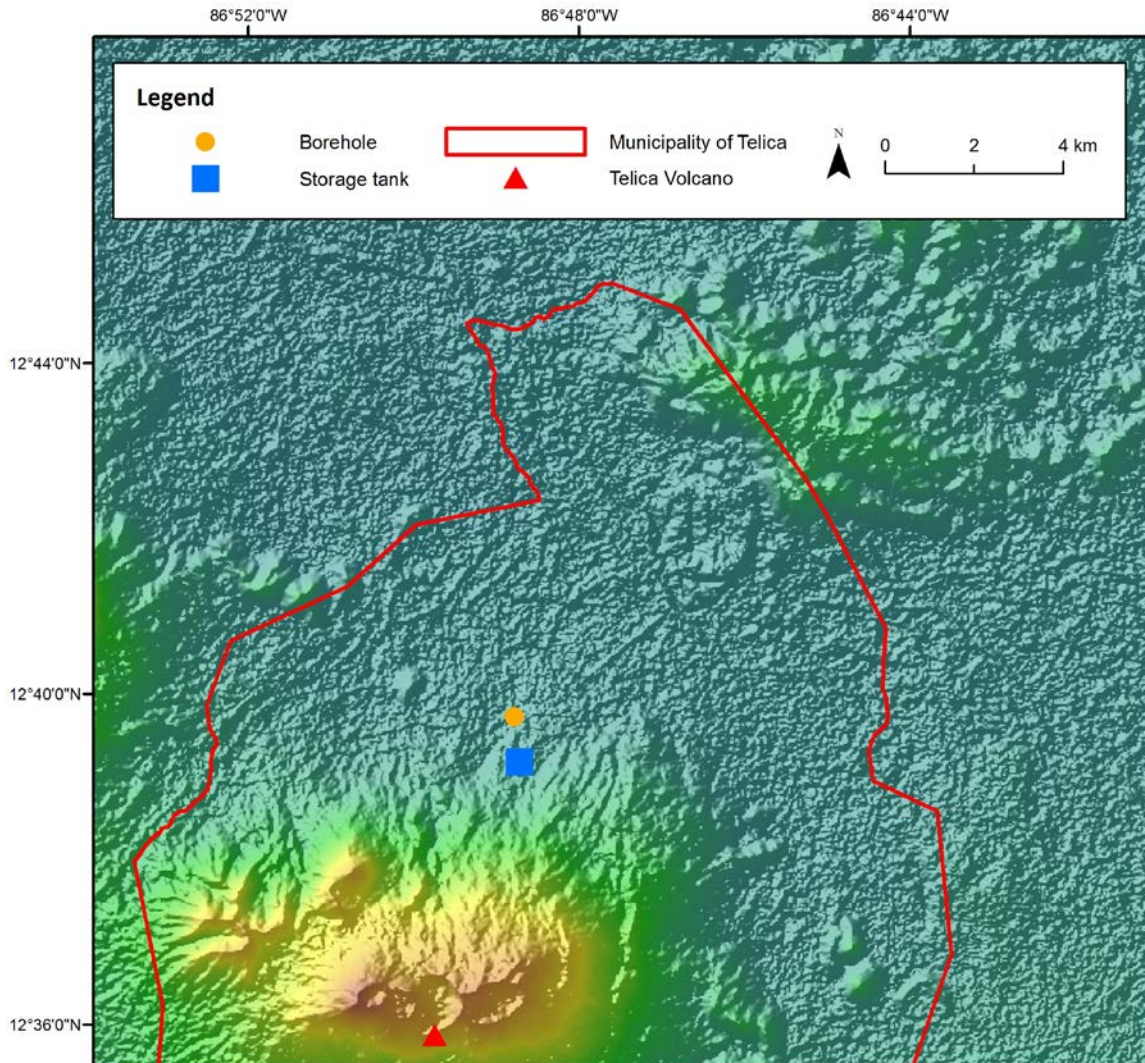
The chosen rural community is located in the western part of the country (Figure 5.1 (a)), north of the active Telica volcano (Longley, 2010). In 2007, it was discovered that well (Figure 5.1 (b)) that supplies water to this community has an arsenic (As) concentration exceeding the WHO guideline of 10  $\mu\text{g/L}$  (Longley, 2010). Since 10 years, a dual water system provides As free drinking water with communal taps through one piped system, and a second piped system supplies the As contaminated water to household connections for other household activities. Two different water sources are used and stored in different reservoirs, located in the higher part of the community. The As free drinking water system is gravity-fed starting in the surrounding mountains, but the capacity is insufficient to meet the water demand of the community and is therefore used for drinking water and cooking alone.

The As rich water is pumped from a drilled water well and As concentrations in this well range from 43 to 50  $\mu\text{g/L}$ , while temperature ranges from 43°C to 50°C. This

water is used for other household activities such as washing, cleaning and bathing; and was the water source for the pilot plant in this study.



(a)



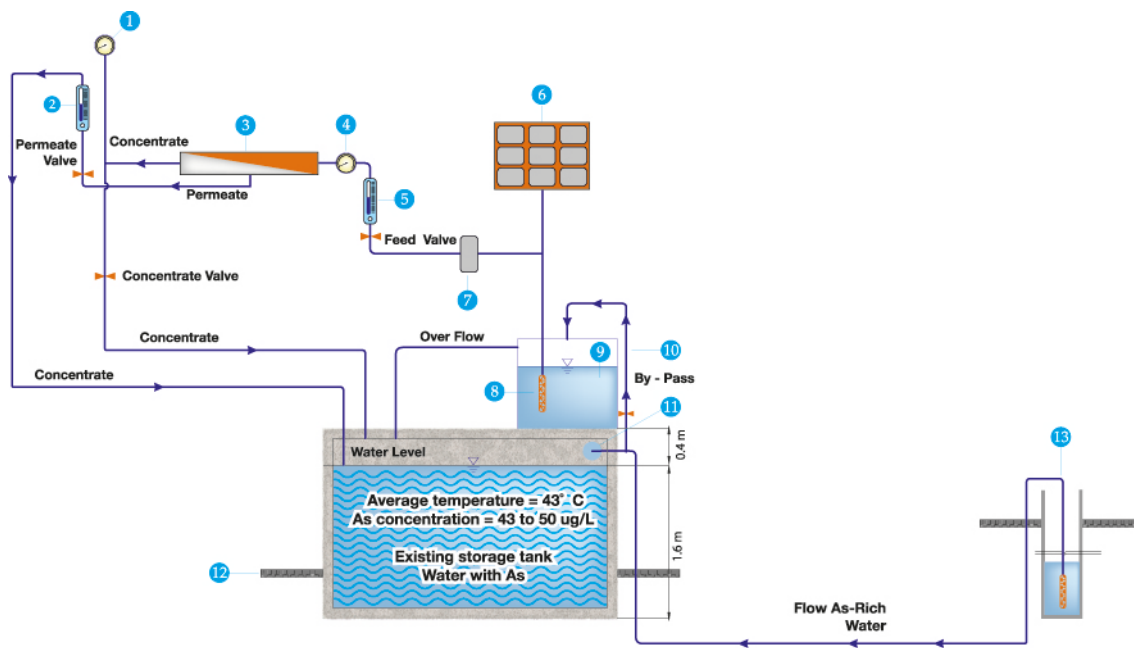
(b)

Figure 5.1 (a) Location of the municipality of Telica. (b) Location of borehole and storage tank .

### 5.2.2 NF membrane filtration pilot unit

A NF membrane filtration pilot unit powered by solar energy was built and operated on site. The NF system was installed on the roof slab of the reservoir that stores the As rich water. The storage tank (40 m<sup>3</sup>) was fed during the day with water pumped from the drilled well located one kilometer away. Consequently, this implies that there was a variation in the temperature of the stored water, as the tank was filling up during the day. The operation of the NF pilot plant was synchronized with the operational hours of the community pump. To keep the temperature constant in the

feed water of the pilot a by-pass system was installed. This system consisted of a 2 m<sup>3</sup> plastic tank (feed tank), constantly fed (pumping hours) by the main pipeline (water from the well). The plastic tank had an overflow, which allowed having a constant fresh water supply, as illustrated in Figure 5.2. The feed water was pumped into the NF system using a submersible solar pump (PS2-1800 HR-23-4, LORENTZ, Germany). The solar pump was powered by three solar panel units (TSM-260-PC, Trina Solar, USA). In order to remove solid particulate material from the feed water, a 5 µm carbon pre-filter was installed (ELGA VEOLIA) before the NF system.



**Figure 5.2** Schematic representation of NF membrane filtration pilot unit. 1. Concentrate pressure meter, 2. Permeate flow meter, 3. Permeate valve, 4. Concentrate valve, 5., 6. Feed pressure meter, 7. Feed flow meter, 8. Feed valve, 9. Solar pump, 10. Solar panels, 11. Buffer tank, 12. By-pass line, 13. Water entrance, 14. Existing As-rich well.

The flow, entering the system, was regulated manually with a feed valve and monitored with a feed flow meter (HRV-3MC). A feed flow of 0.4 m<sup>3</sup>/h was used. All the experiments were conducted with a Dow NF270 – 2540 (DOW FILMTEC™), a negatively charged NF polyamide membrane. The specifications given by the manufacturer indicate that this membrane has an active area of 2.6 m<sup>2</sup> and a maximum operating temperature of 45°C. A Wave cyber pressure vessel (Wave cyber, China) with 2.5" diameter was used to contain the membrane. The pressures in the feed, permeate, and concentrate lines were monitored with a pressure gauge

(MA-50-10-1/4, FESTO, NL). The permeate flow was controlled manually with the concentrate valve, monitoring the permeate flow meter (EK-5EA, Kytola Instruments).

### 5.2.3 NF rejection experiments

#### Overview of experiments

To investigate the effect of elevated temperatures on the performance of low-pressure NF membranes two sets of experiments were conducted. Table 5.1 provides a summary of the experimental conditions for the NF rejection experiments.

**Table 5.1** Overview of pilot plant NF rejection experiments

Experimental Settings	Average temperature	Q feed (m <sup>3</sup> /h)	Q permeate (L/min)	Flux (L/m <sup>2</sup> h)	Recovery
Operation of NF pilot plant at a constant flux and temperature	43.6°C	0.4	0.7	16	10%
Operation of NF pilot plant at different fluxes and temperatures	31°C 35°C 43°C	0.4	0.7, 1 & 1.3	16, 23 & 30	10, 15 & 20%

#### Operation of NF pilot plant at constant flux and temperature

The first set of experiments aimed to evaluate whether or not deterioration in the performance of the NF can occur during the operational run of the system. These experiments were conducted during a six weeks period; fixed flux (16 L/m<sup>2</sup>h) and a fixed temperature (43.6°C) were used. The NF pilot plant was operated during 6 to 7

hours per day. Parameters such as pressure, feed flow, permeate flow, temperature and conductivity were continuously monitored (every 1.5 hours).

Around 150 samples were collected from the feed and the permeate to measure As concentration and physical-chemical parameters. Chemical cleaning was not executed during these experiments, because there was no indication of the occurrence of either scaling or (bio)fouling.

### **Operation of NF pilot plant at different fluxes and temperatures**

The second set of experiments consisted of the evaluation of the NF filtration cycles with fixed temperatures (31,35 & 43.6°C) and varying fluxes (16,23 & 30 L/m<sup>2</sup>h). In order to investigate the effect of flux and temperature on As(V) rejection several rejection experiments with fixed temperatures and various fluxes were performed. For each of the evaluated temperatures (31,35 & 43.6°C), a series of three 2-hour runs were executed. In each run the fluxes recovery was increased (16, 23 & 30 L/m<sup>2</sup>h). For the 43.6°C experiment, source water coming from the well was directly used. For the experiments conducted at the lower temperatures, 31°C and 35°C, it was necessary to collect the water in the feed tank and close the by-pass valve, waiting for the water to cool down: one day (for 35°C) or two (for 31°C) days. For both experiments with cooled water, the permeate and the concentrate returned to the feed tank. All the experiments were performed at least twice. Samples from feed and permeate sampling points were collected every two hours and their physical-chemical parameters were subsequently measured (around 20 samples per experimental condition). Parameters such as pressure, feed and permeate flow, temperature and conductivity were continuously monitored. Chemical cleaning was not applied during these experiments.

#### **5.2.4 Analyses of samples**

Temperature, pH, ORP (oxidation reduction potential) and electrical conductivity of the feed water were measured on-site, using a multimeter (HANNA Instrument).

For the analysis of As (total), Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe (total) and some trace elements (e.g. boron), the samples from the feed, permeate, and concentrate were acidified using 150 µl of HNO<sub>3</sub> (69%) per 15 ml of sample. The concentration of these elements in the samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS Thermo – XSERIES II, Thermo Fisher Scientific) at TU Delft water laboratory. NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were analyzed in a commercial Nicaraguan water laboratory using a Dionex Dx – 100 ion chromatograph. The concentrations of HCO<sub>3</sub><sup>-</sup> were determined using a titrimetric method (702 SM Titrino, Metrohm).

For the As speciation, 200 mL of the raw water were filtered through a 100 mL syringe filled with 50 ml of Amberlite IRA-400 chloride form (anion-exchange resin). As in the raw water and the filtered water was measured using inductively coupled plasma mass spectrometry (ICP-MS Thermo – XSERIES II, Thermo Fisher Scientific) at TU Delft water laboratory. The As concentration in the raw water represents the As total, while the As concentration in the filtered water represents the concentration of As(III) (Clifford et al., 2005). The difference between these two is the concentration of As(V) in the raw water.

## **5.3. Results**

### **5.3.1 Groundwater**

In Nicaragua, the provisional guideline of the World Health Organization (WHO, 2001) has been adopted under the CAPRE normative (CAPRE, 1993)(Regional committee coordinator of potable water supply institutions and sanitation of Central America, Panamá, and Dominican Republic, 1994). Table 5.2 provides an overview of the water quality parameters of the feed water for each of the experimental temperatures. Fe concentrations were low (0.2 mg/L), NH<sub>4</sub> was not detected and ORP values were high (>100 mV), altogether indicating that the groundwater does not originate from a reduced (anoxic) aquifer. This is in-line with the measurement that As(V) is the dominant species (Clifford et al., 2005). And considering the values

of pH and ORP is likely that the As(V) is mainly present as divalent arsenate ( $\text{HAsO}_4^{2-}$ ). The presence of both fluoride and boron indicate - in combination with the elevated temperatures - that the source is geothermally influenced. Furthermore As-rich water sources influence by geothermal sources often present a positive correlation with  $\text{Cl}^-$  (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002).

**Table 5.2** Average natural groundwater composition of geothermally-influenced drinking water well

Parameter	Units	Average Values			CAPRE normative	
		43.6 °C	35 °C	31 °C	Recommended value	Maximum admissible value
pH		6.9	7.1	7.0	6.5 - 8.5	NG
ORP	mV	113.6	116.7	129.6		NG
Dissolved oxygen	mg/L	1.3	NM	NM		NG
Conductivity	$\mu\text{S} / \text{cm}$	830.0	793.3	774.0	400.0	NG
Temperature	°C	43.6	35.3	35.3	18 - 30	NG
$\text{Na}^+$	mg/L	66.2	71.0	69.9	25.0	200.0
$\text{K}^+$	mg/L	13.1	13.5	13.5	NG	10.0
$\text{Mg}^{2+}$	mg/L	14.1	14.3	13.7	7.3	12.2
$\text{Ca}^{2+}$	mg/L	61.6	62.2	60.9	40.0	NG
$\text{Cl}^-$	mg/L	134.4	138.4	122.7	25.0	250.0
$\text{HCO}_3^-$	mg/L	195.7	200.6	193.2		
$\text{SO}_4^{2-}$	mg/L	27.9	28.3	26.6	25.0	250.0
$\text{NH}_4^+$	mg/L	ND	ND	ND		0.5
Fe (total)	mg/L	0.15	NM	NM		0.3
Mn	mg/L	0.0	0.0	0.0		0.5
$\text{F}^-$	mg/L	0.4	0.4	0.4		0.7 - 1.5
Al	mg/L	0.1	0.0	0.1		0.2
Zn	mg/L	0.0	0.0	0.0		3.0
As (total)	$\mu\text{g} / \text{L}$	42.6	42.1	43.2		
As (V)	$\mu\text{g} / \text{L}$	40.0	NM	NM		10
As (III)	$\mu\text{g} / \text{L}$	2.6	NM	NM		

Cd	mg/L	0.0	0.0	0.0	0.05
Cr	mg/L	0.0	0.0	0.0	0.05
Ni	mg/L	0.0	0.0	0.0	0.05
Pb	mg/L	0.0	0.0	0.0	0.01
Sb	mg/L	0.0	0.0	0.0	0.05
Se	mg/L	0.0	0.0	0.0	0.01
B	mg/L	1.5	1.4	1.4	NG
Si	mg/L	56.0	56.5	57.0	NG
Ti	µg / L	6.4	3.7	7.1	NG
V	µg / L	41.2	40.0	41.8	NG
Li	µg / L	71.8	71.3	69.9	NG
Be	µg / L	0.0	0.0	0.0	NG
Sr	µg / L	418.5	417.6	410.9	NG
Mo	µg / L	0.9	0.9	0.9	NG
Ba	µg / L	151.4	149.9	147.0	NG
Tl	µg / L	0.1	0.1	0.1	NG

NM = Not measured

ND = Not detected

NG = No guideline

### 5.3.2 Operation of NF pilot plant at a constant flux and temperature

#### Transmembrane pressure (TMP) and ionic rejection

At a flux of 16 L/m<sup>2</sup>h and a recovery of 10%, a stable transmembrane pressure (TMP) of 1.2 bar was observed during the evaluation period (Figure 5.3), which may be considered a very low operating pressure for polymeric NF membranes. In this period the pilot plant produced an estimated 2.5m<sup>3</sup> (260 liters /day) of drinking water (permeate) and 84.5m<sup>3</sup> of washing/laundry water (concentrate). Water was produced only during the sunny day hours (6-7 hours/day), and based on daily water demand according to World Health Organisation, this would be sufficient to supply drinking water for 2 families (8 to 10 peoples). The temperature of the feed water fluctuated between 43.2 and 44.7°C. Even though operation was intermittent, it may be concluded that the pilot plant operated under stable conditions.

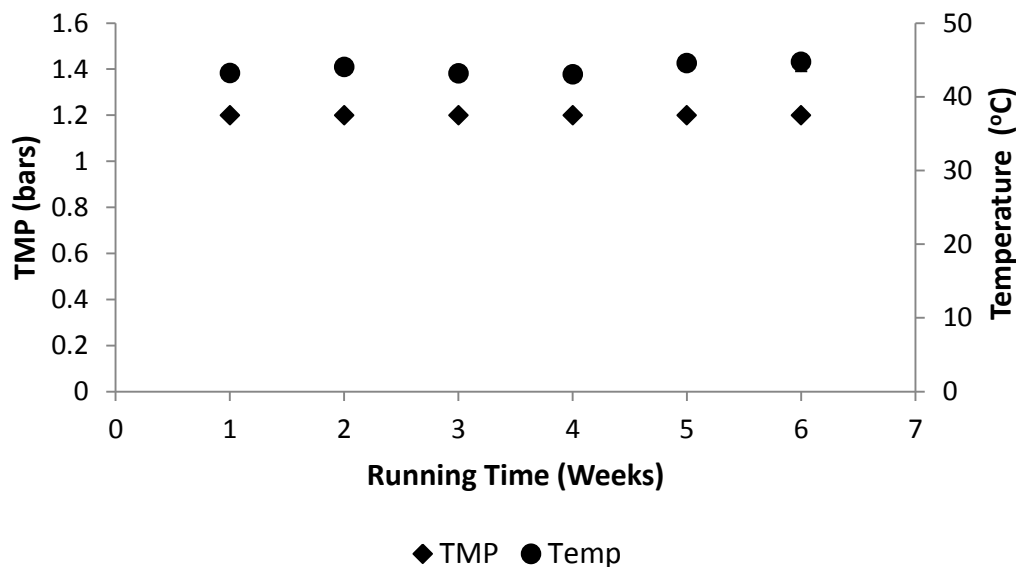


Figure 5.3 Values of TMP and temperature

### Rejection of As(V) at a constant flux and temperature

Figure 5.4 depicts (a) the As (total) rejection at a constant flux (16 L/m<sup>2</sup>h) and constant temperature (43.6°C) and (b) the concentration before (raw water) and after filtration (permeate). A steady (total) As rejection (0.87 to 0.9) was observed during the running period. The As concentration in the permeate was around 5 µg/L, which is below the WHO guideline.

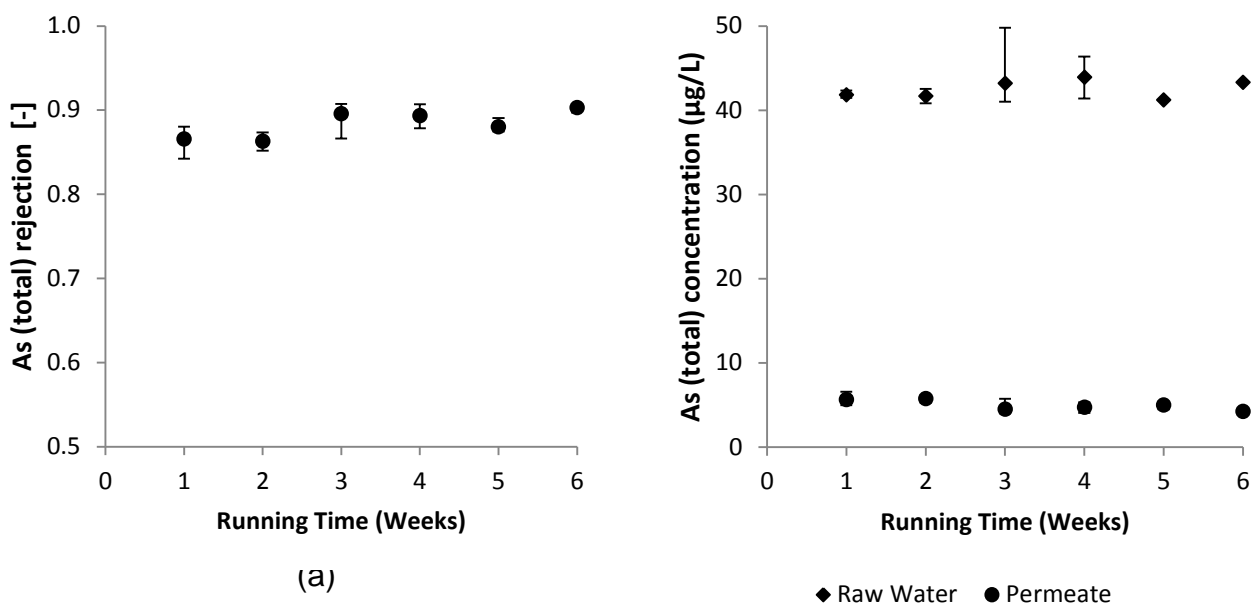


Figure 5.4 (a) As rejection and (b) As concentration in feed water and permeate for the evaluated period.

### Rejection of anion and cation at a constant flux and temperature

Figure 5.5 depicts the average rejection of different monovalent and divalent ions during NF filtration observed during the six-weeks' period. The rejection of  $\text{Cl}^-$  (0.03), a monovalent anion, was considerably lower compared to  $\text{SO}_4^{2-}$  (0.97), a divalent anion. In addition the rejection of  $\text{Na}^+$  (0.06), a monovalent cation, was also lower compared to  $\text{Mg}^{2+}$  (0.32). With the exception of  $\text{Cl}^-$  the rejection of the anions was higher compared to the rejection of the cations. The order of rejection for anions ( $\text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ ) and cations was ( $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$ ). As a consequence of rejection of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  the total hardness decreased with 30%. The  $\text{HCO}_3^-$  concentration decreased from 195 in the feed water to 149 mg/L in the permeate.

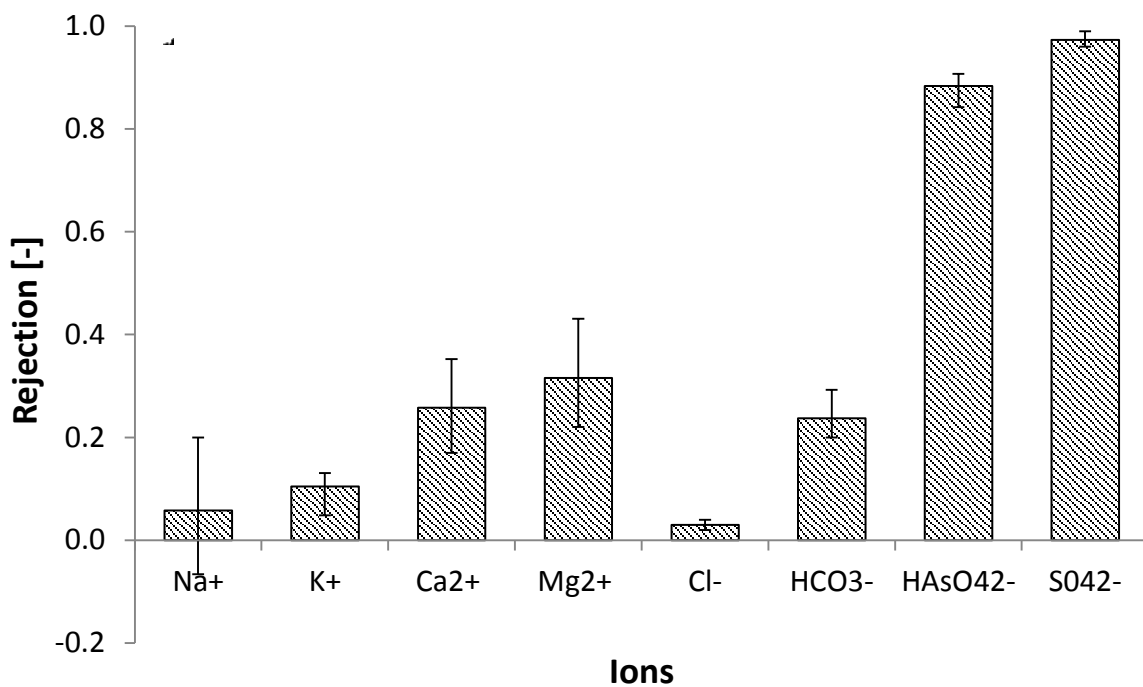
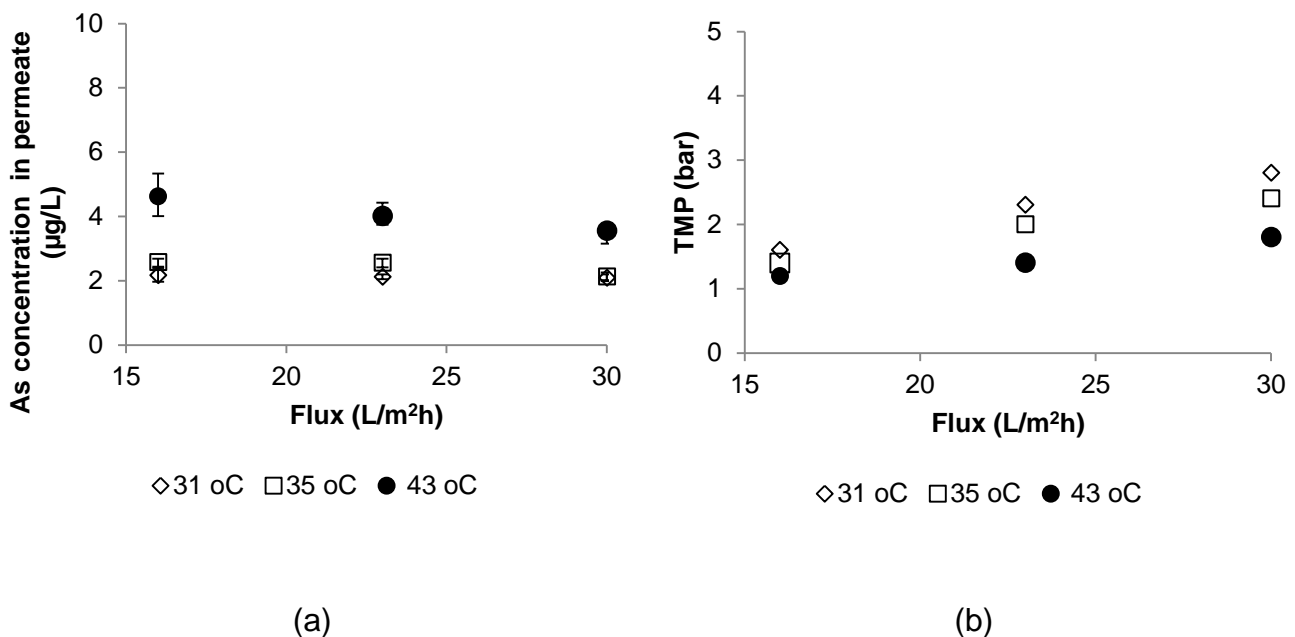


Figure 5.5 Rejection of cations and anions (including arsenic) during the experimental period

### 5.3.3 Operation of NF pilot plant at different fluxes and temperatures

#### Effect of flux and temperature on As(V) rejection

Figure 5.6 (a) depicts the As concentration in the permeate after NF filtration for various fluxes (16, 23 & 30 L/m<sup>2</sup>h) and temperatures (31,35 & 43°C). When the flux increased and temperature decreased, a slight decrease in As concentration in the permeate was observed. However, at lower temperatures as well as higher fluxes, higher operating pressures were required (Figure 5.6 (b)). The As concentration in the permeate decreased from 4.6 to 2 µg/L when the flux increased from 16 to 30 L/m<sup>2</sup>h and the water temperature decreased from 43.6 to 31°C, respectively. As a consequence the pressure increased from 1.2 to 2.8 bar (from 12 to 28 mwc).



**Figure 5.6** Effect of the flux and temperature for (a) concentration of the As(V) in the permeate and (b) TMP as function of flux and temperature.

#### Rejection of anions and cations at different flux and temperature

Table 5.3 presents the anions and cations rejection as function of flux and temperature. With the exception of SO<sub>4</sub><sup>2-</sup>, both at lower temperatures and with higher fluxes the rejection was higher. For all the evaluated fluxes and temperatures there was no variation in the rejection order for all the anions (SO<sub>4</sub><sup>2-</sup> > HAsO<sub>4</sub><sup>2-</sup> > HCO<sub>3</sub><sup>-</sup> >

Cl<sup>-</sup>). On the other hand, as temperature increases, there was a shift in the rejection order for the cations. For 31°C and 35°C ( $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ ) and for 43°C ( $Mg^{2+} > Ca^{2+} > K^+ > Na^+$ ).

**Table 5.3** Comparison of ion rejection during NF filtration for different fluxes and temperatures

Temp	Flux (L/m <sup>2</sup> h)	Ion rejection [-]							
		Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	As(V)	SO <sub>4</sub> <sup>2-</sup>
31°C	16	0.23	0.20	0.37	0.47	0.18	0.35	0.95	0.99
	23	0.28	0.26	0.44	0.54	0.20	0.46	0.95	0.99
	30	0.30	0.26	0.43	0.56	0.20	0.49	0.96	0.99
35°C	16	0.21	0.20	0.34	0.46	0.10	0.36	0.94	0.99
	23	0.21	0.22	0.37	0.46	0.12	0.42	0.94	0.99
	30	0.29	0.24	0.42	0.55	0.14	0.46	0.95	0.99
43°C	16	0.14	0.15	0.28	0.34	0.03	0.26	0.89	0.99
	23	0.14	0.17	0.29	0.38	0.04	0.31	0.91	0.99
	30	0.19	0.21	0.36	0.44	0.06	0.35	0.92	0.99

Table 5.4 presents the water quality of the permeate for the for the tested conditions. At 31°C the permeate could be considered moderately hard water (111 to 125 mg/L CaCO<sub>3</sub>). At 43°C the permeate could be recognized as hard water (130 to 150 mg/L CaCO<sub>3</sub>). Nevertheless, the values of the hardness are in agreement with the values recommended by the CAPRE normative (400 mg/L CaCO<sub>3</sub>)(CAPRE, 1993).For all the other ions the concentration are in the range recommended by the CAPRE normative, consequently there is no need for a remineralization step after NF filtration.

**Table 5.4** Concentration of the major ions in permeate for different fluxes and temperatures

		Ions concentration in permeate [mg/L]						
Temp	Flux (L/m <sup>2</sup> h)	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
31°C	16	53.8	10.7	38.4	7.3	100.0	125.2	0.4
	23	50.3	9.9	34.3	6.2	97.7	104.5	0.4
	30	48.8	10.0	34.9	6.0	98.0	99.3	0.4
35°C	16	55.8	10.9	41.2	7.8	124.7	128.8	0.4
	23	56.1	10.6	39.3	7.8	121.7	116.4	0.4
	30	50.5	10.2	36.0	6.5	118.6	109.0	0.4
43°C	16	57.0	11.1	44.3	9.3	130.4	144.5	0.4
	23	56.7	10.9	43.7	8.7	129.1	135.9	0.4
	30	53.8	10.4	39.3	8.0	126.4	126.6	0.4

## 5.4. Discussion

### 5.4.1 Operation of the NF and water quality in the permeate

At a groundwater temperature of 43°C and operating the NF pilot plant at different fluxes the system required an exceptionally low operational pressure (1.2 to 1.8 bar) and high As(V) rejection (0.89 to 0.95). Pilot studies regarding the NF application for As removal at these high temperatures have not been reported earlier, nevertheless previous studies reported similar rejection for experiments conducted in a range of temperatures between 10°C to 30°C and with operating pressures ranging from 2 to 7 bar (J. Waypa et al., 1997; Oh et al., 2000; Padilla and Saitua, 2010; Saitúa et al., 2005; Saitua et al., 2011). Also, the stability of the TMP indicates that scaling or particulate fouling did not occur in the pilot plant.

Although an increased temperature had a negative effect on the As rejection, As concentrations in the permeate never exceeded 5 µg/L, while the required TMP dropped - depending on the flux - with 0.5 to 1bar. This decrease in required pressure might be of huge benefit in deserted, rural locations where electricity is scarce. Altogether it may be concluded that during the six-week trial, the pilot plant

ran under stable conditions, even though there was only water production during daytime due to the use of a solar pump.

#### **5.4.2 Effect of ion interaction on As rejection at constant flux and temperature**

The order of rejection of  $\text{HAsO}_4^{2-}$  compared with the other anions could be interpreted on the basis of its charge and hydration free energy. Which ultimately are related to the Donnan and size exclusion mechanism respectively. E.g., the lower rejection of  $\text{HAsO}_4^{2-}$  with respect to the rejection of  $\text{SO}_4^{2-}$  observed in our results is in agreement with the order of their hydration free energy ( $\text{SO}_4^{2-} > \text{HAsO}_4^{2-}$ ). Furthermore several studies have reported similar hierarchy in rejection between  $\text{SO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$ . (Nguyen et al., 2009; Saitua et al., 2011; Vrijenhoek and Waypa, 2000).

Anions with lower charge and lower hydration free energy also present lower rejection (Saitua et al., 2011; Tansel, 2012). This could explain the higher rejection of  $\text{HAsO}_4^{2-}$  compared with  $\text{Cl}^-$  and  $\text{HCO}_3^-$  observed in this study, which are in line with the order of their charge ( $\text{HAsO}_4^{2-} > \text{HCO}_3^- = \text{Cl}^-$ ) and their hydration free energy ( $\text{HAsO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$ ). Table 5.5 shows a comparison between the rejection order and thermodynamic and physical properties of the ions, which ultimately are related with the NF rejection mechanisms.

The charge (valence) of the co-ions (anions; same charge as the membrane) could be associated with its concentration in the membrane phase (Peeters et al., 1998; Schaep et al., 1998). The concentration of the co-ions in the membrane (Donnan exclusion mechanism) usually shows a direct relationship with their rejection, i.e. the higher the concentration of the co-ions in the membrane, the lower their rejection (Peeters et al., 1998). Therefore, monovalent anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  will tend to have a lower rejection than divalent anions ( $\text{SO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$ ) as was also observed during our experiments. Furthermore, due to friction forces generated during filtration, anions with a low hydration free energy have the tendency to temporarily decrease the size of its hydrated radius due to the loss of water

molecules that surround its ionic structure (Tansel, 2012) . This characteristic allows the anions with less hydration free energy to pass through the membrane more easily (e.g., Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> compared with SO<sub>4</sub><sup>2-</sup> and HAsO<sub>4</sub><sup>2-</sup>)

The rejection of cations on a negatively charged membrane is may be slightly decreased by their charge (higher charge, less rejection, e.g., Mg<sup>2+</sup> and Ca<sup>2+</sup>), but this is a minor effect. Most important is electro neutrality for the positive ions (Peeters et al., 1998; Saitua et al., 2011; Tansel, 2012). For the differences between positive ions the radius and hydration energy is responsible, e.g., divalent cations which have higher hydration free energy and large hydration radius are better rejected than the monovalent cations (Na<sup>+</sup> and K<sup>+</sup>) as was observed during the experiments in this study.

The presented results showed that unlike the rejection of cations, the sequence of rejection of the anions does not have a strict relationship with their hydrated radius. This could be explained considering that, unlike cations, between anions there is only small variation in their hydration radius (Tansel, 2012).

**Table 5.5** Comparison between rejection order and some thermodynamic and physical properties of the ions

Parameter	Cations	Anions	Reference
Rejection order	(Mg <sup>2+</sup> > Ca <sup>2+</sup> > K <sup>+</sup> > Na <sup>+</sup> )	(SO <sub>4</sub> <sup>2-</sup> > HAsO <sub>4</sub> <sup>2-</sup> > HCO <sub>3</sub> <sup>-</sup> > Cl <sup>-</sup> )	[this study]
Charge	(Mg <sup>2+</sup> = Ca <sup>2+</sup> > K <sup>+</sup> = Na <sup>+</sup> )	(SO <sub>4</sub> <sup>2-</sup> = HAsO <sub>4</sub> <sup>2-</sup> > HCO <sub>3</sub> <sup>-</sup> = Cl <sup>-</sup> )	[-]  (Binder and Zschörnig, 2002; Stumm and Morgan, 2009)
Hydration free energy	(Mg <sup>2+</sup> > Ca <sup>2+</sup> > Na <sup>+</sup> > K <sup>+</sup> )	(SO <sub>4</sub> <sup>2-</sup> > HAsO <sub>4</sub> <sup>2-</sup> > HCO <sub>3</sub> <sup>-</sup> > Cl <sup>-</sup> )	(Nightingale, 1959; Saitua et al., 2011)
Hydrated radius	(Mg <sup>2+</sup> > Ca <sup>2+</sup> > Na <sup>+</sup> > K <sup>+</sup> )	(SO <sub>4</sub> <sup>2-</sup> > Cl <sup>-</sup> > HAsO <sub>4</sub> <sup>2-</sup> = HCO <sub>3</sub> <sup>-</sup> )	

Diffusivity of the ions in the bulk solution	$(\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Na}^+ < \text{K}^+)$	$(\text{HAsO}_4^{2-} < \text{SO}_4^{2-} < \text{HCO}_3^- < \text{Cl}^-)$	(Linde and Jönsson, 1995; Saitua et al., 2011)
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### 5.4.3 Flux and temperature effect on As(V) rejection

As flux increased the As concentration in the permeate decreased, e.g., at 43.6°C when the flux increased from 16 to 30 L/m<sup>2</sup>h the As concentration in the permeate decreased from 4.6 to 2 µg/L. The increase in As(V) rejection due to the increased flux can be ascribed to the so called “dilution effect” (J. Waypa et al., 1997) (Saitua et al., 2011). During filtration, permeate (solution) flow and As(V) (solute) flow are not totally coupled. Although the permeate flow increases, the As(V) flow remains constant. As a consequence, the As(V) concentration decreased.

The hydration-free energy keep an inverse relationship with the temperature, therefore as temperature increases, the hydration-free energy of the As(V) decreases. As a consequence, As(V) could decrease their hydrated radius more easily during filtration. This factor in combination with the thermal expansion of the membrane pores (Dang et al., 2014; Sharma et al., 2003), and the increase of the diffusive transport of the ions across the membrane layer (Brandhuber and Amy, 2001; J. Waypa et al., 1997) could be associated with the decrease of the As(V) rejection when temperature increase, as is observed during the experiments in this study, varying temperature and flux.

### 5.4.4 Gravity-driven NF for As mitigation in rural Nicaragua

The results showed that also at high temperatures it is possible to obtain high rejection of As(V) (0.87 ~ 0.9) during NF filtration of geothermal influenced groundwater, with the additional advantage of requiring low operating pressures (1.2 bar~12mwc). The research was executed with a solar pump, however, at the current pilot plant location with 43°C, a gravity driven system could be a viable option as well.

A 12 meter overhead tank would suffice for reaching the required pressure to operate a gravity-fed NF system, and would as such not require a pump, nor electricity to be operated. In the case of a temperature drop to 31°C one would require an additional 5-12 m of elevation head, so when designing a gravity-fed NF system it is therefore important to prevent loss of heat (e.g., due to long-term storage or pipelines without isolation). Having said this, the gravity-fed NF system might then not require a pump, depending on the local geohydrological situation it might still be necessary to install a groundwater pump for abstraction. Based on the presented research a gravity-fed NF system for As removal from high temperature source waters is feasible at low pressures and is therefore particularly interesting in regions with natural elevations, like the volcanic zones in Nicaragua.

## **5.5. Conclusions**

At a groundwater temperature of 43°C the NF pilot plant in rural Nicaragua could be operated under stable conditions of low recovery (10%) and low pressure (1.2 bar ~12mwc). In these conditions, the permeate of the NF system (~ 5 µg/L) complied with the WHO guideline for drinking water and the concentrate (~ 55 µg/L) could be used by local villagers for daily activities (e.g. washing and bathing.) For the same temperature and with an increase in operating pressure it is possible to run the NF system at higher fluxes and obtained a slight increase in the quality of the permeate. For a proper assessment of the effect of temperature in the life time of the membrane, the frequency of chemical cleanings and the effect of various fluxes and temperatures it would be necessary to investigate operation of the pilot plant for a longer period of time.

For all investigated fluxes and temperatures the order of rejection of As(V) (as  $\text{HAsO}_4^{2-}$ ), compared with the other anions, could be interpreted on the basis of its charge, hydrated radius and hydration free energy. Altogether this study has illustrated that, although polymeric NF membranes have the image to be too expensive, high in maintenance and energy-demanding for low-income countries, NF membranes can be a sustainable barrier for As(V) in rural Nicaragua – specially at high water temperatures.

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## **6. Conclusions and outlook**

### **6.1. Conclusions**

This study presented an overview of the current stage of knowledge of arsenic (As) occurrence and mobilization mechanisms in Nicaragua based on literature review, as well as the interpretation of unpublished information from different institutions and sources. In addition, laboratory and pilot scale experiments were conducted in order to gain more knowledge about the influence of co-occurring ions, ionic strength, water matrix composition and operational parameters during nanofiltration of synthetic and natural geothermal influenced water for As removal. Finally, the use of nanofiltration membranes for As free drinking water production was studied in a rural Nicaraguan community exposed to geothermally influenced water.

Overall, it was found that As has been released into groundwater sources, either directly from geothermal influences or indirectly by reductive dissolution or alkali desorption. Furthermore, it was demonstrated that low-pressure NF membranes can be an effective barrier for As(V) in rural Nicaragua, especially at high water temperatures.

#### **6.1.1 Arsenic occurrence and mobilization mechanisms**

The studies conducted in Nicaragua during the last two decades show an agreement on the geogenic origin of the As contamination in at least 80 rural communities distributed over 34 municipalities. The identified, affected communities are located in the Central and Pacific regions, which belong to the Tertiary volcanic province and to the Depression of Graben (where the active volcanism is concentrated), respectively. Therefore, the source of As contamination in the reported areas is likely to be of volcanic origin (both from volcanic rocks and geothermal fluids). However, As monitoring has been conducted in only 23.5% of the municipalities.

Direct geothermal influences have been reported in some municipalities of Nicaragua Pacific (western part), where volcanic activity is concentrated (consisting of active

and inactive volcanoes). Reductive dissolution could be responsible for As enrichment of reducing groundwater sources in e.g. the municipality of Telica. The water characteristics found in Larreynaga municipality (western part) with the co-occurrence of As and Vanadium, and other trace elements, such as Selenium, Molybdenum, Boron, could indicate alkali desorption as As mobilization mechanism. In six of the mentioned rural communities As poisoning has been responsible for a broad spectrum of skin and pulmonary diseases. Nevertheless, at present, there is no clear oversight of the extension of arsenic contamination and exposed population in Nicaragua.

### **6.1.2 The influence of co-ions on the rejection of As(V) during nanofiltration of high-temperature waters**

Previous lab – scale experiments reported that at 25°C the presence of anions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  could improve the As(V) rejection during nanofiltration. The results described in this thesis suggest that this phenomenon is also temperature dependent, improving the rejection (up to 10%) of As(V) at higher temperatures (50°C). This phenomenon was found to occur for two commercially available NF polyamide membranes (Dow NF270 and Alfa Laval NF) during nanofiltration of a solution containing  $\text{Cl}^-$  (0.6 mM),  $\text{HCO}_3^-$  (0.11 to 1 mM) and As(V) (0.004 mM / 300  $\mu\text{g/L}$ ). As temperature increased (from 25 to 50°C) Dow NF270 rejection increased from 0.87 (25°C) up to 0.97 and 0.93 for mono and divalent As(V),  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ , respectively, at 50°C. As an effect of temperature increase, Alfa Laval NF enhanced the rejection of monovalent (from 0.8 to 0.86) and divalent (from 0.91 up to 0.97) As(V) species. Additionally, an increase of 39% (from 231 Da to 322 Da) and 20% (from 217 Da to 260 Da) in molecular weight cut-off (MWCO) was observed for Dow NF270 and Alfa Laval NF, respectively, as a result of temperature increase (from 25°C to 50°C). However, the results also showed that this phenomenon can vary between different batches (NF-A and NF-B) of the same membrane (Dow NF270). During nanofiltration of a solution containing  $\text{Cl}^-$  (0 to 11 mM),  $\text{HCO}_3^-$  (0.11 to 1 mM) and As(V) (0.004 mM / 300  $\mu\text{g/L}$ ). It was observed that for NF-A, as  $\text{Cl}^-$

concentration increased a higher As(V) rejection (up to 6%) was achieved at 50°C, compared with the rejection obtained at 25°C. On the other hand, this effect was not observed for NF-B, whose rejection of As(V) was similar at 25°C and 50°C. An increase of 25% in MWCO (from 256 Da to 323 Da) was observed for NF-A, which is in agreement with earlier studies and could be attributed to the thermal expansion of the polyamide layer. However, no increase in MWCO was observed for NF-B. At 25°C the MWCO of NF-B (311 Da) was larger than NF-A but as temperature increased to 50°C the MWCO of NF-A became larger than NF-B.

It was found that that the enhancement of As(V) at higher temperatures could not be attributed to changes in the zeta potential of the membrane but mainly to the presence and enhanced mobility of  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , which are considerably more permeable than As(V) species. The enlargement of the pore size and the increase of the mass transfer across the membrane due to the temperature effect thus seemed to be essential to improve the rejection of As(V).

### **6.1.3 The role of operational parameters on As(V) rejection during nanofiltration of geothermal influenced groundwater.**

The influence of operating conditions such as flux (16, 23 & 30 L/m<sup>2</sup>h) and temperature (31 ,35 & 43°C) on the As(V) rejection during pilot-scale nanofiltration of geothermally influenced groundwater in Nicaragua has also been described. The results showed that the optimal flux was 16 L/m<sup>2</sup>h with a recovery of 10%. For a groundwater temperature of 43°C and the mentioned flux, low operational pressure (1.2 bar~12mwc) and a high efficiency (0.87 ~ 0.9) on As(V) rejection was obtained. Furthermore, the quality of the permeate was in agreement with the WHO guideline for drinking water (< 10 µg/L ) and the concentrate (~ 55 µg/L) could be used by local villagers for daily activities (e.g., laundry and bathing).

Considering the low operational pressure and the topography, a gravity-fed NF system for As removal from high temperature source waters was found to be possible.

## 6.2. Outlook

The research presented in this thesis has opened a number of research lines that should be investigated in the future. For instance, a gravity-fed NF system for As (V) removal from high temperature sources appears an effective system for water production in rural volcanic regions. Because its low operating pressures (1.2 bar~12mwc) and high efficiency (0.87 ~ 0.9). Nevertheless, an extended follow-up study is recommended to study e.g. long term effects of temperature on membrane life time, the frequency of chemical cleanings, including the scalability of the pilot plant, used in the described study, and the adoption of the technology in the local Nicaraguan setting, including operation and maintenance and cost recovery. Furthermore, it is necessary to establish for which raw water composition NF can be an effective barrier as a single step treatment for geothermally influenced waters. For example in this type of water Boron can co-occur with As, and, at neutral pH (=7), Boron is mainly found as the uncharged species boric acid. NF has poor rejection of these Boron species, and therefore, if the Boron concentration exceeds 2.4 mg/L (threshold value given by WHO), an additional treatment step should be added (e.g. increasing the pH above 9.2 in order to convert the uncharged boric acid to the negatively charged borate ion). Additionally, for areas where As(III) is present in the water sources, As(III) should be (biologically) oxidised before NF, since As(III) rejection is poor (0.2 ~ 0.6). Therefore, the feasibility and the efficiency of a hybrid system (As(III) biological oxidation – NF) for high temperature waters need to be investigated.

Furthermore, the enhancement of As(V) rejection as a result of temperature increase, found during the lab scale experiments was not replicable during the pilot plant experiments. Therefore, the follow-up research question arises if the difference in behavior between both experiments was an effect of the water matrix composition (e.g. As concentration, presence of other anions) of the natural groundwater. Alternatively a comparison between NF and other As water treatment technologies (e.g. rapid sand filters) should be investigated. This comparison should not only consider the efficiency of the systems but also their acceptability.

Finally, considering that the levels of knowledge on As occurrence, mobilization mechanisms, As speciation and mitigation strategies are far behind of the required

level to provide As-free drinking water to the affected Nicaraguan rural communities, a nationwide As sampling campaign should be executed before being able to start an As mitigation programme. This nationwide sampling campaign should be conducted in two stages:

(1) identification of the As-affected areas. These assessments could be conducted using Arsenic test kits (e.g. Wagtech Arsenator Digital Arsenic Test Kit), providing low cost analyses with enough accuracy to identify As-rich water sources. (2) conduction of physico-chemical analyses in those areas. This will allow the identification of the dominant As species and the presence of co-occurring contaminants. This will aid in the selection of appropriate technologies for arsenic removal (e.g. one single step treatment system for arsenic removal or the use of hybrid systems to remove arsenic in combination with other contaminants) or alternative mitigation strategies (e.g. change of water source).



## 7. Summary

Among the natural contaminants that we can find in water, arsenic (As) is the most carcinogenic substance. The World Health Organization has recommended a provisional concentration of arsenic in drinking water not exceeding 10 µg As /L. Long-term intake of water with high concentrations of As can cause the development of Arsenicosis (arsenic poisoning). Nicaragua's concern about As presence in water sources and its influence on human health began in 1996, when the first documented case of As poisoning in a rural community was reported. In this community, 125 people were found with the characteristic skin lesions of chronic Arsenicosis, after ingesting water from a public well with a As concentration of 132 times the permissible level. According to a study published by UNICEF, in 2004 around 60,000 people were consuming water with high As concentrations, while living in small scattered rural communities or small towns. The number of people who are currently ingesting water with As in rural communities in Nicaragua is unknown. Furthermore, in spite of the awareness of the presence of As in drinking water sources, so far, there is not much practical experience with the use of As removal systems. In 2011 an NGO called Nuevas Esperanzas conducted a study (Action Against Arsenic) for the World Health Organization and determined that around two thousand people have been drinking water contaminated with arsenic for the past two decades in the municipality of Telica (western part of the country). In this region the drinking water sources are influenced by the geothermal fields of the Telica volcano, and used by rural communities. The arsenic concentration in this area ranges between 50 to 900 µg/l and the average temperature is about 34°C. Polyamide negatively-charge nanofiltration (NF) systems have consistently demonstrated a high efficiency for the removal of As(V) from water with ambient temperatures, and it is known from industrial applications that NF is capable of treating water at temperatures up to 65°C. Therefore, the use of nanofiltration (NF) for As removal in rural areas of Nicaragua was studied, where drinking water sources are high in temperature due to geothermal influence. The research methodology consists of three components: (1) review of As occurrence and mobilization mechanisms in Nicaragua, with an emphasis on non peer-reviewed data sources at local institutions, (2) experimental research conducted at the water laboratory of TU Delft, (3) NF pilot plant research in

a Nicaraguan rural community exposed to As-rich drinking water sources due to geothermally influences.

The studies conducted in the last two decades (1996 – 2015) show an agreement on the geogenic origin of the As contamination in Nicaragua. Volcanic rocks and geothermal fluids which are distributed across the country are likely to be the main source of As contamination in drinking water. Depending on the local geochemical conditions, As may have directly entered into the groundwater by geothermally-influenced water bodies, or indirectly by reductive dissolution or alkali desorption. The As contamination has been reported in 80 rural communities, located in 34 municipalities of the country. Arsenicosis has been identified in at least six of those communities.

The lab-scale experiments were conducted in two stages, using a flat-sheet cross-flow module and constant As(V) concentration, in the feed water, of 300 µg/L (0.004mM). For the first stage two commercially available NF polyamide membranes were used (Dow NF270 and Alfa Laval NF). During the experiments of the first stage the effect of high temperatures (25-50°C), as found in geothermally influenced source waters, on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  species (at pH 6, 7 and 8) in a multi-component solution containing  $\text{Cl}^-$  (0.6mM) and  $\text{HCO}_3^-$  (0.11 to 1mM) was studied. As rejection by Dow NF270 increased from 87% (25°C) up to 97% and 93% for mono and divalent As(V), respectively, at 50°C. As rejection by Alfa Laval was enhanced from 80 to 86% for monovalent and from 91 to 97% for divalent As(V) species, respectively, as a result of temperature increase. These results were in contrast to previous studies, conducted with deionized water, where it was found that temperature increase had a negative effect on As(V) rejection. However, the enhancement of As(V) rejection at high temperature in our study was associated with the presence of  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , which are considerably more permeable than both As(V) species.

During the second stage of the lab-scale experiments two different batches (NF-A and NF-B) of Dow NF270 were used. These experiments assessed the effect of co-ions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) and increasing  $\text{Cl}^-$  concentrations on the rejection of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$  As(V) species during NF membrane filtration of high-

temperature water (25°C and 50°C). The rejection of As(V) differed from one batch to another. For NF-A, as Cl<sup>-</sup> concentration increased a higher difference in As(V) rejection (up to 6%) was achieved at 50°C, compared with the rejection obtained at 25°C. The improvement of As(V) rejection due to temperature increase implied that the permeate concentration was reduced from approximately 30 µg/L (at 25°C) to 15 µg/L (at 50°C). However, this effect was not observed for NF-B, whose rejection of As(V) was similar at 25°C and 50°C. The enhancement of As(V) rejection with NF-A at higher temperatures was not attributed to variation in the charge of the membrane (the zeta potential was constant), but to the enlargement of the pore size (MWCO increased) and, as a result, the increase of the mass transfer of Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> across the membrane.

The last component of the thesis consisted of a NF pilot plant, powered by solar panels, that was built and operated in a rural community in Nicaragua, exposed to As-rich drinking water sources due to geothermal influences. The effect of operational parameters such as different fluxes (16, 23 & 30 L/m<sup>2</sup>h) and temperatures (31, 35 & 43°C) on the rejection of As(V) during nanofiltration (NF) of natural geothermal influenced groundwater in Nicaragua were investigated. The results showed that even at high temperatures it was possible to obtain high rejection of As(V) (87-90%) during NF (at recovery of 10% and flux of 16 L/m<sup>2</sup>h) of geothermal influenced groundwater, with the additional advantage of requiring low operating pressures (1.2 bar~12mwc). The permeate concentration (~ 5 µg/L) complied with the WHO guideline for drinking water and the concentrate (~ 55 µg/L) could be used by local villagers for daily activities (e.g., laundry and bathing). For all investigated fluxes and temperatures, the order of rejection of As(V) (as HAsO<sub>4</sub><sup>2-</sup>), compared with the other anions, could be interpreted on the basis of its charge, hydrated radius and hydration free energy. At lower temperatures (31 and 35°C) permeate quality improved slightly (~ 3 µg/L), but, although an increased temperature had a negative effect on the As rejection (contrary to the results obtained from the lab-scale experiments), As concentrations in the permeate never exceeded 5 µg/L, while the required transmembrane pressure (TMP) dropped - depending on the flux – from 0.5 to 1bar. This decrease in required pressure might be of huge benefit at isolated, rural locations, where electricity is scarce.

Altogether this study has illustrated that NF membranes can be an effective barrier for As(V) in rural Nicaragua – also at high water temperatures.

## 8. Samenvatting

Van de natuurlijke verontreinigingen die we in water aantreffen, is arseen (As) de meest kankerverwekkende stof. De World Health Organization (WHO) heeft een voorlopige maximale concentratie van 10 µg As /L in drinkwater aanbevolen. Langdurige inname van water met hoge arseenconcentraties kan de ontwikkeling van arsenicose (arseenvergiftiging) veroorzaken. De bezorgdheid van Nicaragua over de aanwezigheid van As in drinkwaterbronnen en de invloed ervan op de menselijke gezondheid ontstond in 1996, toen voor het eerst een geval van arseenvergiftiging in een plattelandsgemeenschap werd gemeld. In deze gemeenschap werden 125 mensen aangetroffen met de kenmerkende huidafwijkingen van chronische arsenicose, nadat zij water hadden ingenomen uit een openbare bron met een As-concentratie van 132 keer het toegestane niveau. Volgens een door UNICEF gepubliceerde studie consumeerden in 2004 ongeveer 60.000 mensen water met hoge As-concentraties. Deze mensen woonden verspreid op het platteland of in kleine steden. Het aantal inwoners dat momenteel met arseen besmet drinkwater gebruikt op het platteland in Nicaragua is onbekend. Daarbij komt dat er ondanks het besef van de aanwezigheid van arseen in drinkwaterbronnen tot op heden niet veel praktische ervaring is met het gebruik van As-verwijderingssystemen. In 2011 voerde een ngo genaamd Nuevas Esperanzas een onderzoek (Action Against Arsenic) uit voor de World Health Organization waarin vastgesteld werd dat in de afgelopen twee decennia ongeveer tweeduizend mensen in de gemeente Telica (in het westen van het land) met arseen besmet water hebben gedronken. In deze regio worden de drinkwaterbronnen beïnvloed door de geothermische velden van de Telica-vulkaan en gebruikt door plattelandsgemeenschappen. De arseenconcentratie in dit gebied varieert van 50 tot 900 µg/L en de gemiddelde temperatuur is ongeveer 34°C. Negatief geladen polyamide nanofiltratiesystemen hebben consequent een hoog rendement aangetoond voor de verwijdering van As(V) uit water met hoge omgevingstemperaturen en uit industriële toepassingen is bekend dat nanofiltratie (NF) in staat is water te behandelen bij temperaturen tot 65°C. In deze thesis is daarom het gebruik van NF voor de verwijdering van arseen op het platteland van Nicaragua onderzocht, waar drinkwaterbronnen een hoge temperatuur hebben door geothermische invloeden. De onderzoeksmethodologie bestaat uit drie

componenten: (1) een overzicht van het voorkomen van arseen en mobilisatiemechanismen van arseen in Nicaragua, met de nadruk op informatiebronnen (non-collegiaal getoetst) bij lokale instellingen, (2) experimenteel onderzoek uitgevoerd in het waterlaboratorium van de TU Delft, (3) onderzoek met behulp van een NF-pilotinstallatie in een Nicaraguaanse plattelandsgemeenschap die blootgesteld is aan arseenrijke drinkwaterbronnen als gevolg van geothermische invloeden.

De studies die in de afgelopen twintig jaar (1996 – 2015) zijn verschenen zijn het eens over de vermoedelijke geogene oorsprong van de arseenbesmetting in Nicaragua. Vulkanische rotsen die over het hele land zijn verspreid vormen samen met de geothermische grondwaterstromen waarschijnlijk de belangrijkste bron van arseenbesmetting in drinkwater. Arseen kan rechtstreeks in het grondwater terecht zijn gekomen door geothermisch beïnvloede waterlichamen of indirect via het reductief oplossen ervan of door alkalische desorptie, afhankelijk van de lokale geochemische omstandigheden. Arseenbesmetting is gemeld in 80 plattelandsgemeenschappen, verspreid over 34 gemeenten van het land. Arseenvergiftiging is geconstateerd in ten minste zes van die gemeenschappen.

De laboratoriumexperimenten zijn in twee fasen uitgevoerd met behulp van een 'flat-sheet cross-flow module' en een constante As-concentratie in het inkomende water van 300 µg/L (0.004mM). Voor de eerste fase werden twee commercieel verkrijgbare polyamide NF-membranen gebruikt (Dow NF270 en Alfa Laval NF). Tijdens de experimenten van de eerste fase werd het effect van hoge temperaturen (25-50°C), zoals aangetroffen in geothermisch beïnvloede waterbronnen, op de afstoting van monovalente  $\text{H}_2\text{AsO}_4^-$ - en divalente  $\text{HAsO}_4^{2-}$ -complexen (bij pH 6, 7 en 8) bestudeerd in een oplossing met  $\text{Cl}^-$  (0.6mM) en  $\text{HCO}_3^-$  (0.11 tot 1mM). As-afstoting door Dow NF270 steeg van 87% (bij 25°C) tot 97% en 93% respectievelijk voor mono- en divalent As(V) bij 50°C. As-afstoting door Alfa Laval werd verhoogd van 80% naar 86% voor monovalente en van 91% naar 97% voor divalente As(V)-soorten als gevolg van temperatuurstijging. Deze resultaten vormen een contrast met eerdere studies die zijn uitgevoerd met gedeïoniseerd water, waarbij gevonden werd dat temperatuurstijging een negatief effect heeft op As(V)-afstoting. De verbetering van As(V)-afstoting bij hoge temperaturen in ons onderzoek wordt echter geassocieerd

met de aanwezigheid van  $\text{HCO}_3^-$  en  $\text{Cl}^-$ , die aanzienlijk meer doorlatend zijn dan beide As(V)-complexen.

Tijdens de tweede fase van de laboratoriumexperimenten werden twee verschillende partijen (NF-A en NF-B) van Dow NF270 gebruikt. In deze experimenten werden de effecten van  $\text{Cl}^-$  en  $\text{HCO}_3^-$ -ionen en toenemende  $\text{Cl}^-$ -concentraties op de afstoting van  $\text{H}_2\text{AsO}_4^-$  en  $\text{HAsO}_4^{2-}$  tijdens membraanfiltratie bij hoge watertemperaturen ( $25^\circ\text{C}$  en  $50^\circ\text{C}$ ) onderzocht. De afstoting van As(V) verschilde van de ene partij tot de andere. Bij NF-A werd er bij toenemende  $\text{Cl}^-$ -concentraties een hogere As(V)-afstoting bereikt (tot 6% meer) bij  $50^\circ\text{C}$ , vergeleken met de afstoting bij  $25^\circ\text{C}$ . De verbetering van As(V)-afstoting als gevolg van temperatuurstijging wordt bewezen door de verlaging in permeaatconcentratie van ongeveer  $30 \mu\text{g/L}$  (bij  $25^\circ\text{C}$ ) tot  $15 \mu\text{g/L}$  (bij  $50^\circ\text{C}$ ). Dit effect werd echter niet waargenomen voor NF-B, waarvan de afstoting van As(V) vergelijkbaar was bij  $25^\circ\text{C}$  en  $50^\circ\text{C}$ . De versterkte As(V)-afstoting bij NF-A wordt niet toegeschreven aan variatie in de lading van het membraan (het zetapotential was constant), maar aan de vergroting van de poriegrootte (MWCO nam toe) en als gevolg daarvan de toename van de massaoverdracht van  $\text{Cl}^-$  en  $\text{HCO}_3^-$  over het membraan.

Het laatste onderdeel van het onderzoek bestond uit een door zonnepanelen aangedreven NF-pilotinstallatie, gebouwd en getest in een plattelandsgemeenschap in Nicaragua die wordt blootgesteld aan arseenrijke drinkwaterbronnen. In het veld werden de effecten van operationele parameters zoals verschillende fluxen ( $16, 23$  &  $30 \text{ L/m}^2\text{h}$ ) en temperaturen ( $31, 35$  &  $43^\circ\text{C}$ ) op de afstoting van As(V) tijdens nanofiltratie van natuurlijk grondwater in Nicaragua bestudeerd. De resultaten laten zien dat het zelfs bij hoge temperaturen mogelijk is om een hoge afstoting van As(V) (87-90%) te verkrijgen tijdens NF (bij een 'recovery' van 10% en een flux van  $16 \text{ L/m}^2\text{h}$ ) van geothermisch beïnvloed grondwater, met het bijkomende voordeel dat slechts lage drukken ( $1.2 \text{ bar} \sim 12 \text{ mwk}$ ) nodig zijn. De permeaatconcentratie ( $\sim 5 \mu\text{g/L}$ ) voldoet aan de WHO-richtlijnen en het concentraat ( $\sim 55 \mu\text{g/L}$ ) kan door lokale bewoners gebruikt worden voor dagelijkse activiteiten als wassen en baden. Voor alle onderzochte fluxen en temperaturen kon de volgorde van As(V)-afstoting (als  $\text{HAsO}_4^{2-}$ ) vergeleken met de andere anionen, geïnterpreteerd worden op basis van de lading, gehydrateerde straal en vrije hydratatie-energie. Bij lagere temperaturen

(31 en 35°C) verbeterde de permeaatkwaliteit enigszins (~ 3 µg/L), maar hoewel een verhoogde temperatuur een negatief effect had op de As-afstoting (in tegenstelling tot de resultaten verkregen uit het laboratoriumonderzoek), overschreed de arseenconcentratie in het permeaat de 5 µg/L nooit, terwijl de benodigde transmembraandruk daalde – afhankelijk van de flux – van 0.5 tot 1 bar. Deze afname in vereiste druk kan een groot voordeel zijn voor geïsoleerde, landelijke locaties, waar elektriciteit schaars is. Al met al heeft dit onderzoek aangetoond dat NF-membranen een effectieve barrière kunnen vormen voor As(V) op het platteland van Nicaragua – ook bij hoge watertemperaturen.

## 9. CV

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2014–2018	PhD at Delft University of Technology
2010–2012	MSc. Municipal Water and Infrastructure at IHE Delft
1996–2000	Bsc Civil Engineering at National University of Engineering, Nicaragua

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2014 – 2019	Phd researcher	Delft University of Technology
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2012 – 2014	Construction Supervisor	GES Latin America
2005 – 2010	Process Engineer	Environmental Technology
2004-2005	Draughtsman	Purification Technology

## 10. Publications

**B. Gonzalez Rodriguez**, L.C. Rietveld, A.J. Longley ,D. van Halem. “Arsenic contamination of rural community wells in Nicaragua: a review of two decades of experience”. *Science of the Total Environment* 2019; 657: 1441-1449.

**Bayardo Gonzalez**, S.G.J. Heijman, L.C. Rietveld, D. van Halem. “As(V) rejection by NF membranes from high temperature sources for drinking water production”. *Groundwater for Sustainable Development* 2019; 8: 198-204.

**Bayardo Gonzalez**, S.G.J. Heijman, L.C. Rietveld, D. van Halem. “Arsenic removal from geothermal influenced groundwater with low pressure NF pilot plant for drinking water production in Nicaraguan rural communities”. *Science of the Total Environment* 2019 ; 667 : 297-305.

**Bayardo Gonzalez**, S.G.J. Heijman, R. Shang, L.C. Rietveld, D. van Halem. “The effect of co-ions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) and increasing  $\text{Cl}^-$  concentrations on the rejection of As(V) in high temperature water (25°C and 50°C) using nanofiltration membranes”. This article will be submitted for publication.

## 11. Acknowledgements

Supe por primera vez de la problemática de la contaminación de arsénico en fuentes de agua en Nicaragua en el 2010. En esa época me refirieron la historia de una comunidad rural donde encontraron altas concentraciones de arsénico en su pozo comunal. Las autoridades correspondiente anunciaron que clausurarían el pozo. Sin una fuente alterna de agua y sin un sistema de tratamiento para remover arsénico de su única fuente de agua disponible, los pobladores propusieron a las autoridades un trato insólito , la comunidad estaba dispuesto a firmar un documento legal donde hacían constar que asumían las consecuencias de consumir el agua contaminada siempre y cuando no les cerraran el pozo comunal. Esta historia es el génesis de esta investigación en la que he trabajado por los últimos cinco años.

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