# Organic Micropollutant Removal by a Nanofiltration Pilot Plant used to Treat Spring Water from a Wastewater-Irrigated Valley

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**Abstract:** The abundance of freshwater springs in the *Tula Valley* is well documented. Large quantities of untreated wastewater from Mexico City are used for irrigation purposes, with the resultant emerging springs. Studies are needed to assess how safe water is to be supplied to the community. Comparative membrane studies were done on lab-scale, from which NF270 membrane was selected for a pilot plant *in situ* (critical flux 185Lm$^{-2}$h$^{-1}$). The system was successful at removing natural organic matter, hardness and pathogenic content. On-site membrane pretreatment using microfiltration and softening allowed moderate recoveries (60%) and slow permeate flux losses (124-90Lm$^{-2}$h$^{-1}$). Micropollutant (MP) removal was greater than 90% for most of the pharmaceuticals, hormones and phthalates using spiked spring water. However, moderate and variable removals were found when the concentrations of MPs were very low. Molecular structure and hydrophobicity were loosely related to the removal rates of the compounds evaluated, however an accumulating effect on the membrane might be key for higher MP removals. A threshold of concentration could have to be overcome to allow the removal process to achieve a better performance. In consequence, optimization of a large-scale process is the next step to take.

**Keywords:** Nanofiltration, Organic micropollutants, Pathogens removal, Potabilization, Spring water.

## 1. INTRODUCTION

Located 90 km north of Mexico City, the *Tula Valley* receives more than 50m$^3$s$^{-1}$ of wastewater that has been reused for agricultural irrigation without treatment for more than 100 years [1], however the ignorance of the water characteristics, and of its contents point directly to the human health security, and also for the own ecosystem. The use of this wastewater has resulted in significant effects on the soil and crop production of the region, because most of the untreated residual water is used to supply irrigation surfaces, usually with the presence of compounds related. This behavior is showing a gradual increase related with growth. In 1926 were reported 14,000 ha, while 2010 were reached 83,000 ha, equivalent to a doubling rate of irrigation surface every 25 years. In addition soil infiltration rates of 25m$^3$s$^{-1}$ [1], leading over time to the appearance of springs that are used today as fresh water sources by local communities [1]. In the future, this spring water may be used to supply Mexico City increasing demand originated as a consequence of overexploitation of local aquifer. However, currently there are concerns over the safety of using it as a local water supply source. Due to the high concentration of several organic compounds present in the irrigation wastewater [2], the persistence of different organic micropollutants in the springs is seen as an issue, together with the potential impacts on the environment and human health [3-5]. In the case of the Tula spring water, variable concentrations of such compounds have already been found both in surface- and ground-water [1, 2].

Although the content of many micropollutants (MPs) in drinking water has not been regulated, there is a common understanding regarding the need to remove them. This has led to evaluate membrane systems for the organic MPs removal. Studies of wastewater treatment processes using ultrafiltration (UF) membranes have demonstrated their low capacity for removing various MPs unless an additional process (such as a biological type) is associated with them [6-8]. Both reverse osmosis (RO) and nanofiltration (NF) have proven to be significantly effective for the removal of MPs [9-11], but there is usually a variable outcome. Removal percentages change depending on the membrane and the characteristics of the water to be treated. Besides simple filtration, depending on average pore diameter, membrane removal mechanisms include the retention of pollutants based on surface charge interactions and sorption phenomena [12, 13]. Given that even RO membranes (with the smallest pore diameter between 1-5nm) have not always achieved complete retention of diverse MPs, defining the filtration rate and detection threshold of such compounds for a particular system is crucial to establish the effectiveness of the membrane process.

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Several bench-scale studies concerning membrane capabilities have been conducted [14, 15, 6, 16-18] but only few pilot plant or large-scale operations have been described in terms of MPs removal [19-22]. Moreover, changes in configuration from bench-scale systems to larger ones might not yield the same outcomes in terms of operational flux from $3.96e^{-6}ms^{-1}$ to $5.87e^{-6}ms^{-1}$, pressures from 57kPa to135 kPa and maintenance needs.

The Tula Valley, given its long history of wastewater irrigation, faces the challenge in the near future of supply the local population with safe water originating from springs containing MPs. As a consequence, feasible process options are required to achieve it. In this work we focused on the capabilities of three NF membranes to remove MPs, starting with a lab-scale system, and scaling up to an on-site pilot plant in order to determine the MPs and conventional contamination removal, as well as operating conditions over time. A commercial membrane size was identified as a starting point prior to large-scale operation.

## 2. MATERIALS AND METHODS

### 2.1. Lab-Scale Experimental

Initial lab-scale experiments were performed to establish the membrane retention capability of selected organic MPs. An Osmonics® SEPA CF testing unit for flat sheet membranes and spiked spring water was utilized for this purpose. Given the significant hardness of the water as well as its variable natural organic content, prior microfiltration and a chemical softening step were needed to prevent the test membrane from clogging and fouling. The softening chemical doses were optimized (results not shown) and carried out by adding $800mgL^{-1}$ of calcium hydroxide ($Ca(OH)_2$) and $390mgL^{-1}$ of sodium carbonate ($Na_2CO_3$), together with subsequent 0.45μm filtration and pH adjustment to 7.0. The spiked quantities of MPs are presented in Table **1** in the results and discussion section.

Three different flat sheet NF membranes were tested: Dow-filmtec NF90 and NF270, and ESNA1-LF from Nitto Denko Hydranautics. The lab-scale comparison determined MPs removal capability as well as critical flux rates (Table **1**). These were conducted by applying the method developed by Espinasse *et al.* [23], varying operating pressures onto the membrane and measuring the effect on the permeate flux. In all cases, the membrane had an effective transport area of $137cm^2$. The average molecular weight cut off of NF90 and ESNA1 was 200Da, and 170-200Da for NF270. All of the membranes utilised had a manufacturer's reported operating tolerance of T<45°C, $P_{max}$= 600psi and pH 2-11, except for ESNA1 with a pH range of 3-10 units. Temperature was kept for all of the runs at 20°C and pressure was properly controlled.

### 2.2. Experimental Pilot Plant

Based on lab-scale flux results, the 4in diameter spiral wound NF270 membrane (size 4040) was selected to scale up the process and be tested *in situ* at the *Cerro Colorado* spring in the *Tula Valley*. The pilot plant consisted of a membrane unit with a stainless steel cylindrical housing built to fit the 4040 spiral membrane. The effective transfer area was $7.6m^2$. Besides the pumping equipment, the process consisted of two pretreatment stages: a low-pressure microfiltration unit with four layers of polypropylene

**Table 1: Characteristics of Experimental Membranes**

| Manufacturer | Model | Material | Application | MWC (Da) | Flux/Pression ($Lm^{-2}h^{-1}$)/ (MPa) | Free Chlorine Tolerance (ppm) | Retentate % (Species, $mgL^{-1}$) |
|---|---|---|---|---|---|---|---|
| **DOW-FILMTEC** | NF270 | Polyamide Thin-Film composite | TOC removal | 200 | 62.61/0.48<br>53.27/0.48 | < 0.1 | 40-60<br>($CaCl_2$, 500)<br>>97<br>($MgSO_4$, 2000) |
| **DOW-FILMTEC** | NF90 | | Organic compounds removal | 200 | 31.98/0.48<br>40.54/0.48 | < 0.1 | 85-95<br>(NaCl, 2000)<br>>97<br>($MgSO_4$, 2000) |
| **NITTO-HYDRANAUTICS** | ESNA1- LF | | ND | ND | ND | < 0.1 | 89<br>($CaCl_2$ ) |

ND= Not determined; MWC: Molecular weight cut off;

(100–20μm) to reduce natural organic matter content, and a softening stage prior to the membrane inlet (Figure **2**). The softening system was an automatic dual ion exchange unit with resin autoregeneration utilizing NaCl brine solution and 30,000 resin grains in each softening tank. The dual tank guaranteed a non-stop softening operation throughout more than 750 hours of pilot plant study.

The average flow inlet for the pilot plant was 25±1Lmin$^{-1}$ and was kept constant throughout the entire study. This was achieved using a 1.5hp centrifuge pump with the intake positioned in the spring and a jet pump after the softening process to create extra pressure across the membrane. The retentate/permeate ratio depended on the operating pressure and the degree of fouling, but no cleaning aeration or chemical treatment was applied to the membrane during the entire field operation. System variables were followed on-site with suitable manometer and flowmeter instumentation as well as permeate pH and TDS sensors.

### 2.3. Analytical Techniques

For the lab-scale experiments, samples of the inlet water and membrane permeate were taken. For the pilot plant process, the sampling points were raw spring water, the stream immediately after the microfiltration and softening stage, the membrane retentate, and the membrane permeate. Samples were taken and transported in icepacks to the laboratory for determination of physicochemical parameters (TDS and total hardness) and 14 MPs content. TDS and chemical oxygen demand (COD) were measured using *Standard Methods* [24] numbers 2540 C, 2340 C and 5220 C, respectively. Conductivity and pH were determined using an in-line multiparameter testing equipment OAKTON PC 450 referred on Figure **1**.

Microbiological content analysis was carried out in triplicate with a total of eight organisms determined for each sample. These included bacteriophages, faecal coliforms, *Enterococcus faecalis*, *Salmonella* spp., spores of *Clostridium perfringens*, *cysts* of *Giardia* spp., oocysts of *Cryptosporidium* spp., and helminth eggs. Analytical techniques were those described in the *Standard Methods* [24], unless otherwise indicated: *Clostridium perfringens* (spores) using the UK National standard method [25]; bacteriophages with the dual layer method ISO 10705 with *E. coli* WG5 [26]; *Giardia* spp. and *Cryptosporidium* spp. with the epifluorescence method 1623 [27,24]; and helminth eggs with the US E.P.A. method [28]. For all biological methods the limit of detection was zero organisms (or not detected) except for helminth eggs which was defined as 0.2eggL$^{-1}$ with a recovery efficiency of 82% [29].

For MPs, previously filtered triplicate samples were stabilized at pH 2 and then passed through OASIS HLB cartridges (Waters, USA). Subsequently, MP concentrations were determined using the methodology developed by Gibson *et al*. [30]. The MPs studied in this work were selected as a heterogenic group in terms of source (plasticizers, hormones, metabolites, pharmaceuticals and surfactants), and in terms of their

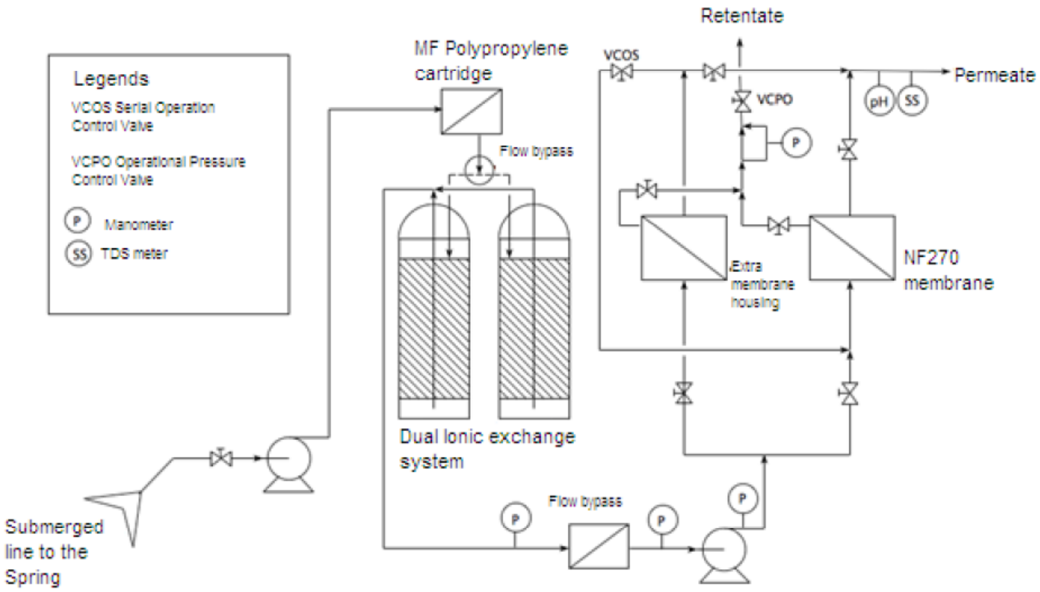

**Figure 1:** Operational diagram of the pilot plant installed at *Cerro Colorado* spring.

physicochemical properties. The studied compounds were: Bisphenol-A (BPA), used commonly in manufacture of plastic bottles, Bis-2-Ethyl-Hexyl-Phthalate (DEHP), employed in flexible PVC articles, and Butyl-Benzyl-Phthalate (BBP), commonly related with production of vinyl foams. Also, Carbamazepine (CBZ), known as an anticonvulsant or an anti-epileptic drug, Gemfibrozil (GFZ), a drug used to lower lipid levels, also Diclofenac (DCF), Ibufpofen (IBU) and Naproxen (NPX), all of them as non-steroidal anti-inflammatory drugs, then, Estrone (E1) and 17β-Estradiol (E2), known as sex hormones. By other hand Salicylic acid (ASL), used most commonly to help remove the outer layer of the skin, and as raw material of acetylsalicylic acid. Finally Nonylphenols (NPS), commonly used in manufacturing oxidants, lubricating oil additives, laundry and dish detergents, and Triclosan (TCS), an antibacterial and antifungal agent found in some consumer products, including toothpaste and soaps. The MPs measurements were made on a HP6890 gas chromatograph coupled to a HP5-MS fused silica column (30mX0.25mm, 0.25mm film thickness) tandem HP5973 mass selective detector. Single ion monitoring (SIM) was used for quantitative analysis.

Clofibric acid (100ng), $[^2H_4]$4-*n*-Nonylphenol (100ng) and $[^2H_4]$ DEHP (100ng) were used as internal quantification determined by a certified laboratory using techniques and procedures referred in APHA, (1995). All of the MPs studied and the derivatization agents (MTBSTFA with 1% *tert*-butyldimethylsilylchlorane and BSTFA with 1% trimethylsilylchloride) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All solvents were HPLC grade from Burdick and Jackson (Morristown, NJ, USA). Deuterated estrogens, $[^2H_4]$estrone, $[^2H_4]$17β-estradiol were obtained from Cambridge Isotopes (Andover, MA, USA).

## 3. RESULTS AND DISCUSSION

### 3.1. Lab Scale Experimental

A comparative performance assessment of membranes ESNA1, NF90 and NF270 was carried out using the flat sheet lab-scale equipment. The high concentrations of calcium (245±12.2mg$CaCO_3L^{-1}$) and magnesium hardness (98±9.7mg$CaCO_3L^{-1}$) in the water, made prior chemical softening treatment necessary in order to reduce membrane scaling by salt deposition. The critical flux values obtained were 75±2.2$Lm^{-2}h^{-1}$, 68±0.4$Lm^{-2}h^{-1}$ and 185±5.3$Lm^{-2}h^{-1}$, with pressure ranges of 65.3±18.9psi, 91.4±20.3psi and 81.3±24.7psi for the ESNA1, NF90 and NF270 membranes, respectively.

Subsequent experiments were conducted with the same flat sheet test equipment to determine MPs removal. The compounds included in this study are listed in the previous section along with their acronyms. Given the variable and low concentrations of these compounds in the spring water [1, 2], it was spiked with additional concentrations (Table **2**) of each MP to better observe removal capabilities. The concentrations in the water were kept well above the limit of detection (LOD) of the relevant analytical technique [30]. The added concentrations were selected to be approximately 10% of the average concentration of the compounds in the raw wastewater of Mexico City.

**Table 2**: **MP Concentrations in the Raw Spring Water, Experimentally Spiked Spring Water, and LOD of the Analytical Technique for Each Compound**

| Compound | Raw spring water Concentration ($ngL^{-1}$) | Added Concentration ($ngL^{-1}$) | Limit of Detection (LOD)* |
|---|---|---|---|
| BPA | 55±5 | 200 | 0.5 |
| DEHP | 87±7 | 700 | 0.5 |
| BBP | 20±4 | 170 | 0.5 |
| CBZ | <LOD | 280 | 0.05 |
| DCF | 97±2 | 300 | 1 |
| E1 | <LOD | 5 | 0.005 |
| E2 | <LOD | 5 | 0.005 |
| GFZ | <LOD | 10 | 0.5 |
| IBU | 86±5 | 300 | 0.25 |
| NPX | 49±7 | 1100 | 0.25 |
| NPS | 21±3 | 2200 | 40 |
| SLC | <LOD | 5000 | 0.25 |
| TCS | 4±0.9 | 120 | 0.1 |

*by Gibson *et al.* (2007)

The MPs removal experiments yielded slight differences among the tested membranes for most of the compounds determined (Figure **2**). Pharmaceuticals were successfully removed by over 80% in general. However, with the exception of TCS, a lower performance was identified for the ESNA1 membrane, especially for CBZ. GFZ and hormones (E1 and E2) were poorly removed by the three tested membranes. BPA as well as phthalates (BBP and DEHP) and the mixture of nonylphenols (NPS) were removed highly successfully.

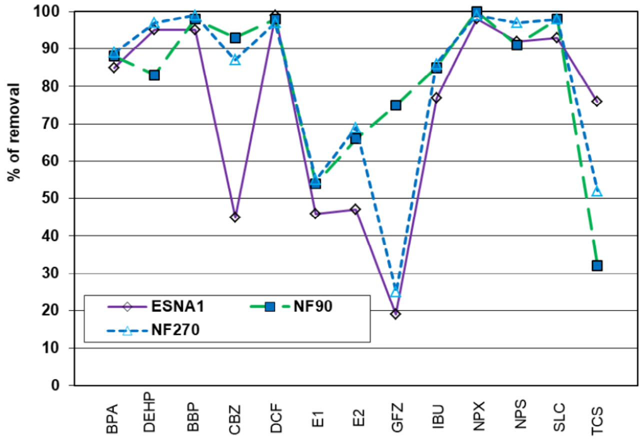

**Figure 2:** Comparative MPs removals from spiked spring water using flat sheet membranes ESNA1, NF90, and NF270 at lab-scale.

No clear relationship was identified for any of the MPs between their removal percentage and molecular hydrophobicity or the functional groups present on the molecule. However, poor removal of TCS and E2 could be related to the short time period of the lab-scale experiments. In consequence these conditions did not allow an accumulation over the membrane that could lead to steric effect retention into the pores [15, 31]; it is noticeable that the lowest removals were obtained for those MPs with the lowest feed concentrations (TCS, GMZ and hormones). According to some previous studies with hormones and other MPs, saturation equilibrium of the MPs onto the membrane was established before constant removal efficiency was obtained [31, 17]. Therefore, apparently, the removal of many compounds depends on accumulation in order to reach the aforementioned equilibrium. A threshold concentration is obtained in the membrane permeate even when such equilibrium has been reached [31]. Thus, if the concentration of the compound to be removed is too low, saturation of the membrane might not be reached, leading to variable retention effectiveness.

Though removal rates were similar for the three membranes, NF270 was selected to be used at pilot plant scale mainly because of the higher critical flux obtained at lab-scale, which was expected to allow a wider operational flux range.

## 3.2. Pilot Plant Performance with Spiked Spring Water

The NF270 membrane pilot plant was assembled and its operational effectiveness evaluated before it was transported and installed *in situ* (at *Cerro Colorado* spring, as mentioned previously). Hydraulic tests with tap water were made to determine pressure/flow ratios (Figure **3**), with the minimal operational pressure of the equipment set at 60psi, obtaining a recovery fraction of 0.29. At 120psi, permeate fraction recovery was 0.51, and at 180psi it was 0.85. However, although a high recovery was desirable, possible limitations were identified regarding the critical flux obtained at flat sheet lab-scale. Thus, optimization of the prior softening step was needed to ensure minimal scaling and maximum operating pressure, and a minimum of 50% of permeate was sought so the operating pressure had to be kept between 120 and 180psi.

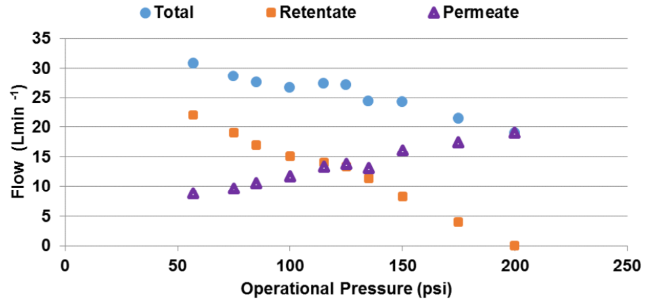

**Figure 3:** Operational pressure and flow capability of the pilot plant using a NF270 4040 membrane module at 20°C.

Spring water softening for the pilot plant evaluation was made using chemical hardness precipitation. Doses of 800mg $Ca(OH)_2L^{-1}$ and 390mg$Na_2CO_3L^{-1}$ were used to reduce hardness to a total value below 100mg $CaCO_3L^{-1}$. Hardness precipitation and filtration with 0.45μm were applied to the water. With this softening procedure, raw spring water calcium hardness was reduced from an average of 607mg$CaCO_3L^{-1}$ to 108±2.5mg$CaCO_3L^{-1}$, and magnesium hardness from 74.9mg $CaCO_3L^{-1}$ to 24.7±0.7mg $CaCO_3L^{-1}$. During the softening step, conductivity increased from 1372±143μ$Scm^{-1}$ to 1826±1.5μ$Scm^{-1}$.

Afterwards, short-term experimental runs were conducted in which softened spring water was spiked to determine MPs removal capability. Raw spring water had higher concentrations of some MPs than those in the flat sheet test, in part due to the variable behavior of the MPs in the spring water. However, concentrations were found to be considerably lower (Table **3**) than those in the wastewater that enters the valley daily and recharges its aquifer. This confirms that the crop irrigation and soil barrier is fairly effective at removing most of the MPs, with only trace quantities remaining in the springs. Phthalate concentrations were the exception, with values above 1000ng$L^{-1}$ in the raw spring water.

**Table 3: MPs Content in Raw and Spiked Spring Water and its Removal by the NF270 Membrane at Pilot Plant Scale**

| Compound | Raw Spring Water ($ngL^{-1}$) | Softened / Doped Spring Water ($ngL^{-1}$) | NF270 Permeate ($ngL^{-1}$) | % Removal | $P_{ow}$* |
|---|---|---|---|---|---|
| BPA | 1004±60 | 10825±2006 | 2554±292 | 76 | 3.32 |
| DEHP | 2008±1330 | 3587±0 | 277±213 | 92 | 9.64 |
| BBP | 77±0 | 20422±627 | <LOD | 100 | 4.77 |
| CBZ | <LOD | 1087±52 | <LOD | 100 | 2.45 |
| DCF | <LOD | 926±94 | 12±0 | 99 | 4.51 |
| E1 | <LOD | 115±75 | <LOD | 100 | 4.15 |
| E2 | <LOD | 59±7 | <LOD | 100 | 3.94 |
| GFZ | 3.4±0.8 | 9.6±2.6 | 7.7±3.5 | 19 | 4.77 |
| IBU | 2.4±1.1 | 366±10 | 5.6±2.2 | 98 | 3.97 |
| NPX | 13±4 | 2153±31 | 24±11 | 98 | 0.22 |
| NPS | 163±4 | 899±42 | 135±7 | 85 | 5.76 |
| SLC | 11±1.2 | 4214±179 | 378±94 | 91 | 2.26 |
| TCS | 218±139 | 1185±12 | 235±21 | 80 | 4.7 |

*a[32], b[22], c[14], d[15], e[18], f[33].

Spiking the samples helped to better determine the membrane effectiveness and over 90% of most of the MPs were removed. As expected from the previous flat sheet tests, very high rates of removal of pharmaceuticals (CBZ, DCF, IBU and NPX) were obtained with the exception of GFZ for which even in spiked water very low concentrations were detected in the feed stream. SLC was significantly high in the spiked water but the removal only reached 91%.

It is important to point out that some of these compounds might be effectively removed not only because of pore size exclusion, but also by surface interactions and membrane saturation as described previously. It is known that surface interaction and even degradation potential are enhanced when a biofilm is present between the stream and the filtering membrane [34]. In the case of the spring water, the bacterial content is minimal as will be shown, so there is little chance of obtaining a biofilm that might result in greater retention capability. Thus, with regard to removal, direct interaction between the membrane and the MPs becomes the most significant cause of removal.

SLC had a moderately high removal of 91%. Its molecular size, adsorption capability onto the membrane and its concentration levels may have played a role in its removal. Pharmaceuticals (CBZ, DCF, IBU and NPX) were much better removed having slightly higher molecular sizes.

TCS, BPA and NPS displayed moderately high removals, while phthalates and hormones were significantly removed. DEHP had a permeate concentration of 277ngL$^{-1}$ that could be considered as it's a passing-through concentration when higher feed quantities are present. Regarding the octanol/water partition coefficients (*$P_{ow}$,* Table **2**), large hydrophobic molecules with many rings and/or branches are as likely to be removed as hydrophilic molecules like pharmaceuticals, as long as sufficient saturation concentrations are reached. Once again higher concentrations might result in higher removal potential, because of an accumulating effect of such compounds onto the membrane. For example, hormone (E1 and E2) removals were found to be better at higher concentrations for the pilot plant than for the flat sheet lab module. Similar results were found for TCS. 50% of an inlet concentration of 120ngL$^{-1}$ was removed by the flat sheet module, while 80% of a concentration ten times higher was removed by the pilot plant, leaving more than 200ngL$^{-1}$ in the permeate. GFZ had the lowest removals, and also the lowest concentrations in both experimental stages. Thus, concentrations in water, especially where a biofilm is absent, could determine a removal potential given the complex interaction with the membrane and among the different molecules that are intended to pass or not pass through the membrane pores. This observation is confirmed by the saturation results presented for hormones in previous work [31, 17]. These spiked spring water studies helped to confirm the removal capabilities of the NF270 membrane for MPs, but it appears that the concentration thresholds present an issue which must be considered to achieve successful treatment. Following this off-site operational test the pilot plant was moved to field operation.

### 3.3. In Situ Pilot Plant Operation

The pilot membrane was installed at *Cerro Colorado* spring in the *Tula Valley*. Given the presence of algae and natural organic matter in the spring water, a microfiltration step was installed between the inlet pump and the softening step, as shown in Figure **1**. For practical operational reasons, the softening process in the field was not driven by chemical precipitation with lime. A continuous resin exchange system was preferred as described in the methodology section. The pilot plant was operated for approximately 750 hours to evaluate permeate quality and operational constraints as a first indication of future large-scale feasibility. The softening process was initially tuned according to the inlet pump supply, and then critical flux tests were carried out for the membrane module to determine operational conditions. A pressure range of 50psi to 200psi was applied over intervals of 3 to 6 hours, yielding flux values between $54Lm^{-2}h^{-1}$ and $111Lm^{-2}h^{-1}$, with no clear critical limit of operational flux or pressure, possibly because operation was continuously below the critical flux obtained in the lab-scale tests on the spring water ($185Lm^{-2}h^{-1} = 5.13x10^{-5}ms^{-1}$). This was attributed to the previous microfiltration and softening steps, which created effective barriers to particulate matter and resulted in hardness reduction. Considering the likely low concentrations of MPs in the spring water, a moderate membrane feed pressure of 170psi was selected with a 60% recovery as standard, maintaining a constant inlet flow of $25Lmin^{-1}$.

Conventional performance parameters are comparatively similar in terms of the mean estimated throughout the entire operation; therefore the obtained values are showed in Table **4**. Organic matter content was determined as COD, with significantly high values ($33mgL^{-1}$) in the spring water, and no reduction after the softening step; however, the NF process was able to decrease COD by 84%. pH was practically constant with only a slight reduction in the permeate stream due to partial demineralization, as evidenced by decreases in conductivity and TDS. Partial conductivity removal was expected, as shown in previous study [18], and it was seen as a beneficial attribute of the process, perhaps rendering the re-mineralization of the permeate stream unnecessary.

Total hardness was effectively reduced by the softening system, but a high standard deviation was obtained for the softening outlet and the retentate stream, given some efficiency fluctuations recorded along the operation stream (Table **4**). At the same time, this proved the hardness removal capability of the membrane because permeate values remained constant despite such variations.

The feed flow remained practically constant through the operation (Figure **4A**), while recovery slowly reduced from an initial value of 60% to almost 45% at the end of more than 700 hours of treatment. Initial flow of retentate increased and slightly overtook the permeate flow values as the membrane worked continuously without any interim maintenance. The maximum permeate flux obtained under operational conditions was $124Lm^{-2}\ h^{-1} = 3.44x10^{-5}ms^{-1}$, and was slowly decreased to a minimum registered value of $90Lm^{-2}h^{-1} = 2.52x10^{-5}ms^{-1}$ after more than 700 hours (Figure **4B**). These results showed that for the specific case of the Tula spring water, suitable pretreatment makes a continuous cleaning strategy for the membrane unnecessary, at least for the first 200 hours of operation, when moderate pressure and recovery are maintained. Nevertheless, for a permanent large-scale system, higher pressures and recoveries have to be sought to optimize the process; thus, a cleaning and maintenance strategy might be helpful to obtain similar

**Table 4: Physicochemical Parameters Estimated Along the Operation of the NF270 Membrane**

| | **Raw Spring Water (mean + SD)** | **Softened Spring Water (mean + SD)** | **Permeate (mean + SD)** | **Retentate (mean + SD)** |
|---|---|---|---|---|
| pH | 7.34±0.34 | 7.26±0.07 | 6.91±0.18 | 7.43±0.13 |
| Conductivity ($\mu Scm^{-1}$) | 1372±304 | 1283±153 | 497±131 | 2240±555 |
| TDS ($mgL^{-1}$) | 1083±62 | 1110±93 | 458±81 | 3887±1786 |
| Total Hardness ($mgCaCO_3L^{-1}$) | 574±261 | 132±167 | 17±9 | 256±301 |
| COD ($mgL^{-1}$) | 33±10 | 37±7 | 5.5±1.5 | 63±13 |

flux loss performance and better recovery at the same time. This is feasible given the fact that 60% recovery was obtained well below a critical flux, and considerably beneath the maximum allowable pressure for the membrane (600psi). It therefore appears that there is still plenty of opportunity for operational optimization adjustments.

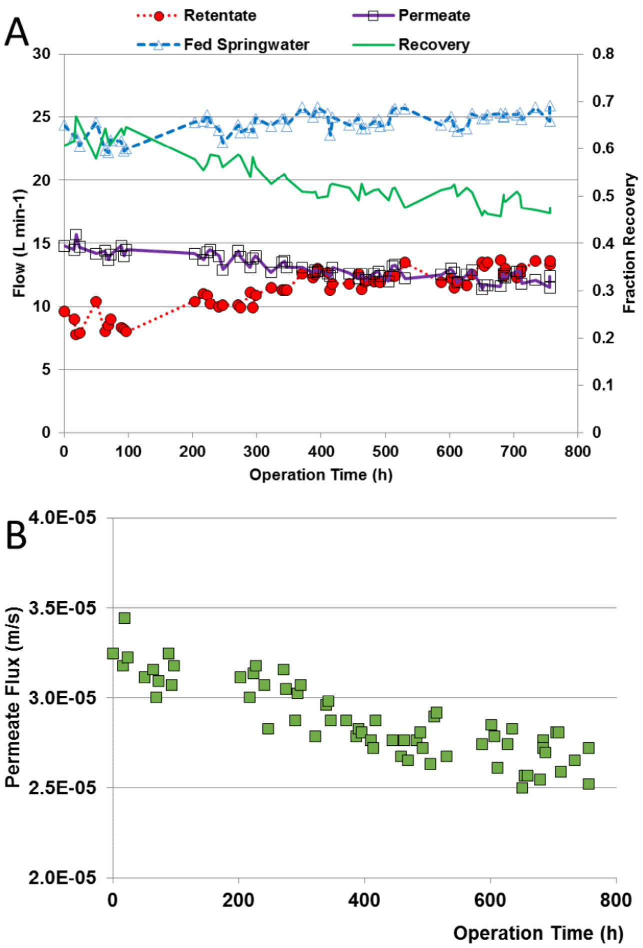

**Figure 4: A.** Pilot plant stream flow performance throughout the experimental period. **B.** Permeate flux throughout the pilot plant operation.

Additional samples were taken to determine the performance of the NF270 membrane for pathogen removal, and make a direct comparison with the current spring water treatment process, which consisted only of chlorine disinfection to be supplied to the local communities. For the microorganisms determined, only a moderate number were detected in the raw spring water: faecal coliforms (14.3±2.9CFU100mL$^{-1}$), *Enterococcus faecalis* (1.7±0.6CFU100mL$^{-1}$), *Salmonella* spp. (1.7±1.2CFU100mL$^{-1}$), spores of *Clostridium perfringens* (9.7±1.5CFU100mL$^{-1}$), *cysts* of *Giardia* spp. (2.5±0.7cystsL$^{-1}$), and oocysts of *Cryptosporidium* spp. (3.0±0.0oocystsL). Any of these pathogens were detected in the membrane permeate. For chlorination of the spring water, most of them were eliminated with exception of 2.0±0.0cystsL$^{-1}$ of *Giardia* spp. and 0.5±0.5oocystsL$^{-1}$ of *Cryptosporidium* spp. The NF270 system proved to be reliable in terms of natural organic matter and pathogen content removal. Additionally, certified lab analysis for organo-chlorine compounds was made at the outlet of the chlorination facility and none were detected. This provided a positive assessment of the state of the current process provided by the local water supplier. However, some disinfection dosage adjustments were recommended to the site's administrators with regard to microorganism removal results.

MPs removal from raw spring water during the field operation was much more challenging given the low concentrations found. Most of the pharmaceuticals and hormones studied were not detected, and the only compounds detected from the original list were at significantly lower and variable concentrations. MPs were determined on five sampling occasions throughout the operation: at initial start-up time (zero hours), then 200, 380, 580 and 750h. The maximum concentrations found (Table **5**) seemed to be very close to the treatable threshold regarding the values obtained in the permeate when the feed concentrations are much higher. This was evident with regard to the moderate or low removals obtained under natural concentrations, where BPA seemed to be the best removed compound. DEHP was not removed at all, and it is noticeable that its concentration in the raw spring water as in the other process streams, is very close in magnitude to the remaining permeate concentration reported for the spiked water experiment. Thus, most of the concentrations obtained in the spring water during the entire operation seemed to be too low and removals much more variable. It appears that the NF process could be more effective above a certain concentration threshold that might be different for each compound. Thus, given their low concentrations, the accumulating mechanism in the membrane and possibly some steric/surface interactions that might help the removal process were absent or incomplete, leading to some removal, but not as high as expected.

Regarding the accumulation phenomenon, all of the concentrations obtained from the process streams were considered to calculate an accumulation rate with the following rationale: $S_i=C_{ia}V_a- C_{ip}V_p - C_{ir}V_r$, where $C_i$ is the concentration of the compound *"i"*, *V* the volumetric flow of each process stream, and *a, p* and *r,* defined for the feed, permeate or retentate, respectively. $S_i$ is the accumulation rate in the system, in other words, how much of the compound is supposed to remain in the membrane domain throughout the operation, according to the experimental MPs concentrations in outlets and inlet. A calculated accumulation rate for the maximum obtained concentrations is presented in Table **5**, and it is assumed to be the instant accumulation rate given the maximum concentrations detected throughout the entire operation. This instant rate is mostly positive for all the significant removals obtained, suggesting that positive accumulation is occurring according to the mass balance, with accumulation favoring removal. On the other hand, the poorest removals are related to a negative instant accumulation rate. All of this is in accordance with the prior observations regarding the need for an accumulating effect in order to reach equilibrium in the removal process. The variability and low concentrations found in the spring water in general prevent such accumulation.

Regarding the MP measurements throughout the operation of the pilot plant, there was considerable variability with often very low concentrations. The average of the instant accumulation rates (Table **5**) was found to be negative. This might be due to the overall balance of the system in which very low accumulation is present and may explain the mostly low removals in comparison with the spiked water experiments. If all of the instant accumulation rates are gathered for the detected compounds (Figure **5**), it is noticeable that most of them are in the negative range, meaning that the retention capability of the membrane is very low. This leads to removal percentages with considerable variability especially if spring water concentrations are very close to the limit of detection, or even within a detectable but low range (≤10ngL$^{-1}$).

**Table 5: Maximum MPs Concentrations for the NF270 Membrane Pilot Plant Operation at the *Cerro Colorado* Spring**

| Compound | Raw Spring Water (mean±SD) (ngL$^{-1}$) | Softened Spring Water (mean±SD) (ngL$^{-1}$) | Permeate (mean±SD) (ngL$^{-1}$) | Retentate (mean±SD) (ngL$^{-1}$) | Removal % | Accumulation at max. Concentration (ngmin$^{-1}$) | Mean Accumulation ±SD (ngmin$^{-1}$) | Mean Spring Water Mass Flow (ngmin$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| BPA | 202±3 | 21±0 | 3±0 | 325±20 | 98% | 1770 | -715 ±2200 | 1349 |
| DEHP | 620±142 | 516±84 | 740±68 | 437±144 | 0% | -22 | -721 ±1689 | 5176 |
| BBP | 4±1 | 6±1 | 2±1 | 5±5 | 50% | 20 | -1041±1785 | 56 |
| NPS | 63±8 | 78±12 | 60±12 | 98±6 | 5% | -963 | -3260±4657 | 862 |
| SLC | 210±20 | 133 ±36 | 167±6 | 29±25 | 20% | 2368 | -278±2089 | 1316 |
| TCS | 30±3 | <LOD | 14±12 | 17±6 | 53% | 354 | -894±1442 | 197 |

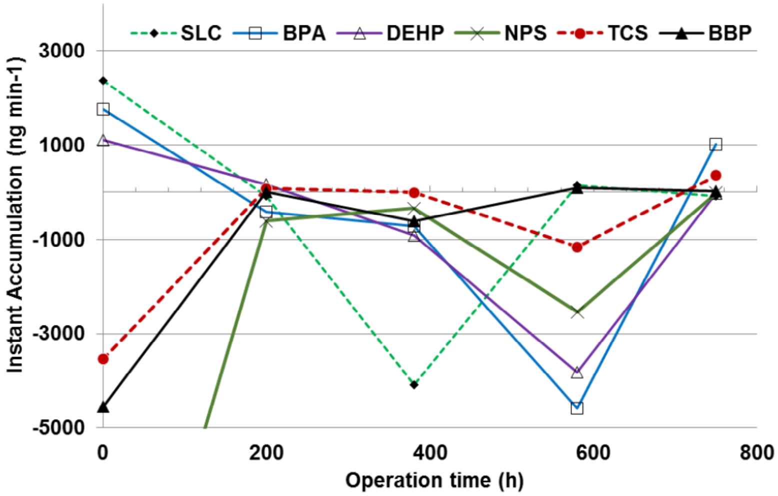

**Figure 5:** Pilot plant MP instant accumulation rates for five MP measurements over 750 hours of operation.

It appears that a concentration threshold may be reached such that the accumulating effect in the compound-membrane interaction allows higher removal percentages. However, it is also evident that in such cases a low percentage of the MPs concentration will eventually pass through the membrane. If concentrations in the spring water are already low, the incomplete removals obtained in this field might be very close or even below the passing-through concentrations that would be obtained from much more polluted water. In any case it is possible that a certain threshold concentration is required for effective MPs removal.

## CONCLUSION

The three NF membranes in lab-scale tests showed similar performance for MPs removal. However, the ESNA1 and NF90 membranes yielded lower critical flux, leading to the selection of NF270 for the pilot scale study. Critical flux determined with the lab-scale flat sheet unit was useful to provide guidance on operational limits for the pilot plant.

Natural organic matter, hardness and low but persistent pathogen content was successfully removed from spring water. A low maintenance regime was feasible for NF270. Pretreatment was implemented using microfiltration and water softening, allowing a slow flux-loss rate throughout the operation of the pilot plant with moderate recoveries. The next step will be optimization of recovery: higher operating pressures and fluxes are feasible if a complete membrane maintenance plan is implemented.

Lab-scale and pilot plant membrane systems showed higher MPs removals with higher feed concentrations. A threshold of such concentrations seems to be needed to achieve high levels of removal for each MP compound. An accumulating effect of MPs onto the membrane might allow more reliable and constant removal efficiency.

Given the low concentrations of the studied MPs in the spring water, moderate NF removal efficiency was sufficient to obtain even lower permeate MP concentrations. Permeate concentrations increased when feed water contained higher concentrations of MPs. Greater insight regarding the potential risks of the passing-through concentrations is needed to determine how safe the treated water really is, and how critical the MPs removal capability of the membranes is when low concentration sources are to be treated for human consumption.

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