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Endocrine Disruptors in Water Sources: Human Health Risks and EDs Removal from Water Through Nanofiltration

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1. Introduction

Water is fundamental for human health and well-being as well as for stimulating diverse socioeconomic activities. Paradoxically, these very activities have contributed to the alteration and deterioration of water supply sources from a microbiological, physical and chemical standpoint, causing sanitary risks for the population. For example: since the end of the 19th century, the role of drinking water in exposing populations to pathogens, and improvements in its quality in order to prevent diarrheic illnesses, has been widely analyzed, debated and documented [1,2]; in the 20th century, epidemiological evidence was found of cutaneous lesions [3] and various types of cancer related to hydroarsenicism [4], as well as dental and skeletal fluorosis related to fluoride in drinking water [5].

In recent decades the problem of these possible public health risks from so-called emergent contaminants (ECs) has been factored into the problem that includes a wide range of compounds whose environmental presence and impact have been proven with the advent of new sensitive and reliable quantitative analytical tools [6]: ECs are bioactive substances synthesized and used for the household, agriculture, livestock, industry, personal care products and hygiene (PCPs), and human and veterinary medicine, including byproducts of production and degradation [7]. However, beyond the concentrations and environmental persistence of ECs,

their relevance lies in the fact that they continue to be released into the environment through various ways which confers ubiquity.

Chemical endocrine disruptors (EDs), which are xenobiotics (compounds exogenous or foreign to living organisms) with potential to alter hormonal regulation and normal endocrine system function, consequently affecting an intact organism, its progeny or subpopulations, are among the wide range of ECs [8]. The evidence of adverse effects on aquatic organisms at relevant environmental concentrations [9,10] is well documented as well as *in vitro*, *in vivo* and epidemiological studies that associate human exposure to these compounds with: obesity, metabolic syndrome, type II diabetes mellitus [11], estrogenic, androgenic and antiandrogenic activity or combinations thereof [12], reproductive, nervous and immune systems effects, as well as some cancers and developmental effects [13].

The presence of EDs in bodies of water is due mainly to the discharge of wastewater that impacts the quality of surface water and groundwater with compounds that are not entirely removed by conventional treatment processes [14,15], which is particularly relevant in areas like the Mezquital Valley (state of Hidalgo, Mexico). The aquifer that supplies the population is recharged with the residual waters used in agricultural irrigation. Another way is through the indirect reuse of treated wastewater for potable water source augmentation. These practices could explain why some pharmaceuticals (Phs) and personal care products (PCPs) have been detected in waters treated for human consumption [16].

The concern regarding human exposure to EDs, in this case through water consumption, is based on five points: 1) evidence of adverse effects on fish and aquatic ecosystems at relevant environmental concentrations [9,10]; 2) documented clinical cases of cancers related to hormones in industrialized nations [8], as well as prevalence of reproductive disorders in adolescents and young men in Europe [17]; 3) *in vivo* studies that show endocrine disruption through exposure to certain ambient chemicals; 4) various chemical compounds classified as EDs or with potential to act as such, have been found in surface water and groundwater [18] and, 5) evidence that suggests that conventional water treatment systems are inefficient in removal of these types of contaminants [16].

The European Union, Germany, England, USA, Australia, Canada and Japan have all installed multi-stage treatment systems that effectively reduce the concentration of EDs in drinking water. The debate has begun over the need for research and regulation, analytical methods, water sources and treated water monitoring, public health and environmental risks, water treatment processes, transformation, transport and fate in the environment of EDs.

In Mexico there are few studies related to the occurrence of EDs in water, as well as few studies that document the efficacy and efficiency of water treatment processes in the removal of ECs and EDs. Considering that the Mezquital Valley is a prime example of an aquifer affected by the reuse of wastewater, and that the occurrence of ECs has been documented in supply wells in the area, the following objectives are proposed:

- a. Analyze and synthesize information regarding the presence of EDs in supply sources and treated waters for potable use, sanitary, environmental and regulatory relevance, treatment processes for removal from water.

- b. Analyze the problems related to ED exposure, specifically arsenic, bisphenol A, alkyl-phenols and their ethoxylates through the use and consumption of water in the Mezquital Valley.
- c. Analyze the technical feasibility of nanofiltration (NF) process to remove mineral and organic compounds from groundwater in the area of the study.
- d. Identify investigation needs regarding the occurrence concentration, persistence, transformation and destination, action mechanisms and risk assessment of EDs in water for human consumption and treatment processes for potable use

2. Endocrine disruptors in drinking water: Public health relevance

By May 16, 2012, the Chemical Abstracts Service [19], had registered over 66.67 million organic and inorganic substances. More than 100,000 man-made chemicals are available on the market including approximately 1,500 new molecules released yearly [20,21] for manufacturing products whose primary use is for human well-being and socioeconomic development. Since the 1990s, EDs have been one of the most controversial issues, attracting the attention of the scientific community, international agencies and organizations, governments and the general public.

The U.S. Environmental Protection Agency defined an endocrine disruptor as “an exogenous agent that interferes with the production, release, transport, metabolism, binding, action, or elimination of natural hormones in the body responsible for the maintenance of homeostasis, reproduction, development, and/ or behavior” [22]; the European Commission defines it as “an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations” [8]. From both definitions it is clear that EDs are compounds that alter hormonal regulation or homeostasis that can cause undesirable adverse effects on health as a result of exposure to a compound whose mechanism or action is endocrine disruption.

2.1. Origin and occurrence of EDs in drinking water

The nature and origin of EDs is diverse and includes groups of compounds such as: active ingredients in medicines with collateral hormonal effect, pesticides and adjuvants for their application, products to increase growth and weight gain in livestock, personal care and hygiene products, flame retardants, chemicals for use in the plastic industry and other frequently used industrial chemicals, natural and synthetic hormones, as well as products for manufacturing consumer goods and degradation by products [20,22-26].

Their impact on public health and wildlife is due to their bioactivity and ubiquity in the environment, as they are introduced unconsciously and permanently in the various environmental compartments. They can be introduced as pure substances or complex mixtures through diverse ways, especially via the flow of treated or untreated wastewaters. These compounds are not totally removed or inactivated by conventional water treatment systems

or by natural processes of self-purification of the receiving bodies (water or ground), frequently reaching groundwater [26-28].

For example, in the Mezquital Valley, the aquifer that supplies the population is recharged mainly with wastewaters from Mexico City from agricultural irrigation; however, while the contamination with EDs, Phs, and other organic compounds originate from these wastewaters, they also originate from the disposal of PCPs and expired or unused medications by households, municipal and hospital wastewater, leachates from landfills and local uncontrolled garbage dumps (Figure 1, adapted from [29]), which is consistent with information published by various authors for other aquifers [29-31].

In this case, as in scenarios of direct or indirect reuse of treated wastewater as water supply source, the main concern is related to the pathogens as well as nitrates, Phs, PCPs and disinfection byproducts with potential to disrupt the endocrine system and affect human and environmental health [29].

In comparison to other chemical compounds, there is little information on the transformation and fate of EDs especially regarding biotransformation, hydrolysis and photo transformation of Phs and PCPs. Their low volatility suggests that their distribution in the environment will occur mainly via aqueous transportation and dispersion through the food chain. The polar and non-volatile nature of Phs impedes their release from water [31], without geographical or climatic borders for these synthetic substances that have been found in areas that are considered to have low pollution levels [32].

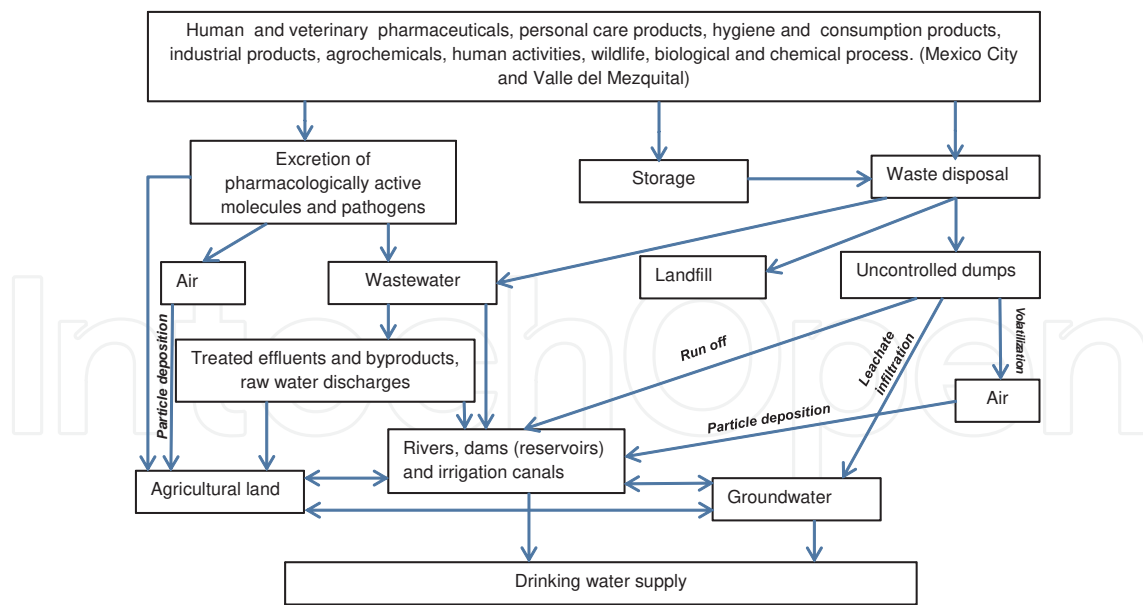


Figure 1. Conceptual model of introduction and transportation of ECs and EDs in the Mezquital Valley.

ECs, EDs and PCPs have been frequently detected in effluents and surface waters that could be present in drinking water. Ultra-trace concentrations (ng/L) of prescription and non-prescription Phs and their metabolites have been reported in samples of drinking water across

the United States. These include caffeine, analgesics, anti-inflammatories (naproxen), anti-convulsants (carbamazepine, phenytoin, primidone) and anxiolytics (meprobamate), xray contrast medium (iopromide), lipid regulators (gemfibrozil), antibiotics or their metabolites, nicotine metabolites, hypotensives (atenolol), synthetic musk, a polycyclic aromatic hydrocarbon compound, a plant sterol, plastic components, an insecticide, surfactants (bisphenol-A, alkylphenols) and degradation products, a fixative used in perfumes and soaps, a flame retardant and a pesticide [16,28,33-36].

In general throughout the water cycle there is a reduction in EDs through absorption, dilution, and biodegradation [24], and yet there are still questions about their fate in the environment. Laboratory studies have shown that bioactivity is reduced over a period of hours to days due to degradation and sorption yet field studies indicate that estrogens are sufficiently mobile and persistent to impact the surface and ground waters [37], while in the ground and sediments where they can persist for long lengths of time (the half-life of clofibric acid, for example, is estimated at 21 years), they reach levels in the g/kg range [23].

Given the ubiquitous nature of EDs, all humans are exposed through different tracks: inhalation, ingestion and dermal contact. Contributing to this is their low biodegradability, air and water transportability, bio accumulation in the trophic chain and transgenerational exposure; fetuses are especially vulnerable because pregnant women accumulate EDs in adipose tissue [38]. As with other environmental chemicals, their effects depend on the concentration and nature of the chemical as well as its route, frequency and intensity with which exposure occurs and in this case the phase of life at which the exposure occurs.

Due to the trace and ultra-trace concentrations in which EDs are found in drinking water, people are commonly exposed in higher quantities through medications and other sources and routes: diet, inhalation of airborne chemical substances and dermal absorption (topical medication or personal care products), which suggests the contribution by drinking water to the overall exposure and its relative importance in assessment of sanitary risks associated with these types of contaminants [39].

Likewise from a risk management viewpoint, it is important to note that the variety and chemical structure of EDs complicates their identification and quantification in water as well as the characterization of the sanitary risks associated with chronic exposure to low or environmentally relevant doses. In addition little is known about the occurrence, toxicity and potential endocrine activity of the products of degradation that may result from the processes of bio and physiochemical transformation that alter the chemical structure of EDs rather than eliminate them.

2.2. Human health effects

2.2.1. Endocrine system

Hormones are produced by the glands that comprise the endocrine system, which is the key to communication within the human organism and control method between the nervous

system and the various functions of the human body such as reproduction, immunity, energy control, metabolism, conduct, growth and development. For example:

- The Thymus gland is the source of immunologic regulatory hormones [35].
- The Hypothalamus gland releases hormones such as oxytocin; it's important in the control of reproductive endocrine processes and stimulate pituitary activity [35,40,41].
- The Pituitary gland releases steroid hormones, such as corticosteroids, androgens, and estrogens; growth hormone, oxytocin. Feedback control signals the endocrine organ (the adrenal gland or gonads), to cease production or release of the endogenous steroid or to stimulate the release of opposing hormones. This homeostatic control in response to endogenous hormones is critical for maintaining proper hormone concentrations [35,40].
- The Thyroid gland releases thyroid hormones (calcitonin and thyroxine), which are receptor nuclear of steroids, regulate metabolism, growth, development, behavior and puberty [35,40,41].
- The Adrenal glands, release corticosteroid hormones, catecholamines to regulate metabolism and behavior [40,41].
- The Pancreas produces insulin and glucagons to regulate blood sugar levels [40].
- The Ovaries and testicles produce sex steroids such as estrogen, progesterone, testosterone (androgens and estrogens) [35,40].

This means that all the physiological systems sensitive to hormones are vulnerable to EDs, including the brain and hypothalamic-neuroendocrine systems, cardiovascular system, mammary gland, adipose tissue, ovary and uterus in females, and testes and prostate in males [25,40].

2.2.2. Endocrine disruption mechanisms

Hormones circulate in the blood stream to modulate cellular and organ function through the union with complex molecular receptors and mechanisms:

- They mimic natural hormones; if exposed to relatively high doses, they join receptors within the cell and block or interfere with the ways through which hormones and receptors are synthesized or controlled [42].
- Binding and activating estrogenic and androgenic receptors N40. There are a number of estrogenic receptors in gonads, liver, brain, and sex organs; union without activation of the receptor would act like anti-estrogenics or anti-androgenics [43-45].
- Binding without activation of the receptor would act like anti-estrogenics or anti-androgenics [43-45].
- Modifying hormonal mechanisms [46], or of the number of hormonal receptors in the cell, or of the production of natural hormones, for example in the thyroid, immune or nervous systems [47].

- Selectively inhibiting DNA transcription; for example, arsenic produces a disruption in the transcription of DNA induced by the glucocorticoids mediated by receptors [47].

The mechanisms described in recent literature also include: a) the alteration of the transcriptional activity of nucleus receptors by modulating co-regulators through mediated degradation of the proteasome as well as by inhibiting histone deacetylase activity and stimulating mitogenic kinase protein activity; b) regulation of the methylation of DNA and c) modulation of lipid metabolism and adipogenesis, which possibly contribute to the current epidemic of obesity [47-50].

2.2.3. Health effects

EDs are structurally similar to many natural hormones; some have lipophilic properties [40], act in extremely low concentrations and therefore can have effects on organisms with low dose exposures [50,51]. As a result, environmental presence in trace and ultra-trace amounts, particularly in water, may be insufficient to cause cellular death or act upon genetic material, yet could result in a source of human exposure and carry sanitary risks for more susceptible segments of the population.

The target hormones for EDs and the effects differ from one compound to another (as shown in Table 1), as well as among species and intra species; for example, there are reports that the median Bisphenol A (BPA) level in human blood and tissues, including in human fetal blood, is higher than the level that causes adverse effects in mice [52].

The time of exposure to EDs in the organism in development is decisive in determining its character and future potential and, even when critical exposure takes place during embryonic development, the clinical manifestations may not be present until adulthood [8,43,45,46]. One compound may act on different target hormones [40] and cause different alterations. A wide and current review of the health risks is found in [22,53]. Some examples of compounds intensively used in Mexico, and their potential effects in humans, are presented in Table 1, as well as their normal application or use and the exposure source. It is worth mentioning that the exposure is involuntary.

2.3. NF as an alternative to remove ECs from water

Between January 2001 and July 2004 the European Union conducted Project Poseidon [64]; among its objectives it proposed conducting integral studies to evaluate and improve the removal of pharmaceuticals and personal care products from residential residual waters using conventional and advanced treatments as well as with potable water. One of the conclusions of the study is that reverse osmosis, nanofiltration and ultrafiltration-powdered activated carbon are powerful processes for the removal of pharmaceuticals and personal care products, among which are found ECs and EDs (suspicious and recognized).

In spite of the conclusions from the POSEIDON Project, the question about the efficacy of NF membranes in removal of emergent contaminants persists. Many studies have been made of this topic [65-73]. The spectrum of tests covers membranes with a molecular weight cut off (MWCO) of 200, 400 and 600 Da, as well as organic compounds with different molecular weights, sizes and physiochemical characteristics.

Example	Use	Involuntary exposure source	Example of adverse effect in humans
Bisphenol A	Plasticizers	Plastic items, packaging foods, beverages, water	Estrogenic [52-55], thyroid hormone, progesterone[40], androgenic. Female breast structural anomalies, premature thelarche, cancer; pubertal timing variations, ovulatory disorders, sexual behavior, prostate cancer [56,57]. Disrupted hypothalamic estrogenic receptor distribution, altered nitric oxide syntheses signaling [57]. Affection of human immune function [58], and disrupted behavior in children associated with early life BPA exposure, especially in girls [59].
Vinclozolin	Fungicides	Foods (fruit, vegetables, cereals), water	Estrogenic, anti-androgenic. Promotes transgenerational adult onset disease such as male infertility, kidney and prostate diseases, immune abnormalities and tumor development [60].
Alkylphenols	Detergents, emulsifiers, agrochemicals	Household items, water, foods (fish)	Estrogenic [40], androgenic. Environmental and health issues continue to cast uncertainty over the human risks of alkylphenols and alkylphenols ethoxylates.
Phthalates	Plasticizers	Plastic items, cosmetics, personal products care, beverages, water	Estrogenic, androgenic, thyroid hormone [40]. Abnormalities such as hypospadias, cryptorchidism, reduced anogenital distance. Oligospermia, germ cell cancer [56]. Neurodevelopment and metabolic endpoints are of concern, since studies of prenatal exposure have found associations with phthalate exposure and lowered IQs, and exposure has been implied as a risk factor for obesity, insulin resistance and diabetes by others [47,50,55].
Diethylstilbestrol	Contraception, hormone replace therapy	Pharmaceuticals. They have been detected in water sources,	Estrogenic. Abnormalities such as hypospadias, cryptorchidism, reduced anogenital distance. Female structural anomalies, breast cancer, structural anomalies, premature thelarche. Prostate cancer [56,61].
Ibuprofen, diclofenac, acetaminophen	Anti-inflammatory, analgesics	wastewater and treated effluents	Candidates may be identified on the basis of simple assumptions regarding their use and activity: a) non estrogenic steroids may react with environmental endocrine receptors or metabolize on their way to the environment and thus form endocrine disruptors; b) many high-volume drugs released to the environment have not yet been tested for their endocrine properties, and some of these are known to interact with the human endocrine system [62].
Bezafibrate, clofibrate, gemfibrozil, fenofibrate	Lipidic regulator		
Atenolol, metoprolol, propranolol	B-blockers, antihypertensives		
Anabolic steroids; trenbolone acetate, melengestrol acetate	Fast growth of meat producing animals	Animal food, soil, wastewater	Androgenic. A placebo-controlled prospective study demonstrated adverse and activating mood and behavioral effects of anabolic steroids [63].

Table 1. Example of possible sources of exposure to EDs and target hormone system.

NF efficiently removes dissolved solids, organic carbon, inorganic ions and organic micro contaminants, both regulated and unregulated, and therefore its capacity is similar to that of reverse osmosis (RO); however, due to higher pressure requirements the latter has higher investment and operational costs. Furthermore the partial discrimination of calcium and bicarbonates of the NF can be advantageous since drinking water distributed through municipal networks should be saturated with calcium carbonate to avoid corrosion [74].

The mechanisms through which RO and NF reject organic compounds are mainly: a) exclusion by size or stericity; b) exclusion by repulsion of charges or ionic exclusion also known as Donnan Effect and c) the physiochemical interaction of the solvent, the solute and the membrane [75].

Size exclusion is associated with the molecular weight cut off of a membrane but this is relative to a certain type of molecule, therefore other molecules with similar molecular weight yet different physiochemical properties may not be rejected at the same rate. In the case of neutral compounds, other geometric descriptors of the molecule are far more useful such as molecular width [76] or hydrodynamic radius, especially for molecules whose radius approaches that of the membrane pores [77].

Exclusion by charge repulsion is a phenomenon in highly typified NF membranes; tests conducted with NF membranes and ultra-low pressure reverse osmosis to retain or reject 9 organic compounds (5 negative ionic charge and 4 neutral) showed that the electrically negative charged compounds were rejected with efficiencies above 91% even with molecular weights lower than the rated molecular weight cut off of the membranes, while the neutral compounds were rejected at much lower rates at levels as low as 12% for 2-naphtol [78].

The interaction between solvent, solute and membrane can lead to misleading results if enough time is not allotted for the process to normalize, since various organic contaminants tend to be adsorbed on the membrane surfaces. As a result, initially they are retained, but once the membrane surface is saturated, the true rejection of the compound can be observed [65,77-81].

NF membranes (MWCO of 200, 300 and 400 Da) and RO membranes (MWCO not reported) have a 90% reject rate of ionic and non-ionic hydrophilic organic compounds such as naproxen, diclofenac, ibuprofen, mecoprop, ketoprofen, gemfibrozil, and primidone and higher for NF membranes with MWCO of 200 Da as well as the RO membranes. Even the NF membrane with MWCO of 300 Da had reject rates of over 90% [68].

Tests conducted with a membrane with a MWCO of 300 Da (Filmtec NF200) to evaluate the removal of hormones and antibiotics with microfiltration showed that in a matrix of drinking water with a mixture of hormones and medications (i.e. hormones with sulfonamides or tetracycline) it is possible to obtain rejects of nearly all of the substances with the exception of testosterone whose reject rate was 95%. The pharmaceuticals tested were tetracyclines, (chlorotetracycline, sulfachloropyridazine, sulfamerazine, sulfametoxazole, sulfametazole) and hormones (estrogen, progesterone, testosterone and 17 α -ethynilestradiol). There is also evidence that the removal efficiency of hormones and sulfonamides was lower when de-ionized water was used and a pure solute [72].

As shown in the previous examples, the results obtained in the laboratory tests on efficiency of NF membranes in the removal of ECs have been very favorable even though it has been shown that compounds with a lower molecular weight, less branched and without ionic charge, were only partially retained.

In pilot applications or full scale, the performance of NF in the control of organic micro contaminants is less documented; even so, there are two pilot systems documented [67, 69] and one municipal plant [73]. The main results of these two applications are described below.

A comparative study between ultra-low pressure reverse osmosis membranes (ULPRO) and NF showed that both types of membrane can reach efficient levels of removal of organic compounds such as pharmaceuticals, pesticides, flame retardants, plasticizers, and nitrogen, similar to that of conventional reverse osmosis, producing water with equal quality as required for indirect potable reuse of treated water. The operational conditions and results show that both types of membrane are viable for reuse projects of treated residual water in which a high quality permeate is required [67].

A NF pilot plant with a capacity of 56.4 L/min was fed with water from an advanced treatment facility for residual water. After the biological treatment, the water was micro filtered and disinfected. The pilot plant operated continuously for 1200 hours (50 days). Ten emergent contaminants were found in the source water (3 plasticizers, [TCEP, TCPP, and TDCPP], acetyl salicylic acid, naproxen, ketoprofen, diclofenac, gemfibrozil, primidone, and carbamazepine) and in all cases removal rates of 75-100% were observed, except during the first 24 hours of operation when efficiencies were lower. However, as the test progressed, an increase in removal of contaminants was observed to the degree that the organic compounds with ionic charge and the neutral ones with greater molecular weight were rejected at a rate of 90%.

A research study was held at a municipal drinking water facility located in the north of Spain. The plant has 3 parallel trains of membrane processes, two of which are reverse osmosis (486 m³/h each one) and one NF (360 m³/h). The facility is fed from groundwater wells, directly influenced by infiltration from Besós River. During the study, five measurement campaigns, aimed at 12 pharmaceutical compounds, were conducted. The results obtained indicate that NF was capable of removing hydrochloratizide, ketoprofen, diclofenac, sotalol, sulfamethoxazole, metopropolol, propifenazone and carbamazepine with efficiency levels above 90%.

Compounds with negative charges like gemfibrozil and mefenamic acid had a low removal rate both in the NF (50% and 30% average), as well in RO (50% and 70% average). Meanwhile, acetaminophen, which has a molecular weight cut off of 151.16 Da., had a removal rate of 44.8% through NF and 73% through reverse osmosis. The authors conclude that the NF and reverse osmosis membranes applied in full-scale are very efficient in removal of almost all pharmaceutical residuals found in water.

Due to advantages NF has over RO, such as lower energy consumption and selective ion discrimination, as well as the capability to remove almost all pharmaceutical residuals found in water it was decided to test a NF process for water treatment at Mezquital Valley.

3. Endocrine disruptors in groundwater sources of Mezquital Valley

3.1. Description of the study site

The Mezquital Valley is located in the central plateau of Mexico, 80 km. from Mexico City in the South central part of the state of Hidalgo. In the municipalities located within the limits of the aquifer of Mezquital Valley (Figure 2), there is an estimated population of 377,951 inhabitants, which represents 14.8% of the total population of the state [82]. The principal economic activity in the region is agriculture, which is distributed in two irrigation districts (03 Tula and 100 Alfajayucan). In the area there are also a petroleum refinery plant, a thermoelectric plant, textile factories and a cement plant, considerable commercial activity, craft production, and the tourist industry is based on spas and hiking in the mountains [83].

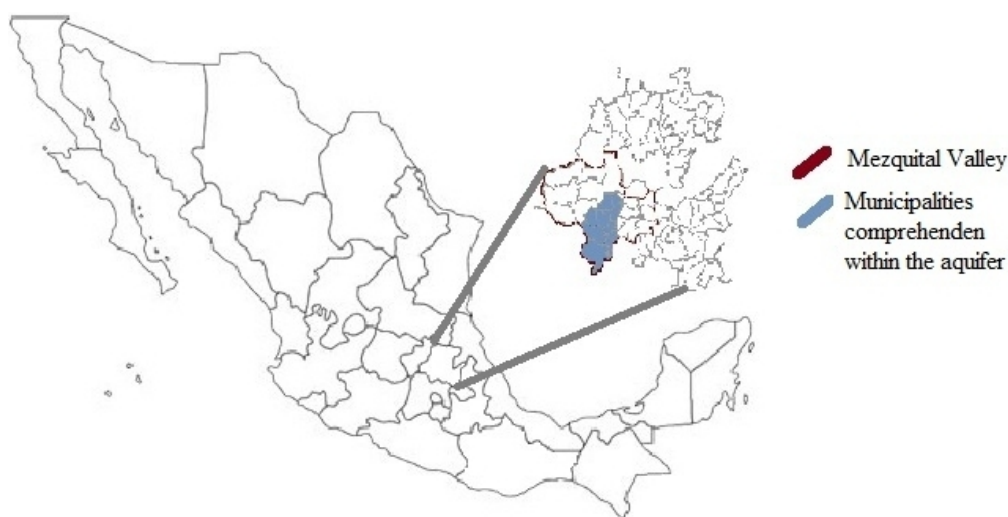


Figure 2. Location of the Mezquital Valley aquifer in Hidalgo State.

The climate is semi-arid, with a high incidence of sunlight and warm temperatures [83]. Average annual precipitation is 450 mm, while evaporation is 2,100 mm; rain is limited to the months of May through October [84].

Within the Mezquital Valley are the irrigation districts 03 Tula and 100 Alfajayucan, representing one of the largest irrigation schemes of residual water in the world. It receives between 50 and 60 m³/s of water (80% residual and 20% pluvial) from Mexico City through the Gran Canal del Desagüe, the Interceptor Poniente, and the Emisor Central (Figure 3)[85,86].

Around 75% of this water [87] is used without formal treatment for irrigation of approximately 85,000 hectares of saline soils that lead to high levels of irrigation (1.5 to 2.2 m) [86]. Approximately 10,000 hectares receive crude residual waters directly, 35,000 hectares receive mixed water (80% residual and 20% from reservoirs and pluvial sources) and 25,000 hectares receive self-purified residual water from the Requena, Endho, Rojo Gomez and Vicente Aguirre reservoirs [88].

The Emisor Central and Emisor Poniente join the Tula River to feed the Endho reservoir (approximately 200 million m³) El Gran Canal empties into the Salado river and reaches the

Tula river beyond the dam [88] (Figure 3). 81% of the main canals and 52% of the lateral canals are not improved or coated, permitting the infiltration and artificial recharge of the aquifer. The water outlets from the aquifer are through springs that lead to the Tula river, extraction through wells, and the rest discharges toward the north and northwest, both superficially (drained by the Salado river) as well as subterranean [85]. The estimated outflow from the springs, which that spread out within the municipalities in the region, range from 100 to 600 L/s, and supply the population [86].

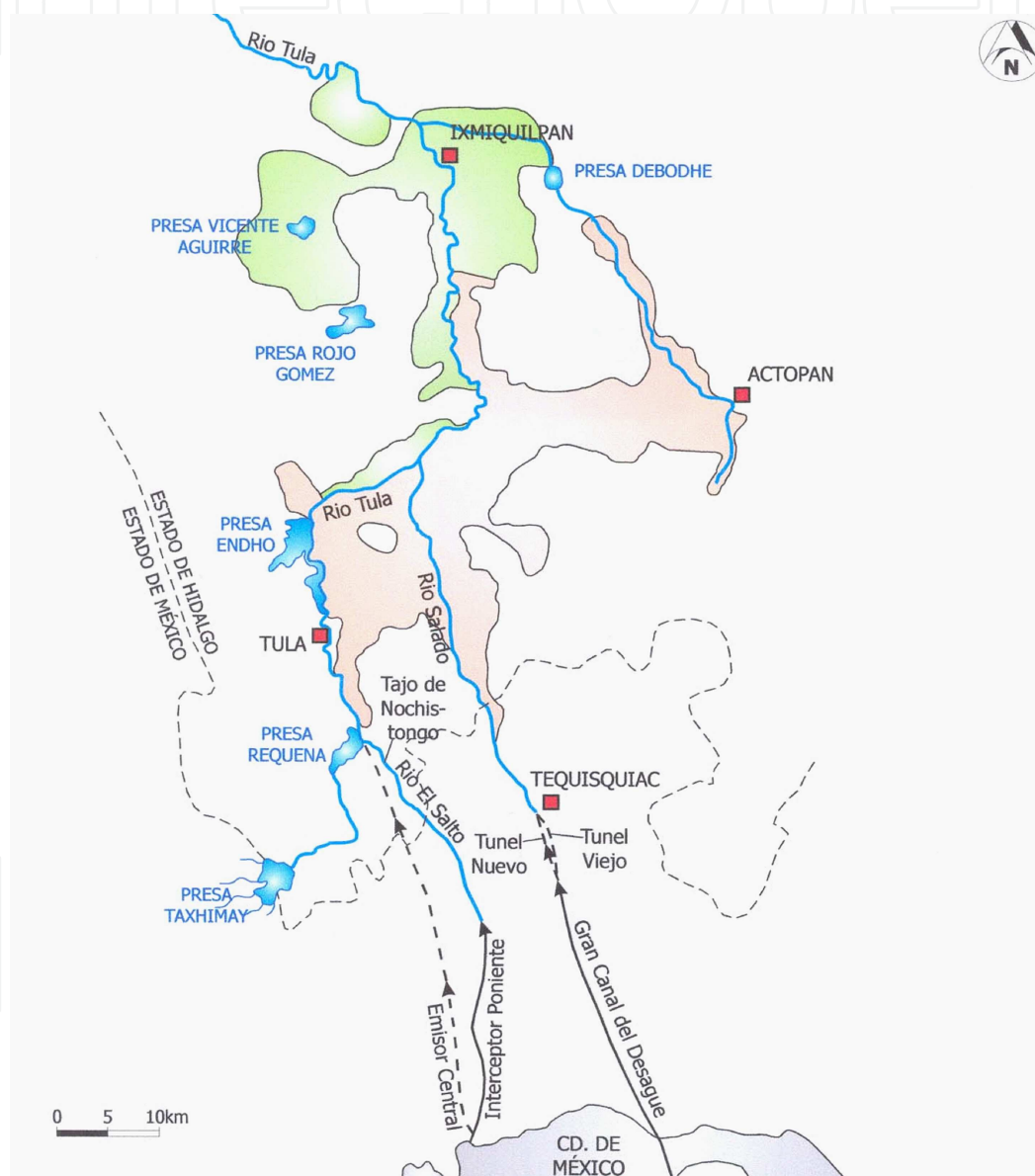


Figure 3. Sanitary sewers from Mexico City to the Mezquital Valley [85].

In the wastewaters, wells and springs in the Valle, sampling has shown traces of volatile and non-volatile organic compounds, phenolic compounds, and some PAHs and PCB's in concentrations in the order of picograms/L. Likewise, the presence of benzylbutylphthalate,

diethylhexyl phthalate, nonylphenol, salicylic acid, carbamazepine, ibuprophen and naproxen, indicate contamination from Phs and PCPs that include recognize and suspicious EDs compounds [87,89,90].

3.2. Sampling sites

For the first monitoring campaign, 19 supply sources were selected (Figure 4) located within the polygon that outlines the aquifer of the Mezquital Valley, and distributed throughout the irrigation zone with untreated wastewater, mixed waters (wastewater and fluvial reservoir water) and at a site to the north of the region to be used as a control site. The 11 sampling sites of wastewater include the water that flows into the Valle via the Emisor Central, residual waters from irrigation canals and one point in the Xotho canal that carries agricultural runoff waters as a point of comparison (Figure 5).

- 2 "Tezoquipa" Well
- 3 "El Tablón" Well
- 4 "Dendhó" Well
- 5 "San Antonio" Well
- 6 "El Refugio" Well
- 7 "Ajacuba" Well
- 8 "Noria Tetepango" Well
- 9 "Doxey" Well
- 10 "Tlaxcoapan" Well
- 11 "Teltipan" Well
- 12 "El Piedhe" Well
- 13 "Atengo" Well
- 14 "Xochitlan" Well
- 15 "Progreso" Spring
- 16 "Progreso" Well
- 17 "Cerro Colorado" Spring
- 18 "Fitzhi" Well
- 19 "Chilcuautla" Well
- 20 "Pedro Ma. Anaya" Well
- 23 "El Llano" Well

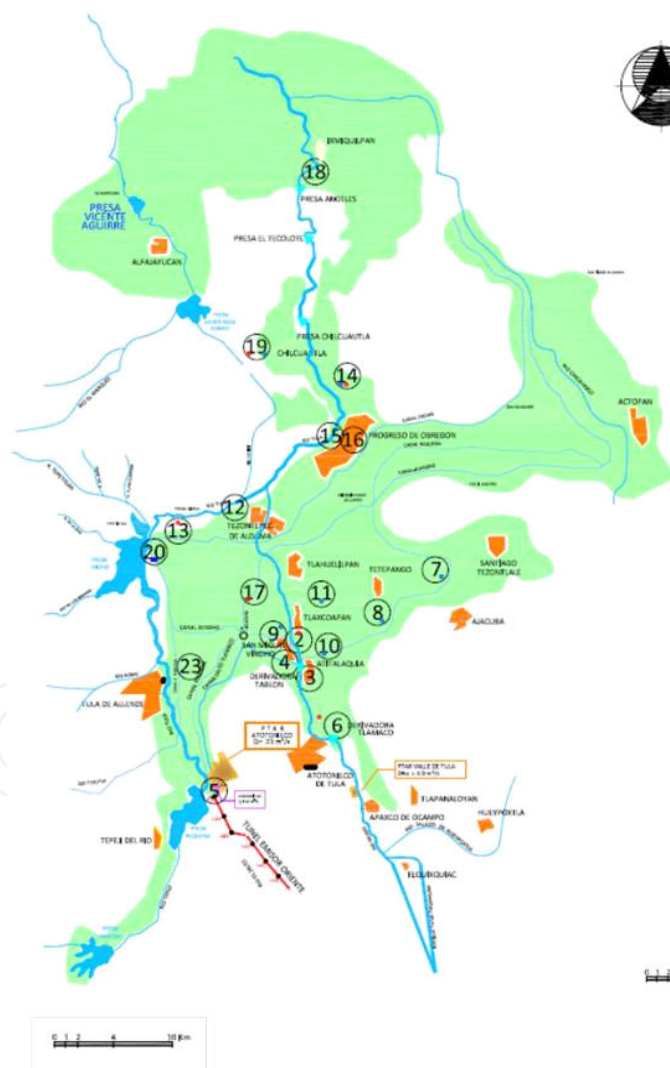


Figure 4. Supply sources.

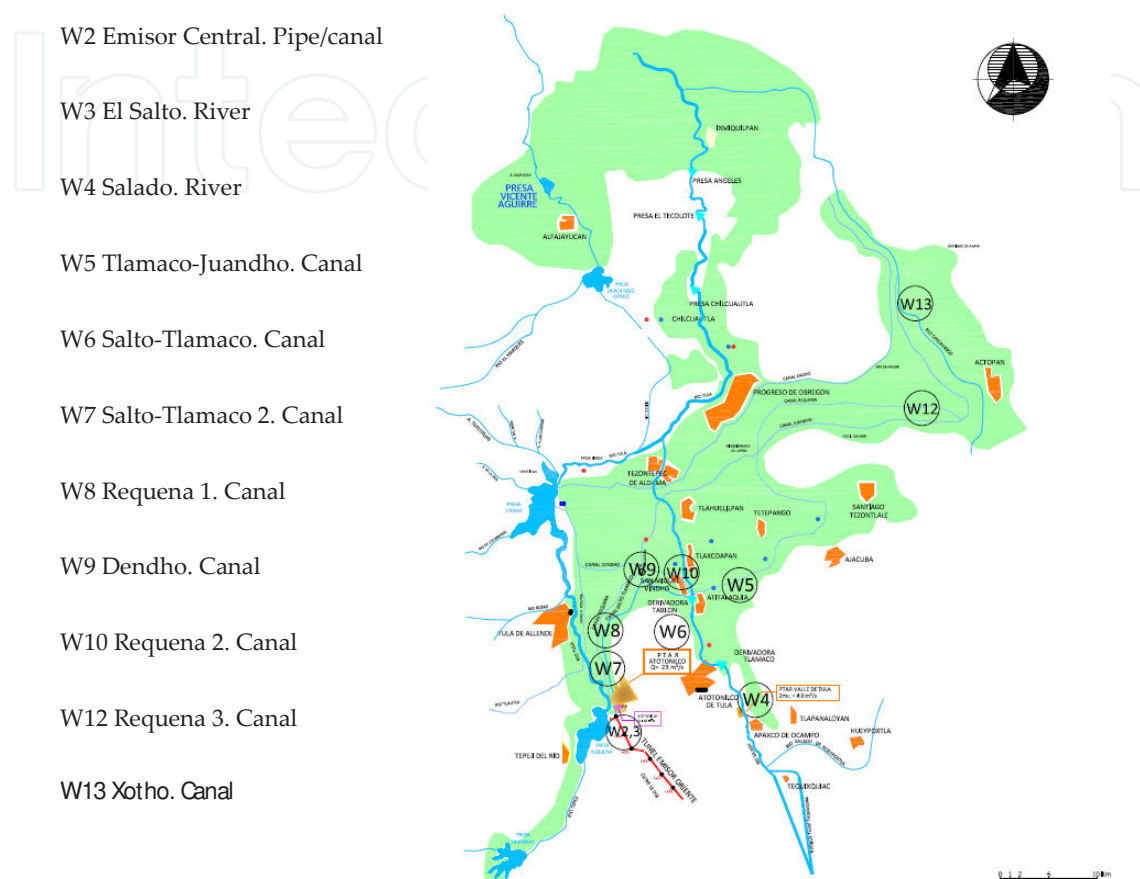


Figure 5. Wastewater sample sites.

A second sampling was later conducted on eight supply sources to test for unregulated organic compounds, phenolic compounds, estrogenic hormones, and a screening for pharmaceuticals, personal care products and progestogenic hormones; a second more specific and selective sampling was conducted of the supply sources in accordance with the following criteria:

- Concentrations of arsenic, fluorides, mercury or lead above maximum allowed limits as established by the Mexican normative for potable waters.
- Abundance (qualitative) of unregulated organic compounds (volatile, semi-volatile and persistent)

The sources selected were: 002 (Tezoquipa), 006 (El Refugio), 013 (Atengo), 014 (Xochitlan), 015 (Progreso spring), 017 (Cerro Colorado spring), 018 (Fitzhi) y 019 (Chilcuautla)

3.3. Sampling

The procedure for gathering water samples to analyze compounds at the trace and ultra-trace levels requires special care in order to not contaminate the samples by physical contact, perspiration or exhalation. For this purpose a cap, powder free gloves and face masks were used while handling, filling, closing, labeling and packaging the containers for storage and transport.

Two people collected the samples; one was designated “dirty hands” and the other “clean hands”. All operations requiring contact with the bottle and transferring the sample from the collection vessel to the bottle were conducted by “clean hands,” and “dirty hands” was responsible for all activities that did not involve direct contact with the sample [91].

3.4. Analytical methods

The samples were analyzed in laboratories accredited by the Entidad Mexicana de Acreditación, and the analytical methods utilized are based on the Mexican Standards or on international methods or those applied in other countries and were implemented, standardized and or validated in the selected test labs for sample analysis. For the analysis of volatile compounds, the samples were gathered in vials of 40 ml, and were kept at a temperature of 4°C during transport to the lab and until their analysis.

The samples were submitted for analysis through a methodology of USEPA Method 5030B [92], using a gas Chromatograph Varian 3800 coupled to a mass spectrometer Saturn 2200 equipped with a capillary column Sample Concentrator Teckmar/Dohrmann Model 3100 and auto sampler Varian Archon for 40 ml. vials.

The analysis of semi-volatile compounds was conducted with US-EPA Method 8270D [93]. Extractions were made in basic, neutral and acidic medium. The fractions obtained were analyzed with gas chromatography-mass spectrometry in total ion monitoring mode. For the analysis of nonphenols, method ASTM-D 7065-06 was applied. Dichloromethane was used to extract the samples. The extracts were concentrated and dried with the use of anhydrous sodium sulphate.

The detection of PPCPs was conducted by AXYS Laboratories in British Columbia Canada. The samples were analyzed following the AXYS method MLA-075: Analytical Procedures for the Analysis of Pharmaceutical and Personal Care Products in Solid, Aqueous and Tissue Samples by LC-MS/MS[91]. This method is suitable for the determination of a suite of pharmaceutical and personal care compounds in aqueous, solid and tissue samples. The analysis requires extraction at two different pH conditions: at pH 10 for analysis of fourteen analytes; and at pH 2.0 for the analysis of the other analytes. Prior to extraction and/or clean-up, samples are adjusted to the required pH and spiked with surrogates. A total of 119 analytes can be identified and quantified. Analysis of the sample extract is performed on a high performance liquid chromatography coupled to a triple quadrupole mass spectrometer. The LC/MS/MS is run in MRM (Multiple Reaction Monitoring) mode and quantification is performed by recording the peak areas of the applicable parent ion/daughter ion transitions. Some analytes are analyzed in the ESI positive mode and some are analyzed in the ESI negative mode.

3.5. Results

3.5.1. Fluoride and heavy metals: Suspected endocrine disrupters

The Mexican standard for drinking water quality [94], among other chemical parameters, limits the concentration of heavy metals, fluoride, organochlorated pesticides, total trihalomethanes and volatile organic compounds. In this framework, only four contaminants with potential to cause endocrine disruption exceeded the established maximum contaminant level: Arsenic (As), Fluorides (F), mercury (Hg) and lead (Pb) [95,96].

The greatest challenge came up in the wells in the south region of the Mezquital Valley (002 through 012 and 23), that are located in the entry zone of the residual waters. In the central and northern zone of the valley high concentrations of fluorides were found (Table 2), which is consistent with data reported in a previous study [85].

Parameter (Max allowable limit)	Supply Source (concentration µg/L or mg/L)
Arsenic (25 µg/L)	Wells: 003 (26), 004 (35.1) y006 (38.7)
Fluorides (1.5 mg/L)	Wells: 004 (1.72), 006 (1.52), 009 (1.62), 012 (1.59); Springs:015 (2.37), 017 (1.64); Wells: 016 (3.32), 018 (3.04), 019 (2.98) 023 (3.77)
Mercury (1 µg/L)	Wells:002 (2), 003(1.1), 006 (2.6), 007 (2.1) y 010 (2.6)
Lead (10 µg/L)	Wells:002 (28), 003(30) y 004 (39)

Table 2. Supply sources and parameters of the Official Norm for Water for Human Consumption and Use that are not met in the study zone.

Chronic exposure to As in drinking water has been strongly associated with increased risks of multiple cancers, heart disease, diabetes mellitus II and reproductive and developmental problems in humans [65].Recent studies suggest that increased human health risks [66],at levels as low as 5-10 ppb, could be mediated, at least partially, through the capacity to alter steroid receptors [97-99].There is evidence that high exposures to F⁻ are associated with decreased thyroid function [100,101], increased activity of the calcitonine and parathyroid, secondary hyperparathyroidism, tolerance to glucose and possible effects over time on reaching sexual maturity [96]. Lead (Pb) and mercury (Hg), can interfere with hormone neurotransmitters and other growth factors, and in both cases any exposure can be considered dangerous to the developing organism [57,102].

3.6. Unregulated organic compounds and estrogens

In the first monitoring campaign, 80 volatile and semi-volatile organic compounds (VSOCs) were identified at a qualitative level. The south zone of the valley showed greater diversity of organic contamination and in the north zone, where the irrigation water is mixed (wastewater and fluvial reservoir water), the water supply sources also showed organic contamination (Table 3 and Table 4), including naphthalene in well 019.

Water sources in the central zone (wells 007, 012, 013 and 015) contained the least diversity of organic compounds, nevertheless, no clear trend can be observed; therefore we assume that human activities within the Valley represent an important contribution to the organic loading (Table 3).

Supply source	Number of organic compound	Supply source	Number of organic compound
002 "Tezoquipa" Well	22	003 "El Tablón" Well	17
004 "Dendhó" Well	17	005 "San Antonio" Well	26
006 "El Refugio" Well	26	007 "Ajacuba" Well	18
008 "Noria Tetepango" Well	20	009 "Doxey" Well	17
010 "Tlaxcoapan" Well	17	011 "Teltipan" Well	22
012 "El Pueche" Well	11	013 "Atengo" Well	17
014 "Xochitlan" Well	22	015 "Progreso" Spring	8
016 "Progreso"	24	017 "Cerro Colorado" Spring	22
018 "Fitzhi" Well	29	019 "Chilcuautla" Well	31
020 "Pedro Ma. Anaya" Well	20	023 "El Llano" Well	17

Table 3. Number of volatile, semi-volatile and fixed organic compounds detected in water supply sources

Sampling site	Number of organic compound	Sampling site	Number of organic compound
AR "002 Emisor Central" Pipe/ canal	56	AR 003 "El Salto" River	37
AR 004 "Salado" River	42	AR 005 "Tlamaco Juandhó" Canal	42
AR 006 "Salto-Tlamaco 1" Canal	56	AR 007 "Salto-Tlamaco 2" Canal	39
AR 008 "Principal Requena 1" Canal	38	AR 009 "Principal Dendhó" Canal	39
AR 010 "Principal Requena 2" Canal	35	AR 012 "Principal Requena 3" Canal	32
AR 013 "Xotho" Canal	15		

Table 4. Number of volatile, semi-volatile and fixed organic compounds detected in wastewater

In the second monitoring campaign conducted during the rainy season all eight supply sources showed VSOCs (173 different ones). Qualitatively, the greatest contamination was observed mainly in the central zone; the source with the highest contamination was 015 with 69 VSOCs followed by 013 with 59 VSOCs; 017, 42; 006 and 014 with 41; 019, 38; 018, 36; and the source least contaminated was Tezoquipa (002) where 32 VSOCs were found.

From both groups of compounds, the following are notorious for their presence in residual waters and supply sources:

- Pesticides: 1,4-dichlorobencene, 1,2-dicloropropane, 3-chloro-2-methyl-1-propene, 1,1-dichloro-1-nitroethane, 1,2,3,4-tetrahydronaphtalene.
- Flavorings and essences: 3-methyl-2-pentanone, 2-methylpentanoic acid, 2-pentanone, 5-methyl-2-hexanone, 2,3-dichloro-2-methylbutane, 3-methyl-2-butanone, 2-propenilesther acetic acid and methanotiol
- Cosmetic formulations, PCPs and industrial uses: ethylbencene, dietilphthalate, 1,2,4-trimethylbenzene, methyl-isobutylcetone, eucaliptol, tetradecane, nonadecane.

Estrogenic hormones such as estrone, 17-β-estradiol, 17-β-estradiol acetate and 17-α-ethiny-lestradiol, were present in both residual waters and supply sources in ultra-trace amounts (ng/L). The highest concentrations were found in the residual water from Mexico City and in the Xotho canal (Table 5 and Table 6). The concentration of hormones in AR00 –Emissor Central and AR003-El Salto and AR004-Salado rivers, AR013-Xotho canal and in 019-Chilcuautla well is notable.

Supply source	Concentration (ng/L)	Supply source	Concentration (ng/L)
002 "Tezoquipa" Well	3.021	003 "El Tablón" Well	0.524
004 "Dendhó" Well	1.228	005 "San Antonio" Well	5.633
006 "El Refugio" Well	1.320	007 " Ajacuba" Well	2.105
008 "Noria Tetepango" Well	ND	009 "Doxey" Well	ND
010 "Tlaxcoapan" Well	0.134	011 "Teltipan" Well	3.105
012 "El Pueche" Well	3.080	013 "Atengo" Well	ND
014 "Xochitlan" Well	0.158	015 "Progreso" Spring"	ND
016 "Progreso"	1.176	017 "Cerro Colorado" Spring	5.660
018 "Fitzhi" Well	2.110	019 "Chilcuautla" Well	11.426
020 "Pedro Ma. Anaya" Well	ND	023 "El Llano" Well	4.510

Table 5. Total estrogens in water supply sources (ND: no detected).

Sampling site	Concentration (ng/L)	Sampling site	Concentration (ng/L)
W "002 Emisor Central" Pipe/ canal	86.032	W 003 "El Salto" River	68.725
W 004 "Salado" River	ND	W 005 "Tlamaco Juandhó" Canal	ND
W 006 "Salto-Tlamaco 1" Canal	76.314	W 007 "Salto-Tlamaco 2" Canal	39.13
W 008 "Principal Requena 1" Canal	11.74	W 009 "Principal Dendhó" Canal	114.599
W 010 "Principal Requena 2" Canal	60.067	W 012 "Principal Requena 3" Canal	33.855
W 013 "Xotho" Canal	12.141		

Table 6. Total estrogens in wastewater (ND: not detected).

In the second monitoring campaign six of the eight supply sources showed contamination from Phs and PCPs (Table 8), in ultra-trace concentrations: erythromycin, sulfamethoxazole (antibiotics), carbamazepine (antiepileptic), methylprednisolone (steroid anti-inflammatory used in cases of allergy), DEET (PCP), caffeine and benzoilecgonine (metabolite of cocaine). Chlofibric acid was found in 002-Tezoquipa (55.5 ng/L) and 003-El Tablón (36.67 ng/L), and AR003-El Salto (41.32 ng/L). The same river also showed traces of gemfibrozil (63.2 ng/L).

Source	Caffeine	Benzoyl-ecgonine	DEET	Methyl-prednisolone	Carba-mazepine	Erithromycin-H ₂ O	Sulfa-methoxasole
002	ND	ND	0.948	12.9	ND	ND	7.25
006	ND	ND	1.64	ND	ND	0.325	ND
013	24.3	4.93	2.01	ND	11.5	1.08	15.9
014	22.9	ND	1.01	ND	ND	0.31	16.7
017	ND	0.318	0.923	5.2	5.24	1.35	10.4
019	ND	ND	1.14	6.59	ND	1.05	22.8

Table 7. Pharmaceuticals and personal care products (concentration in ng/L; ND: not detected).

3.7. Bisphenol A, alkylphenols and alkylphenol-ethoxylates

As previously noted, bisphenol A and alkylphenols, including their ethoxylates, are relevant from a public health standpoint for their potential to alter endocrine processes in humans and aquatic and terrestrial organisms of various taxonomy. They are found in a variety of products of frequent use and are used as an adjuvant in the application of pesticides, which explains why, in the monitoring campaign that took place during the dry season, the highest concentrations were found in residual waters of AR02-Emisor Central and in AR03-El Salto y AR04-Salado rivers, as well as in the irrigation canals in the south zone. Furthermore, the concentrations of these contaminants in the supply sources were not homogenous and there was no obvious trend that suggested that wastewater from Mexico City was the only source of contamination. This is why we concluded that there was an influence from the interior of the Valley (Table 8. and Table 9).

Supply source	Concentration (µg/L)	Supply source	Concentration (µg/L)
002 "Tezoquipa" Well	ND	003 "El Tablón" Well	ND
004 "Dendhó" Well	ND	005 "San Antonio" Well	2.29
006 "El Refugio" Well	ND	007 "Ajacuba" Well	4.23
008 "Noria Tetepango" Well	2.10	009 "Doxey" Well	6.07
010 "Tlaxcoapan" Well	3.7	011 "Teltipan" Well	2.51
012 "El Pudehe" Well	0.18	013 "Atengo" Well	ND
014 "Xochitlan" Well	2.0	015 "Progreso" Spring	ND
016 "Progreso"	ND	017 "Cerro Colorado" Spring	ND
018 "Fitzhi" Well	0.18	019 "Chilcuautila" Well	1.12
020 "Pedro Ma. Anaya" Well	ND	023 "El Llano" Well	ND

Table 8. Total alkylphenols and etoxilates in water supply sources (ND: not detected).

Sampling site	Concentration (µg/L)	Sampling site	Concentration (µg/L)
W "002 Emisor Central" Pipe/canal	41.28	W 003 "El Salto" River	64.57
WW 004 "Salado" River	17.41	W 005 "Tlamaco Juandhó" Canal	40.73
W 006 "Salto-Tlamaco 1" Canal	19.03	W 007 "Salto-Tlamaco 2" Canal	24.29
W 008 "Principal Requena 1" Canal	43.82	W 009 "Principal Dendhó" Canal	94.87
W 010 "Principal Requena 2" Canal	23.84	W 012 "Principal Requena 3" Canal	25.9
W013 "Xotho" Canal	1.52		

Table 9. Total alkylphenols and etoxilates in wastewater.

3.8. Sanitary risks to the Mezquital Valley

Fifty-nine illnesses were identified as the primary causes of general mortality. Diabetes mellitus type II is at the top of the list, and ischemic illnesses of the heart, cerebral vascular ailments, diverse types of cancer (mainly breast, prostate, liver and leukemia) are among the primary causes of death. These diseases are multi-causal and related in great part to diet and life style as well as genetic and epigenetic factors; however environmental exposure to organic and inorganic contaminants can also contribute to the risk of contracting these ailments, which is why it is necessary to conduct studies that allows discovery or estimation of the contribution of water to these diseases.

For both samplings, hazard of exposure to 173 ECs was qualitatively identified, of which 35 are of high priority for their carcinogenic potential or systemic toxicity and among these, for their potential as EDs (acknowledged and suspicious [103-106]) and the frequency with which they were found of note are:

- Cosmetics, PCP and hygienic products formulations: ethylbenzene, octadecanoic acid (stearic acid), octyl-dimethyl-paramino benzoate (Escalol 507) and DEET
- Pharmaceuticals: carbamazepine, methylprednisolone, erythromicine
- Pesticides: 1,4-diclorobenzene
- Industrial uses: 1,2-dichloropropane, benzene, chloroform, n-propylbenzene, tetrahydrofurane, tetrachloroethylene, 1,1,2-trichloroethane
- Plasticizers: di-isobuthylphthalate, dipropylphthalate
- Estrogens: estrone, 17- β -estradiol, 17- β -estradiol acetate and 17- α -ethinylestradiol

By using a methodological approach of health risk assessment and analyzing the results of a survey completed by [107] from 1000 permanent residents in the Mezquital Valley, this study estimated the exposure to contaminants identified as hazardous through the use and consumption of water. The ingested dose via this route was compared to values of toxicity available on The Risk Assessment Information System data bases [108]. The hazard coefficient was obtained for arsenic, fluoride, bisphenol A, nonilphenol, naphthalene, and esters of ftalic acid or ftalates. The hazard coefficient or hazard index (HI) were estimated based on the volume of water consumed, concentration of the analyte in the water, intensity, frequency and magnitude of the oral exposure, body weight and the reference dose for critical effect in the target organ. A HI of 1.0 or less indicates that the exposure poses no health risks.

Hazard Index greater than 1.0 were identified for arsenic, mercury and fluoride, which means there are health risks associated with such substances in drinking water (Table 10). When such indexes are calculated for municipalities, greater hazards are identified. For example: Arsenic HI in Atitalaquia was 7.87 (\pm 5.08), in Progreso 2.29 (\pm 1.13) and in Tlaxcoapan 5.23 (\pm 2.47); Fluoride HI in Atitalaquia was 3.31 (\pm 2.14), in Atotonilco de Tula 2.98 (\pm 1.65), in Chilcuatla 4.68 (\pm 2.65), in Ixmiquilpan 5.40 (\pm 2.81), in Progreso 4.26 (\pm 2.33) and in Tlaxcoapan 3.03 (\pm 1.43).

Analyte	Media HI	Standard deviation	Min HI	Max HI
Arsenic	2.48E+00	4.07E+00	8.22E-03	2.41E+01
Mercury	3.26E-01	4.39E-01	0.00E+00	2.61E+00
Fluoride	3.95E+00	3.28E+00	2.74E-01	2.10E+01
Bisphenol A	7.18E-04	2.12E-03	0.00E+00	1.86E-02
4-Nonylphenol	2.81E-03	3.93E-03	0.00E+00	2.04E-02
Bis-2-(ethylhexyl)-phthalate	9.28E-03	3.51E-02	0.00E+00	3.07E-01
Diethylphthalate	5.78E-06	1.39E-05	0.00E+00	1.09E-04
Dibuthylphthalate	8.94E-04	3.04E-03	0.00E+00	2.68E-02

Table 10. Average Hazard Index from consumption of water with EDs (recognized and suspicious) within Mezquital Valley.

Even though at present it is not possible to associate health risks with chronic ingestion of organic EDs, there is uncertainty about exposure to small doses and the effects in the middle and long terms, besides the concomitant exposure.

3.9. Water treatment test

Pilot scale testing was carried out to make sure NF was effective at removing certain minerals, organic matter and ECs. Two supply sources within the valley were selected for this purpose. The first phase of testing was conducted in the Cerro Colorado spring for 82 consecutive days. This source supplies water to 4 municipalities within the Valley (Mixquiahuala, Progreso, Tepacatepec and Tezontepec). Water characteristics are shown in Table 11. Due to these mineral characteristics of the water (hardness and silica content) up to 72% water recovery can be obtained.

Parameter	Concentration	Unit	Parameter	Concentration	Unit
Cl ⁻	148	mg/L	Na	195.14	mg/L
F ⁻	1.64	mg/L	Hardness	237.1	mg CaCO ₃ /L
HCO ₃ ²⁻	271.53	mg CaCO ₃ /L	SDT	1,147	mg/L
SO ₄	169.96	mg/L	pH	7.16	
SiO ₂	63.1	mg/L			

Table 11. Cerro Colorado Spring water quality.

Pilot scale NF tests were performed with a two stage skid; a 4:2 pressure vessel array with each pressure vessel holding 3 standard elements (NE4040-90 CSM), respectively, was utilized. Through brine recirculation, this design can simulate a two stage full-scale skid, employing six (8" X 40") elements per vessel.

In Figure 6 the pilot installation is shown: The whole treatment train includes sand filtration, a 5 m³ filtered water storage tank, 10 μm cartridge filtration, antifouling agent addition and NF.

The second phase of testing was conducted in the Tezoquipa well, located in Atitalaquia, Hgo. It lasted 36 days. In the first monitoring campaign, we found that the concentration of dissolved solids in this well was among the lowest in the Valley. However, heavy metals were found in the water, which is why it was selected for the second phase of the water treatment test.



Figure 6. Pilot unit including multimedia filtration and NF.

3.9.1. Rejection of mineral and organic compounds

To assess the performance of the NF pilot, six parameters were measured in feed water, permeate and brine: Conductivity, SO_4^{2-} , F^- , Hardness, HCO_3^- and TOC. Figures 7, 8 and 9 show the rejection of those parameters monitored during water treatment tests.

Mineral content rejection, at the beginning of water treatment testing, was 80% (measuring conductivity). This level of efficiency was about 10% below the rejection calculated with the CSM4PRO design software (corresponding to membranes NE4040-90 of CSM). However, as the test progressed, the salt rejection rose to 93%, which was very close to the calculations made by CSM4PRO.

HCO_3^- removal was 92% on average (± 0.9981) while hardness was rejected at a higher rate of 97.46% on average, with a minimum of 95.12 and a maximum of 98.95%.

Sulphate removal was 98.78% on average, with a maximum of 99.57% and a minimum of 95.75%. These results are consistent with the characteristics of the membrane, since it is a negatively charged hydrophobic membrane specialized in the removal of polyvalent anions.

Fluoride rejection oscillated between 80% and 96.77% (Figure 8). The variability in the results could be explained by changes in feed water temperature. Filtered water coming from the spring was stored in the 5m³ tank. The tank was exposed directly to sunlight, causing a rise in water temperature. While samples and measurements were meant to be taken at 13:00 hours, this was not always possible and there was no control over ambient temperatures.

Organic matter, measured as TOC, was rejected at a rate of 82% on average (Figure 9). Nevertheless, its rejection rate varied from 41% to 100%. It is worth mentioning that in two of the four measurements in which removal efficiency was less than 45%, the concentration of TOC in the raw water was lower than 2 ppm; even so the variability is considerable.

With respect to pharmaceuticals and personal care products, laboratory data indicates that the membranes were capable of rejecting all of the sulfamethoxazole% (Table 12).

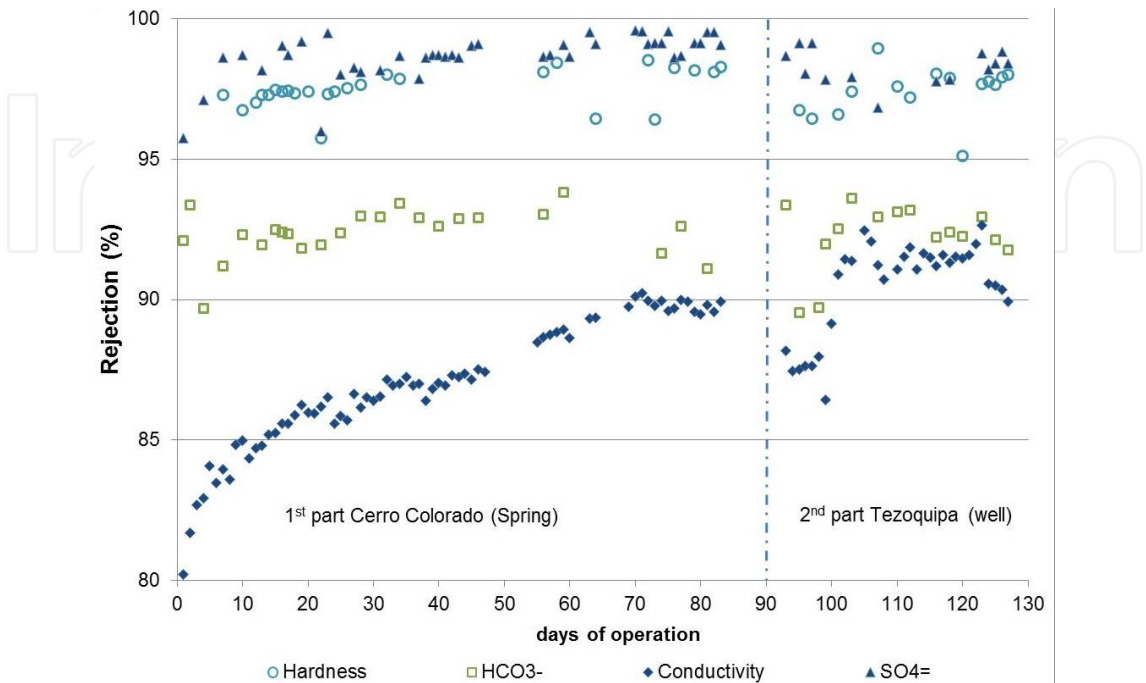


Figure 7. Major ions rejection observed in water tests.

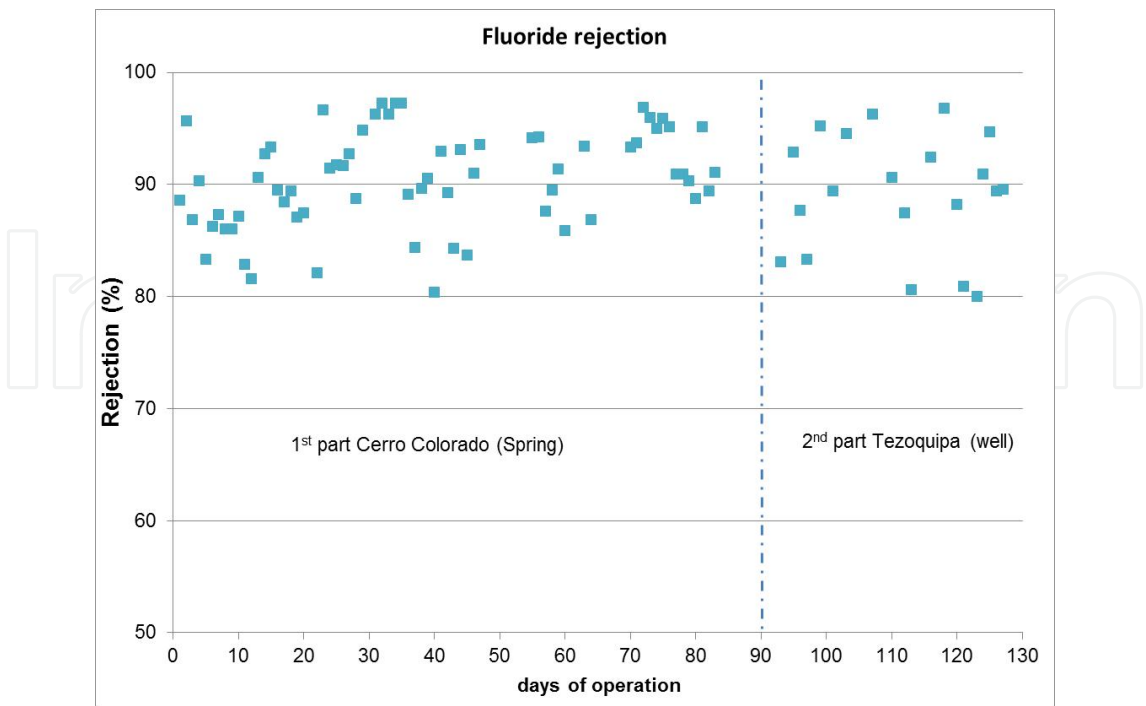


Figure 8. Fluoride removal efficiency observed in water treatment test.

Erythromycin-H₂O and cocaine were found in the brine but not in the feed water or permeate. Given the low concentrations reported (fractions of nanograms), it is plausible that the raw water contained these compounds at non-detectable levels and that they were rejected with great efficiency, causing these substances to reach concentrations at a detectable and quantifiable level.

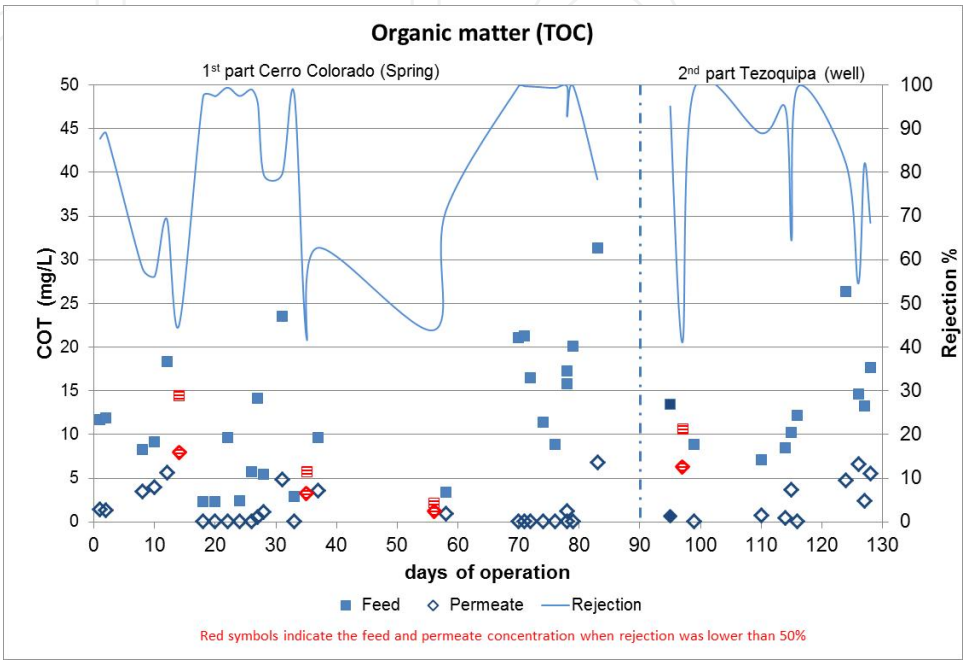


Figure 9. NF performance for organic matter removal.

Site	Compound	Concentration (ng/L)
Raw water	Sulfamethoxazole	7.25
	DEET	0.948
	Methylprednisolone	12.9
Permeate	DEET	2.01
	Methylprednisolone	11
Brine	Caffeine	14.5
	Eritromicina-H ₂ O	0.654
	Sulfamethoxazole	18.8
	Cocaine	0.172
	DEET	0.848

Table 12. Pharmaceuticals and PCPs in water treatment test.

The NF membranes do not appear to be effective in the removal of DEET and are inefficient in the removal of methylprednisolone. The molecular size of DEET is smaller than the

Molecular Weight Cut-Off of the membrane. Also, DEET is a neutral molecule, so negatively charged membranes won't exert electrostatic repulsion. In the case of methylprednisolone, it is of note that it was not found in the brine. This, according to the mass balance, is not possible. In other words, if the concentration in the feed and the permeate streams are the same, the same should be true for the brine.

Overall, groundwater quality within the Valley does not meet the Mexican Drinking Water Quality Standard [94], from a total dissolved solids standpoint [94]. In some sources hardness, sulphate, fluoride and heavy metals like lead, mercury and arsenic are present at concentrations exceeding the MCL. NF was able to reject all these substances at such a rate that the permeate met the Mexican Drinking Water Quality Standard. From the mineral rejection standpoint, NF seems to be an interesting alternative to treat the Mezquital Valley ground water in order to produce drinking water.

4. Conclusions and research needs

In the semi-arid Mezquital Valley, reusing wastewater for agricultural purposes has benefitted aquifer recharge, which has increased the availability of water destined for various human activities, such as drinking water. Nevertheless, the presence of As, F, Hg and Pb and multiple organic pollutants in 19 water sources that were sampled showed a wide variety of potential health risks, including disruptions of the endocrine system.

The Hazard Quotients (HQ) estimated for the EDs (acknowledged and suspected) in the mentioned area indicated risks associated ($HC > 1.0$) with As and F, while no risks were found at the time of the study for organic EDs (phthalates, nonilphenols and bisphenol A). Nevertheless, in water reuse scenarios such as this one, even with the limitations inherent to both point monitoring and considering the lack of scientific knowledge.

It is necessary to emphasize the prevention of human exposure to EDs, considering that: a) the effects of critical exposure during intrauterine, perinatal and puberty periods may not manifest until adulthood; b) the population in the Mezquital Valley is exposed to a mixture of EDs that could lead to the addition, synergy, potentiation or antagonism of effects, and c) it may be assumed that the entire population is potentially exposed to these pollutants since, in qualitative terms, all water sources presented at least one ED.

More monitoring campaigns focusing on EDs in a greater number of supply sources are necessary to quantify the EDs with greater precision and estimate exposure with higher accuracy.

Studies are required to integrate environmental aspects, life style and toxicological research with epidemiology (cohort retrospective study or control cases) that allow associations to be established between EDs exposure with ailments or specific health issues: i.e. diabetes mellitus type II, the development of various types of cancer, reproductive function and processes and neurodevelopment, which are currently of interest to various groups of researchers and the governmental agencies responsible for regulation and policies in health, water and the environment.

On the other hand, the byproducts of the degradation and transformation of a compound can also alter the hormonal system and, while a large number of researchers believe that physico-chemical characteristics of the molecules determine the molecules' behavior and environmental distribution, a greater understanding of their action, transformation and environmental fate are also required to assess and minimize the health risks associated with exposure to EDs in concentrations relevant to drinking water.

Water delivered through public networks must be treated in order to comply with the Mexican Standard for water quality. A NF process will remove mineral pollutants found in the Mezquital Valley. Nevertheless, from an ED standpoint, further tests are needed in order to obtain enough evidence to determine if NF is capable of producing drinking water from these sources, or another process is needed, either as a substitution (like RO) or a complement (like activated carbon).

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