EC PHARMACOLOGY AND TOXICOLOGY
Review Article

Trace Analysis Reveals Pharmaceuticals and Metabolites in Recycled Brackish Water used for Irrigation

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Abstract

The scarcity of water in many areas of our planet earth and the exploding population dictate the use of reclaimed wastewaters for human use and irrigation of fields to grow nutritious crops. The procedures applied in most recycling facilities nowadays, however, leave traces of many kinds of toxic compounds in the reclaimed waters. Nano ultrafiltration is an efficient method that removes these toxins. Application of such filtration technology is imperative and municipal water installation are expected to apply in for their recycled wastewaters.

Keywords: *Pharmaceuticals; Metabolites; Recycled*

Introduction

Scarcity of waters – reuse of municipal wastewaters. Recently, the scarcity of water annoys the Israelis, despite huge investments and establishment of mega-scale seawater desalination plants, Israel [1] suffers from water shortage. These plants supply 80% of the municipal water use of the country. However, the five years drought dried out the natural drinking water sources: fountains, wells rivers, and the lake of Galilee.

Israel treats its municipal wastewater in many local plants, scattered all over the country. These waters are applied only partially for crop production, since the technology applied for the recycling does not eliminate many toxins, and rests of pharmaceuticals. Agrochemicals and toxic metal ions could be detected in the agricultural products cultivated on these waters.

Modern Nano-ultra-filtration methods reduce these toxins to a minimal, legally allowed level. It is reasonable to improve the current way water is reclaimed with this commercially available technology, and refrain from corrupting this precious resource to the sea instead of enforcing the current water supply with the enormous amounts of recycled municipal wastewaters [2]. Recently, the application of microfiltration-reverse osmosis/nanofiltration [3], commercially available, [4] to trace organics removal for municipal wastewater reuse [5]. Nanofiltration is a membrane separation process whose cut-off lies between that of reverse osmosis and ultrafiltration [6]. The commonly used operating pressure is in the range of 0.3 – 4.0 MPa. Cut-offs are specified as being between 180 and 2000 Dalton.

The fate of organic micropollutants (MPs) in a membrane system based on microfiltration (MF) and reverse osmosis/nanofiltration (RO/NF) has been investigated for the case of wastewater reuse. Both an operating full-scale water reuse plant and a pilot plant were employed, with 22 individual organic compounds at their ambient concentrations studied for the former and the latter employing two target compounds over a range of feed concentrations. Results revealed removal efficiencies higher than 75% for most compounds in the full-scale plant, though mass flow studies on all streams revealed a significant imbalance of material for some compounds.

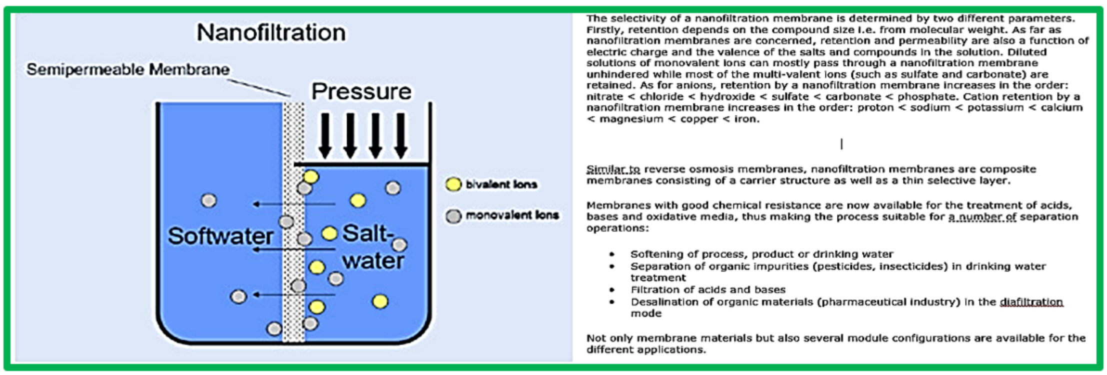

Figure 1: *The nanofiltration technology, credit ref [7,8].*

Japanese researchers [9] used ceramic nanofiltration for removal of rests of organic contaminant in recycled municipal wastewater. (Ceramic nanofiltration (NF) Membrane and Bench-Scale NF Filtration System). An approach to minimize the cost and physical footprint of water recycling (especially in an urban environment) is to replace the filtration-based [10] pre-treatment with an ozone-based process. This is particularly attractive since ozone can be generated onsite and injected directly into the inlet of the NF system without a contact basin. Ozone is a strong oxidant commonly used to decompose organics as part of a water treatment system [11].

Irrigation with treated wastewater: uptake of pharmaceutical and personal care products by common vegetables under field conditions

Water recycling – California's Orange County Water District (OCWD), has a plant that recycles used water returns it to the drinking supply. It is expanding production to 100 million gallons per day, enough for 850,000 people [12].

In arid countries like Israel, Brackish and in particular sewage waters are a source of the precious drinking waters. Purification technologies based on many energy sources renewable and fossils have been presented with remarkable success. However, In recent years pharmaceutical compounds used by humans and livestock are being identified in the vegetable that people consume, due to irrigation with these purified waters.

The situation is not a catastrophe yet, but there is uncertainty about how such minute quantities of bioactive materials are able to affect public health

New research led by Exeter and Plymouth University School of Medicine may find a significant impact on plant growth.

Scientists of the Hebrew University of Jerusalem recently discovered carbamazepine, an anti-epileptic drug, in the urine of people who ate vegetables that were irrigated in treated wastewater. This is one of the first reports to demonstrate that drug contamination in irrigation water results in human exposure to drugs through the consumption of irrigated crops [13].

It is a fact that the same products produced and grown in the soil launched in treated saline wastewater increase their exposure to the drug.

Although the levels detected were much lower than the patients consuming the drug, it is important to assess the availability of commercially available produce [14].

Beyond microbiological safety, concerns have been raised about wastewater contamination recovered by xenobiotics including drugs. This study focuses on mezzanine, an anticonvulsant drug that is found everywhere in returned wastewater, is very persistent in the soil and is taken up by crops. In a randomized controlled trial, researchers demonstrate that healthy people who consume dehydrated wastewater produce secretion of carbamazepine and their metabolites in their urine, while subjects who consume freshwater irrigation produce undetectable or significantly lower levels of carbamazepine. Researchers report that the carbamazepine metabolite pattern at this low.

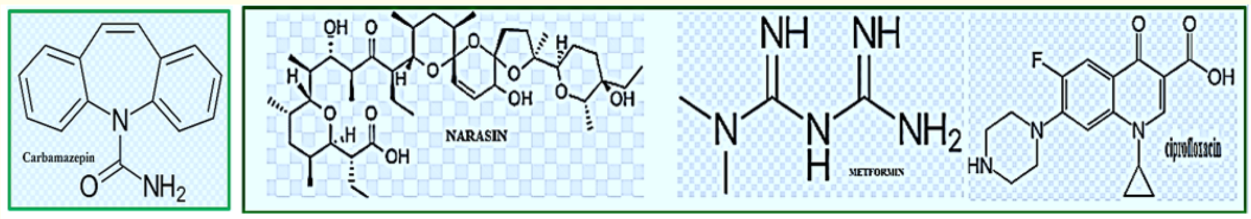

Figure 2: *Drug molecules identified in crops irrigated with "purified" brackish waters.*

The level of exposure is different from that observed at therapeutic doses [15]. The transfer of bioactive drug material from soil to the plants might cause animal and human health risks. The sewage is a potential source for compounds such as human- and veterinary drugs. In the present paper, uptake of the anti-diabetic compound, metformin for example, the antibiotic agent ciprofloxacin and the anti-coccidial narasin in carrot and barley (Hordeumvulgare) are presented. The drug materials were chosen in order to cover various chemical properties, in addition to their presence in relevant environmental matrixes. The root concentration factors (RCF) found in the present study were higher than the corresponding leaf concentration factors (LCF) for the three test pharmaceuticals. The uptake of metformin was higher compared with ciprofloxacin and narasin for all plant compartments analyzed. Metformin was studied more explicitly with regard to uptake and translocation in meadow fescue (Festucapratense), three other carrot cultivars, wheat cereal (Triticumaestivum) and turnip rape seed (Brassicacampestris). Uptake of metformin in meadow fescue was comparable with uptake in the four carrot cultivars (RCF 2-10, LCF approximately 1.5), uptake in wheat cereals were comparable with barley cereals (seed concentration factors, SCF, 0.02 - 0.04) while the accumulation in turnip rape seeds was as high as 1.5.

All three pharmaceuticals produced negative effects on growth and development of carrots when grown in soil concentration of 6-10 mg kg (-1) dry weight [16].

Irrigation with wastewater [17,18]

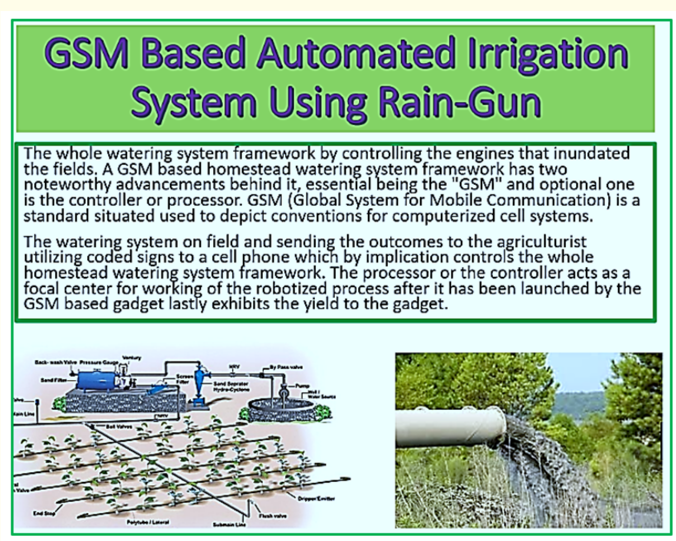

Figure 3

The extent to which the treated wastewater influences crop selection will depend on government policy on effluent irrigation, user goals and wastewater quality.

Irrigation can be defined as applying water to the soil for enabling the moisture essential for plant growth. Irrigation plays a vital role in increasing crop yields and stabilizing production. In arid and semi-arid areas, irrigation is essential for economically viable agriculture, while in moist and humid areas, it is usually required on a complimentary basis.

Irrigation quality requirements are discussed in terms of crop production. The guidelines presented are indicative of their nature and should be adapted to local climate, soil conditions and other factors. In addition, farming practices, such as the type of crop to be grown, irrigation method and agronomic methods will largely determine the degree of quality adjustment of irrigation water.

Far land from a wastewater treatment plant would incur high costs of transporting wastewater to the site and would generally not be suitable. Hence the availability of land for irrigation should be taken into account when designing sewage and wastewater treatment plants should be strategically located with respect to suitable agricultural sites. Ideally, these sites should not be close to residential areas, but even remote lands may not be acceptable to the public if social, cultural or religious attitudes are opposed to wastewater irrigation practices. The potential health hazards associated with wastewater irrigation can make this a highly sensitive issue and public concern will only continue by implementing strict controls. In arid areas, the importance of treated wastewater agriculture means that it is recommended to be as systematic as possible in planning, developing and managing effluent irrigation projects and informing the public at all stages. The ideal goal for site selection is to find a suitable area where long-term effluent can be applied without adverse environmental or public health impacts. It is possible that at some point some potential sites that are within a reasonable distance of the sewerage community can be identified and the problem will be to choose the most suitable area or areas, taking into account all relevant factors. The following basic information about the area below.

Wastewater origins [19]

Industrial wastewater originates from many sources, including iron and steel, food mining, paper pulp, textiles, and chemical industries. Industrial wastewater can be effectively treated by membrane reactors (MBR) (table below) similar to urban wastewater treatment. However, along with the rapid development of industrialization and urbanization or due to the uniqueness of some industries, industrial wastewater and urban wastewater sources contain toxic chemicals such as heavy metals and organic pollutants (TrOCs). They cannot be easily removed by standard water treatment or MBR technologies. Clearing / recovery of heavy metals from wastewater, so we will look at membrane-based technologies for TrOC removal in this section. TrOCs are a diverse group of compounds that include persistent organic compounds (POPs), pesticides, drug-active compounds (PhACs), and endocrine disrupting chemicals (EDCs). The TrOC concentration ranges from 100 ng / L to 100 µg / L in raw wastewater. Even if their contents in wastewater are very small, many are biologically active and can cause acute and chronic toxicity to aquatic organisms and possible harmful effects on human health. Intensive membrane-based technologies have been tested to remove TrOCs, such as MBR, single membrane processes (NF, RO, FO), dual membrane processes (UF + RO, FO + RO), and hybrid processes (MBR or BR (bio-rector) + NF, RO, FO, MD).

Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants

In recent years, many of the contaminants are reported due to ongoing input of environmentally-friendly medications and personal care products (PPCPs) and recent analytical methods. PPCP residues are polluting in drinking water sources, wastewater treatment plants (STPs) and water treatment facilities (WTPs) due to their universal consumption, low metabolic capacity of humans and improper disposal. When partially metabolized PPCPs are transmitted to STPs, they exert adverse effects on biological treatment processes; Therefore, conventional STPs are insufficient when it comes to removing PPCP.

MBR applications in industrial wastewater treatment.

Source	Country	Size of operation	Efficiency
Wool scouring	Japan	Pilot-scale ~ 10 m^3/d	TOD removal > 89%
Pulp mill	Japan	Pilot-scale ~ 10 m^3/d	TOC removal > 85%
Automotive industry	USA	Full-scale 113 m^3/d	COD removal > 94%
Metal transforming	Canada	Pilot-scale 0.2 m^3/d	COD removal > 90%
Cosmetic industry	France	Full-scale	COD removal > 98%
Maize/egg processing	South Africa	Full-scale 500 m^3/d	COD removal > 97%

Figure 4

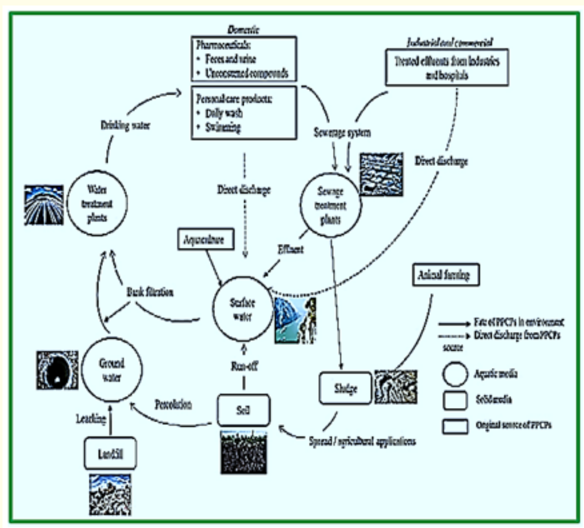

Figure 4

Furthermore, the secreted metabolites may become secondary contaminants and can be further modified in water receiving. Some of advanced treatment systems, including membrane filtration, granular active carbon, and advanced oxidation processes, have been used to efficiently remove individual PPCPs. This review covers the occurrence patterns of some PPCPs in aquatic environments and the techniques adopted to address them in the STP / WTP unit processes operating in different countries.

The purpose of this review is to provide a comprehensive summary of the removal of the fate of PPCPs in various treatment facilities as well as the optimal methods for eliminating them in STP and WTP systems [20].

Many farmers in developing countries are minorities in water irrigation because:

- It is the only water source available for irrigation throughout the year,
- Wastewater irrigation reduces the need to purchase fertilizer,

- Wastewater irrigation involves lower energy costs if the alternative clean water source is deep groundwater wells, or wastewater allows farmers in urban areas to produce high-value vegetables for sale in local markets.

With freshwater resources and unevenly distributed population density around the world, water requirements are already surpassing supply in areas with more than 40% of the world's population. As a result, agriculture has gradually produced its share of non-agricultural uses. As the use of fresh well water for non-agricultural activities produces wastewater, the volume of wastewater increases, depending on the rapidly growing residents, urbanization, improved living conditions and economic development.

Approximately 90% of urban wastewater produced worldwide, especially in low-income countries, remains untreated because the sewer system, physical infrastructure, including pipes, pumps, screens and ducts, etc. used to transport sewage from its source to eventual treatment or disposal is Very expensive. Incredibly expensive wastewater treatment plants require a large amount of energy and are difficult to maintain. Most wastewater from the STPs does not meet the desired treatment standard. As a result, a large amount of urban sewage is dumped directly into water bodies adjacent to the urban communities, polluting downstream water sources [21].

Figure 6: *Brackish and sewage waters pollute freshwater sources (credit ref. [6]).*

Long-term wastewater irrigation of vegetables in real agricultural systems: Concentration of pharmaceuticals in soil, uptake and bioaccumulation in tomato fruits and human health risk assessment [22,23].

Wastewater reuse (WW) for irrigation of vegetable crops is regularly applied worldwide. Such a practice has emerged as enabling the consumption of plant-active substances (PhACs) by plants and their subsequent entry into the food web, which represents an important alternative pathway for human exposure to PhAC levels, with potential health implications. Below is a report on the effects of the long-term (three years in a row) irrigation of two different wastewater treated tomato crops under real farming conditions, on (1) the soil concentration of selected PhACs (i.e. diclofenac, DCF; sulfamethoxazole, SMX; trimethoprim, TMP), (2) the biological accumulation of these PhACs in tomato fruit, and (3) the human risks associated with fruit consumption launched in WW. Results showed that the PhAC concentration tested in both soil and tomato fruits varied according to the qualitative characteristics of the treated wastewater applied and the duration of WW irrigation.

Recently, a growing number of herbal medicine (PC) plant consumption reports have been raised, raising concerns about human exposure through dietary intake. In this study, PC uptake and translocation assessment of cucumber and tomato plants was assessed to elucidate the effects of physicochemical properties on computers, soil type and irrigation quality. Non-union laptops were collected and accumulated at higher levels in plants grown in soil with low organic matter and clay content. While most cucumber and tomato personal computers were in a similar order, their concentration in tomato fruit was much lower than cucumber fruit. This has to do with differences in the physiology of fruit. Our data shows that treated wastewater treatment reduces the bioavailability of acidic computers for the absorption of cucumber plants compared to freshwater irrigation. This study sheds light on factors affecting the uptake of PCs by treated wastewater-grown crops, which play a role in the physicochemical properties of PCs along with the physiological nature of the plant, soil and water quality that together determine its uptake, translocation and accumulation within the plant. Organs. Occurrence of metabolites in the plant implies that it must be present.

Reuse of treated wastewater in agriculture?

As a result of climate change, agriculture will increasingly face yield losses due to drought. The use of alternative freshwater sources, such as wastewater-treated wastewater and wastewater treatment plants, can reduce drought damage. However, these wastewater contains various substances that are foreign to the environment. What are the risks of using these wastewater in agriculture?.

Climate change is expected to increase the impact on agriculture and nature. By 2050, the average drought damage to agriculture as a result of ongoing climate change is expected to be twice as high for the Pleistocene as it is now. Water availability for higher quality applications, such as drinking water production, will be at the same pressure. To manage water scarcity risks, strategies for maintaining fresh water supply are developed in the long run. One of the pillars of these strategies, formulated in Deltaplan Hoge Zandgronden in the South Holland (Delta Plan High Sandy Soils in the South Holland) (DHZ) and the Zoetwatervoorziening Oost-Nederland (ZON), is more efficient use of water resources Locals are available. One of these steps is to reuse fresh wastewater, to complete groundwater at slip level. A possible example is the use of treated wastewater in industries and wastewater treatment plants. Despite a shortage of water in agriculture, industries and wastewater treatment plants are spreading large quantities of wastewater treated daily. In the eastern part of the Netherlands, with an average annual rainfall of almost 300 millimeters (www.klimaatatlas.nl), it was once thought that this amounts to about 40 to 50 millimeters on an annual basis. At the same time, farmers in the area often use groundwater and sometimes also a surface for watering crops. By reusing wastewater for regional water supply, water supply for agriculture is improving and crop yields are increasing, the need for reduced irrigation and pressure on other sources (such as groundwater) is being released.

Figure 7: *Treatment of treated wastewater: Use of pharmaceutical products and personal care by common vegetables under field conditions (Credit) [24,25]. Treated wastewater is an important water resource, but its use for agricultural irrigation faces a barrier: public concern about the potential build-up of pollutants with concern is emerging in human nutrition. In the present study, 19 amount of pharmaceutical care products (PPCPs) were identified and measured in eight vegetables that were watered in treated wastewater under field conditions.*

Pharmaceutical wastewater treatment [26]

Typical Treatment Results	
COD Reduction	> 90%
TSS Reduction	> 99%
Phosphorus Reduction	> 90%[1]
COD Reduction	> 90%
TSS Reduction	> 99%
	[1] with chemical addition

ZeeWeed Features & Benefits	
Feature	**Benefit**
Membrane barrier technology	• Reliable, high quality effluent at all times • Handles shock loads • Reduces treatment chemical costs
Ability to handle high MLSS concentration	• Reduces sludge production and disposal costs
Small system footprint	• Reduces capital costs, clarifiers are not required • System can be placed virtually anywhere
Modular system	• Retrofit existing treatment tanks/infrastructure • "Just-in-time" plant expansion reduces capital costs
Simple to operate	• Reduces labor costs • System can be operated remotely

Figure 8

GE Water Technology Solutions and Processes have developed and promoted MBR (Bioreactor membrane) systems to meet changing market needs. The Zee Weed * MBR system helps manufacturers meet and exceed any direct discharge regulations while simplifying the treatment process. Zee Weed MBR combines membrane filtration with biological treatment. The system replaces conventional treatment and combines clarification, ventilation and filtration into a simple and economical process that reduces capital and operating costs.

Ultrafiltration [27]

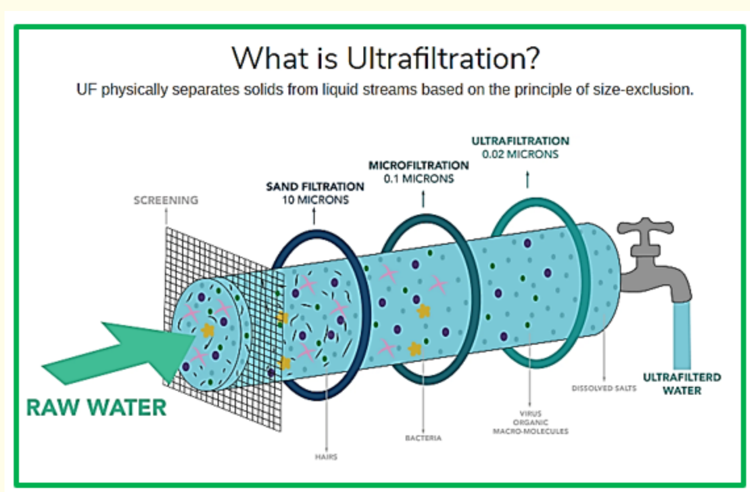

Figure 9

Ultra Filtering – the technology for the removal of traces of pollutants.

Ultra-filtration (UF) is a membrane filtration process similar to reverse osmosis, using hydrostatic pressure to force water through a semi-permeable membrane. The pore size of the ultraviolet membrane is usually 103 - 106 Dalton. Ultra Filtration (UF) is a pressure-driven barrier to hanging solids, bacteria, viruses, endotoxins and other pathogens for producing very high purity water and low erosion density.

Ultrafiltration (UF) is a variety of membrane filtration in which the hydrostatic pressure forces a fluid onto a semi-permeable membrane. Solid and suspended solids of high molecular weight are retained while solutes and low molecular weight water pass through the membrane. Ultra filtration is not fundamentally different from reverse osmosis, microfiltration or nanofiltration, except in terms of the size of the molecules it maintains.

A membrane or, more correctly, a semi-permeable membrane, is a thin layer of material capable of separating materials when a driving force is used across the membrane. Once considered just viable technology for desalination, more and more membrane processes are being removed to remove bacteria and other microorganisms, particulate matter, and natural organic matter, that can impart water, flavors and odors to water and react with disinfectants to create disinfectant byproducts. (DBP).

As membranes and module design progress, capital and operating costs continue to decline. The pressure-driven membrane processes discussed in this fact sheet are micro-filtration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

Safety

With national guidelines (Australia) on recycled water for drinking water published in 2008, with increasing demand on water supply, recycling is going to become more common. The guidelines aim to make sure recycling is done safely, without being sidetracked by the debate over whether recycling is a good or bad idea. The guidelines are aimed at decision-makers and project managers and explain what the risks are and how to manage them.

Although Municipal wastewater and sewage are cleared today all over earth mostly in a microbiological based industry [28], a more delicate treatment targeted at the removal of traces of pharmaceuticals, heavy metal ions, agrochemicals and more organic and inorganic materials by use of ultra Nano-filtration, a high pressure technology which is commercially available needed to upgrade to water to drinking water quality.

Recycled sewage water can safely be used for crop irrigation, according to new research [29,30].

They noted that irrigation of treated crops with treated wastewater is a well-established practice in some desert countries. Israel, for example, recycles about 80 percent of all municipal wastewater in wastewater treatment and plans to raise up to 100 percent by 2020. Estimates say the United States recycles only about 2 to 3 percent. Future water shortages could significantly increase the use of recycled wastewater here and around the world. Water shortages are already affecting almost a billion people.

Several options have been considered as the expensive urban water replacements. They included:

River water, which will require high salinity treatment and high suspended solids, as well as transport to the power plant.

Well, water, which would require the entrepreneur to invest in the well and drilling of a well. Rainwater that is unreliable and requires large storage tanks. Wastewater treatment, which will require long delivery pipes from the central WWTP (wastewater treatment plant).

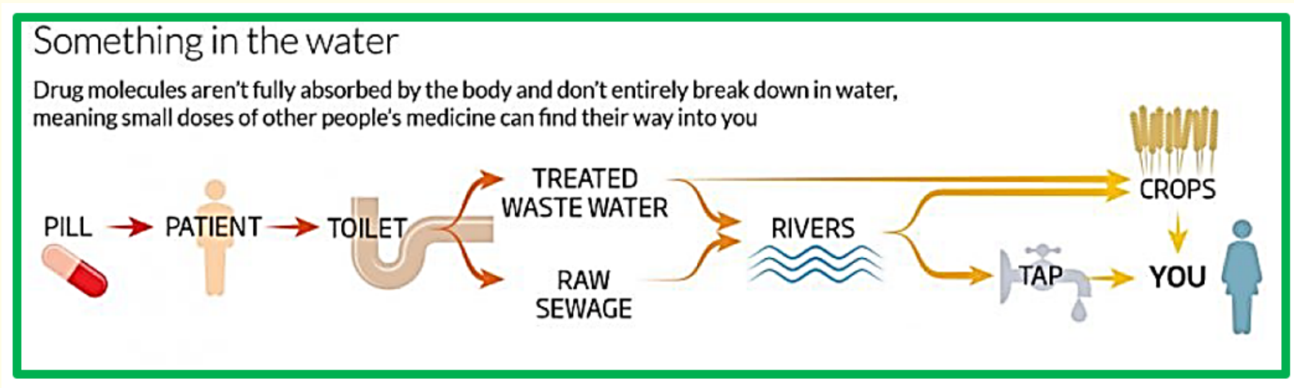

Figure 10

Raw sewage (ie sewage mining), which would require additional treatment and a municipal limit of < 2,000 mg / liter TDS (total dissolved solids (TDS)) for by-product, returned to the sewer. Medicines and personal care products - such as epilepsy, triclosan antibacterial, sedative and caffeine - were low in sedation.

Concluding Remark

Although many trace analytical methods are applied, it became clear that the watering of crops with the currently applied technology is hazardous. The application of nano-ultrafiltration is to be applied in order to remove all toxins from the reclaimed waters.

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