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Priority pollutants and other micropollutants removal in an MBR-RO wastewater treatment system

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ABSTRACT

A small footprint wastewater treatment plant that consists of a membrane bioreactor coupled with a reverse osmosis unit (MBR-RO) has been placed and set in operation for 24 months in the R&D department of the Athens Water Supply and Sewage Company (EYDAP) in order to evaluate the quality of the treated effluent and to explore the feasibility of reuse of the reclaimed water in compliance with the Greek legislation. A sustainable technology called sewer mining (SM) has been applied, which abstracts raw wastewater directly from the sewerage network, treats it on site, and provides water at the point of demand. Monitoring of system's performance was achieved through a series of lab analyses and on-line measurements. In addition to the microbiological and conventional parameters, final effluent was also analyzed for heavy metals, priority pollutants, and other micropollutants in order to examine compliance with the threshold values set in Greece for wastewater reuse of treatment plants with a treatment capacity greater than 100,000 population equivalents. Results showed that the MBR-RO technology achieves a high-quality effluent, suitable for many reuse purposes. The MBR unit managed a substantial reduction of all heavy metals, while the RO unit resulted in heavy metals removal to concentrations below the detection limit. Regarding priority pollutants following MBR treatment, all but chloroform were under the detection limit. The research confirmed the need for RO as a posttreatment level in the case of saline wastewater and/or very strict organic micropollutants threshold values.

Keywords: Sewer mining; Membrane bioreactor; Reverse osmosis; Priority pollutants; Heavy metals; Micropollutants; Water reuse

1. Introduction

During recent years, wastewater treatment schemes such as coupling of the membrane bioreactor (MBR) with the reverse osmosis (RO) have proven to be very effective in eliminating not only conventional but nonconventional pollutants as well, thus producing effluent water of high quality for any type of wastewater reclamation. Thus, the scientific community's attention has shifted to emerging contaminants; how they are produced, what do they cause to humans and the environment and at what level can existing technologies contribute to their removal from the wastewater stream. From these substances, priority pollutants (PPs), heavy metals, and other micropollutants are of paramount importance in wastewater urban reuse, where the legal framework regarding urban reuse is gradually becoming stricter worldwide.

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PPs are substances that pose a danger to both the environment and human health and may be present in water [1]. Within these substances several groups of compounds can be identified such as organotins, volatile organic chemicals (VOCs), polycyclic aromatic hydrocarbons, alkylophenols, pesticides, chlorobenzenes, phthalates, and others [2]. On the other hand, the most commonly detected toxic heavy metals in wastewater include arsenic (As), lead (Pb), mercury (Hg), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), silver (Ag), and zinc (Zn) [3].These metals pose a serious threat to humans and to the aquatic environment since they can be absorbed, accumulated, and biomagnified and can cause several known diseases, due to their toxic nature above certain threshold values [4]. Moreover, it has been found that they can affect several organs such as the kidney and induce malfunctions to the neurological system [5]. It has to be noted that Cd, Hg, and Pb are highly toxic to humans and animals but are less toxic to plants, while Zn, Ni, and Cu, when present in excess concentrations, are more damaging to plants than to humans and animals [6]. Heavy metals and PPs can enter a municipal sewage network through various pathways such as water runoff, groundwater and sanitary, light industrial, domestic or commercial sewage. Several past researches have investigated the source of both PPs [7,8] and heavy metals [9].

The main legislative tool that is being used for the protection of the aquatic environment as well as for armoring water quality, within the European Union (EU), is the Water Framework Directive (2000/60/EC) (WFD). Article 16 of the WFD expresses the EU strategy against pollution of water by chemical substances. Decision 2455/2001/EC introduced an initial list containing priority substances selected from a pool of substances posing "a significant risk to or via the aquatic environment," using the guidelines set in Article 16 of the WFD. The list initially contained 33 priority substances and most of the list's entries refer to organic contaminants (hydrocarbons, organochlorine compounds, organic solvents, pesticides, and chlorophenols), four of them are toxic metals (Cd, Hg, Ni, and Pb) and one is an organometallic compound (tributyltin). WFD makes a distinction between priority substances, for which their emissions should be reduced as far as possible and priority hazardous substances, whose use should be ceased or emissions, discharges and losses should be phased out by 2020. Priority hazardous substances are toxic, persistent and have the tendency to bio-accumulate. However, there is no certain definition for determining priority substances. The first list in the WFD was replaced by Annex II of the Directive on Environmental Quality Standards (Directive 2008/105/EC), also known as the Priority Substances Directive, which set Environmental Quality Standards (EQS) for compounds in surface waters (river, lake, transitional, and coastal). The substances have been classified in two groups, priority and priority hazardous, with the latter raising particular concerns. The Directive 2009/90/EC laid down technical specifications for chemical analysis and monitoring of water status and introduced a list of 11 substances under review for being future entrances in the PP list. Directive 2013/39/EU as the most recent one, brought further additions to the former and updated the initial list of 33 PPs, introducing 12 additional elements, compiling a list of a total of 45 compounds. This continuous upgrade of the EU directives highlights the importance of the water quality standards applied and gives insight to future directions.

The Greek legislation regarding wastewater reuse introduces certain quantitative limits which depend on the type of water reuse. More specifically, the limit values specified in the Greek National legislation regarding wastewater reuse for unrestricted irrigation and urban reuse were introduced by the JMD 145116/2011. The required quality characteristics involve a variety of parametric values concerning agronomic aspects, heavy metals, micropollutants, and microbiological indicators (in terms of *Escherichia coli*). Supplementing the quality criteria, reference is made to the minimum requirements with respect to the treatment schemes to be adopted for each type of reuse. Regarding heavy metals and PPs, there are two separate tables for each category which incorporate 19 and 40 compounds, respectively. An amendment of the Joint Ministerial Decision 145116/2011 (JMD) occurred via the Government Gazette B 69/2016 (GG), which introduced 3 new PPs and more detailed quality standards.

In this context, monitoring of heavy metals and PPs becomes crucial in water reclamation applications. One of the technologies that steadily gains popularity aiming to substitute freshwater in nonpotable uses is called sewer mining (SM). This practice focuses on draining wastewater directly from the sewage network, while the treatment takes place at the point of use. It belongs to the group of decentralized options for water recycle/reuse, targeting mainly urban reuse and, therefore, it is considered appropriate to examine a wide spectrum of substances, including heavy metals and PPs.

For the goal of examining the quality of the reclaimed wastewater of a SM unit, an innovative small footprint SM packaged treatment unit for urban reuse, consisting of a MBR coupled with a RO unit, has been installed in the R&D department of the Athens Water Supply and Sewerage company (EYDAP) in the Metamorphosis region. Taking into consideration the criteria for urban water reuse set in the Greek legislation, which impose advanced treatment, and at the same time the need for mobile, compact, and distributed wastewater treatment units within the urban framework, MBR proved to be the most suitable type of treatment. MBRs require less space than traditional activated sludge systems due to the shorter hydraulic retention time in the bioreactor. MBR is the best-fit solution when high-quality effluent with greater reuse potential is required, compact plants are considered, land limitations are expected, reduced footprint is required and potential reduction of sludge volume due to high SRT values is desirable. The use of RO as a posttreatment level is considered in the case of reuse of saline wastewater. Therefore, within the context of SW and decentralized treatment, a combination of MBR, followed by an RO unit, when needed (in the case of saline water), presents a great potential for the treatment of raw sewage of various sources, being able to produce reclaimable water that falls very well in the concept of applying multiple barriers to protect public health and is also in line with the strict advanced treatment demands set in the Greek legislation for urban reuse. Finally, the total cost of reclaimable water, including operating and capital expenditure (OPEX and CAPEX), is not prohibitive; in the case of retrieving 100 m^3 of wastewater per day; the cost

is around 0.86 € m^{-3} when only MBR is applied and 1.07 € m^{-3} when MBR-RO is applied [10].

In view of the above, this is one of the few studies that test a SM unit in real conditions and aims at assuring that the reclaimed water complies with the quality standards set by the Greek legislation. It should be underlined that in the case study presented, the MBR unit only would have sufficed wastewater treatment requirements. The addition of the RO unit was decided to provide additional data on the treatment performance of an MBR-RO system. In other words, the objective of this study was to examine the presence of certain heavy metals, PPs and other micropollutants in municipal wastewater and to access the performance of an MBR-RO pilot system in relation to the efficiency of their removal.

2. Materials and methods

2.1. Description of the MBR-RO pilot system

Dual-membrane processes, such as the coupling of an ultrafiltration (UF) with an RO, are gaining ground in the process of retrieving municipal wastewater, owing to their high performance and simplicity in operation. UF membranes are the equivalent of secondary treatment of wastewater, whereas RO acts as the polishing treatment step. The suspended solids are removed by UF membranes while RO membranes remove dissolved solids, organic and ionic matter. An MBR can implement the secondary treatment of sewage and generate an effluent that conforms with the qualitative criteria needed for being an influent stream of an RO unit, and hence MBR-RO is a promising combination for the treatment of raw sewage for water reclamation [11,12].

Fig. 1 presents the flow chart of the unit. Feed wastewater is pumped from the local sewerage network to the satellite wastewater treatment plant (WWTP). The wastewater stream is then directed from the inlet pumping station to the equalization tank, which consists of a compact fine screen-grit system and a biotube filter and is the location where preliminary treatment takes place. From there, the pretreated sewage is overflowing to the main treatment units, that is, biological treatment with MBR and finally an RO unit.

The first occurring biological process is denitrification, which is materialized inside an anoxic tank equipped with a proper mixing device. Afterwards, the mixed liquor enters the aeration tank, where the biological processes of sludge stabilization and nitrification as well as oxidation of the organic load oxidation take place. Suspended solids are separated from the treated effluent as a result of the application

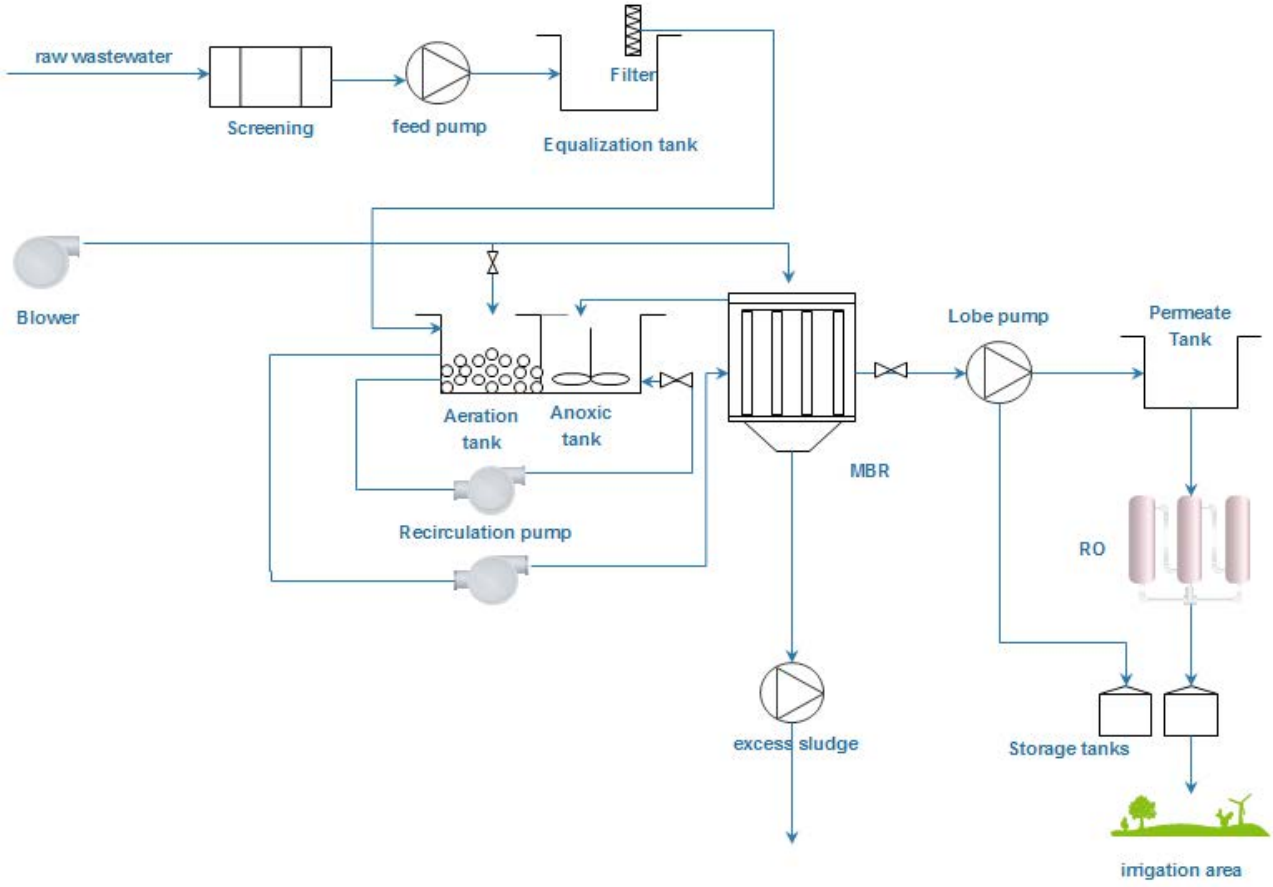

Fig. 1. Schematic presentation of the MBR-RO unit.

of a UF membrane. The installed membrane consists of UF modules that operate under negative pressure, with a filtration course going from the external region of the modules toward the internal one. Thus, solids are withheld in the retentate on the outside, whereas the permeate passes through the modules and is then directed by a lobed pump to a permeate tank, while excess sludge is transmitted back to sewage network. The content of the permeate tank is eventually guided into the RO unit. The use of RO as a post-treatment level is needed in order to achieve compliance with the environmental standards as in the case of saline wastewater. Moreover, the unit has a mode in which the RO unit is by-passed and the permeate ends up directly into the effluent tank. Table 1 summarizes the characteristics of both the MBR and RO membranes as well as those of the pilot unit.

An aeration system that consists of blowers and coarse bubble diffusers is responsible for cleaning the membranes, thus guarding the membranes from fouling and particle deposition. However, this process is not adequate for maintaining membrane permeability, thus two more procedures of membrane cleaning have been applied. The first one is the backflushing mode; the lobbed pump inverts its rotation sense and having a direction opposite to the normal filtration, it transfers a part of the produced permeate outside of the UF modules in order to detach excess material. The other method is maintenance cleaning; chemical cleaning cycles consisting of sodium hypochlorite (NaOCl) and citric acid that reach the membranes by backflushing clean water that is enriched with those chemicals through dosage pumps.

2.2. Analytical methods

The monitoring process consisted of sampling from three distinct points of the pilot unit. Specifically, regarding conventional pollutants, the samples were collected, on a weekly basis, from the MBR influent and permeate and the RO effluent. On the other hand, the monitoring process of micropollutants consisted of four repetitions of sample collection with the use of a 1 L laboratory glass bottle, with samples from the influent stream, the MBR permeate, and the RO effluent. It has to be noted that the minimum number of sampling repetition for micropollutants set in the Greek legislation is two per year. The type of sample drawn from the inlet stream was a composite sample retrieved from an equalization tank, in which the sewage remained for 1 d. The MBR permeate and RO effluent samples were drawn from two storage tanks with 3 h retention time. Wastewater characteristics (chemical oxygen demand, biochemical oxygen demand, total suspended solids, total volatile solids, sludge volume index, total phosphorus, total nitrogen, ammoniacal and nitrate nitrogen, chlorides, total and fecal coliforms, and *E. coli*) were determined according to Standard Methods [13]. For the detection of heavy metals in the inlet flow and the MBR effluent, the method used was inductively coupled plasma mass spectrometry (ICP-MS), while for the RO effluent the selected method was inductively coupled plasma optical emission spectrometry. For the PPs three different approaches were followed, depending on the chemical; purge and trap gas chromatography–mass spectrometry (T&P/GC-MS), gas chromatography coupled to tandem mass spectrometry (GC-MS/MS), liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Finally, ecotoxicity assessment was performed using as an indicator the survival rate of *Daphnia magna* (mortality at 48 h) in both MBR permeate and RO effluent, the results of which were compared with a control sample. Table 2 enlists all PPs measured, accompanied by their detection method and the corresponding limit of detection (LOD). The PPs under examination are the ones that are specified in the Greek legislation, which poses qualitative limitations to the effluent water of all WWTPs with population equivalent greater than 100,000. Furthermore, apart from the substances specified in the Greek legislation, complementary compounds that are part of the list of micropollutants composed by the US Environmental Protection Agency (EPA) were also investigated.

3. Results and discussion

3.1. Raw wastewater characterization

The influent of the pilot unit was tested for the occurrence of certain heavy metals, trace elements, and PPs that are specified in the Greek legislation for water reuse. Concerning heavy metals, the substances under investigation were the ones specified in Table 4 of Annex II of the JMD 145116/2011. From a total of 19 compounds measured (18 enlisted in the

Table 1
Membrane and pilot system characteristics

Membrane characteristics	MBR	RO	Pilot parameters	MBR	RO
Manufacturer	KOCH Membrane systems	Filmtech membranes	Manufacturer	Chemitec	Chemitec
Module type	PSH 34	XLE 4040	Configuration	Hollow fiber	Spiral wound
Nominal pore size	0.03 μm	–	Operation mode	Continuous	
Surface area	34 m^2	8.1 m^2	Permeate volume(m^3 d^{-1})	10	–
Material	PVDF	Polyamide thin-film composite	Specific air demand based on membrane area (SADm) (m^3 air m^{-2} membrane area h^{-1})	0.45	–
Salt rejection	–	99%	Operating pressure (bar)	–0.6 to 0.6	3–10

Table 2
List of examined micropollutants together with their respective detection method, measurement units and LOD

Substance (mg L^{-1})	Method	Measurement	LOD
Aluminum (Al)	OE 072-93 (ICP-MS)	μg L^{-1}	0.2
Arsenic (As)	OE 072-93 (ICP-MS)	μg L^{-1}	0.003
Beryllium (Be)	OE 072-93 (ICP-MS)	μg L^{-1}	0.01
Boron (B)	OE 072-93 (ICP-MS)	μg L^{-1}	0.13
Cadmium (Cd)	OE 072-93 (ICP-MS)	μg L^{-1}	0.001
Chromium (Cr)	OE 072-93 (ICP-MS)	μg L^{-1}	0.01
Cobalt (Co)	OE 072-93 (ICP-MS)	μg L^{-1}	0.001
Copper (Cu)	OE 072-93 (ICP-MS)	μg L^{-1}	0.03
Iron (Fe)	OE 072-93 (ICP-MS)	μg L^{-1}	0.06
Lead (Pb)	OE 072-93 (ICP-MS)	μg L^{-1}	0.005
Lithium (Li)	OE 072-93 (ICP-MS)	μg L^{-1}	0.5
Manganese (Mn)	OE 072-93 (ICP-MS)	μg L^{-1}	0.005
Mercury (Hg)	OE 072-93 (ICP-MS)	μg L^{-1}	0.01
Molybdenum (Mo)	OE 072-93 (ICP-MS)	μg L^{-1}	0.035
Nickel (Ni)	OE 072-93 (ICP-MS)	μg L^{-1}	0.001
Selenium (Se)	OE 072-93 (ICP-MS)	μg L^{-1}	0.0035
Sodium (Na)	OE 072-93 (ICP-MS)	μg L^{-1}	0.0015
Vanadium (V)	OE 072-93 (ICP-MS)	μg L^{-1}	0.002
Zinc (Zn)	OE 072-93 (ICP-MS)	μg L^{-1}	0.05
Bromates (BrO_3)	OE 072-85 (LC-MS/MS)	μg L^{-1}	0.06
1,2-Dichloroethane (EDC)	OE 072-88 (GC-MS)	μg L^{-1}	0.05
Vinyl chloride (CH_2CHCl)	OE 072-88 (GC-MS)	μg L^{-1}	0.04
Trihalomethane (THMs)	OE 072-88 (GC-MS)	μg L^{-1}	0.04
Chloroform ($CHBr_3$)	OE 072-88 (GC-MS)	μg L^{-1}	0.04
Bromoform ($CHBr_3$)	OE 072-88 (GC-MS)	μg L^{-1}	0.05
Bromodichloromethane ($CHBrCl_2$)	OE 072-88 (GC-MS)	μg L^{-1}	0.04
Dibromochloromethane ($CHBr_2Cl$)	OE 072-88 (GC-MS)	μg L^{-1}	0.05
Tri-tetrachloroethylene	OE 072-88 (GC-MS)	μg L^{-1}	0.03
Trichloroethylene (TCE)	OE 072-88 (GC-MS)	μg L^{-1}	0.05
Tetrachloroethylene (PCE)	OE 072-88 (GC-MS)	μg L^{-1}	0.03
Benzo (a) pyrene	OE 072-80 (GC-MS/MS)	μg L^{-1}	0.0025
Polycyclic aromatic hydrocarbons (PAH)	OE 072-80 (GC-MS/MS)	μg L^{-1}	0.0025
Benzo (b) fluoranthene	OE 072-80 (GC-MS/MS)	μg L^{-1}	0.0025
Benzo (k) fluoranthene	OE 072-80 (GC-MS/MS)	μg L^{-1}	0.0025
Indeno (1,2,3-c,d) pyrene	OE 072-80 (GC-MS/MS)	μg L^{-1}	0.0025
Benzene	OE 072-88 (GC-MS)	μg L^{-1}	0.03
Acrylamide (C_3H_5ClO)	OE 072-96 (LC-MS/MS)	μg L^{-1}	0.04
Epichlorohydrin (C_3H_5ClO)	OE 072-87 (GC-MS)	μg L^{-1}	0.07
Di-(2-ethyl hexyl) phthalate (DEHP)	OE 072-120 (LC-MS/MS)[a]	μg L^{-1}	–
Pentachlorophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
2-Chlorophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
2,4-Dinitrophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
4-Chloro-3-methylphenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
2-Nitrophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
4-Nitrophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
4-*n*-Nonyphenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
4-*tert*-Octyphenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
Bisphenol A	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
2,4,6-Trichlorophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
2,4-Dichlorophenol	OE 072-84 (GC-MS/MS)	μg L^{-1}	0.125
Pesticides total	OE 072-79 (GC-MS/MS)	μg L^{-1}	0.006–0.02
C_{10}-C_{13} chloroalkanes	ISO 12010[a]	μg L^{-1}	0.4
Tributyltin cation	ISO 17353[a]	μg L^{-1}	0.003
Penta-brominated diphenyl ether	EPA 1614[a]	μg L^{-1}	0.0031
Acute toxicity test: Determination of the inhibition of the mobility of *Daphnia magna*	ISO 6341[a]	TU	–

[a]Determinations outside accreditation scope.

JMD plus Sodium (Na)), all but two were identified in the examined wastewater. Beryllium (Be) and Mercury (Hg) were measured below their respective LOD, which was 0.01 μg L^{-1}. The rest of the examined metals, that is, aluminum (Al), arsenic (As), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), molybdenum (Mo), selenium (Se), sodium (Na), copper (Cu), iron (Fe), lithium (Li), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn), were found to be present in the inlet stream.

In a study performed by Sörme and Lagerkvist [9], regarding urban wastewater, it was found that Cu mostly derives from households, specifically from copper pipes and taps. In the case of Zn, the load is equally divided between households and businesses (mainly car wash enterprises), while Pb originates mostly from commercial activities. Another study suggests that in the case of Cu, Pb, and Zn, light industrial sources are the major contributors [8]. Moreover, the influent analysis is in good agreement with other studies regarding the ranking of concentration magnitude of metals in raw wastewater. More specifically, the occurrence of heavy metals in urban wastewater seems to follow –with slight variations – this sequence: Fe >> Al > Zn > Mn > Cr > Cu > Ni > Pb > Cd [14–16]. The influent metal concentration order produced from this study is Fe > Al > Zn > Na > B > Mn > Cu > Pb > Ni > Li > Cr > As > V > Mo > Se > Cd > Co, which agrees in most part with the aforementioned sequence.

Regarding PPs, from all substances enlisted in Table 6 of Annex IV JMD 145116/2011, only five were present in wastewater samples. More specifically, these were chloroform ($CHCl_3$), trichloroethylene (TCE), tetrachloroethylene (PCE), benzene (C_6H_6), and di(2-ethyl hexyl) phthalate (DEHP), none of which is considered as a hazardous priority substance. Moreover, bromoform ($CHBr_3$), which is not enlisted in the Greek legislation, was also found to be present in the wastewater. All of the aforementioned compounds belong to the VOC PPs. TCE and PCE are widely used and are characterized as persistent VOC contaminants that permeate soil and groundwater and can be responsible for long-term contamination [17]. Contamination by these compounds and other chlorinated solvents is a common phenomenon in the environment and derives from the intensive use of dry cleaning agents, degreasing solvents, and paint strippers. They are also used in the production of anesthetics and refrigerants [16]. After use, these chemical substances are usually not properly disposed, thus contributing to contamination. $CHCl_3$ and $CHBr_3$ belong to the trihalomethanes (THMs), which are one of the most abundant and extensively studied disinfection by-products and were among the first regulated substances in relation to drinking water. THM compounds have been identified as genotoxic mutagens and have been linked with cancer to the digestive or genitourinary organs [18]. Concerning $CHCl_3$, a study of Rule et al. [8] has found that it is the only solvent that was found to have concentration greater than its LOD on domestic level. While chloroform concentration in that study was found greater in domestic sewage, for TCE and PCE the authors suggest that dry cleaning was the reason why their concentration was greater in samples retrieved from the town center, where commercial activities take place. Another study indicates that $CHCl_3$ has a far greater concentration in the water supply in comparison with domestic sewage, proposing that chlorination must be the main source of chloroform in wastewater [19]. DEHP is a chemical used mainly for PVC production and its presence in wastewater is one of the most dominant ones among plasticizers. As a highly hydrophobic substance with a half-life in biological treatment of around 25 d, DEHP can act as an indicator for the removal of hydrophobic emerging contaminants [17]. In a previous study, it was found to be the most abundant of all six detected PPs and this abundance has been verified in past researches as well [20]. Moreover, it has been shown that the concentration of DEHP is correlated with precipitation events, where it increases when wet weather conditions are observed [20]. As part of the phthalates family, DEHP is toxic in several body systems [25], and this is the reason why it is listed as PP in many countries [21–23].

3.2. MBR-RO removal efficiency

The operational parameters of the unit at the time of sampling are presented in Table 3. Moreover, results concerning nutrients, organic and microbial load are presented in Table 4. It is evident that the system completely eliminated microbial load and achieved high removal of organic and inorganic contaminants, a fact that was presented in detail in a previous publication [10].

As far as MBR is concerned, heavy metals removal occurs predominantly through chemical and biochemical mechanisms. These mechanisms are biosorption, bioaccumulation, sorption, and precipitation. More specifically, biosorption is a rapid process that involves sorption of metal ions on the external surface of microorganisms, while sorption refers to extracellular biopolymers and other particles found in wastewater. Bioaccumulation refers to heavy metals penetration within microbial cells. Finally, precipitation depends on heavy metals solubility [24,25]. Among the target heavy metals, Ni, Cu, Zn, Co, and Fe at low concentrations (micronutrients) are necessary for microorganisms growth, while others (Hg, Cd, Pb, As, Au, and Sn) have no metabolic value for the organism [26].

The MBR unit of the pilot system exhibited high removal rates for some heavy metals, averaging over 80% for Pb, Zn,

Table 3
MBR operational parameters

Parameter	Value
Flow (Q) (m^3 d^{-1})	12
Hydraulic retention time (HRT) (h)	3
Solid retention time (SRT) (d)	20
Organic loading (F M^{-1}), gCOD (gMLVSS d) $^{-1}$	0.38
Suspended solids (MLSS) (g L^{-1})	9.2
Volatile solids (MLVSS) (g L^{-1})	7.4
Sludge removal (W) (L d^{-1})	84
Filtration flux (J), (L m^{-2} h^{-1})	15–20
Filtration flow (Q_{filtr}) (L h^{-1})	500
Filtration time (min)	10
Backflushing flow (Q_{back}) (L h^{-1})	1,000
Backflushing time (min)	1

Table 4
Performance of the MBR-RO system for the treatment of municipal waste

Parameter	MBR influent	MBR permeate	RO effluent
TSS (mg L^{-1})	106 (40–295)	≤5	≤5
VSS (mg L^{-1})	95 (34–240)	≤5	≤5
TDS (mg L^{-1})	Not measured	672 (737–661)	179 (234–105)
COD (mg L^{-1})	342 (166–649)	25 (≤10–55)	≤10 (≤10–14)
CODs (mg L^{-1})	172 (80–241)	25 (≤10–55)	≤10 (≤10–14)
BOD_5 (mg L^{-1})	Not measured	1.05 (0.2–2.42)	1.01 (0.2–2)
NH_4-N (mg L^{-1})	60 (20–79)	0.3 (0.09–0.7)	Not measured
TN (mg L^{-1})	Not measured	Not measured	9 (6–17)
TP (mg L^{-1})	9 (6–11)	7 (6–8)	≤5
Conductivity (μS cm^{-1})	1,500 (1,250–1,600)	1,300 (1,000–1,530)	250 (160–650)
CL^- (mg L^{-1})	165 (133–213)	161 (129–199)	58 (16–136)
Turbidity (NTU)	Not measured	0.06 (0.03–0.3)	–
TC (CFU (100 mL)$^{-1}$)	$>10^7$	91 (7–470)	ND[a]
FC (CFU (100 mL)$^{-1}$)	$>10^7$	5 (ND[a]–19)	ND[a]
EC (CFU (100 mL)$^{-1}$)	$>10^7$	4 (ND[a]–19)	ND[a]

The values presented refer to average values (range).
[a]Not detected.

and Al (95%, 82%, and 81%, respectively). On the other hand, lower removal rates, between 60% and 80%, were recorded for Fe (78%), Cu (76%), V (65%), and Mn (62%) and much lower removal rates were observed for Co (42%), Se (40%), Cr (33%), Ni (32%), B (28%), Na (18%), and Li (13%). The elimination of Cd was complete, whereas on average, the reduction of the concentration of As and Mo from the inlet stream to the MBR permeate was insignificant. There are also others studies that have reported low As removal rate using MBR systems [27,28].

The membranes of the particular UF MBR system reject particles with size greater than 0.03 μm (nominal membrane pore size) and thus heavy metals of equivalent size. Therefore, all heavy metals bonded to the layer's biocells are removed by the MBR system. In most cases, the system achieved an appreciable metal reduction, indicating that metals are mostly insoluble attached to the mixed liquor suspended solids.

The behavior of metals in the treatment of wastewater using MBR systems is the subject of research in several studies [29–31]. The general metals removing trend from the MBR in decreasing order is the following: Cd > Pb > Zn > Al > Fe > Cu > V > Mn > Co > Se > Cr > Ni > B > Na > Li (Table 5). The trend obtained in this work is only indicative, and variations may be observed compared with other studies due to differences in system's operating conditions, active sludge properties and liquid waste composition. These results are in good agreement with Carletti et al. [32], who reported high removal (in the order of 70%) during wastewater treatment in an MBR unit for some heavy metals such as Fe, Pb, Cu, Ni and Al, while for metals such as As, Hg, and Zn, the MBR efficiency was lower. Also the results are consistent with Bolzonella et al. [29] that categorized metals into three groups depending on removal efficiency obtained by MBR or conventional activated sludge systems: the ones that are easily removed, exhibiting removal rates over 75% (Al, Ag, Ba, Cd, Cr, Cu, Fe, Hg, Sn, V), metals that were partially removed with removal efficiencies ranging from 40% to 60% (Co, Mn, Ni, Pb, Zn) and metals that are difficult to remove and displaying removals of lower than 25% (As, B, Se).

Following MBR, RO managed to sharply reduce the concentration of most heavy metals. More specifically, RO achieved complete removal of Co, Se, V and high removal of Al, Fe, Ni, As, Mo, Zn and Mn with removal rates averaging 97%, 97%, 96%, 94%, 93%, 91%, and 90%, respectively. On the other hand, lower removal rates but over 60% were recorded for Pb (87%), Cu (67%), Na (67%), and Cr (61%), while much lower removal rates were observed for Li (56%) and B(23%). Fig. 2, illustrates the performance of the system with respect to heavy metals removal.

Concerning PPs that were present in the inlet stream, most of them were not detected in the MBR effluent with the exception of $CHCl_3$, the concentration of which was reduced by about 30% from the influent to the MBR effluent. An additional 57% removal was obtained through the RO treatment. It should be underlined that all PPs had effluent values consistently below the limit values set out in Greek legislation. Fig. 3 illustrates the concentration of PPs in the influent, MBR permeate and RO effluent.

Table 5 presents the average (± standard deviation) of the target compounds concentration in the influent, the MBR effluent and the RO effluent. Based on these results it can be concluded that the system produced a high-quality treated effluent, in-line with the strict qualitative standards set by the Greek legislation. Table 6 provides a review comparison of the removal rate for each target compound with the respective ones from other studies.

Based on the data provided in Table 5, it is evident that Pb, Cu, Zn, Fe, Al, Cd are removed with great efficiency in all studies assessing the performance of MBR units, which might be an indication that these heavy metals are present mostly in particulate form. According to Malamis et al. [33],

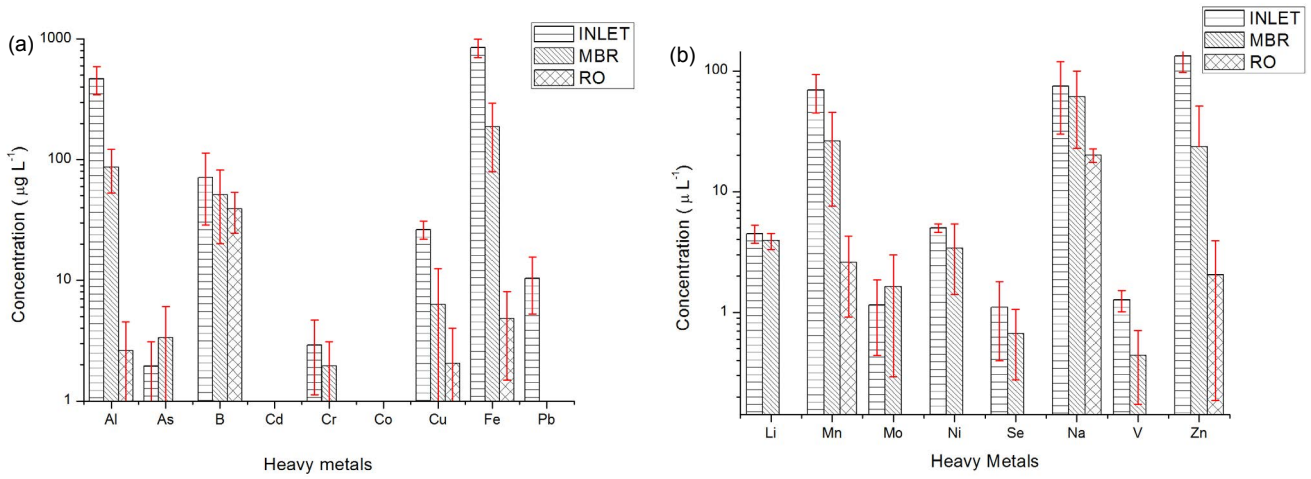

Fig. 2. Heavy metals' average concentrations in the inlet, MBR permeate, and RO effluent (a) depicts Al, As, B, Cd, Cr, Co, Cu, Fe, Pb and (b) depicts Li, Mn, Mo, Ni, Se, Na, V, Z.

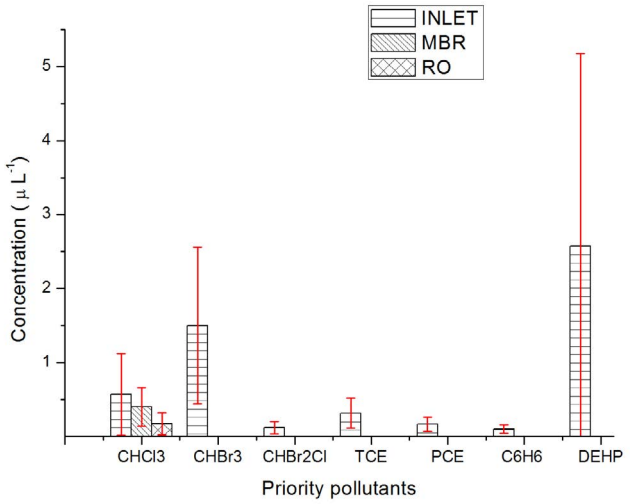

Fig. 3. Average concentrations of PPs in the inlet, MBR permeate, and RO effluent.

divalent and trivalent metals are more easily attached to activated sludge in relation to the monovalent metals and, therefore, MBR achieved higher removal rates for the former substances. This explains the less effective removal of Na and Li by the MBR. All studies agreed that the removal rate of As was far lower than the rest of the metals, while the removal of Ni presented the highest variation among the studies. Regarding Mn, this study as well as the research of Mansell et al. [37] produced lower removal rates than the rest of the studies. Finally, the comparison conducted by Fatone et al. [34] between the removal rates of an MBR and a conventional activated sludge process (CASP) revealed that for most of the involved metals, the removal rates of the MBR were higher compared with the CASP values, validating that the higher removal of suspended solids, where pollutants are sorbed, leads to more efficient metal removal. It has to be noted that the differences between these studies can be attributed to differences in the operating conditions and more specifically differences in SRT, HRT as well as in membrane characteristics, for example, the membrane pore size and material. Moreover, the initial concentrations in the inlet stream vary from one study to another and so does the removal rate potential.

Regarding the PPs that were present in the influent, most of the studies found in literature present mostly the effluent concentration. In such a study, it was found that for $CHCl_3$, C_6H_6, TCE, and PCE, the effluent concentration of an MBR that was used as advanced treatment in a WWTP, was below the LOQ, while the concentration of DEHP was 1.4 μg L^{-1} [41]. In the same study, all five substances were found to be present in the effluent stream of conventional WWTPs, which highlight the ability of the MBR to reduce such PPs below detectable concentrations. The average removal rates achieved in conventional WWTP have been reported to be around 70% for $CHCl_3$, 93% for C_6H_6, 79% for TCE, 81% for PCE, and 95% for DEHP [42].

One of the most investigated substances is DEHP. In an experiment using municipal solid waste leachate with high concentration of DEHP (804 μg L^{-1}), a hollow fiber microfiltration MBR managed a removal rate of over 98% [43]. In another study using tertiary treatment with micrograin activated carbon (μGAC), DEHP was one of the few members of the group of compounds that at 20 gμGAC m^{-3} recorded poor elimination (<30%) [44]. In relation to $CHCl_3$, a previous study found that hydrophobic UF membrane outperforms hydrophilic NF and RO membranes, by yielding a retention coefficient of 81% and argues that the filtration cake that is formed during the UF process enhances the removal of $CHCl_3$ [45]. This contradicts the findings of the current study that reveals a low removal rate of the $CHCl_3$ by the MBR. The low removal rate may be caused by the chlorination during the cleaning protocol of the membranes, where the dissolved organic matter reacts with chlorine to produce several by-products, among which are THMs. Comparing the efficiency of the RO with respect to the removal of $CHCl_3$, a previous study found that RO can remove at least 80% of the inflowing $CHCl_3$, in contrast with the 50% rate observed in this study, and also concluded that by increasing its concentration from 100 to 500 μg L^{-1} the rate decreased [46]. Regarding C_6H_6, a study

Table 5
Concentrations of detected PPs and heavy metals in the influent, MBR permeate, and RO effluent streams (in μg L^{-1}) refer to average value (± standard deviation)

Substance (μg L^{-1})	Inlet wastewater	MBR permeate	RO effluent	MBR removal rate (%)	RO removal rate (%)	Legislation limit[a] (max value)
Al	468 (±122)	87 (±34.5)	2.6 (±1.92)	81	97	5,000
As	1.95 (±1.14)	3.35 (±2.67)	0.205 (±0.14)	–	94	100
B	71 (±42)	51 (±30.8)	39 (±14.4)	28	24	2,000
Be	ND[b]	ND[b]	ND[b]	–	–	100
Cu	26 (±4.5)	6.3 (±6.2)	ND[b]	76	67	200
Cd	0.141 (±0.1)	ND[b]	ND[b]	>99	–	10
Cr	2.9 (±1.78)	1.95 (±1.12)	0.755 (±0.78)	33	61	100
Co	0.92 (±0.53)	0.53 (±0.31)	ND[b]	42	>99	50
Fe	847 (±146)	187 (±108)	4.8 (±3.3)	78	97	3,000
Li	4.5 (±0.78)	3.9 (±0.6)	1.7 (±0.98)	13	56	2,500
Mn	69 (±24)	26.3 (±18.8)	2.6 (±1.68)	62	90	200
Hg	ND[b]	ND[b]	ND[b]	–	–	2
Ni	5 (±0.4)	3.4 (±1.99)	ND[b]	32	96	200
Pb	10.37 (±5.12)	0.51 (±0.3)	ND[b]	95	87	100
Mo	1.15 (±0.71)	1.64 (±1.35)	0.12 (±0.08)	–	93	10
Se	1.1 (±0.7)	0.665 (±0.39)	ND[b]	40	>99	2
Na	74,500 (±12,700)	61,000 (±3,830)	20,000 (±2,650)	18	67	70,000[c]
V	1.3 (±0.25)	0.44 (±0.27)	ND[b]	65	>99	100
Zn	132 (±35)	23.55 (±27.47)	2.055 (±1.87)	82	91	2,000
Chloroform ($CHCl_3$)	0.98 (±0.57)	0.4 (±0.26)	0.17 (±0.15)	30	58	2.5
Bromoform ($CHBr_3$)	1.5 (±0.83)	ND[b]	ND[b]	>99	–	–
Trichloroethylene (TCE)	0.32 (±0.2)	ND[b]	ND[b]	>99	–	10
Tetrachloroethylene (PCE)	0.19 (±0.165)	ND[b]	ND[b]	>99	–	10
Benzene (C_6H_6)	0.1 (±0.06)	ND[b]	ND[b]	>99	–	5
Di-(2-ethyl hexyl) phthalate (DEHP)	2.57 (±2.6)	ND[b]	ND[b]	>99	–	10
Acute toxicity test: Determination of the inhibition of the mobility of *Daphnia magna*	Not measured	Not applicable[d]	Not applicable[d]			TU50≤1

[a]The limit values set in Greek legislation for wastewater reuse for unrestricted irrigation and/or industrial reuse (Joint Ministerial Decision 354/8-3-2011).
[b]Not detected (see Table 2 for LOD values).
[c]Refer to agronomic characteristics of reusable treated wastewater for irrigation (JMD 354/8-3-2011).
[d]The undiluted sample immobilized <50% of the *Daphnia* at 48 h.

conducted on four MBRs in different sites (one full scale and three pilot scale) revealed that for influent concentration similar to the one of this study, the removal was over 92%, with the compound being under the LOD in the effluent stream [47]. Finally, in constructed wetlands, another type of secondary treatment, the removal of $CHCl_3$ has been reported to be around 67%, the removal of DEHP has been found to range from 20% to 50% and for benzene the removal rate recorded a wide range from low values up to complete removal [48].

4. Conclusions

According to the findings of this study, it is anticipated that wastewater treatment through MBR-RO systems can produce a treated water of excellent quality that meets the standards that are specified in the Greek National legislation regarding wastewater reclamation for urban reuse. Most of the micropollutants detected in the primary effluent were reduced to levels below the detection limit, while the ones traceable in the effluent stream had concentration far smaller than the one dictated in the Greek legislation. Such a dual membrane scheme in the context of a SM application has proven to be a viable solution for water reuse in combination with freshwater saving in highly urbanized, space-limited environments. The future prospects of advanced treatment technologies such as the MBR-RO are significant, considering the ever increasing need for technologies that provide with ample water sources and sufficiently protect the existing ones.

Table 6
Comparison of MBR, RO, and combined MBR-RO removal rates for selected metals and PPs

MBR	MBR-RO	Reference
Al (81%), B (28%), Cd (>99%), Cr (33%), Co (42%), Cu (76%), Fe (78%), Pb (95%), Li (13%), Mn (62%), Ni (32%), Se (40%), Na (18%), V (65%), Zn (82%), $CHCl_3$ (30%), TCE (>99.9%), PCE (>99.9%), C_6H_6 (>99.9%), DEHP (>99%), C_6H_6 (>99%)	Al (>99%), As (89%), B (45%), Cd (>99), Cr (74%), Co (>99%), Cu (92%), Fe (>99), Pb (>99), Li (>99%), Mn (96%), Mo (>99%), Ni (98%), Se (>99), Na (73%), V (>99%), Zn (98%), $CHCl_3$ (70%)	Present study
Cu (90%), Fe (85%), Mn (82%), Zn (75%), Cr (80%), Pb (73%), Ni (67%), Mg (61%), Na (30%)	Cu (>97.1%), Fe (>99.3%), Mn (>99.1%), Zn (>99.8%), Ni (>90.9%), Pb (>99.2%), Cr (>99%), Mg (98.5), Na (95.7%)	[33]
Cu (94.9%), Zn (94.4%), Fe (97.2%), As (48.4%), Pb (74%), Ni (85.9%), Cr (75%), Al (97.5), Cd (>27.1)	–	[34]
As (33.5%)[a], Cd (>90%)[a], Cr (>95%)[a], Cu (84%)[a], Ni (54%)[a], Pb (60.3%)[a]		[35]
Cu (31.3%)[b], Zn (59.6%)[b], Ni (33.7%)[b], Co (60.9%)[b], Cr (47.4%)[b], As (45.7 %)[b], Pb (80%)[b], Cd (86.3%)[b], B (85.7%)[b]	–	[36]
As (>2%)[c], Pb (58%)[c], Cu (>81%)[c], Fe (>88%)[c], Mn (>54%)[c], Zn (26%)[c], PCE (>99.9%)[c], $CHCl_3$ (>99.9)[c]	–	[37]
Zn (97%), Fe (99%), Mn (92%), Pb (72%)	–	[38]
Ni (>99%), Pb (>99%), Cr (89%), Cu (49%)	Cu (>99%), Cr (>99%)	[39]

[a]Values refer to the average of the four runs.
[b]Refer to average value.
[c]Metal data retrieved indirectly through Conklin et al. [40], who used the raw data to extract the removal rates (values refer to a Zenon pilot unit).

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