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Mozaffari, M. H., Shafiepour, E., Mirbagheri, S. A., Rakhshandehroo, G., Wallace, S., & Stefanakis, A. I. (2021). Hydraulic characterization and removal of metals and nutrients in an aerated horizontal subsurface flow “racetrack” wetland treating primary-treated oil industry effluent. *Water Research*, 200, 117220.
<https://doi.org/10.1016/j.watres.2021.117220>.

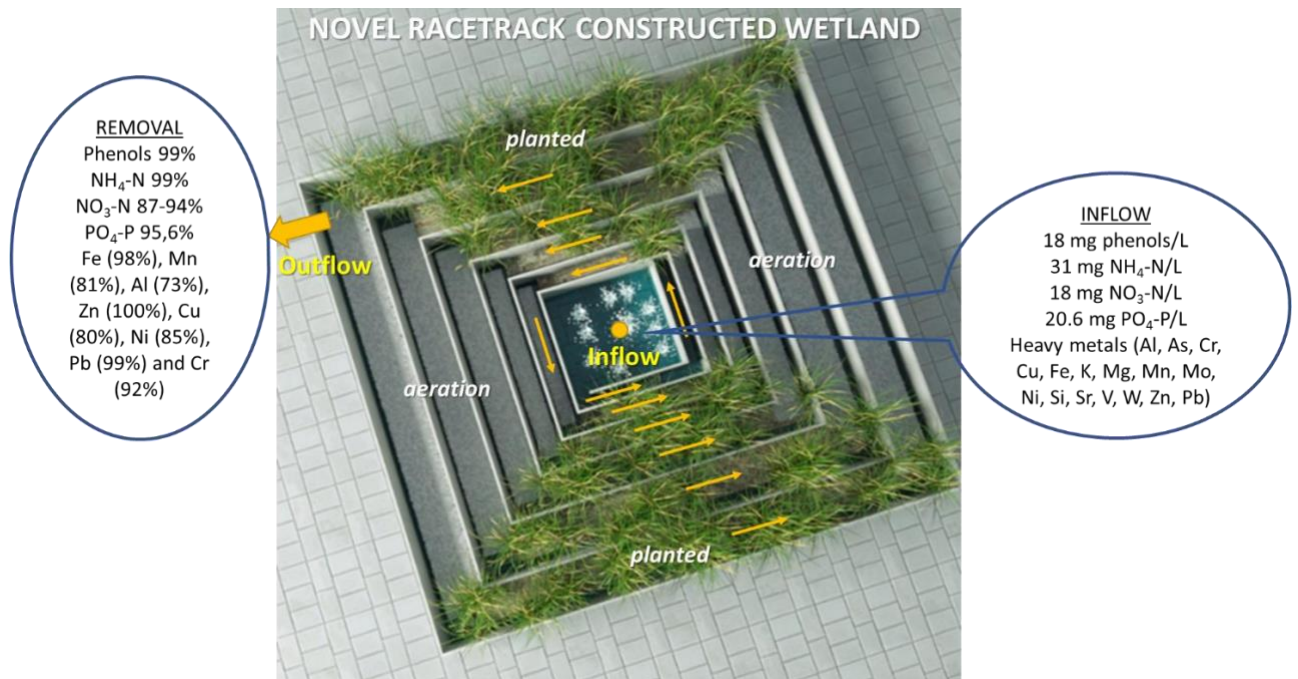
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GRAPHICAL ABSTRACT



Hydraulic characterization and removal of metals and nutrients in an aerated horizontal subsurface flow “racetrack” wetland treating primary-treated oil industry effluent

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Highlights

- Novel ‘racetrack’ constructed wetland design tested for the first time
- Treatment of oil refinery effluent rich in heavy metals, phenols and nutrients
- Positive role of plants and artificial aeration found, even at low retention time of 1.3 days
- High heavy metals removal (up to 98%), complete degradation of phenols and ammonia
- Higher *k*-rates calculated than literature findings for other wetland systems

1 Hydraulic characterization and removal of metals and nutrients in an aerated 2 horizontal subsurface flow “racetrack” wetland treating primary-treated oil 3 industry effluent

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21 Abstract

Constructed wetlands (CW) are an attractive technology due to their operational simplicity and low life-cycle cost. It has been applied for refinery effluent treatment but mostly single-stage designs (e.g., vertical or horizontal flow) have been tested. However, to achieve a good treatment efficiency for industrial effluents, different treatment conditions (both aerobic and anaerobic) are needed. This means that hybrid CW systems are typically required with a respectively increased area demand. In addition, a strong aerobic environment that facilitates the formation of iron, manganese, zinc and aluminum precipitates cannot be established with passive wetland systems, while the role of these oxyhydroxide compounds in the further co-precipitation and removal of heavy metals such as copper, nickel, lead, and chromium that can simplify the overall treatment of industrial wastewaters is poorly understood in CW. Therefore, this study tests for the first time an innovative CW design that combines an artificially aerated section with a non-aerated section in a single unit applied for oil refinery wastewater treatment. Four pilot units were tested with different design (i.e., planted/unplanted, aerated/non-aerated) and operational (two different hydraulic loading rates) characteristics to estimate the role of plants and artificial aeration and to identify the optimum design configuration. The pilot units received a primary refinery effluent, i.e., after passing through a dissolved air flotation unit. The first-order removal of heavy metals under aerobic conditions is evaluated, along with the removal of phenols and nutrients. High removal rates for Fe (96-98%), Mn (38-81%), Al (49-73%), and Zn (99-100%) generally as oxyhydroxide precipitates were found, while removal of Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (60-92%) under aerobic conditions was also observed, likely through co-precipitation. Complete phenols and ammonia nitrogen removal was also found. The first-order rate coefficient (k) calculated from the collected data demonstrates that the tested CW represents an advanced wetland design reaching higher removal rates at a smaller area demand than the common CW systems.

Keywords: aerated wetland; constructed wetland; refinery effluent; phenols; heavy metals; tracer test

1. Introduction

Polluted water from industrial sites represents a major environmental threat for ecosystems and public health by virtue of historic operational practices, incidents and leakages during storage and transport (Langwaldt and Puhakka, 2000; Stefanakis et al., 2020a). These wastewaters typically have a complex composition with a large variety of pollutants of different nature and properties such as heavy metals, organic matter, nutrients, solids, color, salinity, amid of other inorganic and toxic compounds (Wu et al., 2015; Stefanakis, 2018; Ramirez et al., 2019). Among them, heavy metals are considered one the most problematic. Many industrial wastewaters have varying levels of metals that derive from their operation and require further treatment prior the release to the environment or reuse at the operation sites. In particular, heavy metals are frequently found in effluents from refineries and generally the petrochemical industry (Wu et al., 2015; Mustapha et al., 2018; Stefanakis et al., 2018; Jain et al., 2020).

Various technologies and processes have been applied for the treatment of refinery effluents, e.g., membrane bioreactors, activated sludge, anaerobic reactors, ozonation etc. (Stefanakis, 2020a; Jain et al., 2020). The green technology of Constructed wetlands (CW) has also been used for petroleum derived water treatment though the respective applications are limited (Ji et al., 2007; Johnson et al., 2008; Wallace et al., 2011; Stefanakis et al., 2016; Stefanakis, 2020a). The positive aspects of CW include lower investment for infrastructure, significantly lower operation and maintenance cost, ecological character, tolerance to flowrate variations, no use of chemicals for the treatment,

among others (Kadlec and Wallace, 2009; Stefanakis, 2019). In addition, CW can handle varying contaminant loads and treat many constituents of concern at the same time and more effectively than some physical and chemical processes (Stefanakis, 2016; Gorito et al., 2017). These advantages account for the growing interest and increasing number of CW applications for the treatment of various industrial wastewater sources such as from the chemical and petrochemical industry (Wallace et al., 2011; Stefanakis et al., 2016; Stefanakis, 2020a), the oil and gas exploration (Stefanakis et al., 2018; Jain et al., 2020; Stefanakis, 2020b), the food industry such as dairy farms and olive mills (Tatoulis et al., 2017; Wu et al., 2015), and agro-industries such as glass industry, tanneries, cork processing wastewater (Gholipour et al., 2020; Gomes et al., 2018; Ramirez et al., 2019), among others.

The application of CW technology for refinery effluent treatment is not widely reported, although current knowledge indicates that CW can be specifically designed and built for the removal of target-constituents from refinery effluents. A few studies on vertical flow CW (VFCW) and horizontal subsurface flow CW designs (HSFCW) are also available in the international literature (Gillespie et al., 2000; Stefanakis et al., 2016; Mustapha et al., 2018; Jain et al., 2020). HSFCW are inherently oxygen-transfer limited systems, thus, anaerobic digestion (methanogenesis) becomes a salient contributor to the removal of the various constituents (Kadlec and Wallace, 2009). On the other hand, artificial aeration in CW is an advanced design that increases the phytoremediation potential of CW for heavy metals removal such as Cu^{+2} (Xin et al., 2019), while it also enhances the biodegradation rate under an aerobic environment (Del Rio et al., 2006; Stefanakis et al., 2019).

However, the vast majority of the published literature studies single CW units that utilize only one wetland design (e.g., vertical or horizontal or surface flow), while the aerated CW has barely been

tested for refinery effluent treatment. This means that a CW system for refinery effluent typically has a high areal footprint. However, the refinery effluent composition would require a combination of different environments, i.e., aerobic and anaerobic conditions, to achieve effective removal rates for the various pollutants especially for nitrogen and heavy metals. This could potentially be done with the use of hybrid (i.e., multistage) CW systems but this would further increase the land area demand. Therefore, the present study proposes and investigates an advanced CW design as a new innovative solution that combines in the same unit different treatment conditions necessary for the effective removal of pollutants of diverse nature aiming at providing a wetland treatment solution with smaller area demand than the existing CW designs. Therefore, the main research goal of this study is to test for the first time this innovative CW design at pilot scale for the effective treatment of process waters from a refinery. The specific goals is to determine the role of plants, substrate, hydraulic retention time and aeration in treating the refinery effluent with focus on the load removal of a series of heavy metals and nutrients.

2. Materials and methods

2.1. Study location

Four pilot-scale HSFCW units (planted and unplanted) with an innovative design were built outdoors at the Khajeh-Nasir Toosi University (35°45'48.0"N 51°24'33.9"E) with different design characteristics, i.e., planted, unplanted (i.e., sand filters), with and without artificial aeration. Wastewater volume was collected from the Tehran oil refinery effluent. This facility, located southern of Tehran City (35°32'24.7"N 51°25'37.7"E), is the second largest refinery in Iran and is one of the oldest refineries with an oil refining capacity of approximately 110,000 barrels per day, and a water consumption of nearly 505 m³/h (Bidhendi et al., 2010). It is considered as the best

performing refinery for the sake of Environmental Protection Act in Iran. The current wastewater treatment plant of the refinery consists of the DAF unit, followed by an aeration tank, a sedimentation tank and sand filtration unit, while the final effluent is discharged to agricultural fields or recycled in the industrial process. The effluent of the dissolved air flotation (DAF) unit was used for this study, since the DAF system achieves high recovery rates of the residual oil and it is preferred to remain in operation.

2.1. Pilot-scale CW design

The base unit of the innovative design (called “Racetrack wetland”) of each CW was fabricated out of clear acrylic plastic with a total flow path length of 12.8 m, mean channel width of 7.65 cm, and an effective depth of 0.2 m. The flow path was wrapped in a spiral configuration (Fig. 1a), such that each pilot cell required only 0.86 m² of area. The inflow point was at the centre of the unit and the water followed a meandric subsurface flow path, with the outflow point at one corner of the unit (Figs. 1 and 2). The structural design of the tested ‘Racetrack Wetland’ (RW) system furnishes two different environments (Fig. 2): a planted section without aeration (total length of planted section 6.3 m) and an unplanted section with aeration (total length of unplanted section 5.7 m). The aerated unplanted section constituted 44% of the total wetland area and included irrigation tubes in the center of the flow path with specific drippers that provided 0.6 L/min air flowrate at air pressure of 100 mbar. Aeration in the CW was based on previous systems used in North America and Europe (Wallace, 2002), using a 0.175 kW air blower capable of delivering up to 626.8 L/m²/min. The unplanted sections were filled with a graded, washed silica sand (size 0.8 - 1.2 mm, porosity 24%). The same media was used in the planted sections, but with the addition of 5% clay on the top 2 cm, to allow for the plant establishment in the silica soil. The inlet section at

137 the center of the unit had dimensions of 26x26 cm, while the outlet section had a length of 80 cm
138 and width 15.5 cm, while coarser gravel (6-7 mm) was used at the inlet and outlet sections to
139 facilitate the flow distribution (Fig. 3). *Cyperus alternifolius* plants of approx. 1 week old were
140 harvested from local water courses at the distance of 35 kilometers from Tehran Oil Refinery and
141 then immediately planted in the planted section of the CW design, covering 56% of the total
1421 wetland area.

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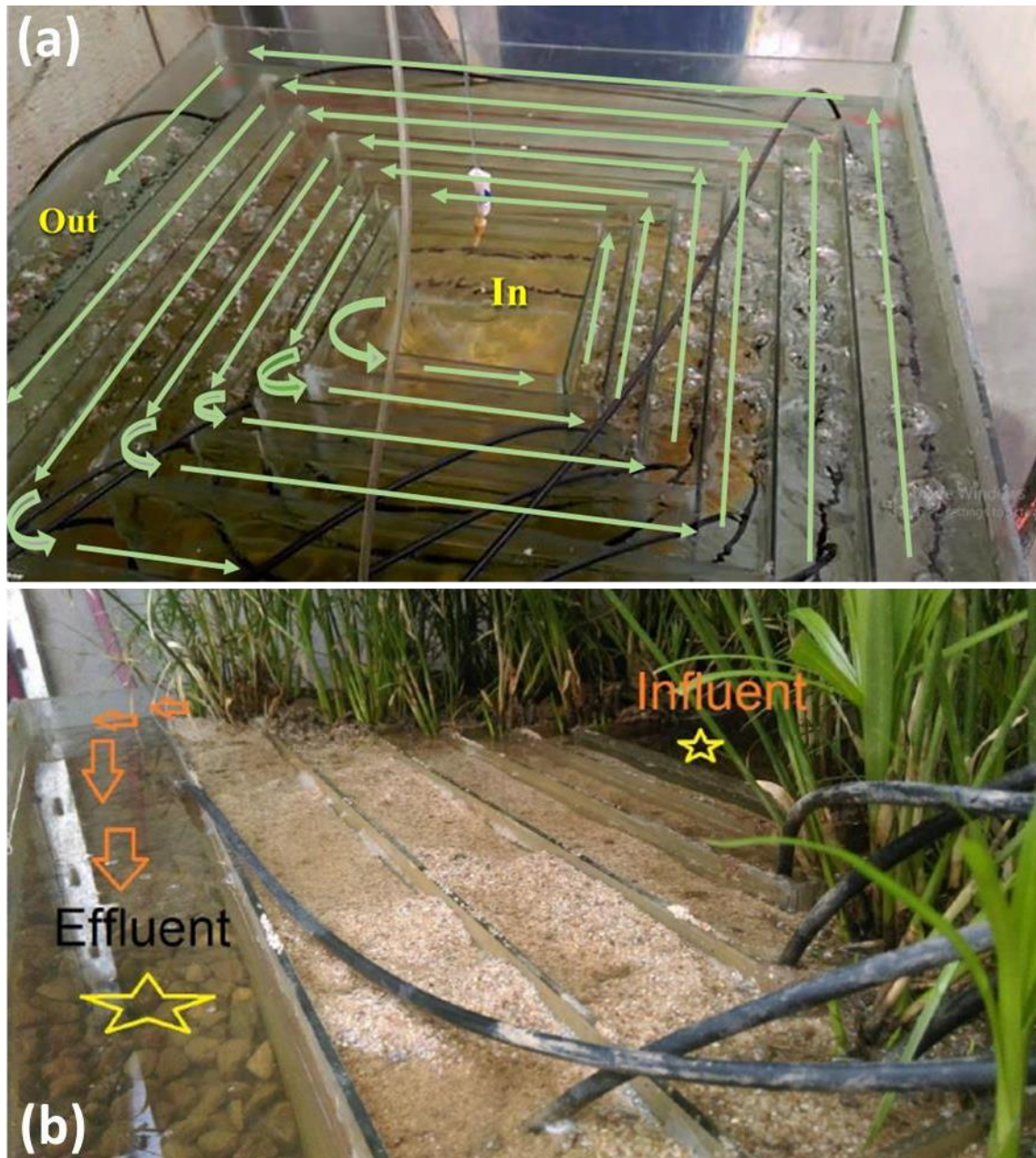


Figure 1. (a) Racetrack wetland configuration with aeration (base unit without substrate or vegetation), and (b) the unplanted and planted sections, the coarse gravel at the inlet and outlet sections, and the influent and effluent sampling points.

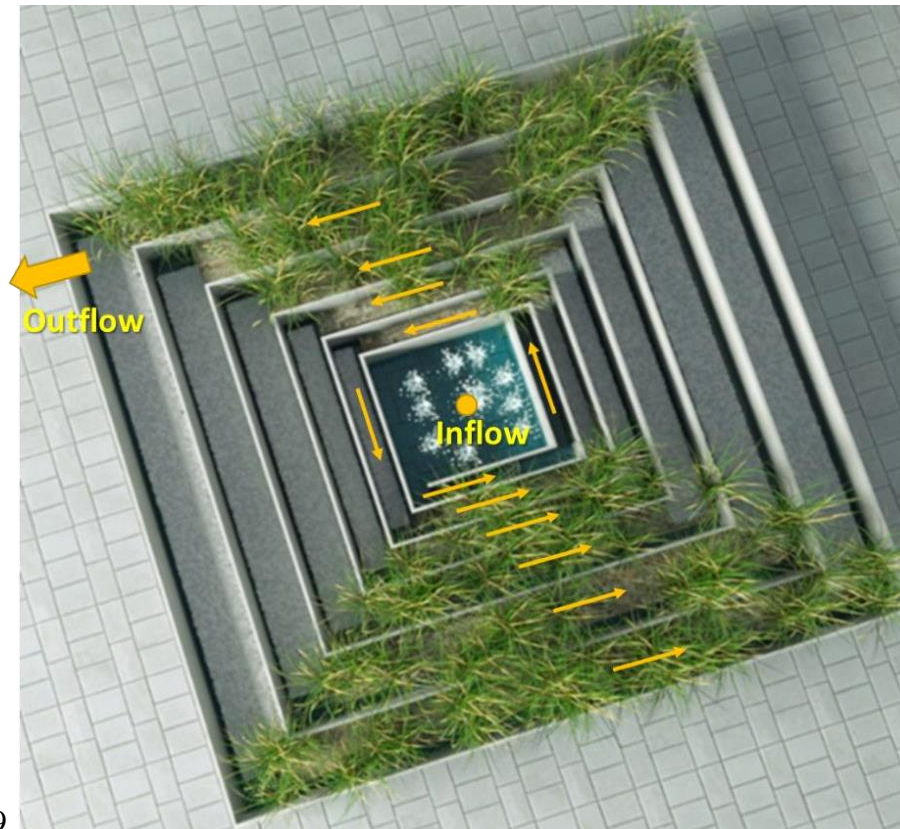


Figure 2. Schematic representation (top view) of the planted and non-planted sections of the racetrack wetland unit and the meandric flow path.

Four similar pilot RW units were built and operated in parallel to examine the effects of plant, substrate and aeration in the wetland performance, distinctly, with the following configuration: one pilot unit only with substrate (RW-S), one pilot unit with substrate and forced bed aeration (RW-SA), one pilot unit with substrate planted with *Cyperus alternifolius* (RW-SP), and one pilot unit with substrate planted with *Cyperus alternifolius* and with forced bed aeration (RW-SPA).

Once the pilot RW units were built and planted, a solution of 10 mL of a natural liquid fertilizer (NPK 7-4-7, Iranian plant company) mixed with 100 mL of tap water was added to each RW twice per week to cover the nutrients requirement for the initial growth period of the plants and biofilm (Ramond et al., 2012). The feeding with the NPK solution lasted the first 3 months after planting, in order to assist plant adoption to the new environment and sufficient penetration depth of plant roots into the substrate (Qureshi et al., 2005). After that start-up period, tracer tests were carried out for a period of 2 weeks. Once the tracer tests were completed, the refinery effluent was collected in a large tank that fed the CW units and the feeding of the pilot CWs started. The first 3 weeks of operation with the refinery effluent were considered a necessary period for the system to adopt to the feed water after the start-up period, hence no samples were taken (Kadlec and Wallace, 2009; Ramirez et al., 2019). After that period, another batch of refinery effluent was collected and fed, and the sampling and monitoring started. Two flowrates, i.e., 0.20 and 0.67 mL/s, were selected corresponding to the target hydraulic retention times (HRT) of 4 days and 1 day, respectively. Tracer tests were used to determine more accurately the actual HRT at the two different flowrates. The low flowrate (0.2 mL/s) was first applied to the four CWs to evaluate their removal performance. Afterwards, the high low flowrate (0.67 ml/s) was applied and the samples taking started again after a week to allow for the adoption of the system to the new flowrate (Schultze-Nobre et al., 2017; Tatoulis et al., 2017; Gomes et al., 2018).

2.3. Sampling and analytical methods

Samples were taken after each HRT cycle, i.e., every 3.2 days for operation period under the first HRT (HLR of 0.2 mL/s) and every 1.3 days for operation period under the second HRT (HLR of 0.67 mL/s) and a total of 18 samplings were carried out per pilot unit (9 per HRT). The total

duration of the experiment was 6 months. Wastewater samples were collected from the influent and effluent points (Fig. 1b) and analyzed immediately to determine the following parameters: pH, Al (aluminum), As (arsenic), Ce (Cerium), Cr (Chromium), Cu (Copper), Fe (iron), K (potassium), Li (lithium), Mg (Magnesium), Mn (Manganese), Mo (Molybdenum), Ni (Nickel), Pb (lead), Sc (Scandium), Se (Selenium), Si (Silicon), Sn (Tin), Sr (Strontium), Ta (Tantalum), Th (Thorium), V (Vanadium), W (Tungsten), Zn (Zinc), total phenols, ammonia nitrogen (NH₄-N), nitrate (NO₃-N) and orthophosphate (PO₄-P). Heavy metals were measured via inductively coupled plasma–mass spectrometry (ICP–MS) according to Standard Method 1640 EPA (APHA, 1999). Nitrogen species (NH₄-N, NO₃-N) were measured via spectrophotometry (T80 UV, PG instrument LTD) according to Standard Method 4500-NO₃-N and ASTM D1426 for NH₄-N. Orthophosphate (PO₄-P) were measured via spectrophotometry (T80 UV, PG instrument LTD) according to Standard Method 4500-P-C. Total phenols was measured via spectrophotometry (T80 UV, PG instrument LTD) using Standard Method ASTM D1783, and pH was determined by a VIVOSUN PH Meter Digital PH Tester Pen for Water. Conductivity was measured with a conductivity meter (MS1-IMP403-24) and converted to salinity. Tracer tests were conducted using NaCl.

2.4. Calculations and statistical analysis

To estimate the removal performance, the removal rates of the various parameters were calculated, assuming that the rate coefficients can be described by the means of a first-order removal laws. Considering the flowrates, the HRT, the CW surface area and the concentrations of the various parameters, the first-order reaction rate coefficients (*k*-rates) for wastewater applied and treated in HSFCW were calculated based on the equation (Tarutis et al., 1999; Kadlec and Wallace, 2009):

$$k = (Q \times (\ln C_{in} - \ln C_{out})) / A$$

where, Q is the inflow (m^3/day), A the surface area (m^2), C_{in} the influent concentration (mg/L), C_{out} the effluent concentration (mg/L) and k the first-order rate coefficient (m/d).

First-order reaction rate coefficients (k -rates) were calculated from the observed removals and tracer studies (number of the tanks in series) and were compared to those previously reported in the literature. The nominal HRT was calculated based on the void volume of the saturated media without considering the inlet and outlet sections of the units.

Statistical analysis was performed using the SPSS software (SPSSInc., Chicago, IL, USA; Version 12.0). The data was analysed through one-way analysis of variance (ANOVA) at the 95% significance level ($p \leq 0.05$) to compare the performance of the CW units in the removal of the various parameters. Post Hoc pair comparisons were also performed to test equal variations, using Tukey's honestly significant difference test. Homogeneity of variance tests (Levene) were bypassed, since the number of data points for each group was the same.

3. Results and discussion

3.1. Tracer experiment results

Prior to start measuring the treatment performance, tracer experiments were performed in the RW-SP unit (non-aerated, planted system) at the two different flowrates, i.e., 0.67 and 0.2 mL/s that correspond to the target HRT of 1 day and 4 days, respectively. Sodium chloride (NaCl) was used as a tracer at 1,000 mg/L concentration. Electrical conductivity was measured to obtain the response curve. Tracer data was analyzed using the gamma function distribution method (Kadlec and Wallace, 2009). The actual HRT values were 1.37 and 3.16 days, respectively, with the associated number of tanks-in-series ($NTIS$) of 6.4 and 12.32 (Fig. 3). Tracer recoveries were 70% and 51% for the high and low flowrate, respectively.

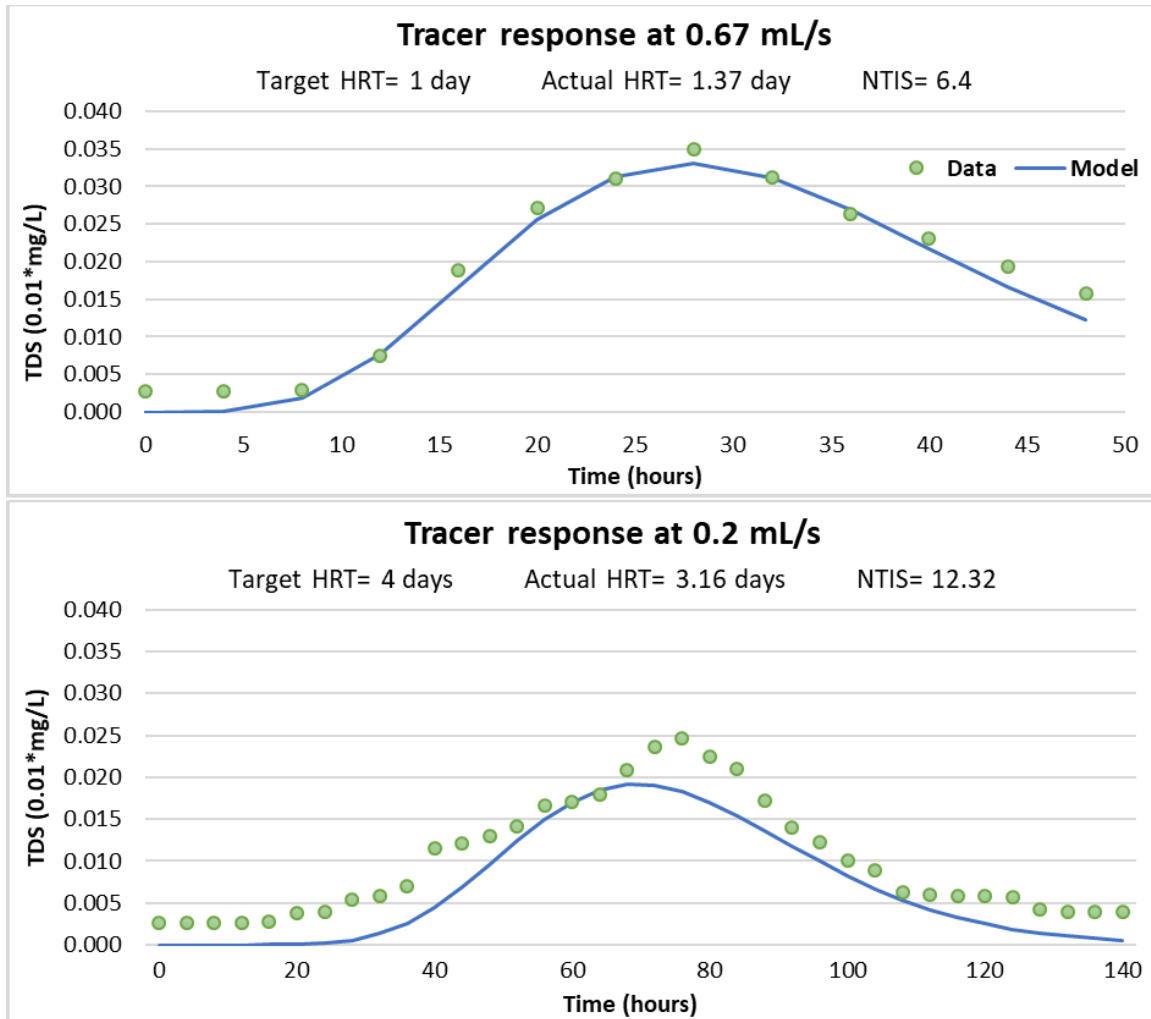


Figure 3. Tracer response curve for the targeted 1-day and 4-days HRT.

Testing the system at the two different flowrates indicated different hydraulic performances. While the variation in the HRT was roughly proportional to the applied flowrate and more or less expected, the degree of internal mixing (*NTIS*) shifted from 12.32 (HRT of 3.16 days) to 6.4 (HRT of 1.37 days). This was likely caused by higher flow velocities at the higher flowrate, resulting in a greater degree of internal mixing, despite the length to width ratio of the system being

237 approximately 7.7. As a point of reference, the reported mean *NTIS* value for HSFCW over 37
238 tracer studies is 11.0 (Kadlec and Wallace, 2009). It is expected that the operation of the aeration

system would increase the internal mixing (Boog, 2013; Boog et al., 2014). A comparable aerated HSFCW at an experimental facility in Germany had an NTIS value of 4.5 while continually aerated (Boog, 2013), although the system had a length to width ratio of 3.9.

3.1. Overall treatment performance

Table 1 shows the influent and effluent values and the respective removal rates of the various parameters at the flowrate of 0.2 mL/s (HRT of 3.16 days) and Table 2 at the flowrate of 0.67 mL/s (HRT of 1.37 days). First-order reaction rate coefficients (k -rates) were calculated based on the observed removals and tracer tests and compared to other results in the literature (Table 3). The removal rates of the various heavy metals are presented in Fig. 4 for both HRT tested, while Fig. 4 shows the removal rates for nitrogen, phosphorus and phenols.

In general, the aerobic conditions in the wetland (aided by the aeration system) allowed relatively high removal rates for Fe (96-98%), Mn (38-92%), Al (63-73%), and Zn (99%) at both HRT (Fig. 3), generally as oxyhydroxide precipitates. Removal of Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (63-92%) under aerobic conditions was also observed (Fig. 3), likely through co-precipitation. These removal rates appear to be higher than typically reported figures for passive CW systems (Aslam et al., 2007; Mustapha et al., 2018). The average pH values of the influent (6.8-7.5) and effluent from all units (7.1-7.5), i.e., close to the neutral zone, also indicate that there was no negative interference to the major metal removal mechanisms (i.e., adsorption, precipitation, sedimentation, plant uptake) (Nyquist and Greger, 2009). The effluent pH values were also within the Iranian standards for environmental discharge and effluent reuse (6-8.5; IEAP,

2008).

262 **Table 1.** Average influent (IN) and effluent (EFF) concentrations ($\mu\text{g/L}$), respective treatment
263 performance (Removal, %) and inlet mass load ($\text{g/m}^2/\text{yr}$) of the pilot RW units at the HRT of 1.37
264 days ($n=9$).

Parameter	IN ($\mu\text{g/L}$)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load ($\text{g/m}^2/\text{yr}$)
		EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	
Al	300	110	63.3	105	65.0	100	66.7	80	73.3	2.20
As	4.37	2.43	44.4	2.15	50.8	2.25	48.5	2.16	50.6	0.032
Ce	1	0.1	90.0	0.26	74.0	0.05	95.0	0.054	94.6	0.007
Cr	6.19	1	83.8	1.52	75.4	0.48	92.2	0.62	90.0	0.045
Cu	30.58	7.76	74.6	11.95	60.9	6.21	79.7	8.0	73.8	0.224
Fe	3580	70	98.0	160	95.5	68	98.1	142	96.0	26.3
K	6510	3440	47.2	4110	36.9	1860	71.4	2080	68.0	47.7
Li	34.62	20.32	41.3	26.61	23.1	21.31	38.4	25.2	27.2	0.254
Mg	27900	22290	20.1	27050	3.0	22170	20.5	22980	17.6	204.6
Mn	130	80	38.5	30	76.9	80	38.5	25	80.8	0.953
Mo	22.29	9.33	58.1	12.83	42.4	4.62	79.3	6.58	70.5	0.163
Ni	52.96	15.95	69.9	14.5	72.6	16.01	69.8	7.87	85.1	0.388
Sc	18.53	4.32	76.7	3.73	79.9	2.9	84.3	1.8	90.3	0.136
Se	14.27	8.97	37.1	8.89	37.7	6.5	54.4	7.1	50.2	0.105
Si	10190	8630	15.3	8040	21.1	6410	37.1	7001	31.3	74.7
Sn	1.57	1.37	12.7	1.49	5.1	0.65	58.6	0.98	37.6	0.012
Sr	2480	1390	44.0	1710	31.0	1480	40.3	2025	18.3	18.2
Ta	0.25	0.13	48.0	0.17	32.0	0.11	56.0	0.16	36.0	0.002
Th	1.05	0.09	91.4	0.1	90.5	0.06	94.3	0.07	93.3	0.008
V	101	3.36	96.7	3.64	96.4	2.63	97.4	2.52	97.5	0.741
W	2.28	0.68	70.2	1.35	40.8	0.39	82.9	0.85	62.7	0.017
Zn	12820	80	99.4	180	98.6	113	99.1	128	99.0	94.0

Pb	62	1.78	97.1	1.82	97.1	0.8	98.7	1.1	98.2	0.455
Phenols	638	3.3	99.5	2.9	99.5	1.7	99.7	0.9	99.9	4.679
NO₃-N	18000	12100	32.8	13900	22.8	8300	53.9	9100	49.4	132.0
NH₄-N	31000	11300	63.5	20	99.9	20	99.9	18	99.9	227.4
PO₄-P	20600	20600	0.0	20600	0.0	1000	95.1	1000	95.1	151.1

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267 **Table 2.** Average influent (IN) and effluent (EFF) concentrations (µg/L), respective treatment
268 performance (Removal, %) and inlet mass load (g/m²/yr) of the pilot RW units at the HRT of 3.16
269 days (n=9).

Parameter	IN (µg/L)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load (g/m ² /yr)
		EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	
Al	300	153	49.0	120	60.0	108	64.0	91	69.7	7.38
As	4.37	3.2	26.8	2.9	33.6	3.1	29.1	0.9	79.4	0.11
Ce	1	0.12	88.0	0.13	87.0	0.05	95.0	0.05	95.0	0.02
Cr	6.19	2.3	62.8	2.5	59.6	0.48	92.2	0.62	90.0	0.15
Cu	30.58	8.8	71.2	13.4	56.2	7.01	77.1	8.8	71.2	0.75
Fe	3580	91	97.5	95	97.3	71	98.0	152	95.8	88
K	6510	2,050	68.5	4,110	36.9	1,930	70.4	760	88.3	160
Li	34.62	13.86	60.0	30.1	13.1	19.5	43.7	21.5	37.9	0.85
Mg	27900	15,390	44.8	20,015	28.3	14,510	48.0	15,310	45.1	686
Mn	130	30	76.9	10	92.3	39	70.0	10	92.3	3.20
Mo	22.29	7.37	66.9	18.4	17.5	5.93	73.4	6.61	70.3	0.55
Ni	52.96	12.18	77.0	11.63	78.0	12.52	76.4	13.71	74.1	1.30
Sc	18.53	4.29	76.8	3.89	79.0	4.2	77.3	3.5	81.1	0.46
Se	14.27	5.4	62.2	5.8	59.4	3.5	75.5	3.55	75.1	0.35

Si	10190	8,040	21.1	8,005	21.4	7,011	31.2	7,000	31.3	251
Sn	1.57	0.97	38.2	1.54	1.9	0.73	53.5	1.29	17.8	0.04
Sr	2480	890	64.1	2,130	14.1	980	60.5	1,560	37.1	61
Ta	0.25	0.2	20.0	0.24	4.0	0.06	76.0	0.08	68.0	0.01
Th	1.05	0.09	91.4	0.11	89.5	0.07	93.3	0.08	92.4	0.03
V	101	3.57	96.5	3.5	96.5	3.1	96.9	3.2	96.8	2.48
W	2.28	0.79	65.4	0.79	65.4	0.79	65.4	0.79	65.4	0.06
Zn	12820	60	99.5	130	99.0	78	99.4	91	99.3	315
Pb	62	2.6	95.8	2.62	95.8	1.3	97.9	1.36	97.8	1.52
Phenol	638	7.8	98.8	4.9	99.2	18	97.2	2.3	99.6	15.7
NO₃-N	18000	16500	8.3	17300	3.9	1100	93.9	2400	86.7	442.4
NH₄-N	31000	17300	44.2	20	99.9	6500	79.0	20	99.9	761.6
PO₄-P	20600	20600	0.0	20600	0.0	900	95.6	890	95.7	506.1

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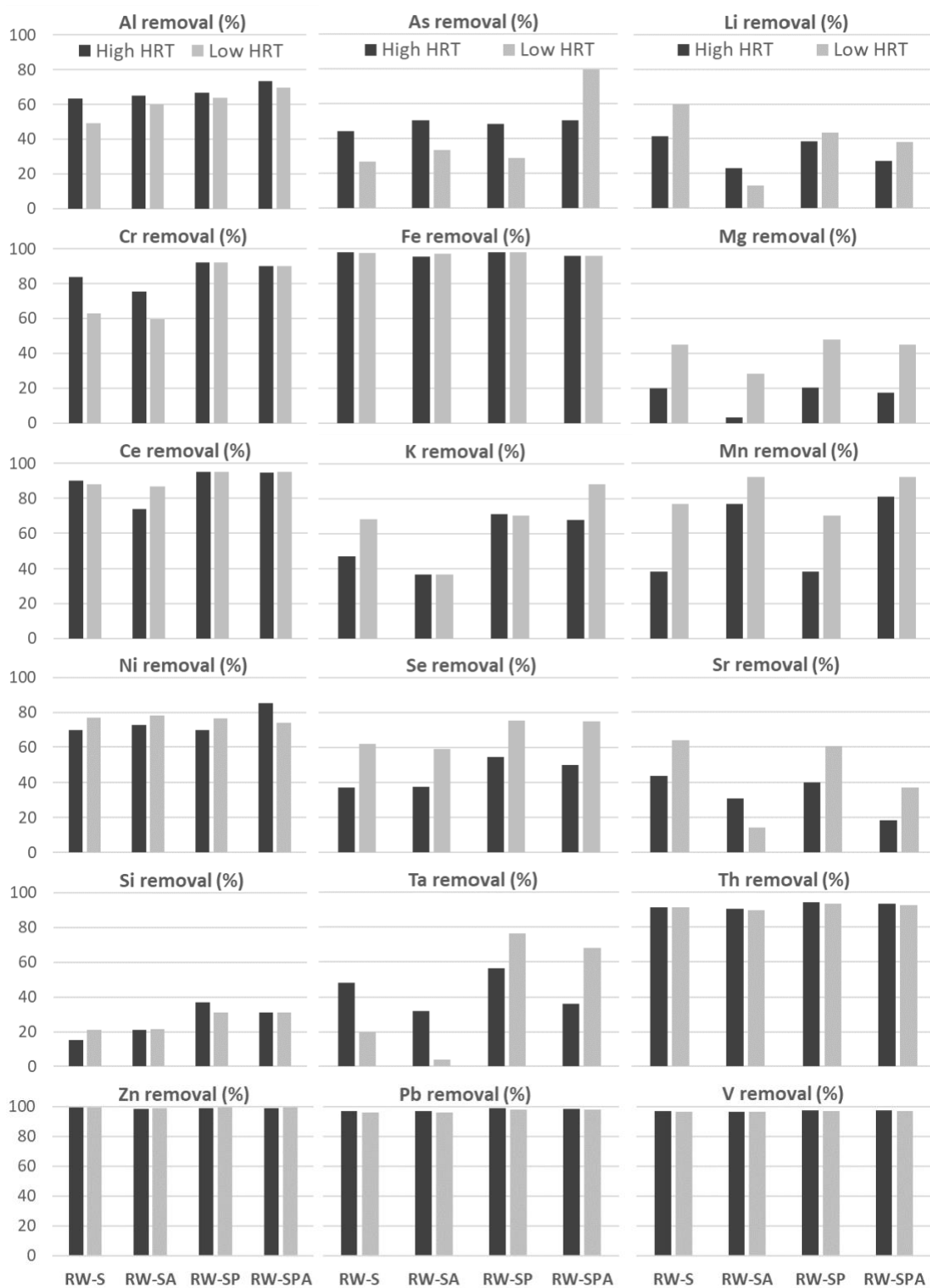


Figure 4. Removal rates of heavy metals in the four pilot CW units at the two HRT tested; low

273 (1.37 days) and high (3.16 days).

Phenols were completely removed in the units under both HRT (Fig. 4), which is in agreement with results from other studies (Stefanakis et al., 2016; Schultze-Nobre et al., 2017; Gomes et al., 2018; Jain et al., 2020). $\text{NH}_4\text{-N}$ reached high removal in the planted units (Fig. 4) and was practically completely removed in the aerated RW units apparently due to the higher dissolved oxygen availability provided by plant roots and mostly by artificial aeration for the nitrification process (Kadlec and Wallace, 2009; Mustapha et al., 2018; Stefanakis et al., 2019). As a result, the first-order reaction rate coefficients (k ; Table 4) estimated for these parameters were limited by the complete removal of the mass loading, and further investigation of removal of these parameters, especially phenols, in aerated CW is warranted. $\text{NO}_3\text{-N}$ removal was limited at a certain level due to the enhanced aeration and conditions conducive to extensive denitrification did not occur in the tested pilot configurations, although higher removal rates were measured in the planted units probably due to higher plant uptake (Stefanakis et al., 2019). Phosphorus removal in the system was attributable to short-term plant biomass uptake over the duration of the study period, as indicated by the high removal rates measured only in the planted units.

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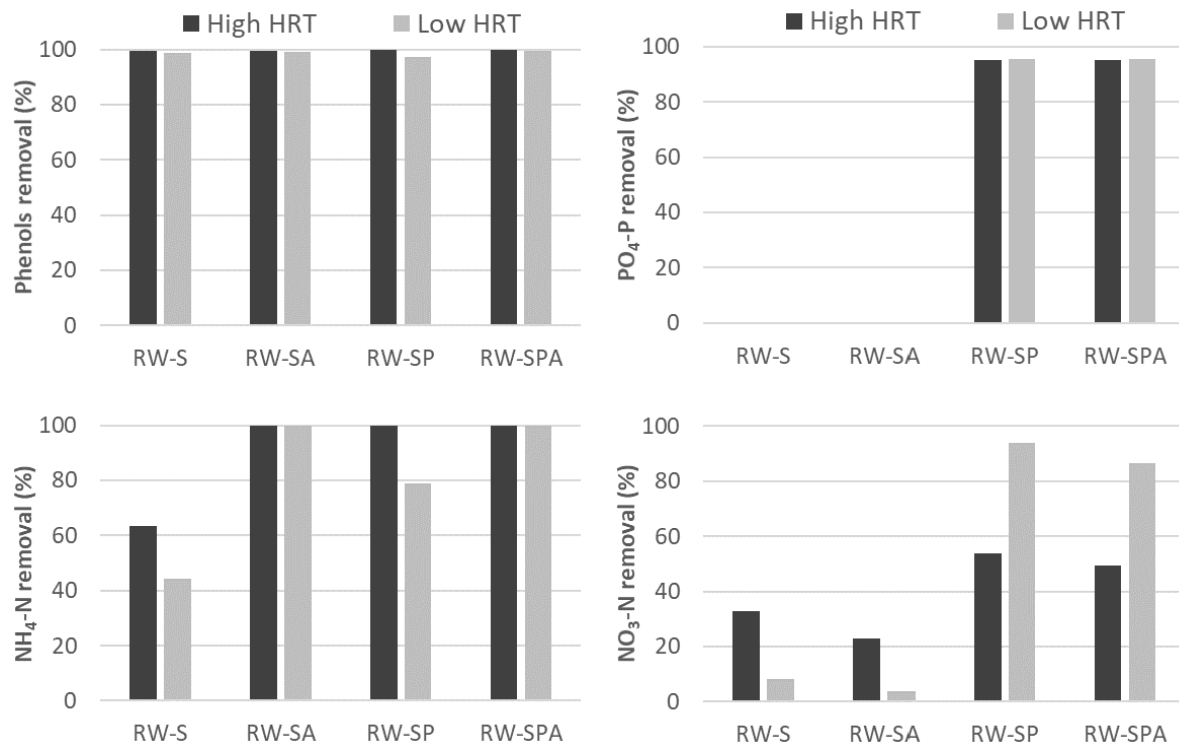


Figure 5. Removal rates of phenols, ammonia nitrogen, nitrate and phosphorus in the four pilot

CW units at the two HRT tested; low (1.37 days) and high (3.16 days).

Table 3. First-order reaction rate coefficients (k) for the racetrack wetland design and comparison with available literature data.

Parameter	This Study	Other Studies
Fe	219–290 m/yr (1.37 d HRT, range for all units) 82-107 m/yr (3.16 d HRT, range for all units)	42 m/yr (Manyin et al., 1997) 66 m/yr (Tarutis et al., 1999)
Mn	169 m/yr (1.37 d HRT with aeration)	21 m/yr (SF; Tarutis et al., 1999)

	71-88 m/yr (1.37 d HRT without aeration)	10-60 m/yr (HSF with river gravel; Sikora et al., 2000) 100-600 m/yr (HSF with limestone; Sikora et al., 2000)
Cu	54-97 m/yr (1.37 d HRT, range for all units) 23-39 m/yr (3.16 d HRT, range for all units)	80 m/yr (SF, estimated; Kanagy et al., 2008)
Ni	81-82 m/yr (1.37 d HRT, range for all units) 29-42 m/yr (3.16 d HRT, range for all units)	15-18 m/yr (SF+HSF; Sinicrope et al., 1992)
Pb	219-284 m/yr (1.37 d HRT, range for all units) 95-121 m/yr (3.16 d HRT, range for all units)	104 m/yr (SF, estimated; Kanagy et al., 2008)
Cr	52-57 m/yr 1.37 d HRT, unplanted) 148-168 m/yr (1.37 d HRT, planted) 34-46 m/yr (3.16 d HRT, unplanted) 59-66 m/yr (3.16 d HRT, planted)	25-35 m/yr (SF+HSF; Sinicrope et al., 1992) 20-80 m/yr (SF; Kadlec and Srinivasan, 1995) 3-64 m/yr (Kadlec and Wallace, 2009)
Zn	360-450 m/yr (1.37 d HRT, range for all units)	28 m/yr (SF+HSF; Sinicrope et al., 1992) 55-121 m/yr (SF; Gillespie et al., 2000) 21-42 m/yr (SF, estimated; Dorman et al., 2009)

	118-146 m/yr (3.16 d HRT, range for all units)	
Phenols	96 -165 m/yr (1.37 d HRT, planted with aeration) 152-201 m/yr (3.16 d HRT, planted with aeration)	8-17 m/yr (HSF, estimated; Rossmann et al., 2012) 107.2 m/yr (HSF; Stefanakis et al., 2016) 98.9 m/yr (HSF; Tatoulis et al., 2017) 100 m/yr (SF, estimated; Polprasert and Dan, 1994) 76 m/yr (SF, unplanted; Tang and Lu, 1993) 150 m/yr (SF, planted; Tang and Lu, 1993) 100 m/yr (SF, estimated; Dong and Lin, 1994)
NH ₄ -N	233-237 m/yr (planted with aeration) 13.8 m/yr (1.37 d HRT, unplanted, no aeration) 24.4 m/yr (3.16 d HRT, unplanted, no aeration)	960,6 m/yr (VF, planted with aeration; Stefanakis et al., 2019) 589 m/yr (HSF, planted with aeration; Stefanakis, 2020b) 2.9 m/yr (HSF, planted without aeration; Nivala et al., 2019) 22.4 m/yr (HSF, planted without aeration; Stefanakis et al., 2016)
NO ₃ -N	0.9-2.0 m/yr (1.37 d HRT, unplanted) 51-73 m/yr (1.37 d HRT, planted) 6.0-9.3 m/yr (3.16 d HRT, unplanted) 16-19 m/yr (3.16 d HRT, planted)	75 m/yr (HSF, planted with aeration; Nivala et al., 2019) 65.1 m/yr (VF, planted with aeration; Stefanakis et al., 2019) 96.4 m/yr (HSF, planted with aeration; Stefanakis, 2020b) 3.9 m/yr (HSF, planted without aeration; Nivala et al., 2019)

296 3.2. Removal of metals

297 As seen in Tables 1 and 2, a removal rate was detected for all measured metals, albeit at varying
298 mass loading rates and removal percentages. Generally, heavy metals removal can be attributed to
299 the (i) adsorption onto the wetland substrate (sand, gravel) and organic matter (plant roots), (ii)
300 air/water interactions, which generally lead to an aerobic (oxidizing) environment, especially in
301 the pilot units with artificial aeration, resulting in precipitation and co-precipitation of metals, and
302 (iii) uptake and assimilation in plant biomass (Sheoran and Sheoran, 2006; Kadlec and Wallace,
303 2009; García et al., 2010).

304 Iron (Fe) loading rates were 26 and 88 g/m²/yr at the two flowrates with corresponding removals
305 of 96-98% (Fig. 3). These loading rates are far below those recommended for CWs treating mine
306 drainage, which are in the range of 3,650 – 7,300 g/m²/yr (Hedin et al., 1994; PIRAMID
307 Consortium, 2003; Nyquist and Greger, 2009). The Fe effluent values of all pilot CWs were also
308 below the national limit for environmental discharge (300 µg/L; IEAP, 2008). The absence of high
309 organic loads and the respectively limited oxygen demand within the wetlands in the present study,
310 as well as the external aeration provided to the system, generally supports the hypothesis that Fe
311 was removed as an oxyhydroxide precipitate (Fe(OH)₃). It is proposed that Fe removal in CWs is
312 a first-order process, with reaction rate coefficients (*k*) estimated at 42 m/yr (Manyin et al., 1997)
313 and 66 m/yr (Tarutis et al., 1999). Analysis of the data from this study yielded *k*-rates between 82-
314 107 m/yr at the longer HRT (3.16 days) and 219-290 m/yr at the shorter retention time (1.37 days)
315 (Table 3). Since virtually all Fe was removed in the CW, the higher reaction rate coefficients
316 indicate that Fe removal occurred quickly within the system.

Manganese (Mn) loads were 0.95 and 3.2 g/m²/yr at the two flowrates (Tables 1 and 2), which is considerably lower than the 182.5 g/m²/yr recommended for CWs treating mine drainage (PIRAMID Consortium, 2003). Mn removal was consistently higher in the CW units with artificial aeration at both flowrates. At the HRT of 1.37 days, Mn removal was 70-77% without aeration and 92% with aeration (Fig. 3); for the HRT of 3.16 days, Mn removal was 38.5% without aeration and 77-81% with aeration (Fig. 3). As the kinetics for Mn oxidation and precipitation are generally slower compared to Fe (Hedin and Nairn, 1993) and Mn removal is not significant in aerobic CWs with low Fe concentration (Hallberg and Johnson, 2005), the enhancement of the aerobic conditions in the aerated wetlands could potentially have aided in Mn removal. The Mn effluent values of all pilot CWs were also below the national limit for environmental discharge (50 µg/L; IEAP, 2008). Mn removal as a first-order process in CWs has been proposed. Data analysis indicated reaction rate coefficients (*k*) of 169 m/yr for the optimum conditions (highest loading with aeration), and 71-88 m/yr (highest loading without aeration) (Table 3). In the literature, 21 m/yr has been proposed for surface flow (SF) CW (Tarutis et al., 1999). For HSFCWs (without aeration), rates of 10-60 m/yr for river gravel and 100-600 m/yr for limestone-based systems have been estimated (Sikora et al., 2000).

Aluminum (Al) can form hydroxide precipitates under oxidizing conditions, which are strongly associated with phosphorus retention. Al loads were 2.2 and 7.4 g/m²/yr (Tables 1 and 2), compared to loads of approximately 0.44 g/m²/yr observed for municipal wastewater applications of non-aerated HSFCWs (Vymazal and Krása, 2003). The removal percentages in this study ranged from 63-73% at the HRT of 3.16 days, and 49-70% at the HRT of 1.37 days (Fig. 3), indicating that longer HRT resulted in better Al removal. Respective figures for Al reported in the literature are approximately 70% (Gensemer and Playle, 1999), and are comparable to this study.

Copper (Cu) loads were 0.75 and 0.22 g/m²/yr at the two flowrates (Tables 1 and 2), with removal percentages between 56-80%. While Cu removal is often associated with reducing conditions and sulfide precipitation, removal under aerobic conditions via co-precipitation with Fe and Mn oxyhydroxide precipitates is also possible. For mining applications, loading rates of 3,650 g/m²/yr (sulfide producing conditions) and 18.25 g/m²/yr (aerobic conditions) have been proposed (PIRAMID Consortium, 2003), which are considerably higher than this study. The Cu effluent values of all pilot CWs were below the national limit for environmental discharge (20 µg/L; IEAP, 2008). Cu removal as a first-order process under aerobic conditions is a possibility (Tarutis et al., 1999). If Cu removal is through co-precipitation with Fe and Mn, and those metals follow a first-order process, reaction rate coefficients (*k*) can also be estimated for Cu. Data analysis indicates *k*-rates of 23-39 m/yr at the lower HRT, and 54-97 m/yr at the higher HRT (Table 3). In a pilot-scale SFCW treating oil produced water, Cu removal data indicated a *k*-rate of 80 m/yr (Kanagy et al., 2008).

Nickel (Ni) loads were 1.30 and 0.39 g/m²/d at the two flowrates, with removal percentages between 70-85% (HRT of 3.16 days) and 74-77% (HRT of 1.37 days) (Tables 1 and 2). While Ni removal is often associated with reducing conditions and sulfide precipitation, removal under aerobic conditions through co-precipitation with Fe and Mn oxyhydroxide precipitates is also possible. For mining applications, loading rates of 730 g/m²/yr (sulfide producing conditions) and 14.6 g/m²/yr (aerobic conditions) have been proposed (PIRAMID Consortium, 2003), which are considerably higher than this study. Ni removal as a first-order process under aerobic conditions is a possibility (Tarutis et al., 1999), but data sets to estimate a first-order reaction rate coefficient (*k*) are limited. Data from a SF + HSF CW at Sacramento, California resulted in estimated *k*-rates of 15-18 m/yr (Sinicrope et al., 1992), at Ni loading rates of 5.5-6.7 g/m²/yr (Kadlec and Wallace,

2009). Data from this study yields k -rate estimates of 29-48 m/yr (HRT of 3.16 days) and 81-82 m/yr (HRT of 1.37 days) (Table 3).

Lead (Pb) loads were 1.52 and 0.46 g/m²/yr at the two flowrates (Tables 1 and 2). Almost all Pb was removed (96-99%; Fig. 3), which is consistent with the formation of very insoluble sulfate and carbonate precipitates (DeVolder et al., 2003). The Pb effluent values of all pilot CWs were below the national limit (50 µg/L; IEAP, 2008). Pb removal as a first-order process has been proposed, but previous data sets did not allow for the estimation of a k -rate (Kadlec and Wallace, 2009). Data from this study yields k -rate estimates of 95-121 m/yr at the lower HRT and 219-284 m/yr at the higher HRT (Table 3). Since virtually all Pb was removed at both HRTs, the use of the higher k -rate estimates appears justified. In a pilot-scale SFCW treating oil produced water, Pb removal data indicated a k -rate of approximately 104 m/yr (Kanagy et al., 2008).

Chromium (Cr) loads were 0.15 and 0.05 g/m²/yr at the two flowrates (Tables 1 and 2). Cr removal was affected by plants' presence. The removal in the unplanted units were 75-84% (low loading rate) and 60-63% (high loading rate), and 90-92% in the planted units at both loading rates (Fig. 3). On the other hand, the artificial aeration did not appear to influence Cr removal. The Cr influent and effluent values of all pilot CWs were below the national limit for environmental discharge (50 µg/L; IEAP, 2008). Cr can be removed through co-precipitation with Fe and Mn oxyhydroxide precipitates; the first-order modeling approach applied to those metals can also be applied to Cr. A summary of Cr removal data estimated k -rate coefficients ranging from 3-64 m/yr, with a median value of 19 m/yr (Kadlec and Wallace, 2009). Data from SFCW and HSFCW mesocosms at Sacramento, California treating municipal wastewater yielded k -rate estimates of 25-35 m/yr (Sinicrope et al., 1992), and data from a SFCW mesocosm treating petroleum wastewater yielded k -rate estimates of 20-80 m/yr (Kadlec and Srinivasan, 1995). In a pilot-scale SFCW treating ash

basin water, Cr removal data suggested k -rates of 29-36 m/yr (Dorman et al., 2009). In this study, the unplanted units resulted in k -rate estimates of 34-46 m/yr (HRT of 3.16 days) and 52-57 m/yr (HRT of 1.37 days) and the planted units in 59-66 m/yr (HRT of 3.16 days) and 148-168 m/yr (HRT of 1.37 days) (Table 3).

Zinc (Zn) loads were 315 and 94 g/m²/yr at the two flowrates (Tables 2 and 3). Zn was almost completely removed (99%; Fig. 3), which is consistent with the formation of insoluble carbonate precipitates, and through co-precipitation with Fe and Mn oxyhydroxide precipitates (Younger et al., 2002; Kadlec and Wallace, 2009). In comparison, recommendations for loading rates for mine water treatment range from 14.6 g/m²/yr (PIRAMID Consortium, 2003) up to 2,555 g/m²/yr (Younger et al., 2002). The Zn effluent values of all pilot CWs were below the national limit for environmental discharge (500 µg/L; IEAP, 2008). Zn removal can be considered a first-order process. For a SFCW and HSFCW mesocosm at Sacramento, California, the estimated k -rate was 28 m/yr (Sinicrope et al., 1992), while for a SFCW treating oil refinery effluent, the k -rate for Zn removal was estimated at 55-121 m/yr at two different loading rates (Gillespie et al., 2000; Kadlec and Wallace, 2009). In a pilot-scale CW treating oil produced water (Kanagy et al., 2008), Zn removal data indicated a k -rate of approximately 15 m/yr. In another pilot-scale SFCW treating ash basin water, Zn removal data suggested k -rates of 21-42 m/yr (Dorman et al., 2009). In this study, the estimated k -rates ranged from 118-146 m/yr (low HRT) to 360-450 m/yr (high HRT) (Table 3).

3.3. Phenols

Phenol was essentially completely removed in all systems (Fig. 4), as the influent (638 µg/L) was removed to close to non-detect concentrations (0.9-18 µg/L; Tables 1 and 2). First order rate

coefficients (k) ranged from 152 – 201 m/yr (HRT of 3.16 days) and 96 – 165 m/yr (HRT of 1.37 days). It is reported that aerobic biodegradation is the main phenol removal mechanism in CW (Kurzbaum et al., 2010; Rossmann et al., 2012; Stefanakis et al., 2016), though anaerobic degradation is also possible (Kumaran and Paruchuri, 1997). Similarly, high removal rates for phenols are reported in CW studies in the literature, even for higher influent concentrations. Data from a series of pilot-scale HSFCW treating coffee processing wastewater in Brazil (Rossmann et al., 2012) suggests phenol degradation k -rates of 8-17 m/yr. A pilot HSFCW treating cork boiling wastewater in Portugal suggests k -rates between 35-42 m/yr (Gomes et al., 2018). In a series of pilot studies using SFCW (Polprasert et al., 1996), data indicated a phenol degradation k -rate of approximately 100 m/yr. In a study of planted and unplanted SFCW channels in China, k -rates for phenol degradation were estimated at 150 m/yr (planted) and 76 m/yr (unplanted) (Tang et al., 1993). In a study at a petroleum facility, a full-scale SFCW (50 ha) had an estimated k -rate of approximately 100 m/yr for phenol removal (Dong and Lin, 1994). Complete phenols removal and a k rate of 107.2 m/yr was found in a HSFCW system treating groundwater contaminated with phenols and petroleum derivatives (Stefanakis et al., 2016). A similar phenols removal k rate of 98.9 m/yr is reported for a HSFCW treating pre-treated olive mill wastewater (Tatoulis et al., 2017).

3.4. Nitrogen

Ammonia nitrogen ($\text{NH}_4\text{-N}$) removal (nitrification) occurred in all pilot units at both loading rates (influent of 31,000 $\mu\text{g/L}$, effluent of 18-20 $\mu\text{g/L}$; Tables 1 and 2), with corresponding k -rates of 233-237 m/yr (Table 3). $\text{NH}_4\text{-N}$ removal was strongly influenced by the presence of aeration (Fig. 4). It is likely the actual k -rates are higher, since the systems ran out of $\text{NH}_4\text{-N}$ with essentially

complete removal. In a similar study, an aerated HSFCW in Germany had an estimated k -rate of 1,540 m/yr vs. 2.9 m/yr for a non-aerated system (Table 3; Nivala et al., 2019). A high k -rate of 960.6 m/yr was also estimated for an aerated VFCW in the UK operating as tertiary treatment stage (Stefanakis et al., 2019), while an aerated second-stage HSFCW in Oman suggests k -rate of 589 m/yr (Stefanakis, 2020b). In both these systems under different climates, complete ammonia removal occurred as well, indicating the positive impact of artificial aeration on aerobic nitrification (Stefanakis et al., 2019).

Ammonia removal was also influenced by the presence of vegetation (Tables 1 and 2), since the presence of plants promotes the biofilm development and the related aerobic oxidation of $\text{NH}_4\text{-N}$ by microorganisms (Stefanakis, 2016). Many studies report that plants' presence favor ammonia removal (Kadlec and Wallace, 2009; Stefanakis et al., 2016; Schultze-Nobre et al., 2017). The shorter duration trial (HRT of 1.37 days) had an estimated k -rate of 39 m/yr, whereas at the longer HRT (3.16 days), the estimated k -rate was 233 m/yr (since the system ran out of $\text{NH}_4\text{-N}$). Without plants or aeration, k -rates were lower, 13.8 m/yr (HRT of 1.37 days) and 24.4 m/yr (HRT of 3.16 days), respectively. Respective k -rate of 22.4 and 39.9 m/yr are reported for HSF systems treating contaminated groundwater and cork boiling wastewater (Stefanakis et al., 2016; Gomes et al., 2018).

Nitrate ($\text{NO}_3\text{-N}$) removal (denitrification) also occurred but at lower levels. Nitrate concentrations decreased from influent values, despite the conversion of $\text{NH}_4\text{-N}$ to oxidized forms of nitrogen within the pilot systems. Aeration possibly impacted $\text{NO}_3\text{-N}$ removal, as more $\text{NH}_4\text{-N}$ was converted to oxidized forms of nitrogen, and the aerobic conditions were not conducive to complete denitrification. For systems without vegetation, estimated k -rates with and without aeration were 0.9-2.0 m/yr (HRT of 1.37 days) and 6.0-9.3 m/yr (HRT of 3.16 days), respectively.

With vegetation, $\text{NO}_3\text{-N}$ removal rates increased (Fig. 4), potentially due to plant uptake considering that ammonia is completely oxidized and nitrate remain the only available nitrogen form for plant uptake, as well as due to the potential presence of more bioavailable carbon in the system, but again, $\text{NO}_3\text{-N}$ removal rates were possibly by aeration. However, the presence of non-aerated sections in the design possibly limited the effect of the aeration in the denitrification extent in the system. The fact that aeration also enhances the microbial growth (Chazarenc et al., 2009; Nivala et al., 2020) indicates that nitrate removal should be a combination of microbial oxidation and plant uptake. Estimated k -rates with and without aeration were 51-73 m/yr (HRT of 1.37 days) and 16-19 m/yr (HRT of 3.16 days). In a similar study, an aerated HSFCW in Germany (Nivala et al., 2019) had an estimated k -rate of 75 m/yr with aeration and 3.9 m/yr without aeration, since $\text{NO}_3\text{-N}$ was not produced in the non-aerated wetland. Similar k -rates of 65.1 and 96.4 m/yr were also estimated for an aerated VFCW in the UK (Stefanakis et al., 2019) and an aerated HSFCW in Oman (Stefanakis, 2020b), with the latter receiving small amounts of raw wastewater (step-feeding) to increase the carbon availability, hence the higher rate observed.

3.5. Phosphorus

Phosphorus ($\text{PO}_4\text{-P}$) removal only occurred when vegetation was present in the system, since it is known that $\text{PO}_4\text{-P}$ removal in CW systems is generally lower compared to other pollutants and mostly depends on the adsorption capacity of the substrate media and the uptake by plants to cover their growth needs (Kadlec and Wallace, 2009; García et al., 2010; Stefanakis, 2016). For the trials conducted with vegetation, phosphorus uptake was essentially complete (95-98%) with effluent concentrations close to detection limits. The applied phosphorus loads of 151 and 507 $\text{g/m}^2\text{/yr}$ (at

477 the low and high loading rates) greatly exceeds the amount of phosphorus required to support the

plant biomass cycle (Kadlec and Wallace, 2009). As a result, it is anticipated that the system would saturate with phosphorus in a longer-term study as the plant community matures and the media gets gradually saturated.

3.6. Optimum design configuration

The tested design proved to be efficient in treating the refinery effluent reaching higher removal rates for most of the tested parameters. The different pilot units revealed the significant role of plants in the overall performance, as the planted bed (RW-SP) showed better removal rates for all parameters than the unplanted unit (RW-S) (Tables 2 and 3), with statistically significant removals ($p<0.05$) occurring for nitrogen and phosphorus and many heavy metals (Al, Ce, Cr, K, Mo, Sc, Se, Si, Sn, Sr, Ta, W). The performance appears to be further enhanced with the addition of the aerated section (RW-SPA; Tables 2 and 3). Artificial aeration seems to improve ($p<0.05$) the removal of ammonia nitrogen, Al, As, K, Mn, Sc, and Se compared to the planted non-aerated unit (RW-SP). On the other hand, when the aeration was applied in the unplanted unit (RW-SA), it did not improve the overall performance. Among the two HRT tested, high removals were observed even for the smaller HRT of 1.4 days with slightly higher removal rates compared to the removals under the HRT of 3.2 days and with statistical significance ($p<0.05$) occurring for nitrate, Al, As, K, Li, Mg, Mn, Ni, Se, Sr, and Ta.

The advantage of the tested design arises from the comparison with other wetland designs applied for similar effluent treatment. The surface flow CW is widely applied for such effluents, but it has a significantly higher area demand due to the prolonged HRT required, e.g., 20 days under similar hydraulic load of 0.06 m/d (Mustafa et al., 2018). A VFCW operating at 0.07 m/d and a HRT of 2

500 days showed a lower performance for nutrients though receiving a much lower influent

concentration since it received a secondary refinery effluent (Mustapha et al., 2015; 2018). A HSFCW was also tested for diesel contaminated water at different levels, resulting in optimum removal conditions of 63 days retention time (Al-Baldawi et al., 2014). In a review paper on refinery effluent treatment in CW, the HRT range reported varies between 2.1-90 days, with the majority of the systems being in the range above 10 days (Jia et al., 2020). In the same review study, the positive role of plants and aeration is also indicated, while the HSFCW is reported to be the design with the better performance.

4. Conclusions

Petroleum refinery effluents represent a major industrial pollution source of significant concern due to its toxic and harmful nature. Established biological methods are not very effective in the remediation of these effluents, while advanced oxidation processes, although effective, are expensive to install and operate. In this study, the technology of Constructed Wetlands was applied for refinery effluent containing heavy metals, phenols and nitrogen as a sustainable nature-based treatment solution. An innovative CW design forming a meandric ‘racetrack’ shape and combining different treatment environments (aerobic and anaerobic) was tested for the first time at pilot-scale. Different construction (non-aerated, artificial aeration, planted and unplanted) and operation (different hydraulic loading rates) parameters were studied to determine the optimum design for effective performance. The first-order removal of metals and the simultaneous removal of phenols and nutrients from the oil refinery wastewater were calculated. The planted unit with artificial aeration managed to reach high removal rates for Fe (96-98%), Mn (38-81%), Al (49-73%), Zn (99-100%), Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (60-92%) even at the short HRT of

523 1.3 days, while complete removal of phenols and full nitrification was also found. As the calculated

524 first-order removal coefficients showed, the overall performance of this novel design exceeded the
525 reported efficiency of the common CW designs and implies the potential to further apply and test
526 it for other industrial effluents.

527

528 **Authorship contribution statement**

529 Mozaffari M.S: Conceptualization, Writing - review, Visualization, Investigation, Data curation.

530 Shafiepour E.: Project administration. Mirbagheri S.A.: Resources, Funding acquisition

531 Rakhshandehroo G.: Methodology, Funding acquisition. Wallace S.: Conceptualization, Formal

532 analysis, Data curation. Stefanakis A.I.: Formal analysis, Data curation and analysis, Writing -

5335 original draft, Writing - review

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535 **Acknowledgements**

536 This study work was supported by the Civil Engineering Department, Shiraz University and the

5375 Khajeh Nasir Toosi University of Technology.

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Hydraulic characterization and removal of metals and nutrients in an aerated horizontal subsurface flow “racetrack” wetland treating primary-treated oil industry effluent

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Highlights

- Novel ‘racetrack’ constructed wetland design tested for the first time
- Treatment of oil refinery effluent rich in heavy metals, phenols and nutrients
- Positive role of plants and artificial aeration found, even at low retention time of 1.3 days
- High heavy metals removal (up to 98%), complete degradation of phenols and ammonia
- Higher k -rates calculated than literature findings for other wetland systems

Abstract

Constructed wetlands (CW) are an attractive technology due to their operational simplicity and low life-cycle cost. It has been applied for refinery effluent treatment but mostly single-stage designs (e.g., vertical or horizontal flow) have been tested. However, to achieve a good treatment efficiency for industrial effluents, different treatment conditions (both aerobic and anaerobic) are needed. This means that hybrid CW systems are typically required with a respectively increased area demand. In addition, a strong aerobic environment that facilitates the formation of iron, manganese, zinc and aluminum precipitates cannot be established with passive wetland systems, while the role of these oxyhydroxide compounds in the further co-precipitation and removal of heavy metals such as copper, nickel, lead, and chromium that can simplify the overall treatment of industrial wastewaters is poorly understood in CW. Therefore, this study tests for the first time an innovative CW design that combines an artificially aerated section with a non-aerated section in a single unit applied for oil refinery wastewater treatment. Four pilot units were tested with different design (i.e., planted/unplanted, aerated/non-aerated) and operational (two different hydraulic loading rates) characteristics to estimate the role of plants and artificial aeration and to identify the optimum design configuration. The pilot units received a primary refinery effluent, i.e., after passing through a dissolved air flotation unit. The first-order removal of heavy metals under aerobic conditions is evaluated, along with the removal of phenols and nutrients. High removal rates for Fe (96-98%), Mn (38-81%), Al (49-73%), and Zn (99-100%) generally as oxyhydroxide precipitates were found, while removal of Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (60-92%) under aerobic conditions was also observed, likely through co-precipitation. Complete phenols and ammonia nitrogen removal was also found. The first-order rate coefficient (k) calculated from the collected data demonstrates that the tested CW represents an advanced wetland design reaching higher removal rates at a smaller area demand than the common CW systems.

Keywords: aerated wetland; constructed wetland; refinery effluent; phenols; heavy metals; tracer test

1. Introduction

Polluted water from industrial sites represents a major environmental threat for ecosystems and public health by virtue of historic operational practices, incidents and leakages during storage and transport (Langwaldt and Puhakka, 2000; Stefanakis et al., 2020a). These wastewaters typically have a complex composition with a large variety of pollutants of different nature and properties such as heavy metals, organic matter, nutrients, solids, color, salinity, amid of other inorganic and toxic compounds (Wu et al., 2015; Stefanakis, 2018; Ramirez et al., 2019). Among them, heavy metals are considered one the most problematic. Many industrial wastewaters have varying levels of metals that derive from their operation and require further treatment prior the release to the environment or reuse at the operation sites. In particular, heavy metals are frequently found in effluents from refineries and generally the petrochemical industry (Wu et al., 2015; Mustapha et al., 2018; Stefanakis et al., 2018; Jain et al., 2020).

Various technologies and processes have been applied for the treatment of refinery effluents, e.g., membrane bioreactors, activated sludge, anaerobic reactors, ozonation etc. (Stefanakis, 2020a; Jain et al., 2020). The green technology of Constructed wetlands (CW) has also been used for petroleum derived water treatment though the respective applications are limited (Ji et al., 2007; Johnson et al., 2008; Wallace et al., 2011; Stefanakis et al., 2016; Stefanakis, 2020a). The positive aspects of CW include lower investment for infrastructure, significantly lower operation and maintenance cost, ecological character, tolerance to flowrate variations, no use of chemicals for the treatment,

among others (Kadlec and Wallace, 2009; Stefanakis, 2019). In addition, CW can handle varying contaminant loads and treat many constituents of concern at the same time and more effectively than some physical and chemical processes (Stefanakis, 2016; Gorito et al., 2017). These advantages account for the growing interest and increasing number of CW applications for the treatment of various industrial wastewater sources such as from the chemical and petrochemical industry (Wallace et al., 2011; Stefanakis et al., 2016; Stefanakis, 2020a), the oil and gas exploration (Stefanakis et al., 2018; Jain et al., 2020; Stefanakis, 2020b), the food industry such as dairy farms and olive mills (Tatoulis et al., 2017; Wu et al., 2015), and agro-industries such as glass industry, tanneries, cork processing wastewater (Gholipour et al., 2020; Gomes et al., 2018; Ramirez et al., 2019), among others.

The application of CW technology for refinery effluent treatment is not widely reported, although current knowledge indicates that CW can be specifically designed and built for the removal of target-constituents from refinery effluents. A few studies on vertical flow CW (VFCW) and horizontal subsurface flow CW designs (HSFCW) are also available in the international literature (Gillespie et al., 2000; Stefanakis et al., 2016; Mustapha et al., 2018; Jain et al., 2020). HSFCW are inherently oxygen-transfer limited systems, thus, anaerobic digestion (methanogenesis) becomes a salient contributor to the removal of the various constituents (Kadlec and Wallace, 2009). On the other hand, artificial aeration in CW is an advanced design that increases the phytoremediation potential of CW for heavy metals removal such as Cu^{+2} (Xin et al., 2019), while it also enhances the biodegradation rate under an aerobic environment (Del Rio et al., 2006; Stefanakis et al., 2019).

However, the vast majority of the published literature studies single CW units that utilize only one wetland design (e.g., vertical or horizontal or surface flow), while the aerated CW has barely been

tested for refinery effluent treatment. This means that a CW system for refinery effluent typically has a high areal footprint. However, the refinery effluent composition would require a combination of different environments, i.e., aerobic and anaerobic conditions, to achieve effective removal rates for the various pollutants especially for nitrogen and heavy metals. This could potentially be done with the use of hybrid (i.e., multistage) CW systems but this would further increase the land area demand. Therefore, the present study proposes and investigates an advanced CW design as a new innovative solution that combines in the same unit different treatment conditions necessary for the effective removal of pollutants of diverse nature aiming at providing a wetland treatment solution with smaller area demand than the existing CW designs. Therefore, the main research goal of this study is to test for the first time this innovative CW design at pilot scale for the effective treatment of process waters from a refinery. The specific goals is to determine the role of plants, substrate, hydraulic retention time and aeration in treating the refinery effluent with focus on the load removal of a series of heavy metals and nutrients.

2. Materials and methods

2.1. Study location

Four pilot-scale HSFCW units (planted and unplanted) with an innovative design were built outdoors at the Khajeh-Nasir Toosi University (35°45'48.0"N 51°24'33.9"E) with different design characteristics, i.e., planted, unplanted (i.e., sand filters), with and without artificial aeration. Wastewater volume was collected from the Tehran oil refinery effluent. This facility, located southern of Tehran City (35°32'24.7"N 51°25'37.7"E), is the second largest refinery in Iran and is one of the oldest refineries with an oil refining capacity of approximately 110,000 barrels per day, and a water consumption of nearly 505 m³/h (Bidhendi et al., 2010). It is considered as the best

performing refinery for the sake of Environmental Protection Act in Iran. The current wastewater treatment plant of the refinery consists of the DAF unit, followed by an aeration tank, a sedimentation tank and sand filtration unit, while the final effluent is discharged to agricultural fields or recycled in the industrial process. The effluent of the dissolved air flotation (DAF) unit was used for this study, since the DAF system achieves high recovery rates of the residual oil and it is preferred to remain in operation.

2.1. Pilot-scale CW design

The base unit of the innovative design (called “Racetrack wetland”) of each CW was fabricated out of clear acrylic plastic with a total flow path length of 12.8 m, mean channel width of 7.65 cm, and an effective depth of 0.2 m. The flow path was wrapped in a spiral configuration (Fig. 1a), such that each pilot cell required only 0.86 m² of area. The inflow point was at the centre of the unit and the water followed a meandric subsurface flow path, with the outflow point at one corner of the unit (Figs. 1 and 2). The structural design of the tested ‘Racetrack Wetland’ (RW) system furnishes two different environments (Fig. 2): a planted section without aeration (total length of planted section 6.3 m) and an unplanted section with aeration (total length of unplanted section 5.7 m). The aerated unplanted section constituted 44% of the total wetland area and included irrigation tubes in the center of the flow path with specific drippers that provided 0.6 L/min air flowrate at air pressure of 100 mbar. Aeration in the CW was based on previous systems used in North America and Europe (Wallace, 2002), using a 0.175 kW air blower capable of delivering up to 626.8 L/m²/min. The unplanted sections were filled with a graded, washed silica sand (size 0.8 - 1.2 mm, porosity 24%). The same media was used in the planted sections, but with the addition of 5% clay on the top 2 cm, to allow for the plant establishment in the silica soil. The inlet section at

137 the center of the unit had dimensions of 26x26 cm, while the outlet section had a length of 80 cm
138 and width 15.5 cm, while coarser gravel (6-7 mm) was used at the inlet and outlet sections to
139 facilitate the flow distribution (Fig. 3). *Cyperus alternifolius* plants of approx. 1 week old were
140 harvested from local water courses at the distance of 35 kilometers from Tehran Oil Refinery and
141 then immediately planted in the planted section of the CW design, covering 56% of the total
1421 wetland area.

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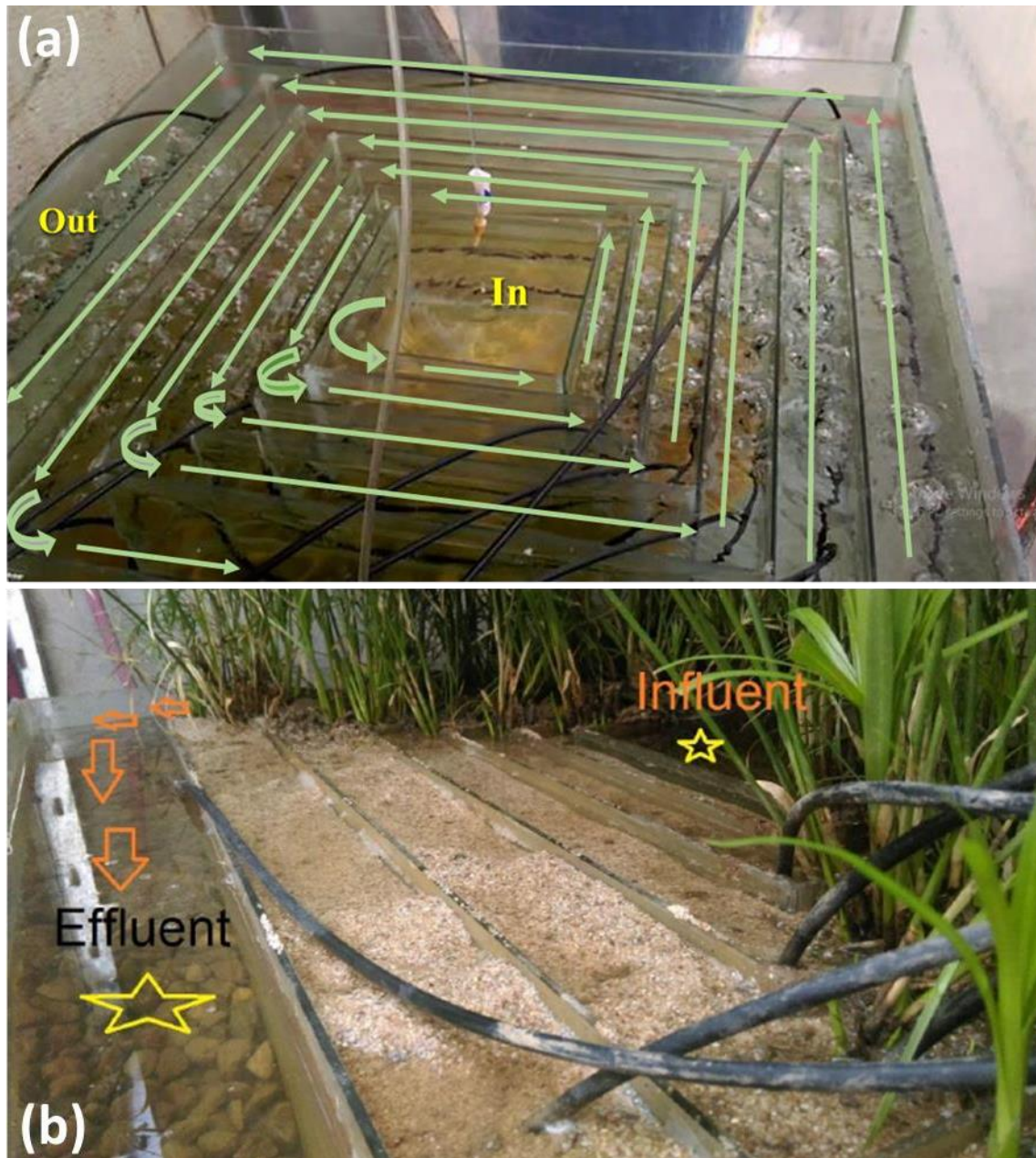


Figure 1. (a) Racetrack wetland configuration with aeration (base unit without substrate or vegetation), and (b) the unplanted and planted sections, the coarse gravel at the inlet and outlet sections, and the influent and effluent sampling points.

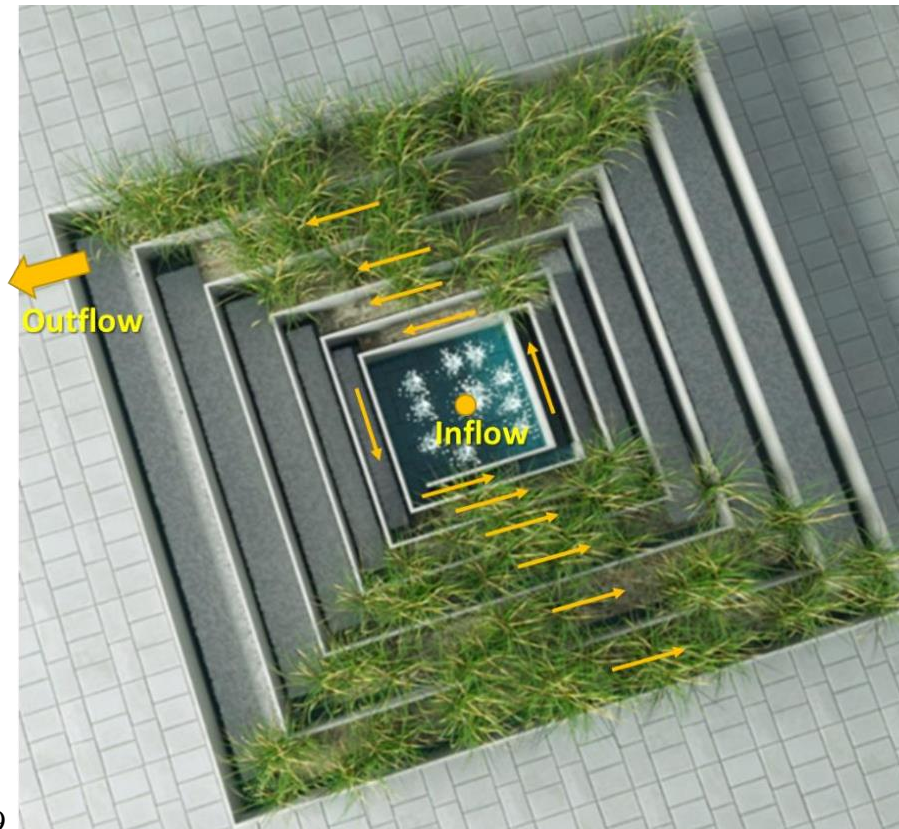


Figure 2. Schematic representation (top view) of the planted and non-planted sections of the racetrack wetland unit and the meandric flow path.

Four similar pilot RW units were built and operated in parallel to examine the effects of plant, substrate and aeration in the wetland performance, distinctly, with the following configuration: one pilot unit only with substrate (RW-S), one pilot unit with substrate and forced bed aeration (RW-SA), one pilot unit with substrate planted with *Cyperus alternifolius* (RW-SP), and one pilot unit with substrate planted with *Cyperus alternifolius* and with forced bed aeration (RW-SPA).

Once the pilot RW units were built and planted, a solution of 10 mL of a natural liquid fertilizer (NPK 7-4-7, Iranian plant company) mixed with 100 mL of tap water was added to each RW twice per week to cover the nutrients requirement for the initial growth period of the plants and biofilm (Ramond et al., 2012). The feeding with the NPK solution lasted the first 3 months after planting, in order to assist plant adoption to the new environment and sufficient penetration depth of plant roots into the substrate (Qureshi et al., 2005). After that start-up period, tracer tests were carried out for a period of 2 weeks. Once the tracer tests were completed, the refinery effluent was collected in a large tank that fed the CW units and the feeding of the pilot CWs started. The first 3 weeks of operation with the refinery effluent were considered a necessary period for the system to adopt to the feed water after the start-up period, hence no samples were taken (Kadlec and Wallace, 2009; Ramirez et al., 2019). After that period, another batch of refinery effluent was collected and fed, and the sampling and monitoring started. Two flowrates, i.e., 0.20 and 0.67 mL/s, were selected corresponding to the target hydraulic retention times (HRT) of 4 days and 1 day, respectively. Tracer tests were used to determine more accurately the actual HRT at the two different flowrates. The low flowrate (0.2 mL/s) was first applied to the four CWs to evaluate their removal performance. Afterwards, the high low flowrate (0.67 ml/s) was applied and the samples taking started again after a week to allow for the adoption of the system to the new flowrate (Schultze-Nobre et al., 2017; Tatoulis et al., 2017; Gomes et al., 2018).

2.3. Sampling and analytical methods

Samples were taken after each HRT cycle, i.e., every 3.2 days for operation period under the first HRT (HLR of 0.2 mL/s) and every 1.3 days for operation period under the second HRT (HLR of 0.67 mL/s) and a total of 18 samplings were carried out per pilot unit (9 per HRT). The total

duration of the experiment was 6 months. Wastewater samples were collected from the influent and effluent points (Fig. 1b) and analyzed immediately to determine the following parameters: pH, Al (aluminum), As (arsenic), Ce (Cerium), Cr (Chromium), Cu (Copper), Fe (iron), K (potassium), Li (lithium), Mg (Magnesium), Mn (Manganese), Mo (Molybdenum), Ni (Nickel), Pb (lead), Sc (Scandium), Se (Selenium), Si (Silicon), Sn (Tin), Sr (Strontium), Ta (Tantalum), Th (Thorium), V (Vanadium), W (Tungsten), Zn (Zinc), total phenols, ammonia nitrogen (NH₄-N), nitrate (NO₃-N) and orthophosphate (PO₄-P). Heavy metals were measured via inductively coupled plasma–mass spectrometry (ICP–MS) according to Standard Method 1640 EPA (APHA, 1999). Nitrogen species (NH₄-N, NO₃-N) were measured via spectrophotometry (T80 UV, PG instrument LTD) according to Standard Method 4500-NO₃-N and ASTM D1426 for NH₄-N. Orthophosphate (PO₄-P) were measured via spectrophotometry (T80 UV, PG instrument LTD) according to Standard Method 4500-P-C. Total phenols was measured via spectrophotometry (T80 UV, PG instrument LTD) using Standard Method ASTM D1783, and pH was determined by a VIVOSUN PH Meter Digital PH Tester Pen for Water. Conductivity was measured with a conductivity meter (MS1-IMP403-24) and converted to salinity. Tracer tests were conducted using NaCl.

2.4. Calculations and statistical analysis

To estimate the removal performance, the removal rates of the various parameters were calculated, assuming that the rate coefficients can be described by the means of a first-order removal laws. Considering the flowrates, the HRT, the CW surface area and the concentrations of the various parameters, the first-order reaction rate coefficients (*k*-rates) for wastewater applied and treated in HSFCW were calculated based on the equation (Tarutis et al., 1999; Kadlec and Wallace, 2009):

$$k = (Q \times (\ln C_{in} - \ln C_{out})) / A$$

where, Q is the inflow (m^3/day), A the surface area (m^2), C_{in} the influent concentration (mg/L), C_{out} the effluent concentration (mg/L) and k the first-order rate coefficient (m/d).

First-order reaction rate coefficients (k -rates) were calculated from the observed removals and tracer studies (number of the tanks in series) and were compared to those previously reported in the literature. The nominal HRT was calculated based on the void volume of the saturated media without considering the inlet and outlet sections of the units.

Statistical analysis was performed using the SPSS software (SPSSInc., Chicago, IL, USA; Version 12.0). The data was analysed through one-way analysis of variance (ANOVA) at the 95% significance level ($p \leq 0.05$) to compare the performance of the CW units in the removal of the various parameters. Post Hoc pair comparisons were also performed to test equal variations, using Tukey's honestly significant difference test. Homogeneity of variance tests (Levene) were bypassed, since the number of data points for each group was the same.

3. Results and discussion

3.1. Tracer experiment results

Prior to start measuring the treatment performance, tracer experiments were performed in the RW-SP unit (non-aerated, planted system) at the two different flowrates, i.e., 0.67 and 0.2 mL/s that correspond to the target HRT of 1 day and 4 days, respectively. Sodium chloride (NaCl) was used as a tracer at 1,000 mg/L concentration. Electrical conductivity was measured to obtain the response curve. Tracer data was analyzed using the gamma function distribution method (Kadlec and Wallace, 2009). The actual HRT values were 1.37 and 3.16 days, respectively, with the associated number of tanks-in-series ($NTIS$) of 6.4 and 12.32 (Fig. 3). Tracer recoveries were 70% and 51% for the high and low flowrate, respectively.

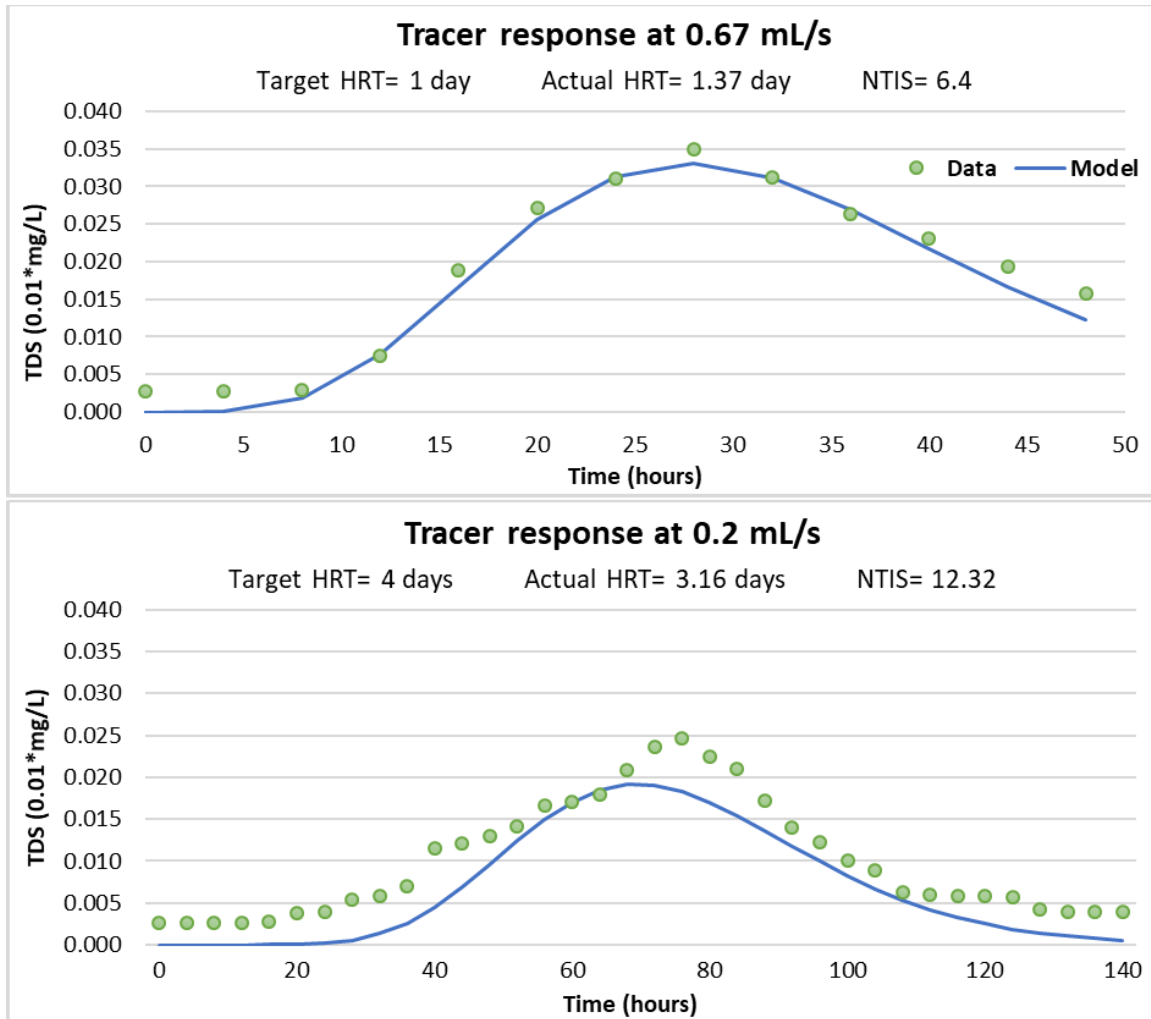


Figure 3. Tracer response curve for the targeted 1-day and 4-days HRT.

Testing the system at the two different flowrates indicated different hydraulic performances. While the variation in the HRT was roughly proportional to the applied flowrate and more or less expected, the degree of internal mixing (*NTIS*) shifted from 12.32 (HRT of 3.16 days) to 6.4 (HRT of 1.37 days). This was likely caused by higher flow velocities at the higher flowrate, resulting in a greater degree of internal mixing, despite the length to width ratio of the system being

237 approximately 7.7. As a point of reference, the reported mean *NTIS* value for HSFCW over 37
238 tracer studies is 11.0 (Kadlec and Wallace, 2009). It is expected that the operation of the aeration

system would increase the internal mixing (Boog, 2013; Boog et al., 2014). A comparable aerated HSFCW at an experimental facility in Germany had an NTIS value of 4.5 while continually aerated (Boog, 2013), although the system had a length to width ratio of 3.9.

3.1. Overall treatment performance

Table 1 shows the influent and effluent values and the respective removal rates of the various parameters at the flowrate of 0.2 mL/s (HRT of 3.16 days) and Table 2 at the flowrate of 0.67 mL/s (HRT of 1.37 days). First-order reaction rate coefficients (*k*-rates) were calculated based on the observed removals and tracer tests and compared to other results in the literature (Table 3). The removal rates of the various heavy metals are presented in Fig. 4 for both HRT tested, while Fig. 4 shows the removal rates for nitrogen, phosphorus and phenols.

In general, the aerobic conditions in the wetland (aided by the aeration system) allowed relatively high removal rates for Fe (96-98%), Mn (38-92%), Al (63-73%), and Zn (99%) at both HRT (Fig. 3), generally as oxyhydroxide precipitates. Removal of Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (63-92%) under aerobic conditions was also observed (Fig. 3), likely through co-precipitation. These removal rates appear to be higher than typically reported figures for passive CW systems (Aslam et al., 2007; Mustapha et al., 2018). The average pH values of the influent (6.8-7.5) and effluent from all units (7.1-7.5), i.e., close to the neutral zone, also indicate that there was no negative interference to the major metal removal mechanisms (i.e., adsorption, precipitation, sedimentation, plant uptake) (Nyquist and Greger, 2009). The effluent pH values were also within the Iranian standards for environmental discharge and effluent reuse (6-8.5; IEAP,

2008).

262 **Table 1.** Average influent (IN) and effluent (EFF) concentrations ($\mu\text{g/L}$), respective treatment
263 performance (Removal, %) and inlet mass load ($\text{g/m}^2/\text{yr}$) of the pilot RW units at the HRT of 1.37
264 days ($n=9$).

Parameter	IN ($\mu\text{g/L}$)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load ($\text{g/m}^2/\text{yr}$)
		EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	EFF ($\mu\text{g/L}$)	Rem (%)	
Al	300	110	63.3	105	65.0	100	66.7	80	73.3	2.20
As	4.37	2.43	44.4	2.15	50.8	2.25	48.5	2.16	50.6	0.032
Ce	1	0.1	90.0	0.26	74.0	0.05	95.0	0.054	94.6	0.007
Cr	6.19	1	83.8	1.52	75.4	0.48	92.2	0.62	90.0	0.045
Cu	30.58	7.76	74.6	11.95	60.9	6.21	79.7	8.0	73.8	0.224
Fe	3580	70	98.0	160	95.5	68	98.1	142	96.0	26.3
K	6510	3440	47.2	4110	36.9	1860	71.4	2080	68.0	47.7
Li	34.62	20.32	41.3	26.61	23.1	21.31	38.4	25.2	27.2	0.254
Mg	27900	22290	20.1	27050	3.0	22170	20.5	22980	17.6	204.6
Mn	130	80	38.5	30	76.9	80	38.5	25	80.8	0.953
Mo	22.29	9.33	58.1	12.83	42.4	4.62	79.3	6.58	70.5	0.163
Ni	52.96	15.95	69.9	14.5	72.6	16.01	69.8	7.87	85.1	0.388
Sc	18.53	4.32	76.7	3.73	79.9	2.9	84.3	1.8	90.3	0.136
Se	14.27	8.97	37.1	8.89	37.7	6.5	54.4	7.1	50.2	0.105
Si	10190	8630	15.3	8040	21.1	6410	37.1	7001	31.3	74.7
Sn	1.57	1.37	12.7	1.49	5.1	0.65	58.6	0.98	37.6	0.012
Sr	2480	1390	44.0	1710	31.0	1480	40.3	2025	18.3	18.2
Ta	0.25	0.13	48.0	0.17	32.0	0.11	56.0	0.16	36.0	0.002
Th	1.05	0.09	91.4	0.1	90.5	0.06	94.3	0.07	93.3	0.008
V	101	3.36	96.7	3.64	96.4	2.63	97.4	2.52	97.5	0.741
W	2.28	0.68	70.2	1.35	40.8	0.39	82.9	0.85	62.7	0.017
Zn	12820	80	99.4	180	98.6	113	99.1	128	99.0	94.0

Pb	62	1.78	97.1	1.82	97.1	0.8	98.7	1.1	98.2	0.455
Phenols	638	3.3	99.5	2.9	99.5	1.7	99.7	0.9	99.9	4.679
NO₃-N	18000	12100	32.8	13900	22.8	8300	53.9	9100	49.4	132.0
NH₄-N	31000	11300	63.5	20	99.9	20	99.9	18	99.9	227.4
PO₄-P	20600	20600	0.0	20600	0.0	1000	95.1	1000	95.1	151.1

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267 **Table 2.** Average influent (IN) and effluent (EFF) concentrations (µg/L), respective treatment
268 performance (Removal, %) and inlet mass load (g/m²/yr) of the pilot RW units at the HRT of 3.16
269 days (n=9).

Parameter	IN (µg/L)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load (g/m ² /yr)
		EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	
Al	300	153	49.0	120	60.0	108	64.0	91	69.7	7.38
As	4.37	3.2	26.8	2.9	33.6	3.1	29.1	0.9	79.4	0.11
Ce	1	0.12	88.0	0.13	87.0	0.05	95.0	0.05	95.0	0.02
Cr	6.19	2.3	62.8	2.5	59.6	0.48	92.2	0.62	90.0	0.15
Cu	30.58	8.8	71.2	13.4	56.2	7.01	77.1	8.8	71.2	0.75
Fe	3580	91	97.5	95	97.3	71	98.0	152	95.8	88
K	6510	2,050	68.5	4,110	36.9	1,930	70.4	760	88.3	160
Li	34.62	13.86	60.0	30.1	13.1	19.5	43.7	21.5	37.9	0.85
Mg	27900	15,390	44.8	20,015	28.3	14,510	48.0	15,310	45.1	686
Mn	130	30	76.9	10	92.3	39	70.0	10	92.3	3.20
Mo	22.29	7.37	66.9	18.4	17.5	5.93	73.4	6.61	70.3	0.55
Ni	52.96	12.18	77.0	11.63	78.0	12.52	76.4	13.71	74.1	1.30
Sc	18.53	4.29	76.8	3.89	79.0	4.2	77.3	3.5	81.1	0.46
Se	14.27	5.4	62.2	5.8	59.4	3.5	75.5	3.55	75.1	0.35

Si	10190	8,040	21.1	8,005	21.4	7,011	31.2	7,000	31.3	251
Sn	1.57	0.97	38.2	1.54	1.9	0.73	53.5	1.29	17.8	0.04
Sr	2480	890	64.1	2,130	14.1	980	60.5	1,560	37.1	61
Ta	0.25	0.2	20.0	0.24	4.0	0.06	76.0	0.08	68.0	0.01
Th	1.05	0.09	91.4	0.11	89.5	0.07	93.3	0.08	92.4	0.03
V	101	3.57	96.5	3.5	96.5	3.1	96.9	3.2	96.8	2.48
W	2.28	0.79	65.4	0.79	65.4	0.79	65.4	0.79	65.4	0.06
Zn	12820	60	99.5	130	99.0	78	99.4	91	99.3	315
Pb	62	2.6	95.8	2.62	95.8	1.3	97.9	1.36	97.8	1.52
Phenol	638	7.8	98.8	4.9	99.2	18	97.2	2.3	99.6	15.7
NO₃-N	18000	16500	8.3	17300	3.9	1100	93.9	2400	86.7	442.4
NH₄-N	31000	17300	44.2	20	99.9	6500	79.0	20	99.9	761.6
PO₄-P	20600	20600	0.0	20600	0.0	900	95.6	890	95.7	506.1

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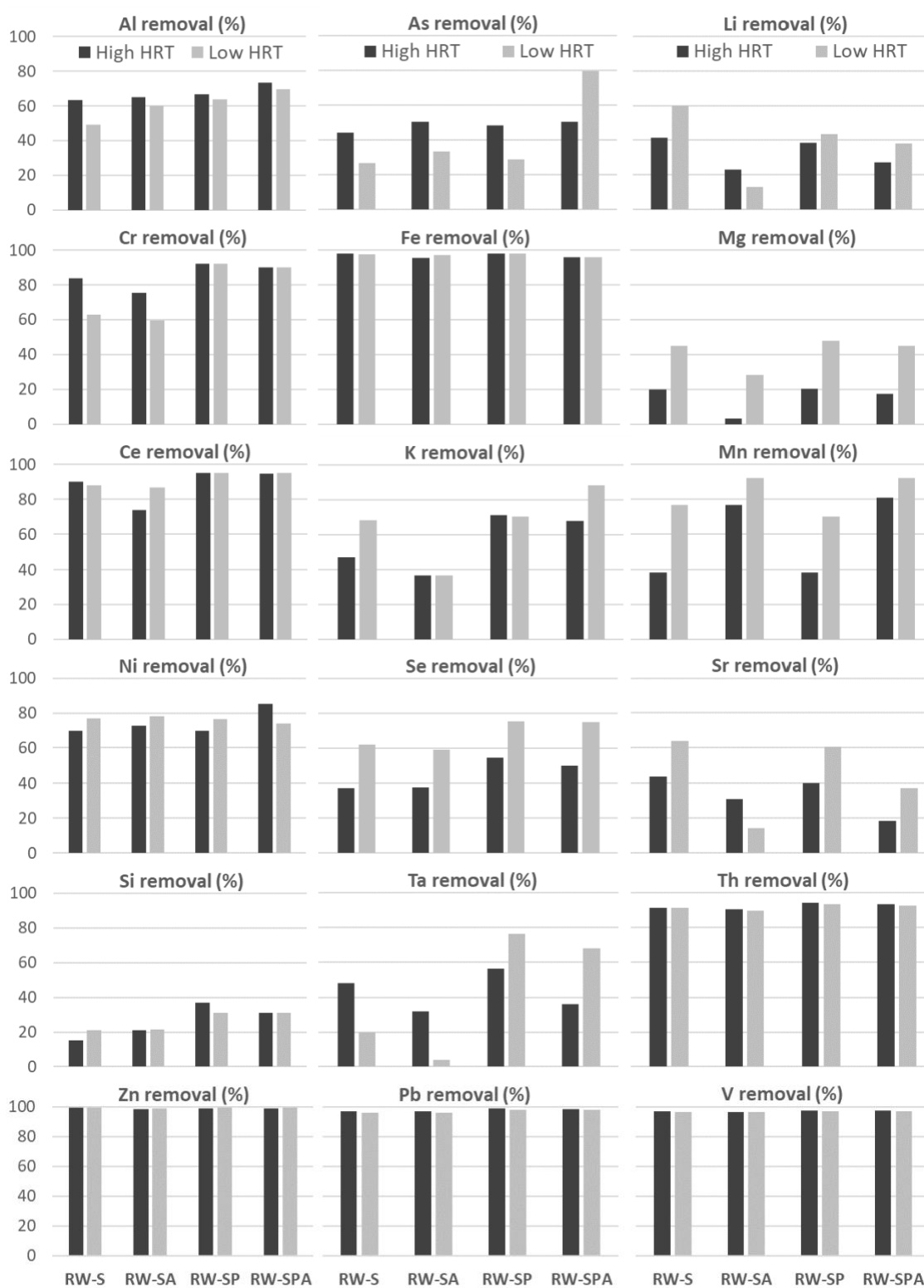


Figure 4. Removal rates of heavy metals in the four pilot CW units at the two HRT tested; low

273 (1.37 days) and high (3.16 days).

Phenols were completely removed in the units under both HRT (Fig. 4), which is in agreement with results from other studies (Stefanakis et al., 2016; Schultze-Nobre et al., 2017; Gomes et al., 2018; Jain et al., 2020). $\text{NH}_4\text{-N}$ reached high removal in the planted units (Fig. 4) and was practically completely removed in the aerated RW units apparently due to the higher dissolved oxygen availability provided by plant roots and mostly by artificial aeration for the nitrification process (Kadlec and Wallace, 2009; Mustapha et al., 2018; Stefanakis et al., 2019). As a result, the first-order reaction rate coefficients (k ; Table 4) estimated for these parameters were limited by the complete removal of the mass loading, and further investigation of removal of these parameters, especially phenols, in aerated CW is warranted. $\text{NO}_3\text{-N}$ removal was limited at a certain level due to the enhanced aeration and conditions conducive to extensive denitrification did not occur in the tested pilot configurations, although higher removal rates were measured in the planted units probably due to higher plant uptake (Stefanakis et al., 2019). Phosphorus removal in the system was attributable to short-term plant biomass uptake over the duration of the study period, as indicated by the high removal rates measured only in the planted units.

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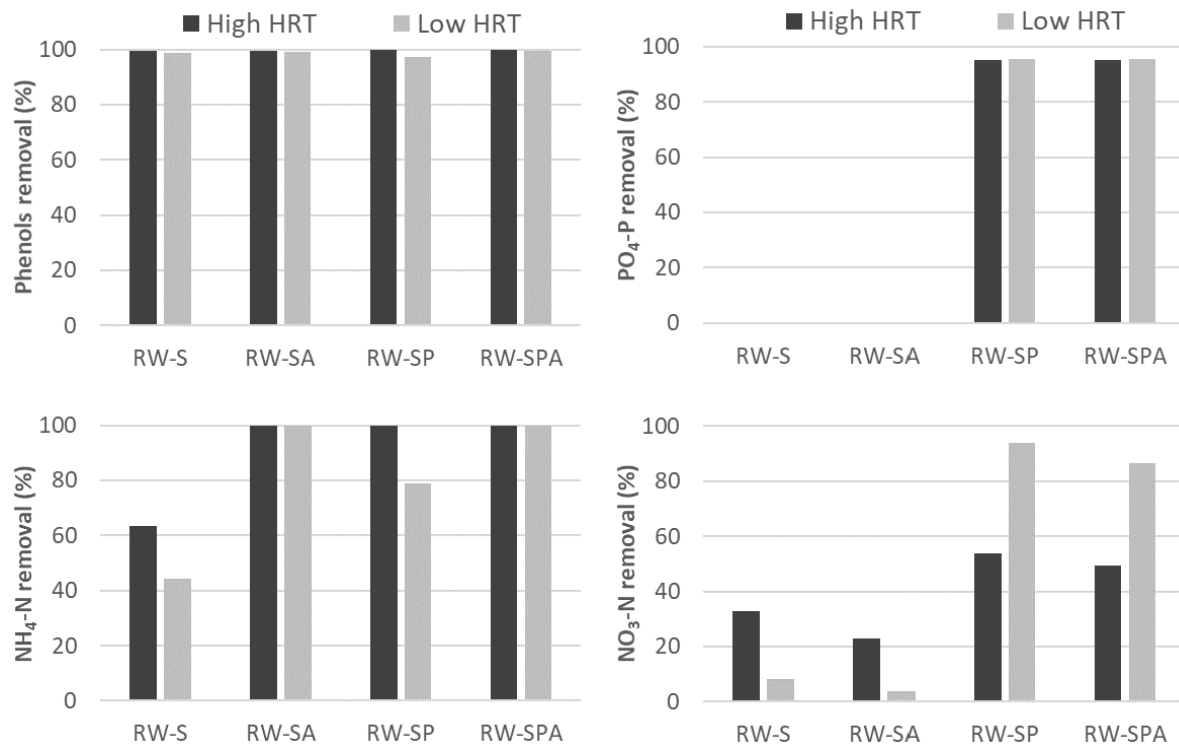


Figure 5. Removal rates of phenols, ammonia nitrogen, nitrate and phosphorus in the four pilot

CW units at the two HRT tested; low (1.37 days) and high (3.16 days).

Table 3. First-order reaction rate coefficients (k) for the racetrack wetland design and comparison with available literature data.

Parameter	This Study	Other Studies
Fe	219–290 m/yr (1.37 d HRT, range for all units)	42 m/yr (Manyin et al., 1997)
	82-107 m/yr (3.16 d HRT, range for all units)	66 m/yr (Tarutis et al., 1999)
Mn	169 m/yr (1.37 d HRT with aeration)	21 m/yr (SF; Tarutis et al., 1999)

	71-88 m/yr (1.37 d HRT without aeration)	10-60 m/yr (HSF with river gravel; Sikora et al., 2000) 100-600 m/yr (HSF with limestone; Sikora et al., 2000)
Cu	54-97 m/yr (1.37 d HRT, range for all units) 23-39 m/yr (3.16 d HRT, range for all units)	80 m/yr (SF, estimated; Kanagy et al., 2008)
Ni	81-82 m/yr (1.37 d HRT, range for all units) 29-42 m/yr (3.16 d HRT, range for all units)	15-18 m/yr (SF+HSF; Sinicrope et al., 1992)
Pb	219-284 m/yr (1.37 d HRT, range for all units) 95-121 m/yr (3.16 d HRT, range for all units)	104 m/yr (SF, estimated; Kanagy et al., 2008)
Cr	52-57 m/yr 1.37 d HRT, unplanted) 148-168 m/yr (1.37 d HRT, planted) 34-46 m/yr (3.16 d HRT, unplanted) 59-66 m/yr (3.16 d HRT, planted)	25-35 m/yr (SF+HSF; Sinicrope et al., 1992) 20-80 m/yr (SF; Kadlec and Srinivasan, 1995) 3-64 m/yr (Kadlec and Wallace, 2009)
Zn	360-450 m/yr (1.37 d HRT, range for all units)	28 m/yr (SF+HSF; Sinicrope et al., 1992) 55-121 m/yr (SF; Gillespie et al., 2000) 21-42 m/yr (SF, estimated; Dorman et al., 2009)

	118-146 m/yr (3.16 d HRT, range for all units)	
Phenols	96 -165 m/yr (1.37 d HRT, planted with aeration) 152-201 m/yr (3.16 d HRT, planted with aeration)	8-17 m/yr (HSF, estimated; Rossmann et al., 2012) 107.2 m/yr (HSF; Stefanakis et al., 2016) 98.9 m/yr (HSF; Tatoulis et al., 2017) 100 m/yr (SF, estimated; Polprasert and Dan, 1994) 76 m/yr (SF, unplanted; Tang and Lu, 1993) 150 m/yr (SF, planted; Tang and Lu, 1993) 100 m/yr (SF, estimated; Dong and Lin, 1994)
NH ₄ -N	233-237 m/yr (planted with aeration) 13.8 m/yr (1.37 d HRT, unplanted, no aeration) 24.4 m/yr (3.16 d HRT, unplanted, no aeration)	960,6 m/yr (VF, planted with aeration; Stefanakis et al., 2019) 589 m/yr (HSF, planted with aeration; Stefanakis, 2020b) 2.9 m/yr (HSF, planted without aeration; Nivala et al., 2019) 22.4 m/yr (HSF, planted without aeration; Stefanakis et al., 2016)
NO ₃ -N	0.9-2.0 m/yr (1.37 d HRT, unplanted) 51-73 m/yr (1.37 d HRT, planted) 6.0-9.3 m/yr (3.16 d HRT, unplanted) 16-19 m/yr (3.16 d HRT, planted)	75 m/yr (HSF, planted with aeration; Nivala et al., 2019) 65.1 m/yr (VF, planted with aeration; Stefanakis et al., 2019) 96.4 m/yr (HSF, planted with aeration; Stefanakis, 2020b) 3.9 m/yr (HSF, planted without aeration; Nivala et al., 2019)

296 3.2. Removal of metals

297 As seen in Tables 1 and 2, a removal rate was detected for all measured metals, albeit at varying
298 mass loading rates and removal percentages. Generally, heavy metals removal can be attributed to
299 the (i) adsorption onto the wetland substrate (sand, gravel) and organic matter (plant roots), (ii)
300 air/water interactions, which generally lead to an aerobic (oxidizing) environment, especially in
301 the pilot units with artificial aeration, resulting in precipitation and co-precipitation of metals, and
302 (iii) uptake and assimilation in plant biomass (Sheoran and Sheoran, 2006; Kadlec and Wallace,
303 2009; García et al., 2010).

304 Iron (Fe) loading rates were 26 and 88 g/m²/yr at the two flowrates with corresponding removals
305 of 96-98% (Fig. 3). These loading rates are far below those recommended for CWs treating mine
306 drainage, which are in the range of 3,650 – 7,300 g/m²/yr (Hedin et al., 1994; PIRAMID
307 Consortium, 2003; Nyquist and Greger, 2009). The Fe effluent values of all pilot CWs were also
308 below the national limit for environmental discharge (300 µg/L; IEAP, 2008). The absence of high
309 organic loads and the respectively limited oxygen demand within the wetlands in the present study,
310 as well as the external aeration provided to the system, generally supports the hypothesis that Fe
311 was removed as an oxyhydroxide precipitate (Fe(OH)₃). It is proposed that Fe removal in CWs is
312 a first-order process, with reaction rate coefficients (*k*) estimated at 42 m/yr (Manyin et al., 1997)
313 and 66 m/yr (Tarutis et al., 1999). Analysis of the data from this study yielded *k*-rates between 82-
314 107 m/yr at the longer HRT (3.16 days) and 219-290 m/yr at the shorter retention time (1.37 days)
315 (Table 3). Since virtually all Fe was removed in the CW, the higher reaction rate coefficients
316 indicate that Fe removal occurred quickly within the system.

Manganese (Mn) loads were 0.95 and 3.2 g/m²/yr at the two flowrates (Tables 1 and 2), which is considerably lower than the 182.5 g/m²/yr recommended for CWs treating mine drainage (PIRAMID Consortium, 2003). Mn removal was consistently higher in the CW units with artificial aeration at both flowrates. At the HRT of 1.37 days, Mn removal was 70-77% without aeration and 92% with aeration (Fig. 3); for the HRT of 3.16 days, Mn removal was 38.5% without aeration and 77-81% with aeration (Fig. 3). As the kinetics for Mn oxidation and precipitation are generally slower compared to Fe (Hedin and Nairn, 1993) and Mn removal is not significant in aerobic CWs with low Fe concentration (Hallberg and Johnson, 2005), the enhancement of the aerobic conditions in the aerated wetlands could potentially have aided in Mn removal. The Mn effluent values of all pilot CWs were also below the national limit for environmental discharge (50 µg/L; IEAP, 2008). Mn removal as a first-order process in CWs has been proposed. Data analysis indicated reaction rate coefficients (*k*) of 169 m/yr for the optimum conditions (highest loading with aeration), and 71-88 m/yr (highest loading without aeration) (Table 3). In the literature, 21 m/yr has been proposed for surface flow (SF) CW (Tarutis et al., 1999). For HSFCWs (without aeration), rates of 10-60 m/yr for river gravel and 100-600 m/yr for limestone-based systems have been estimated (Sikora et al., 2000).

Aluminum (Al) can form hydroxide precipitates under oxidizing conditions, which are strongly associated with phosphorus retention. Al loads were 2.2 and 7.4 g/m²/yr (Tables 1 and 2), compared to loads of approximately 0.44 g/m²/yr observed for municipal wastewater applications of non-aerated HSFCWs (Vymazal and Krása, 2003). The removal percentages in this study ranged from 63-73% at the HRT of 3.16 days, and 49-70% at the HRT of 1.37 days (Fig. 3), indicating that longer HRT resulted in better Al removal. Respective figures for Al reported in the literature are approximately 70% (Gensemer and Playle, 1999), and are comparable to this study.

Copper (Cu) loads were 0.75 and 0.22 g/m²/yr at the two flowrates (Tables 1 and 2), with removal percentages between 56-80%. While Cu removal is often associated with reducing conditions and sulfide precipitation, removal under aerobic conditions via co-precipitation with Fe and Mn oxyhydroxide precipitates is also possible. For mining applications, loading rates of 3,650 g/m²/yr (sulfide producing conditions) and 18.25 g/m²/yr (aerobic conditions) have been proposed (PIRAMID Consortium, 2003), which are considerably higher than this study. The Cu effluent values of all pilot CWs were below the national limit for environmental discharge (20 µg/L; IEAP, 2008). Cu removal as a first-order process under aerobic conditions is a possibility (Tarutis et al., 1999). If Cu removal is through co-precipitation with Fe and Mn, and those metals follow a first-order process, reaction rate coefficients (*k*) can also be estimated for Cu. Data analysis indicates *k*-rates of 23-39 m/yr at the lower HRT, and 54-97 m/yr at the higher HRT (Table 3). In a pilot-scale SFCW treating oil produced water, Cu removal data indicated a *k*-rate of 80 m/yr (Kanagy et al., 2008).

Nickel (Ni) loads were 1.30 and 0.39 g/m²/d at the two flowrates, with removal percentages between 70-85% (HRT of 3.16 days) and 74-77% (HRT of 1.37 days) (Tables 1 and 2). While Ni removal is often associated with reducing conditions and sulfide precipitation, removal under aerobic conditions through co-precipitation with Fe and Mn oxyhydroxide precipitates is also possible. For mining applications, loading rates of 730 g/m²/yr (sulfide producing conditions) and 14.6 g/m²/yr (aerobic conditions) have been proposed (PIRAMID Consortium, 2003), which are considerably higher than this study. Ni removal as a first-order process under aerobic conditions is a possibility (Tarutis et al., 1999), but data sets to estimate a first-order reaction rate coefficient (*k*) are limited. Data from a SF + HSF CW at Sacramento, California resulted in estimated *k*-rates of 15-18 m/yr (Sinicrope et al., 1992), at Ni loading rates of 5.5-6.7 g/m²/yr (Kadlec and Wallace,

2009). Data from this study yields k -rate estimates of 29-48 m/yr (HRT of 3.16 days) and 81-82 m/yr (HRT of 1.37 days) (Table 3).

Lead (Pb) loads were 1.52 and 0.46 g/m²/yr at the two flowrates (Tables 1 and 2). Almost all Pb was removed (96-99%; Fig. 3), which is consistent with the formation of very insoluble sulfate and carbonate precipitates (DeVolder et al., 2003). The Pb effluent values of all pilot CWs were below the national limit (50 µg/L; IEAP, 2008). Pb removal as a first-order process has been proposed, but previous data sets did not allow for the estimation of a k -rate (Kadlec and Wallace, 2009). Data from this study yields k -rate estimates of 95-121 m/yr at the lower HRT and 219-284 m/yr at the higher HRT (Table 3). Since virtually all Pb was removed at both HRTs, the use of the higher k -rate estimates appears justified. In a pilot-scale SFCW treating oil produced water, Pb removal data indicated a k -rate of approximately 104 m/yr (Kanagy et al., 2008).

Chromium (Cr) loads were 0.15 and 0.05 g/m²/yr at the two flowrates (Tables 1 and 2). Cr removal was affected by plants' presence. The removal in the unplanted units were 75-84% (low loading rate) and 60-63% (high loading rate), and 90-92% in the planted units at both loading rates (Fig. 3). On the other hand, the artificial aeration did not appear to influence Cr removal. The Cr influent and effluent values of all pilot CWs were below the national limit for environmental discharge (50 µg/L; IEAP, 2008). Cr can be removed through co-precipitation with Fe and Mn oxyhydroxide precipitates; the first-order modeling approach applied to those metals can also be applied to Cr. A summary of Cr removal data estimated k -rate coefficients ranging from 3-64 m/yr, with a median value of 19 m/yr (Kadlec and Wallace, 2009). Data from SFCW and HSFCW mesocosms at Sacramento, California treating municipal wastewater yielded k -rate estimates of 25-35 m/yr (Sinicrope et al., 1992), and data from a SFCW mesocosm treating petroleum wastewater yielded k -rate estimates of 20-80 m/yr (Kadlec and Srinivasan, 1995). In a pilot-scale SFCW treating ash

basin water, Cr removal data suggested k -rates of 29-36 m/yr (Dorman et al., 2009). In this study, the unplanted units resulted in k -rate estimates of 34-46 m/yr (HRT of 3.16 days) and 52-57 m/yr (HRT of 1.37 days) and the planted units in 59-66 m/yr (HRT of 3.16 days) and 148-168 m/yr (HRT of 1.37 days) (Table 3).

Zinc (Zn) loads were 315 and 94 g/m²/yr at the two flowrates (Tables 2 and 3). Zn was almost completely removed (99%; Fig. 3), which is consistent with the formation of insoluble carbonate precipitates, and through co-precipitation with Fe and Mn oxyhydroxide precipitates (Younger et al., 2002; Kadlec and Wallace, 2009). In comparison, recommendations for loading rates for mine water treatment range from 14.6 g/m²/yr (PIRAMID Consortium, 2003) up to 2,555 g/m²/yr (Younger et al., 2002). The Zn effluent values of all pilot CWs were below the national limit for environmental discharge (500 µg/L; IEAP, 2008). Zn removal can be considered a first-order process. For a SFCW and HSFCW mesocosm at Sacramento, California, the estimated k -rate was 28 m/yr (Sinicrope et al., 1992), while for a SFCW treating oil refinery effluent, the k -rate for Zn removal was estimated at 55-121 m/yr at two different loading rates (Gillespie et al., 2000; Kadlec and Wallace, 2009). In a pilot-scale CW treating oil produced water (Kanagy et al., 2008), Zn removal data indicated a k -rate of approximately 15 m/yr. In another pilot-scale SFCW treating ash basin water, Zn removal data suggested k -rates of 21-42 m/yr (Dorman et al., 2009). In this study, the estimated k -rates ranged from 118-146 m/yr (low HRT) to 360-450 m/yr (high HRT) (Table 3).

3.3. Phenols

Phenol was essentially completely removed in all systems (Fig. 4), as the influent (638 µg/L) was removed to close to non-detect concentrations (0.9-18 µg/L; Tables 1 and 2). First order rate

coefficients (k) ranged from 152 – 201 m/yr (HRT of 3.16 days) and 96 – 165 m/yr (HRT of 1.37 days). It is reported that aerobic biodegradation is the main phenol removal mechanism in CW (Kurzbaum et al., 2010; Rossmann et al., 2012; Stefanakis et al., 2016), though anaerobic degradation is also possible (Kumaran and Paruchuri, 1997).

Similarly, high removal rates for phenols are reported in CW studies in the literature, even for higher influent concentrations. Data from a series of pilot-scale HSFCW treating coffee processing wastewater in Brazil (Rossmann et al., 2012) suggests phenol degradation k -rates of 8-17 m/yr. A pilot HSFCW treating cork boiling wastewater in Portugal suggests k -rates between 35-42 m/yr (Gomes et al., 2018). In a series of pilot studies using SFCW (Polprasert et al., 1996), data indicated a phenol degradation k -rate of approximately 100 m/yr. In a study of planted and unplanted SFCW channels in China, k -rates for phenol degradation were estimated at 150 m/yr (planted) and 76 m/yr (unplanted) (Tang et al., 1993). In a study at a petroleum facility, a full-scale SFCW (50 ha) had an estimated k -rate of approximately 100 m/yr for phenol removal (Dong and Lin, 1994). Complete phenols removal and a k rate of 107.2 m/yr was found in a HSFCW system treating groundwater contaminated with phenols and petroleum derivatives (Stefanakis et al., 2016). A similar phenols removal k rate of 98.9 m/yr is reported for a HSFCW treating pre-treated olive mill wastewater (Tatoulis et al., 2017).

3.4. Nitrogen

Ammonia nitrogen ($\text{NH}_4\text{-N}$) removal (nitrification) occurred in all pilot units at both loading rates (influent of 31,000 $\mu\text{g/L}$, effluent of 18-20 $\mu\text{g/L}$; Tables 1 and 2), with corresponding k -rates of 233-237 m/yr (Table 3). $\text{NH}_4\text{-N}$ removal was strongly influenced by the presence of aeration (Fig. 4). It is likely the actual k -rates are higher, since the systems ran out of $\text{NH}_4\text{-N}$ with essentially

complete removal. In a similar study, an aerated HSFCW in Germany had an estimated k -rate of 1,540 m/yr vs. 2.9 m/yr for a non-aerated system (Table 3; Nivala et al., 2019). A high k -rate of 960.6 m/yr was also estimated for an aerated VFCW in the UK operating as tertiary treatment stage (Stefanakis et al., 2019), while an aerated second-stage HSFCW in Oman suggests k -rate of 589 m/yr (Stefanakis, 2020b). In both these systems under different climates, complete ammonia removal occurred as well, indicating the positive impact of artificial aeration on aerobic nitrification (Stefanakis et al., 2019).

Ammonia removal was also influenced by the presence of vegetation (Tables 1 and 2), since the presence of plants promotes the biofilm development and the related aerobic oxidation of $\text{NH}_4\text{-N}$ by microorganisms (Stefanakis, 2016). Many studies report that plants' presence favor ammonia removal (Kadlec and Wallace, 2009; Stefanakis et al., 2016; Schultze-Nobre et al., 2017). The shorter duration trial (HRT of 1.37 days) had an estimated k -rate of 39 m/yr, whereas at the longer HRT (3.16 days), the estimated k -rate was 233 m/yr (since the system ran out of $\text{NH}_4\text{-N}$). Without plants or aeration, k -rates were lower, 13.8 m/yr (HRT of 1.37 days) and 24.4 m/yr (HRT of 3.16 days), respectively. Respective k -rate of 22.4 and 39.9 m/yr are reported for HSF systems treating contaminated groundwater and cork boiling wastewater (Stefanakis et al., 2016; Gomes et al., 2018).

Nitrate ($\text{NO}_3\text{-N}$) removal (denitrification) also occurred but at lower levels. Nitrate concentrations decreased from influent values, despite the conversion of $\text{NH}_4\text{-N}$ to oxidized forms of nitrogen within the pilot systems. Aeration possibly impacted $\text{NO}_3\text{-N}$ removal, as more $\text{NH}_4\text{-N}$ was converted to oxidized forms of nitrogen, and the aerobic conditions were not conducive to complete denitrification. For systems without vegetation, estimated k -rates with and without aeration were 0.9-2.0 m/yr (HRT of 1.37 days) and 6.0-9.3 m/yr (HRT of 3.16 days), respectively.

With vegetation, $\text{NO}_3\text{-N}$ removal rates increased (Fig. 4), potentially due to plant uptake considering that ammonia is completely oxidized and nitrate remain the only available nitrogen form for plant uptake, as well as due to the potential presence of more bioavailable carbon in the system, but again, $\text{NO}_3\text{-N}$ removal rates were possibly by aeration. However, the presence of non-aerated sections in the design possibly limited the effect of the aeration in the denitrification extent in the system. The fact that aeration also enhances the microbial growth (Chazarenc et al., 2009; Nivala et al., 2020) indicates that nitrate removal should be a combination of microbial oxidation and plant uptake. Estimated k -rates with and without aeration were 51-73 m/yr (HRT of 1.37 days) and 16-19 m/yr (HRT of 3.16 days). In a similar study, an aerated HSFCW in Germany (Nivala et al., 2019) had an estimated k -rate of 75 m/yr with aeration and 3.9 m/yr without aeration, since $\text{NO}_3\text{-N}$ was not produced in the non-aerated wetland. Similar k -rates of 65.1 and 96.4 m/yr were also estimated for an aerated VFCW in the UK (Stefanakis et al., 2019) and an aerated HSFCW in Oman (Stefanakis, 2020b), with the latter receiving small amounts of raw wastewater (step-feeding) to increase the carbon availability, hence the higher rate observed.

3.5. Phosphorus

Phosphorus ($\text{PO}_4\text{-P}$) removal only occurred when vegetation was present in the system, since it is known that $\text{PO}_4\text{-P}$ removal in CW systems is generally lower compared to other pollutants and mostly depends on the adsorption capacity of the substrate media and the uptake by plants to cover their growth needs (Kadlec and Wallace, 2009; García et al., 2010; Stefanakis, 2016). For the trials conducted with vegetation, phosphorus uptake was essentially complete (95-98%) with effluent concentrations close to detection limits. The applied phosphorus loads of 151 and 507 $\text{g/m}^2\text{/yr}$ (at

477 the low and high loading rates) greatly exceeds the amount of phosphorus required to support the

plant biomass cycle (Kadlec and Wallace, 2009). As a result, it is anticipated that the system would saturate with phosphorus in a longer-term study as the plant community matures and the media gets gradually saturated.

3.6. Optimum design configuration

The tested design proved to be efficient in treating the refinery effluent reaching higher removal rates for most of the tested parameters. The different pilot units revealed the significant role of plants in the overall performance, as the planted bed (RW-SP) showed better removal rates for all parameters than the unplanted unit (RW-S) (Tables 2 and 3), with statistically significant removals ($p<0.05$) occurring for nitrogen and phosphorus and many heavy metals (Al, Ce, Cr, K, Mo, Sc, Se, Si, Sn, Sr, Ta, W). The performance appears to be further enhanced with the addition of the aerated section (RW-SPA; Tables 2 and 3). Artificial aeration seems to improve ($p<0.05$) the removal of ammonia nitrogen, Al, As, K, Mn, Sc, and Se compared to the planted non-aerated unit (RW-SP). On the other hand, when the aeration was applied in the unplanted unit (RW-SA), it did not improve the overall performance. Among the two HRT tested, high removals were observed even for the smaller HRT of 1.4 days with slightly higher removal rates compared to the removals under the HRT of 3.2 days and with statistical significance ($p<0.05$) occurring for nitrate, Al, As, K, Li, Mg, Mn, Ni, Se, Sr, and Ta.

The advantage of the tested design arises from the comparison with other wetland designs applied for similar effluent treatment. The surface flow CW is widely applied for such effluents, but it has a significantly higher area demand due to the prolonged HRT required, e.g., 20 days under similar hydraulic load of 0.06 m/d (Mustafa et al., 2018). A VFCW operating at 0.07 m/d and a HRT of 2

500 days showed a lower performance for nutrients though receiving a much lower influent

concentration since it received a secondary refinery effluent (Mustapha et al., 2015; 2018). A HSFCW was also tested for diesel contaminated water at different levels, resulting in optimum removal conditions of 63 days retention time (Al-Baldawi et al., 2014). In a review paper on refinery effluent treatment in CW, the HRT range reported varies between 2.1-90 days, with the majority of the systems being in the range above 10 days (Jia et al., 2020). In the same review study, the positive role of plants and aeration is also indicated, while the HSFCW is reported to be the design with the better performance.

4. Conclusions

Petroleum refinery effluents represent a major industrial pollution source of significant concern due to its toxic and harmful nature. Established biological methods are not very effective in the remediation of these effluents, while advanced oxidation processes, although effective, are expensive to install and operate. In this study, the technology of Constructed Wetlands was applied for refinery effluent containing heavy metals, phenols and nitrogen as a sustainable nature-based treatment solution. An innovative CW design forming a meandric ‘racetrack’ shape and combining different treatment environments (aerobic and anaerobic) was tested for the first time at pilot-scale. Different construction (non-aerated, artificial aeration, planted and unplanted) and operation (different hydraulic loading rates) parameters were studied to determine the optimum design for effective performance. The first-order removal of metals and the simultaneous removal of phenols and nutrients from the oil refinery wastewater were calculated. The planted unit with artificial aeration managed to reach high removal rates for Fe (96-98%), Mn (38-81%), Al (49-73%), Zn (99-100%), Cu (61-80%), Ni (70-85%), Pb (96-99%) and Cr (60-92%) even at the short HRT of

523 1.3 days, while complete removal of phenols and full nitrification was also found. As the calculated

524 first-order removal coefficients showed, the overall performance of this novel design exceeded the
525 reported efficiency of the common CW designs and implies the potential to further apply and test
526 it for other industrial effluents.

527

528 **Authorship contribution statement**

529 Mozaffari M.S: Conceptualization, Writing - review, Visualization, Investigation, Data curation.
530 Shafiepour E.: Project administration. Mirbagheri S.A.: Resources, Funding acquisition
531 Rakhshandehroo G.: Methodology, Funding acquisition. Wallace S.: Conceptualization, Formal
532 analysis, Data curation. Stefanakis A.I.: Formal analysis, Data curation and analysis, Writing -
5335 original draft, Writing - review

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535 **Acknowledgements**

536 This study work was supported by the Civil Engineering Department, Shiraz University and the
5375 Khajeh Nasir Toosi University of Technology.

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Hydraulic characterization and removal of metals and nutrients in an aerated horizontal subsurface flow “racetrack” wetland treating oil industry effluent

List of Tables

Table 1. Average influent (IN) and effluent (EFF) concentrations ($\mu\text{g/L}$), respective treatment performance (Removal, %) and inlet mass load ($\text{g/m}^2/\text{yr}$) of the pilot RW units at the HRT of 1.37 days ($n=9$).

Table 2. Average influent (IN) and effluent (EFF) concentrations ($\mu\text{g/L}$), respective treatment performance (Removal, %) and inlet mass load ($\text{g/m}^2/\text{yr}$) of the pilot RW units at the HRT of 3.16 days ($n=9$).

Table 3. First-order reaction rate coefficients (k) for the racetrack wetland design and comparison with available literature data.

Table 1

Parameter	IN (µg/L)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load (g/m ² /yr)
		EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	
Al	300	110	63.3	105	65.0	100	66.7	80	73.3	2.20
As	4.37	2.43	44.4	2.15	50.8	2.25	48.5	2.16	50.6	0.032
Ce	1	0.1	90.0	0.26	74.0	0.05	95.0	0.054	94.6	0.007
Cr	6.19	1	83.8	1.52	75.4	0.48	92.2	0.62	90.0	0.045
Cu	30.58	7.76	74.6	11.95	60.9	6.21	79.7	8.0	73.8	0.224
Fe	3580	70	98.0	160	95.5	68	98.1	142	96.0	26.3
K	6510	3440	47.2	4110	36.9	1860	71.4	2080	68.0	47.7
Li	34.62	20.32	41.3	26.61	23.1	21.31	38.4	25.2	27.2	0.254
Mg	27900	22290	20.1	27050	3.0	22170	20.5	22980	17.6	204.6
Mn	130	80	38.5	30	76.9	80	38.5	25	80.8	0.953
Mo	22.29	9.33	58.1	12.83	42.4	4.62	79.3	6.58	70.5	0.163
Ni	52.96	15.95	69.9	14.5	72.6	16.01	69.8	7.87	85.1	0.388
Sc	18.53	4.32	76.7	3.73	79.9	2.9	84.3	1.8	90.3	0.136
Se	14.27	8.97	37.1	8.89	37.7	6.5	54.4	7.1	50.2	0.105
Si	10190	8630	15.3	8040	21.1	6410	37.1	7001	31.3	74.7
Sn	1.57	1.37	12.7	1.49	5.1	0.65	58.6	0.98	37.6	0.012
Sr	2480	1390	44.0	1710	31.0	1480	40.3	2025	18.3	18.2
Ta	0.25	0.13	48.0	0.17	32.0	0.11	56.0	0.16	36.0	0.002
Th	1.05	0.09	91.4	0.1	90.5	0.06	94.3	0.07	93.3	0.008
V	101	3.36	96.7	3.64	96.4	2.63	97.4	2.52	97.5	0.741
W	2.28	0.68	70.2	1.35	40.8	0.39	82.9	0.85	62.7	0.017
Zn	12820	80	99.4	180	98.6	113	99.1	128	99.0	94.0
Pb	62	1.78	97.1	1.82	97.1	0.8	98.7	1.1	98.2	0.455
Phenols	638	3.3	99.5	2.9	99.5	1.7	99.7	0.9	99.9	4.679
NO₃-N	18000	12100	32.8	13900	22.8	8300	53.9	9100	49.4	132.0

NH₄-N	31000	11300	63.5	20	99.9	20	99.9	18	99.9	227.4
PO₄-P	20600	20600	0.0	20600	0.0	1000	95.1	1000	95.1	151.1

Table 2.

Parameter	IN (µg/L)	RW-S		RW-SA		RW-SP		RW-SPA		Inlet mass load (g/m²/yr)
		EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	EFF (µg/L)	Rem (%)	
Al	300	153	49.0	120	60.0	108	64.0	91	69.7	7.38
As	4.37	3.2	26.8	2.9	33.6	3.1	29.1	0.9	79.4	0.11
Ce	1	0.12	88.0	0.13	87.0	0.05	95.0	0.05	95.0	0.02
Cr	6.19	2.3	62.8	2.5	59.6	0.48	92.2	0.62	90.0	0.15
Cu	30.58	8.8	71.2	13.4	56.2	7.01	77.1	8.8	71.2	0.75
Fe	3580	91	97.5	95	97.3	71	98.0	152	95.8	88
K	6510	2,050	68.5	4,110	36.9	1,930	70.4	760	88.3	160
Li	34.62	13.86	60.0	30.1	13.1	19.5	43.7	21.5	37.9	0.85
Mg	27900	15,390	44.8	20,015	28.3	14,510	48.0	15,310	45.1	686
Mn	130	30	76.9	10	92.3	39	70.0	10	92.3	3.20
Mo	22.29	7.37	66.9	18.4	17.5	5.93	73.4	6.61	70.3	0.55
Ni	52.96	12.18	77.0	11.63	78.0	12.52	76.4	13.71	74.1	1.30
Sc	18.53	4.29	76.8	3.89	79.0	4.2	77.3	3.5	81.1	0.46
Se	14.27	5.4	62.2	5.8	59.4	3.5	75.5	3.55	75.1	0.35
Si	10190	8,040	21.1	8,005	21.4	7,011	31.2	7,000	31.3	251
Sn	1.57	0.97	38.2	1.54	1.9	0.73	53.5	1.29	17.8	0.04
Sr	2480	890	64.1	2,130	14.1	980	60.5	1,560	37.1	61
Ta	0.25	0.2	20.0	0.24	4.0	0.06	76.0	0.08	68.0	0.01
Th	1.05	0.09	91.4	0.11	89.5	0.07	93.3	0.08	92.4	0.03
V	101	3.57	96.5	3.5	96.5	3.1	96.9	3.2	96.8	2.48
W	2.28	0.79	65.4	0.79	65.4	0.79	65.4	0.79	65.4	0.06
Zn	12820	60	99.5	130	99.0	78	99.4	91	99.3	315
Pb	62	2.6	95.8	2.62	95.8	1.3	97.9	1.36	97.8	1.52
Phenol	638	7.8	98.8	4.9	99.2	18	97.2	2.3	99.6	15.7
NO₃-N	18000	16500	8.3	17300	3.9	1100	93.9	2400	86.7	442.4

NH₄-N	31000	17300	44.2	20	99.9	6500	79.0	20	99.9	761.6
PO₄-P	20600	20600	0.0	20600	0.0	900	95.6	890	95.7	506.1

Table 3.

Parameter	This Study	Other Studies
Fe	219–290 m/yr (1.37 d HRT, range for all units) 82-107 m/yr (3.16 d HRT, range for all units)	42 m/yr (Manyin et al., 1997) 66 m/yr (Tarutis et al., 1999)
Mn	169 m/yr (1.37 d HRT with aeration) 71-88 m/yr (1.37 d HRT without aeration)	21 m/yr (SF; Tarutis et al., 1999) 10-60 m/yr (HSF with river gravel; Sikora et al., 2000) 100-600 m/yr (HSF with limestone; Sikora et al., 2000)
Cu	54-97 m/yr (1.37 d HRT, range for all units) 23-39 m/yr (3.16 d HRT, range for all units)	80 m/yr (SF, estimated; Kanagy et al., 2008)
Ni	81-82 m/yr (1.37 d HRT, range for all units) 29-42 m/yr (3.16 d HRT, range for all units)	15-18 m/yr (SF+HSF; Sinicrope et al., 1992)
Pb	219-284 m/yr (1.37 d HRT, range for all units) 95-121 m/yr (3.16 d HRT, range for all units)	104 m/yr (SF, estimated; Kanagy et al., 2008)
Cr	52-57 m/yr 1.37 d HRT, unplanted)	25-35 m/yr (SF+HSF; Sinicrope et al., 1992) 20-80 m/yr (SF; Kadlec and Srinivasan, 1995)

	148-168 m/yr (1.37 d HRT, planted) 34-46 m/yr (3.16 d HRT, unplanted) 59-66 m/yr (3.16 d HRT, planted)	3-64 m/yr (Kadlec and Wallace, 2009)
Zn	360-450 m/yr (1.37 d HRT, range for all units) 118-146 m/yr (3.16 d HRT, range for all units)	28 m/yr (SF+HSF; Sinicrope et al., 1992) 55-121 m/yr (SF; Gillespie et al., 2000) 21-42 m/yr (SF, estimated; Dorman et al., 2009)
Phenols	96 -165 m/yr (1.37 d HRT, planted with aeration) 152-201 m/yr (3.16 d HRT, planted with aeration)	8-17 m/yr (HSF, estimated; Rossmann et al., 2012) 107.2 m/yr (HSF; Stefanakis et al., 2016) 98.9 m/yr (HSF; Tatoulis et al., 2017) 100 m/yr (SF, estimated; Polprasert and Dan, 1994) 76 m/yr (SF, unplanted; Tang and Lu, 1993) 150 m/yr (SF, planted; Tang and Lu, 1993) 100 m/yr (SF, estimated; Dong and Lin, 1994)
NH ₄ -N	233-237 m/yr (planted with aeration) 13.8 m/yr (1.37 d HRT, unplanted, no aeration) 24.4 m/yr (3.16 d HRT, unplanted, no aeration)	960,6 m/yr (VF, planted with aeration; Stefanakis et al., 2019) 589 m/yr (HSF, planted with aeration; Stefanakis, 2020b) 2.9 m/yr (HSF, planted without aeration; Nivala et al., 2019) 22.4 m/yr (HSF, planted without aeration; Stefanakis et al., 2016)

NO ₃ -N	0.9-2.0 m/yr (1.37 d HRT, unplanted)	75 m/yr (HSF, planted with aeration; Nivala et al., 2019)
	51-73 m/yr (1.37 d HRT, planted)	65.1 m/yr (VF, planted with aeration; Stefanakis et al., 2019)
	6.0-9.3 m/yr (3.16 d HRT, unplanted)	96.4 m/yr (HSF, planted with aeration; Stefanakis, 2020b)
	16-19 m/yr (3.16 d HRT, planted)	3.9 m/yr (HSF, planted without aeration; Nivala et al., 2019)

Hydraulic characterization and removal of metals and nutrients in an aerated horizontal subsurface flow “racetrack” wetland treating oil industry effluent

List of Figures

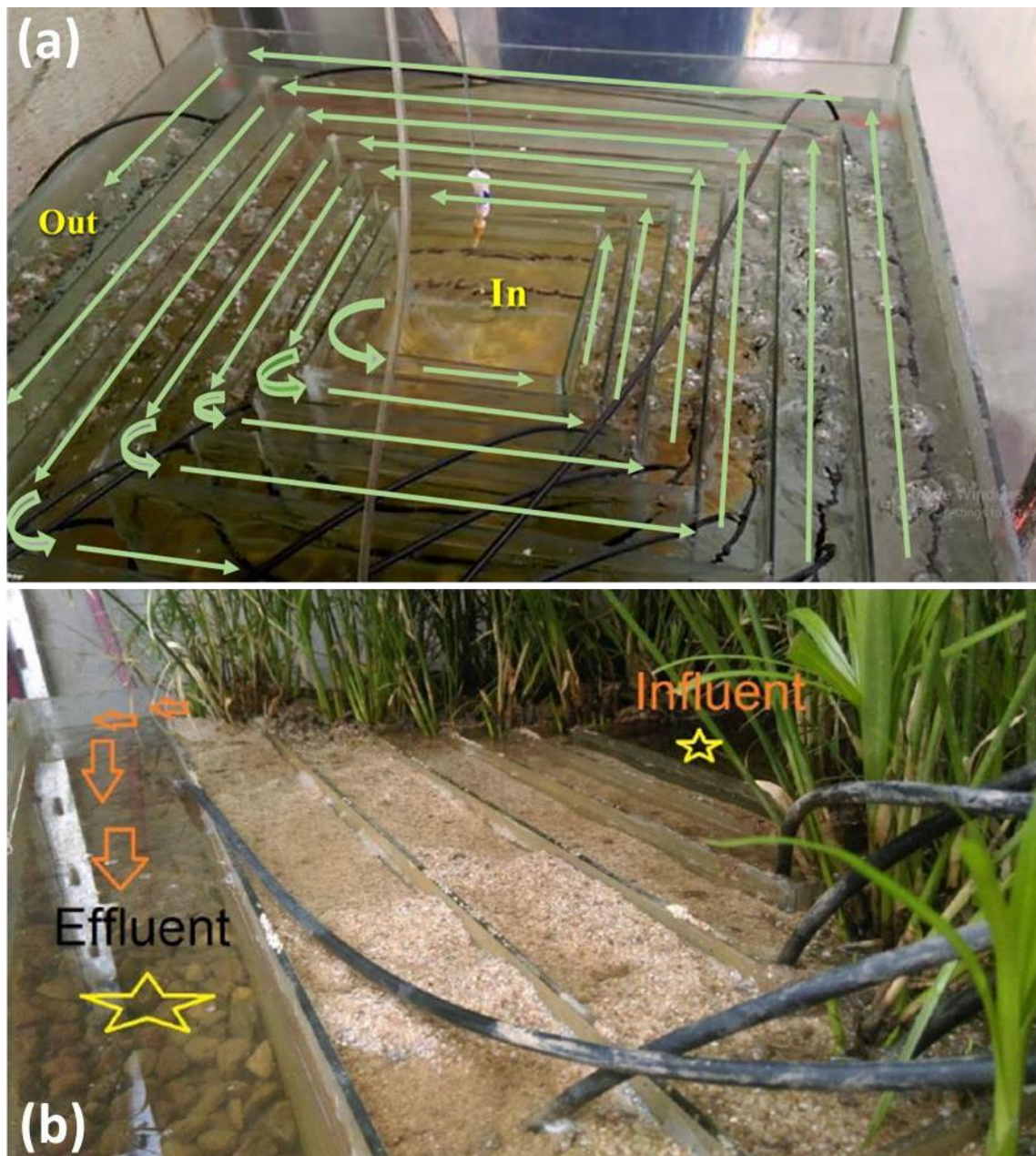


Figure 1. (a) Racetrack wetland configuration with aeration (base unit without substrate or vegetation), and (b) the unplanted and planted sections, the coarse gravel at the inlet and outlet sections, and the influent and effluent sampling points.

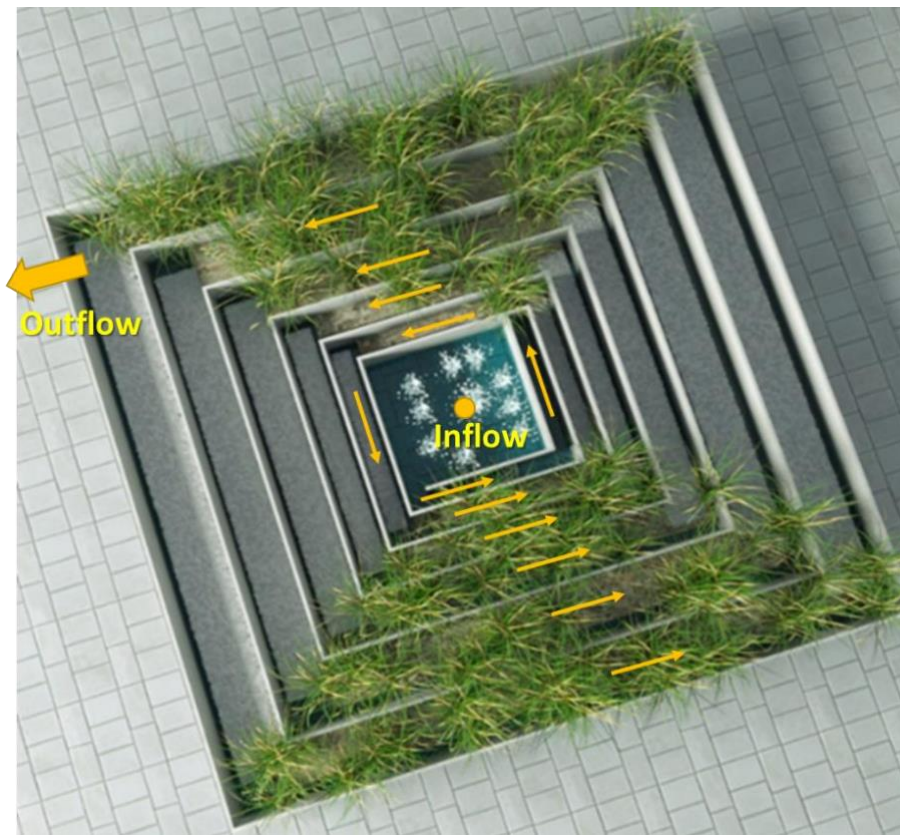


Figure 2. Schematic representation (top view) of the planted and non-planted sections of the racetrack wetland unit and the meandric flow path.

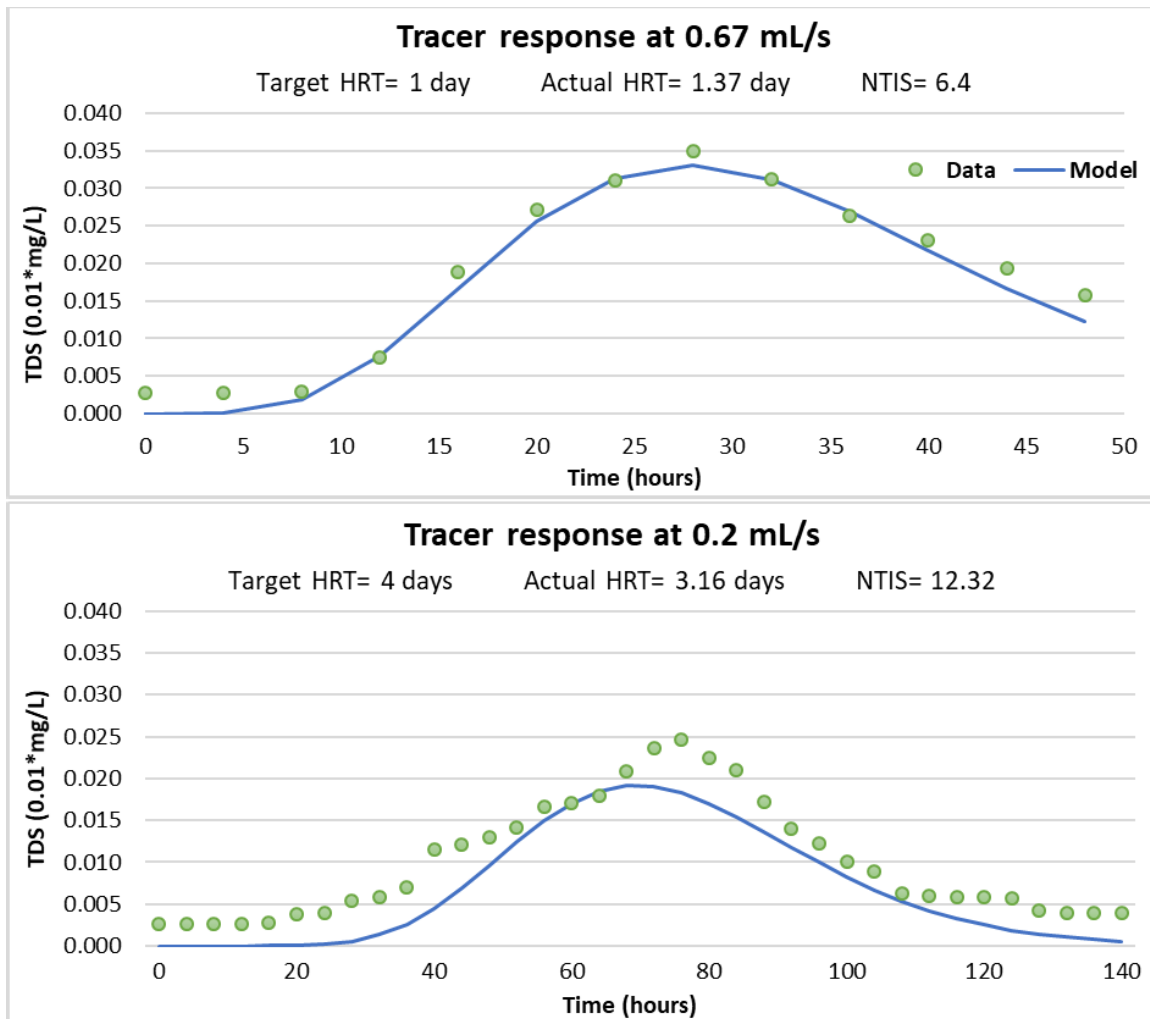


Figure 3. Tracer response curve for the targeted 1-day and 4-days HRT.

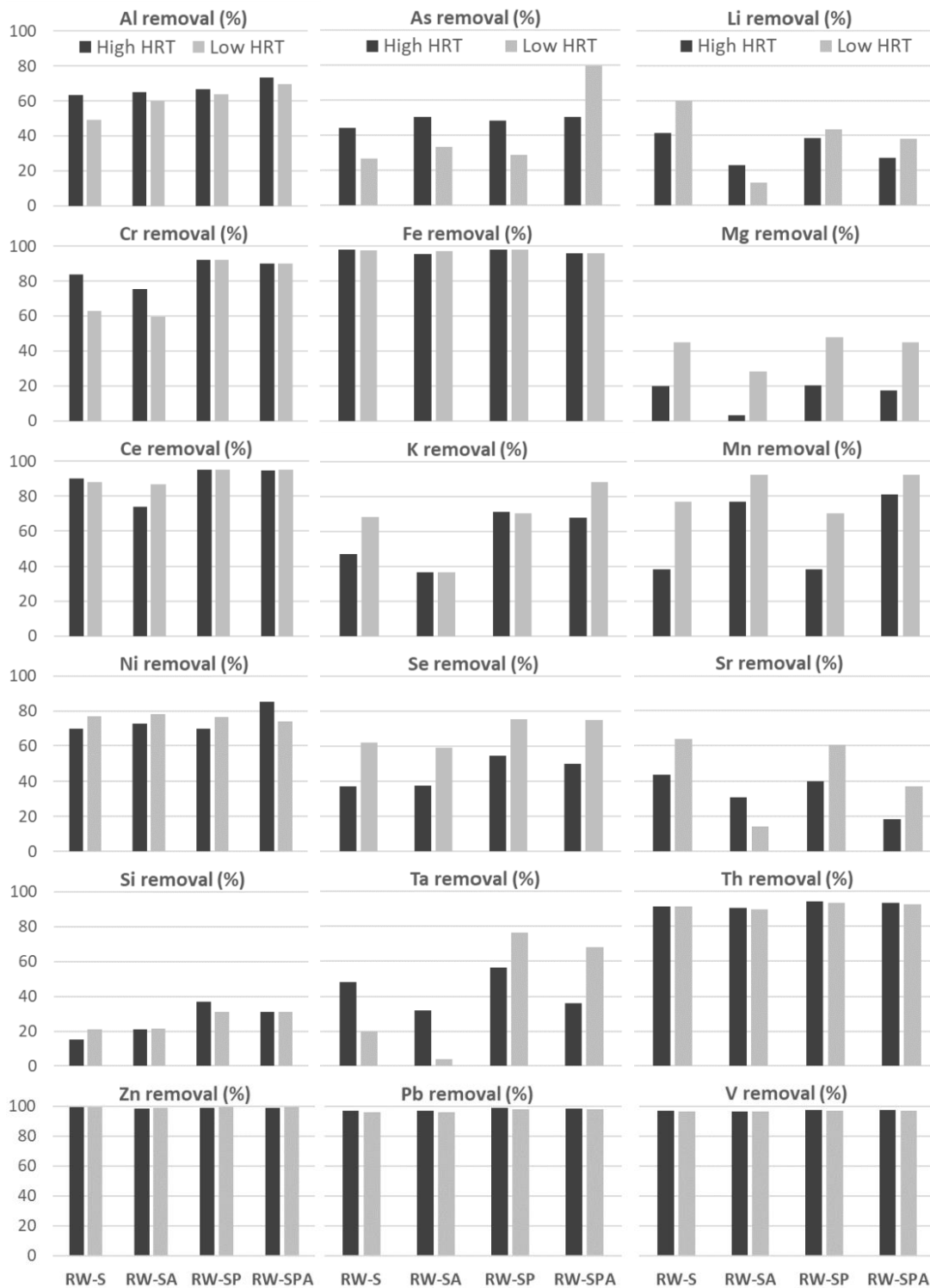


Figure 4. Removal rates of heavy metals in the four pilot CW units at the two HRT tested; low (1.37 days) and high (3.16 days).

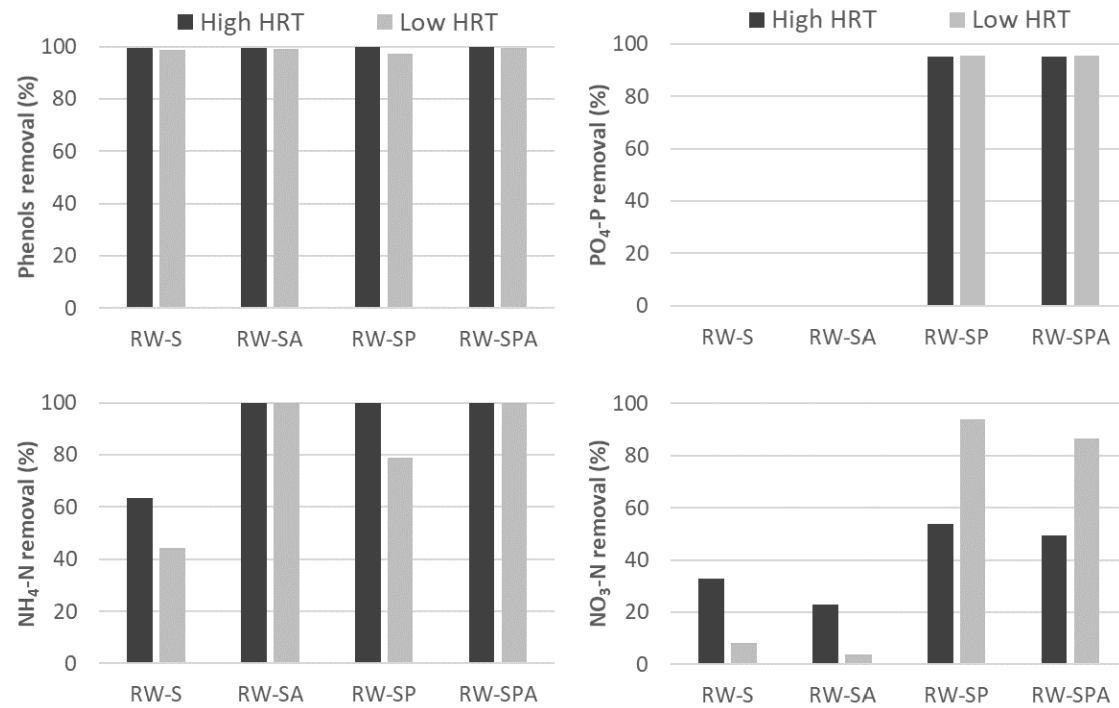


Figure 5. Removal rates of phenols, ammonia nitrogen, nitrate and phosphorus in the four pilot CW units at the two HRT tested; low (1.37 days) and high (3.16 days).

