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Probabilistic human health risk assessment of linear alkylbenzene sulfonate (LAS) in water samples from Anzali Wetland, southwest of the Caspian Sea

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ABSTRACT

Linear alkyl benzene Sulfonate (LAS) is a major anionic surfactant utilized in detergents around the world and is subsequently a ubiquitous water contaminant. This paper deals with assessing human health risk due to LAS in Anzali Wetland between different age groups. Water samples were collected from 50 stations in the wetland. LAS concentration was determined by spectrophotometry at 650 nm. The risk quotients (RQ) index was used to assess the human health risk assessment of LAS in the wetland. Based on the results, the health risk index was lower than 0.2 in all stations, indicating that there is no LAS contaminant risk for human health in this wetland. However, due to the presence of the different unregulated discharge of wastewater to the wetland, without strong policies to control and management, the risk of contamination may increase in the future.

Key words: Anzali Wetland, Detergents, Linear alkyl benzene sulfonate (LAS), Health risk assessment, Risk quotients (RQs).

INTRODUCTION

Today, the entry of urban, industrial and domestic wastewater into the aquatic ecosystems pose serious risks to the ecological health of water resources (Scott & Jones 2000; Alkhadher *et al.* 2015). Most urban sewage systems contain a range of diverse pollutants, which their entrance into the body of water can create many risks. Of the main contaminations in urban sewage are detergents (Scott & Jones 2000; Babaei & Khodaparast 2010; Ebrahimi *et al.* 2010)with cleansing properties (Pérez-López *et al.* 2018). The detergents consist of surfactants, builders (e.g. tripolyphosphate), boosters, fillers, and auxiliary compounds (Scott & Jones 2000; Hajian Nejad *et al.* 2012). They are used in the formulation of pesticides as well as for dispersion of marine oil spills. So, their manufacture, application and exposure aer widespread. They enter the sea by the running rivers or directly through the poor or unregulated wastewater management of adjacent towns and industrial zones (Uedeme-Naa and Erondu 2016) as recent studies have reported their presence in various environments(Alkhadher *et al.* 2015; Sakai *et al.* 2017; Jones-Costa *et al.* 2018; Riyahi Bakhtiari *et al.* 2018). Among different detergents, surfactants, also known as surface-active substances, have specific physicochemical features such as the ability to reduce surface tension between different media, and solubility in polar and nonpolar solutions. Hence, they are used in different aspects of human activities which resulted in its systematic emission and increased mobility between different environmental elements (Ruman *et al.* 2017; Thomas *et al.* 2017). Surfactants are mainly of four types: anionic, nonionic, cationic and amphoteric (Mungray & Kumar 2009; Pérez-López *et al.* 2018). A major anionic surfactant is Linear alkyl benzene sulfonate (LAS) which globally used due to its performance, cost/performance proportion, flexibility and environmental safety record (Oyoroko & Ogamba 2017; Thomas *et al.* 2017). LAS contains a benzene ring attached to a linear alkyl chain and sulfonated at the para position. There are typically 10 to 14 carbon atoms in its linear alkyl chain (Jensen *et al.* 2001; Gong *et al.* 2016). The annual global consumption of LAS is approximately 2.8×10^6 tons and this number has been steadily increasing (Zhou *et al.* 2018). After use, LAS is released to the sewage systems and is decomposed by microbes partially.

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Although microbial activity can reduce the final concentration of LAS of wastewater, in high concentrations, normal decomposition is inefficient and high concentrations of LAS have been found in surface water (Zhou *et al.* 2018). The entrance, distribution, and dispersion of these compounds into water resources leading to different hurt to biological and non-biological parts of aquatic ecosystems. From the point view of non-biological aspects, detergents lead to reduce the surface tension of the water, disruption of the water purification processes (coagulation and sedimentation processes), foaming on the water surface that reduces transfer of oxygen to water and cause the negative visual effects (Perkowski *et al.* 2006; Pérez-López *et al.* 2018), increase the cost of wastewater purification and alter the flavor (Tadros 2006; Ebrahimi *et al.* 2010; Mousavi *et al.* 2010). Detergents in biological systems cause disrupt bio-membranes, alter the state and quality of the protein (Jensen 1999), disruption of biological function (Ivanković & Hrenović 2010), exerts direct and, earnest inhibitory effects on the growth, reproduction, and physiological functions of aquatic organisms by influencing membrane permeability, enzyme activity and tissue structure. They also increase the dissolution of pollutants in water leading to more damages to the aquatic organisms living environments (Zhou *et al.* 2018).

The toxic effects of surfactants to aquatic vertebrates, mostly fish, have been documented in the literature. Fish seem to take up anionic LAS through gills. So that, scientific findings have revealed that the concentrations of some LAS homologs in the liver and internal organs of juvenile rainbow trout increase rapidly, suggesting that they quickly enter systemic circulation (Ivanković & Hrenović 2010). Given the dependence of the human food chain on aquatic ecosystems and aquatic organisms, especially fish, these materials re-enter our system of life in short or long cycles and endanger the health of humans (Fleming *et al.* 2006). On the other hand, different studies suggest that sometimes fewer detergents do not play a direct role in the mortality of an organism, but their mixture with another chemical can significantly increase mortality. For example, in a study on the effect of a mixture of anionic detergents with allowable concentration and non-lethal of Parnol.j (a detergent containing 20% LAS) and n-heptan in *Diapomus forbesi*, the results showed an increase in mortality from 10 to 50% (Piri & Fallahi 1998). In another study, Golami *et al.* (2007) reported the effects of individual and mixed of heavy metals (lead and cadmium) and detergents (LAS) on *Rutilus frisii kutum* from the Caspian Sea. Their results indicated that the detergents have a catalytic effect, leading to the intensified penetration of heavy metals into the cells as well as higher toxicity of pollutant mixtures than their individual forms.

In their study, the concentration of LAS and cadmium mixtures caused a reduction of 50% of the fish population (LC_{50}) was 0.047 mg L^{-1}, and the concentration of LAS and copper mixtures reducing the fish population by 50%, was 0.99 mg L^{-1} (Gholami *et al.* 2007). Imandel *et al.* (2001) reported that dishwashing liquid containing 17% effective LAS, 0.1% formalin, 5% diethanolamine and 2% lauramide than two other detergents including hand washing powder (containing 22% LAS) and machine washing powder (containing 10% LAS) without the aforementioned materials, exhibited more severe effects on mortality of *Rutilus frisii kutum* and *Abramis brama orientalis*. Bradai *et al*. (2016) suggest that LAS, at concentrations similar to those observed in wastewater treatment plants outlets, can lead to a tumor promotion effect on the colon cancer cells through increasing cell proliferation, in association with the overexpression of Elongation Factor 2 and Dipeptidyl Peptidase 3 proteins, and a down-regulation of 14-3-3 protein theta. They concluded that more attention should be paid to the adverse effects of toxicants even at low non-cytotoxic concentrations. In this regard, toxicity predictive models are a beneficial tool for providing a risk assessment that can be useful to determine the toxicity range of each surfactant and the different test organisms to select efficient surfactants with a lower impact on the aquatic environment (Lechuga *et al.* 2016). It is useful to define risk by identifying and, if possible, characterizing and quantifying the magnitude of risk for particular extremely vulnerable groups or subgroups within the population (US EPA 2005). Among various pollutants, health risk assessment of LAS, as a pollutant with vast application and dispersion as well as a high potential for contaminating surface water resource seems to be very important.

Anzali Wetland is inevitably under the threat of intensive anthropogenic activities such as dumping pollutants into rivers, municipal wastewaters of Rasht, Anzali, and other cities in this area, agricultural runoff, waste disposal, industrial wastewaters and ecotourism exploitation, as well as shipping industry waste that discharge oil into this wetland (Zamani-Ahmadmahmoodi *et al.* 2013; Hassanzadeh *et al.* 2014). Given the importance of this issue, the main purpose of this study is to evaluate the human health risks of LAS in different age groups, after measuring in Anzali wetland, which is one of the sites registered in the Ramsar Convention in 1975. In this study, Risk Quotients (RQ) index used to measure health risk in different age groups in this wetland.

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MATERIALS AND METHODS

Study area

Anzali Wetland is located at the southwest of the Caspian Sea with an area of about 193 km^2. It was registered as an international wetland in Ramsar Convention in 1975. The catchment of the wetland covers an area of about 3610 km^2 and is bounded by the Caspian Sea in the north, the Alborz mountain range in the south, the Talysh Mountains in the west, and the Sefidrud Delta in the east. Approximately 93.525 and 196.020 ha of the catchment area are covered by farmlands (particularly rice farms) and forestlands, respectively (Jamshidi & Bastami 2016). The wetland includes four separate parts: the eastern, southern (also known as Siyahkashim), central, and western (Abkenar) parts (Hassanzadeh *et al.* 2014; Navabian *et al.* 2020). This wetland is known as a main habitat for foraging and breeding of fish species. Over 150 species of migrant birds visit the wetland every year, making this body of water as an important ecological stopover site for migrating birds (Shariati *et al.* 2018).

Sampling Method

In the spring 2018, 50 stations in Anzali Wetland (eastern, central, western and southern parts) and the area around the wetland were selected for water sampling based on proximity to urban communities, ease of access (to parts of the wetland with no dense vegetation), different uses (residential, harbor and transport, agriculture, industrial) as well as sewage and canal entrances to the wetland from Rasht, Sowmehsara and Bandar Anzali (Fig. 1).

Sampling was performed from the water column (0-50 cm), with 3 repetitions. Water samples were placed in 1-L polyethylene bottles that previously washed with distilled water and then immediately transferred to the laboratory to prepare for analysis.

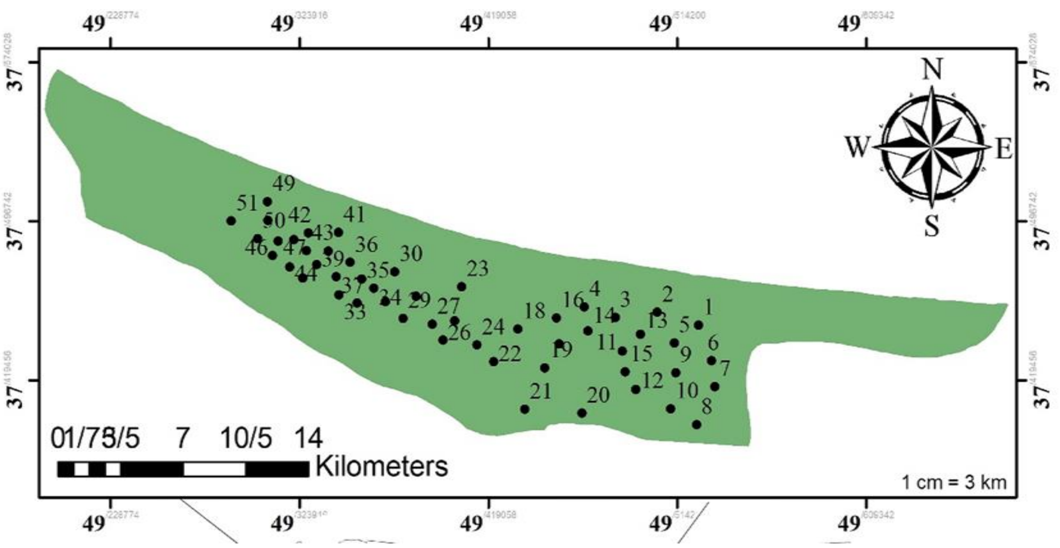

Fig. 1. Sampling station map in Anzali Wetland.

Extraction and chemical analysis of LAS

Reagents: Sodium dodecylbenzene sulfonate 99% was purchased from Sigma-Aldrich. Methylene blue (Merck Millipore), sodium tetraborate 98% (Liaoning, China), Phenolphthalein (Merck Millipore) were also used.

The following solutions were prepared:

1-A stock solution of 1 g L^{-1} LAS: This solution is obtained by dissolving 1 g sodium dodecyl benzene sulfonate in 750 mL-distilled water and transmitting it to pH 7 using sodium hydroxide solution.

2-The standard solution of 10 mg L^{-1} LAS: It is obtained by dilution with a ratio of 1/100 stock solutions. Preparation of standard solutions in the range of 0 – 2.5 mg L^{-1} using a standard solution of 10 mg L^{-1} for drawing calibration chart.

3-Methylene blue soluble adjusted in low pH acidity, g L^{-1} (13.3 mM): 0.1 g methylene blue was dissolved in 100 mL tetraborate buffer solution (10 mM). The pH of this solution was adjusted in the range of 5-6 and kept in a topaz-colored glass container.

4-Sodium tetraborate buffer solution 50 mM at pH=10.5: Dissolving 19 g sodium tetraborate ($Na_2B_4O_7$. 10 H_2O) in 850 mL distilled water. pH was maintained at 10.5 to 11.

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5-Phenolphthalein detector: Dissolving 1 g of phenolphthalein in 50 mL ethanol (C_2H_5OH, 95%) and simultaneously stirring up, adding 50 mL water.
After sampling, 5 mL of the sample was added in a glass tube and alkalized by adding sodium tetraborate (50 mM) to reach pH 10.5. A volume of 200 μL was needed to change the color of phenolphthalein (PH > 8.3). Then 100 μL methylene blue was added to the solution and stirred up, followed by adding 4 mL chloroform. Thereafter, the solution was shaken thoroughly for 30 seconds, and left for 5 min, then the organic phase was read using a spectrophotometer at a wavelength of 650 nm. Moreover, using the calibration curve and absorbed wavelength, we measured the LAS concentration (Jurado *et al.* 2006). The method was optimized by recovery studies before the determination of kinds and quantities of LASs on collected samples. Recovery studies were carried out by spiking samples, which did not contain any LASs, with known volumes of the appropriate working mixtures of Sodium dodecylbenzene sulfonate in triplicate. The limit of detection calculated as the product of the standard deviation at the lowest validation level with the Student t-values was found to be 0.004 mg L^{-1}. The efficiency of the method was evaluated by spiking control samples with Sodium dodecylbenzene sulfonate at various concentration levels. So, the recovery obtained was 102% with RSD values below 15%.

Human health risk assessment method
Characterization of human health risk was based on risk quotients (RQs) evaluation, by considering the distinguished life stages in order to improve the accuracy of risk assessment. RQ was calculated for every detected LAS within the water samples by dividing the maximum measured concentration in the water (MC) by the corresponding drinking water equivalent level (DWEL) (equation 1) (Sharma *et al.* 2019).

$$RQ = MC/DWEL \quad \textbf{(1)}$$

It is often simpler to convert the acceptable daily intake (ADI) into a corresponding water concentration, such as DWEL. So, the comparison of chemical concentrations measured in drinking water is simpler than ADIs. The DWEL was calculated using equation 2.

$$DWEL = (ADI\ (or\ RSD) * BW)/(DWI * AB * FOE) \quad \textbf{(2)}$$

Where ADI (μg/kg/day) is the acceptable daily intake or risk specific dose (RSD) for non-carcinogenic and carcinogenic effects, respectively. Values of ADI (or RSD) for each identified LAS were received from the literature (According to literature, its amount is 4.5 mg L^{-1}) (HERA 2013). BW is the median body weight (70 kg for adults) of age-specific groups, DWI is the daily drinking water intake (2 liters per day are considered for an adult) of age-specific groups, AB, the gastrointestinal absorption, rate assumed to be 1 for all the studied compounds and FOE is related to the frequency of exposure (350 days/365 days). Age groups were selected according to the guidance provided by the Environmental Protection Agency (EPA) (US EPA 2005). An RQ value >1 indicated the potential risk to human health. An RQ value between 0.2 and 1 requires a more detailed assessment, whereas RQ ≤ 0.2 considered as any significant concern for human health (Sharma *et al.* 2019).

RESULTS
According to the findings, The LAS concentration ranged 0.01-3.93 with an average of 1.70 mg L^{-1}. The lowest amount was recorded at station 50, while highest at station 8. The highest concentration was observed between the stations 1 and 20, which are located at the eastern part of the wetland (Fig. 1). The results of health risk assessment calculations in the wetland water samples are presented in Table 1. The RQ value was in the range of 0.0001 to 0.0240 (averaged 0.0056). The lowest amounts were recorded at stations 29 and 50, while the highest at station 8. The results of the Health Risk Index calculations, as well as the risk classification based on the RQ index are given in Fig. 2. The results of the RQ index classification (including no risk, moderate and high risks) exhibited that there is no risk at all stations. The calculations of health risk assessment in the Anzali Wetland water for different age groups are presented in Table 2. For all age group, DWEL ranged from 22.83 to 150.95 mg L^{-1}, while mean RQs ranged from 0.0113 to 0.0746. The highest average RQ was recorded at Station 8, while the lowest at Station 50. In addition, the RQ for different age groups was found to be as the following order: 0-3 months > 3-6 months > 6-12 months > 1-2 years > 3-6 years > 2-3 years > 6-11 years > 11-16/ >18 years > 16-18 years. The comparison of risk assessment results indicated that at Station 8, the value of RQ for all age groups

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was higher than in the other stations. According to the available data, there is no significant risk in any of the age groups, even in lower age groups with higher susceptibility.

Table 1. Results of health risk assessment in the Anzali Wetland water samples.

DWEL: 164.063			**Mean RQ: 0.0056**		
station	**LAS (mg L^{-1})**	**RQ**	**station**	**LAS (mg L^{-1})**	**RQ**
1	2.21	0.0135	26	0.17	0.0010
2	3.37	0.0205	27	1.49	0.0091
3	2.95	0.0180	28	2.11	0.0129
4	3.09	0.0188	29	0.02	0.0001
5	1.76	0.0107	30	2.34	0.0143
6	2.87	0.0175	31	1.08	0.0066
7	2.09	0.0127	32	2.07	0.0126
8	3.93	0.0240	33	1.39	0.0085
9	1.96	0.0119	34	1.34	0.0082
10	3.48	0.0212	35	0.59	0.0036
11	3.23	0.0197	36	1.2	0.0073
12	1.32	0.0080	37	0.78	0.0048
13	1.87	0.0114	38	2.02	0.0123
14	2.54	0.0155	39	1.65	0.0101
15	3.56	0.0217	40	1.03	0.0063
16	2.45	0.0149	41	1.19	0.0073
17	3.02	0.0184	42	0.84	0.0051
18	2.65	0.0162	43	0.32	0.0020
19	3.13	0.0191	44	0.06	0.0004
20	3.24	0.0197	45	0.08	0.0005
21	2.04	0.0124	46	0.84	0.0051
22	1.45	0.0088	47	1.03	0.0063
23	1.49	0.0091	48	0.47	0.0029
24	0.26	0.0016	49	0.08	0.0005
25	0.93	0.0057	50	0.01	0.0001

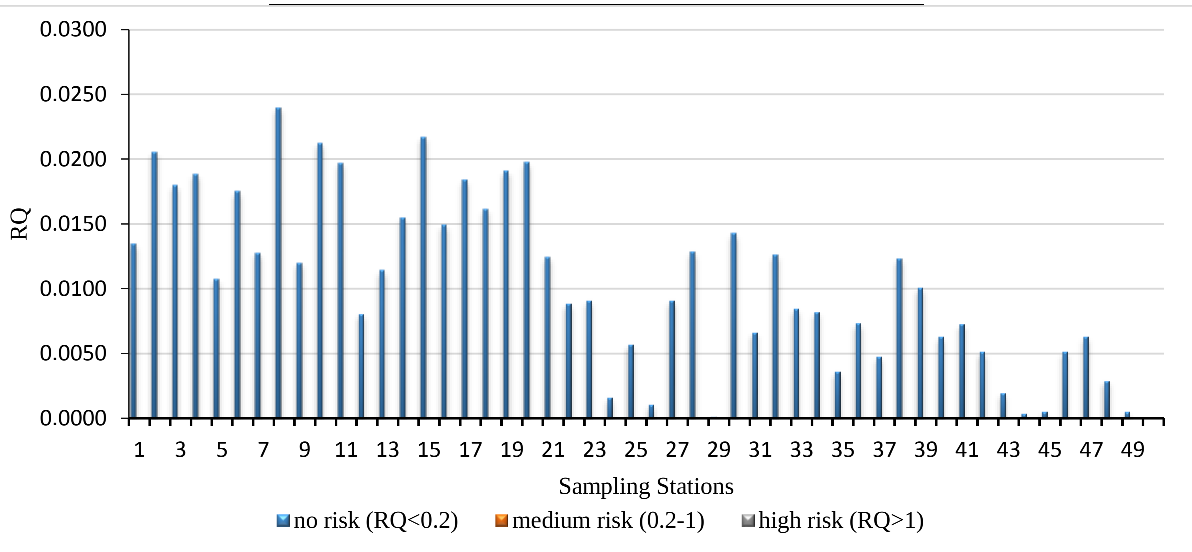

Fig. 2. Health Risk Index (RQ) calculations along with the risk classification based on the RQ index.

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Table 2. Health risk assessment calculations in the Anzali Wetland water samples for different age groups.

DWEL	**22.83**	**29.61**	**37.34**	**66.18**	**77.94**	**76.78**	**108.87**	**138.16**	**150.95**	**137.87**	
station number	**0-3 months**	**3-6 months**	**6-12 months**	**1-2 years**	**2-3 years**	**3-6 years**	**6-11 years**	**11-16 years**	**16-18 years**	**adult(>18 years)**	**mean**
1	0.0968	0.0746	0.0592	0.0334	0.0284	0.0288	0.0203	0.0160	0.0146	0.0160	0.0388
2	0.1476	0.1138	0.0902	0.0509	0.0432	0.0439	0.0310	0.0244	0.0223	0.0244	0.0592
3	0.1292	0.0996	0.0790	0.0446	0.0379	0.0384	0.0271	0.0214	0.0195	0.0214	0.0518
4	0.1354	0.1044	0.0828	0.0467	0.0396	0.0402	0.0284	0.0224	0.0205	0.0224	0.0543
5	0.0771	0.0594	0.0471	0.0266	0.0226	0.0229	0.0162	0.0127	0.0117	0.0128	0.0309
6	0.1257	0.0969	0.0769	0.0434	0.0368	0.0374	0.0264	0.0208	0.0190	0.0208	0.0504
7	0.0916	0.0706	0.0560	0.0316	0.0268	0.0272	0.0192	0.0151	0.0138	0.0152	0.0367
8	0.1722	0.1327	0.1052	0.0594	0.0504	0.0512	0.0361	0.0284	0.0260	0.0285	0.0690
9	0.0859	0.0662	0.0525	0.0296	0.0251	0.0255	0.0180	0.0142	0.0130	0.0142	0.0344
10	0.1525	0.1175	0.0932	0.0526	0.0447	0.0453	0.0320	0.0252	0.0231	0.0252	0.0611
11	0.1415	0.1091	0.0865	0.0488	0.0414	0.0421	0.0297	0.0234	0.0214	0.0234	0.0567
12	0.0578	0.0446	0.0353	0.0199	0.0169	0.0172	0.0121	0.0096	0.0087	0.0096	0.0232
13	0.0819	0.0632	0.0501	0.0283	0.0240	0.0244	0.0172	0.0135	0.0124	0.0136	0.0328
14	0.1113	0.0858	0.0680	0.0384	0.0326	0.0331	0.0233	0.0184	0.0168	0.0184	0.0446
15	0.1560	0.1202	0.0953	0.0538	0.0457	0.0464	0.0327	0.0258	0.0236	0.0258	0.0625
16	0.1073	0.0828	0.0656	0.0370	0.0314	0.0319	0.0225	0.0177	0.0162	0.0178	0.0430
17	0.1323	0.1020	0.0809	0.0456	0.0387	0.0393	0.0277	0.0219	0.0200	0.0219	0.0530
18	0.1161	0.0895	0.0710	0.0400	0.0340	0.0345	0.0243	0.0192	0.0176	0.0192	0.0465
19	0.1371	0.1057	0.0838	0.0473	0.0402	0.0408	0.0287	0.0227	0.0207	0.0227	0.0550
20	0.1419	0.1094	0.0868	0.0490	0.0416	0.0422	0.0298	0.0235	0.0215	0.0235	0.0569
21	0.0894	0.0689	0.0546	0.0308	0.0262	0.0266	0.0187	0.0148	0.0135	0.0148	0.0358
22	0.0635	0.0490	0.0388	0.0219	0.0186	0.0189	0.0133	0.0105	0.0096	0.0105	0.0255
23	0.0653	0.0503	0.0399	0.0225	0.0191	0.0194	0.0137	0.0108	0.0099	0.0108	0.0262
24	0.0114	0.0088	0.0070	0.0039	0.0033	0.0034	0.0024	0.0019	0.0017	0.0019	0.0046
25	0.0407	0.0314	0.0249	0.0141	0.0119	0.0121	0.0085	0.0067	0.0062	0.0067	0.0163
26	0.0074	0.0057	0.0046	0.0026	0.0022	0.0022	0.0016	0.0012	0.0011	0.0012	0.0030
27	0.0653	0.0503	0.0399	0.0225	0.0191	0.0194	0.0137	0.0108	0.0099	0.0108	0.0262
28	0.0924	0.0713	0.0565	0.0319	0.0271	0.0275	0.0194	0.0153	0.0140	0.0153	0.0371
29	0.0009	0.0007	0.0005	0.0003	0.0003	0.0003	0.0002	0.0001	0.0001	0.0001	0.0004
30	0.1025	0.0790	0.0627	0.0354	0.0300	0.0305	0.0215	0.0169	0.0155	0.0170	0.0411
31	0.0473	0.0365	0.0289	0.0163	0.0139	0.0141	0.0099	0.0078	0.0072	0.0078	0.0190
32	0.0907	0.0699	0.0554	0.0313	0.0266	0.0270	0.0190	0.0150	0.0137	0.0150	0.0364
33	0.0609	0.0470	0.0372	0.0210	0.0178	0.0181	0.0128	0.0101	0.0092	0.0101	0.0244
34	0.0587	0.0453	0.0359	0.0202	0.0172	0.0175	0.0123	0.0097	0.0089	0.0097	0.0235
35	0.0258	0.0199	0.0158	0.0089	0.0076	0.0077	0.0054	0.0043	0.0039	0.0043	0.0104
36	0.0526	0.0405	0.0321	0.0181	0.0154	0.0156	0.0110	0.0087	0.0079	0.0087	0.0211
37	0.0342	0.0263	0.0209	0.0118	0.0100	0.0102	0.0072	0.0056	0.0052	0.0057	0.0137
38	0.0885	0.0682	0.0541	0.0305	0.0259	0.0263	0.0186	0.0146	0.0134	0.0147	0.0355
39	0.0723	0.0557	0.0442	0.0249	0.0212	0.0215	0.0152	0.0119	0.0109	0.0120	0.0290
40	0.0451	0.0348	0.0276	0.0156	0.0132	0.0134	0.0095	0.0075	0.0068	0.0075	0.0181
41	0.0521	0.0402	0.0319	0.0180	0.0153	0.0155	0.0109	0.0086	0.0079	0.0086	0.0209

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Continue Table 2

DWEL	22.83	29.61	37.34	66.18	77.94	76.78	108.87	138.16	150.95	137.87	
station number	0-3 months	3-6 months	6-12 months	1-2 years	2-3 years	3-6 years	6-11 years	11-16 years	16-18 years	Adult (>18 years)	mean
42	0.0368	0.0284	0.0225	0.0127	0.0108	0.0109	0.0077	0.0061	0.0056	0.0061	0.0148
43	0.0140	0.0108	0.0086	0.0048	0.0041	0.0042	0.0029	0.0023	0.0021	0.0023	0.0056
44	0.0026	0.0020	0.0016	0.0009	0.0008	0.0008	0.0006	0.0004	0.0004	0.0004	0.0011
45	0.0035	0.0027	0.0021	0.0012	0.0010	0.0010	0.0007	0.0006	0.0005	0.0006	0.0014
46	0.0368	0.0284	0.0225	0.0127	0.0108	0.0109	0.0077	0.0061	0.0056	0.0061	0.0148
47	0.0451	0.0348	0.0276	0.0156	0.0132	0.0134	0.0095	0.0075	0.0068	0.0075	0.0181
48	0.0206	0.0159	0.0126	0.0071	0.0060	0.0061	0.0043	0.0034	0.0031	0.0034	0.0083
49	0.0035	0.0027	0.0021	0.0012	0.0010	0.0010	0.0007	0.0006	0.0005	0.0006	0.0014
50	0.0004	0.0003	0.0003	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002
mean	0.0746	0.0575	0.0456	0.0257	0.0218	0.0222	0.0156	0.0123	0.0113	0.0123	

DISCUSSION

The concentration order of LAS was as follows: the eastern > central> Siyahkashim> western parts of the wetland. Which may be due to: 1-The development of industrial area and towns, and consequently an increased entry of domestic and industrial wastewater, and pollutants made by tourists in the eastern part of the wetland and 2-Receiving agricultural and rural wastewater in the central part compared to other parts. The lowest LAS concentrations were observed in western and SiyahKashim stations which may be due to the higher distances of these parts from densely-populated areas, the absence of human activities and also less amounts of detergents and LAS-containing products discharged to these parts. In addition, Siyahkashim is one of the protected areas, which may play a significant role in lower amounts of pollutant in this part. However, agricultural wastes from around discharge to this part, and because of utilizing LAS in the chemical fertilizer formulation, these parts may affect by LAS contamination (Hassanzadeh *et al.* 2014; Riyahi Bakhtiari *et al.* 2018; Shariati *et al.* 2018). Furthermore, some factors such as the sampling season, time, water hardness, length of the alkyl chain, amount of wastewater treatment (primary and secondary purification) and the type of wastewater treatment (aerobic and anaerobic) can also influence the rate of decomposition and concentration of LAS in the water. Dadaye Ghandi *et al*. (2005) assessed the amount of surfactant and their seasonal trend in Anzali Wetland. Their results indicated that the highest concentration of surfactant was found in Pirbazar station in the range between 0.176 and 0.422 mg L^{-1}, while the lowest in the south Caspian Sea station (0.049 to 0.098 mg L^{-1}). The Pirbazar River station exhibited the highest amount of LAS due to receiving untreated wastewater from Rasht city and also the surrounding villages. In addition, the results of their study revealed that the annual average concentration of LAS was 0.137 mg L^{-1}, and the highest average was found in winter (0.169 mg L^{-1}) while the lowest in spring (0.104 mg L^{-1}). Comparing the mean concentration of LAS in their study (0.137 mg L^{-1}) with that of our study (1.70 mg L^{-1}), indicates an elevated LAS concentration over time. Based on our results, the RQ Index was lower than 0.2 in all stations, indicating that there is no risk for human health due to LAS pollution in Anzali Wetland (Fig. 2). Similarly, the results of health risk assessment exhibited that the RQ index in all age groups was lower than 0.2 indicating no risk due to LAS contamination in these groups (Table 2). The results also indicated that in the 0-3 month-age group, the RQ index was higher than in the others, revealing the susceptibility of this group to LAS contamination, in accordance with the results of De Jesus Gaffney *et al*. (2015). In 1 to 12-month-old infants, due to rapid growth and weight gain, increased proportion of body fat, increased skin permeability, deficiencies in hepatic enzyme activity, immature immune system functions, high oxygen requirements (leading to higher inhalation rates) and lower renal function, the level of vulnerability and sensitivity to LAS seems to be higher. Since childhood is a time of fast developments in behavior and physiology, when conducting an exposure assessment, these significant variations should be considered. Children of all ages busy in dangerous behaviors that can increase environmental exposure. Physically, the metabolic rate and the activity levels in children are higher than those of adults. So, children consume more water and food per unit of body weight than adults. The higher metabolic rate in children compared to adults may result in exposure to more chemicals produced by metabolic processes. The skin of babies (especially newborns) is more permeable to many environmental

Caspian J. Environ. Sci. Vol. 18 No. 4 pp. 345~356 Received: Jan. 18. 2020 Accepted: June 28. 2020
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chemicals than the skin of elderly children and adults. Similarly, in infants, the blood-brain barrier is less well developed. Some studies show that lead can be absorbed more effectively from the gastrointestinal tract in very young children than in adults, although this is affected by many variables (e.g., iron and calcium status)(US EPA 2005). Also, babies and adults display discrepancy in their metabolism and excretion of absorbed environmental contaminants leading to a potential discrepancy in biologically-efficient dose. In babies, metabolic pathways are usually less developed than in adults. Depending on the specific substances involved, metabolic disorders may increase or decrease the toxicity of environmental factors. Babies' liver and kidneys (younger than 1 year) are also less efficient in removing certain environmental toxicants from the bloodstream than adolescents (US EPA 2005). Our results exhibited that the mean RQ in Station 8 was higher in all age groups than the other stations, followed by stations 15 and 10 which displayed the higher values respectively. As aforementioned, one of the reasons for the high value of this index in these stations seems to be their proximity to pollution sources compared to the other stations. Moreover, the RQ index at Station 50 in all age groups was lower than at the other stations which may be due to low LAS concentrations in the western and Siyahkashim, since these parts are located far from populated areas and less influenced by human activities. Many studies focused on health risk assessment using the RQ Index. Leung *et al*. (2013) once working on the human health risk assessment of pharmaceuticals in tap water in China reported that the risk is low. Similarly, Yang *et al*. (2017) in their studies on the human health risk assessment of micro-pollutants in groundwater using the RQ index reported that all of the micro-pollutants detected from groundwater in different age groups posed no appreciable concern to human health, when considered individually. They stated that more researches are needed to determine the long-term potential risks of micro-pollutant mixtures to humans. Besides, Sharma *et al*. (2019) assessed the risk of emerging contaminants in the surface and groundwater of Gangez River, India, concluding that pollutants do not pose a risk to humans, but they have a moderate ecological risk.

In a similar study, Hoshiari *et al*. (2019) assessed the ecological and health risk of LAS in the Dorodzan Dam, Fars Province, Iran reporting that the LAS concentration in its water was lower than the limits allowed by the standard organizations (WHO, EPA and Iranian Environmental Protection Agency) and does not pose any risk to human health and the ecological aspects of the dam. Their results also revealed that the RQ index in 0-3 month-old-infants was higher than in the other groups, similar to our results.

Field observations and various studies in Anzali Wetland have indicated that most pollutants of industrial, urban and residential units of coastal populations in Guilan Province, especially untreated sewage from Rasht city through the Goharrud and Zarrinehrud rivers discharge to this wetland and are thus transported to the sea (Dadaye Ghandi *et al.* 2005; Rahbar Hashemi *et al.* 2013; Riyahi Bakhtiari *et al.* 2018; Varedi 2011). Although evidence suggests the entry of industrial and domestic wastewater into the wetland, but the LAS health risk calculations do not exhibit significant concern for human health.

Factors such as the entry of numerous rivers into the wetland (11 main rivers), heavy rainfalls, the decomposition and oxidation of LAS, and the sedimentation of pollutants in the floor, can reduce its concentration in water. In a study conducted by Riyahi Bakhtiari *et al*. (2018), the concentration of linear alkylbenzenes (LABs) in the sediment samples of Anzali Wetland was in a range of 394.12 to 109305.26 ng g^{-1} dw. The concentrations of ΣLABs (sum of Linear Alkyl benzenes) in the eastern part were significantly higher than those in the other parts, similar to the results of our study. They suggested that LABs are powerful indicators to trace anthropogenic sewage contamination and also highlighted the necessity of sewage treatment plants to be founded around the wetland, especially in the vicinity of the eastern and central parts. Therefore, due to the deposition of pollutants on the bottom of aquatic ecosystems, the simultaneous study on sediment along with water samples can be useful in assessing the exact risk of contaminants. Also, various studies have reported that surfactants sometimes act as an exacerbating agent for the toxicity of other pollutants such as heavy metals and hydrocarbons (Jensen 1999; Dadaye Ghandi *et al.* 2005; Abedini *et al.* 2006; Babaei and Khodaparast 2010). Therefore, continuous monitoring on the increased presence of these pollutants in the aquatic ecosystems is needed, followed by further studies on water, sediment and organisms as well as the health risk assessments of LABs in combination with other pollutants.

CONCLUSION

The entry of high quantities of urban and industrial wastewater and other pollutants into Anzali Wetland has left irreparable damage and in addition to reducing water quality, the aquatic ecosystems and organisms, food safety

Caspian J. Environ. Sci. Vol. 18 No. 4 pp. 345~356 Received: Jan. 18. 2020 Accepted: June 28. 2020
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and human health have also been put at risk. Although the results of this study showed that LAS measured in Anzali Wetland posed no significant concern for human health, but it is possible that the risk of this pollutant significantly be increased in combination with other pollutants and chemicals. Given that this study was carried out in a short time, we recommend conducting long-term and seasonal studies to achieve complete confidence concerning to the health of this wetland ecosystem. Also, we strongly recommend to calculate the risk of LAS in combination with other pollutants and to investigate the antagonistic or synergistic effects of this contaminant on the flora and fauna as well as human.

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محاسبه ریسک سلامت احتمالی آلکیل بنزن سولفانات خطی (LAS) در نمونه آب تالاب انزلی، جنوب غربی دریای خزر

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چکیده

آلکیل بنزن سولفانات خطی (LAS) یک سورفاکتانت آنیونی مهم است که به طور گسترده در سراسر جهان به عنوان ترکیب اصلی مواد شوینده و پاک‌کننده استفاده می شود و متعاقباً یک آلاینده فراوان در آب است. با توجه به اهمیت این موضوع، این مقاله به محاسبه ریسک سلامت LAS در گروه‌های سنی مختلف در تالاب انزلی پرداخته است. ۵۰ ایستگاه در این تالاب برای نمونه‌گیری انتخاب شد. پس از انتقال نمونه‌های آب جمع‌آوری شده به آزمایشگاه، غلظت LAS با استفاده از دستگاه اسپکتروفتومتری در طول موج ۶۵۰nm تعیین شد. یافته‌های پژوهش، دامنه غلظت LAS را mg/L ۳/۹۳- ۰/۰۱ نشان داد. ریسک سلامت LAS با استفاده از شاخص RQ محاسبه شد. براساس نتایج به دست آمده مشخص شد شاخص RQ در کل ایستگاه‌ها کمتر از ۰/۲ است که نشان‌دهنده عدم وجود ریسک احتمالی LAS در آب تالاب انزلی برای سلامت انسان است. با وجود این، به دلیل ورودی‌های مختلف فاضلاب به این تالاب با ارزش، در صورت عدم کنترل و مدیریت فاضلاب‌های ورودی به تالاب، در آینده احتمال خطر برای سلامت انسان وجود خواهد داشت.

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