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A reconnaissance study of pharmaceuticals, pesticides, perfluoroalkyl substances and organophosphorus flame retardants in the aquatic environment, wild plants and vegetables of two Saudi Arabia urban areas: Environmental and human health risk assessment

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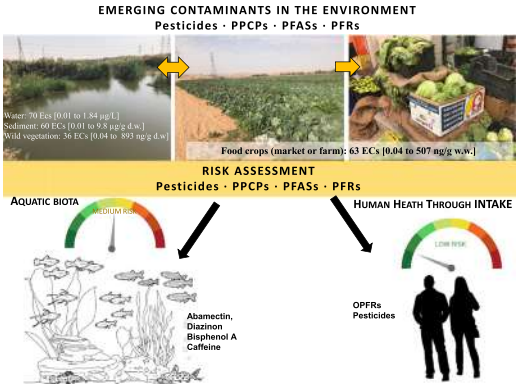
HIGHLIGHTS

- Of 131 emerging contaminants, 87 belonging to all kinds tested were in the samples.
- Content of PPCPs>Pesticides>OPFRs> PFASs except for wild vegetation in Al-Jubail
- Significant differences in pesticide content between Riyadh and Al-Jubail samples
- Caffeine, bisphenol A, diazinon and abamectin showed the highest ecological risk.
- Level of contamination in food does not indicate serious threat to population health.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the occurrence of 12 organophosphorus flame retardants (OPFRs), 64 pesticides, 21 perfluoroalkyl substances (PFASs) and 34 pharmaceuticals and personal care products (PPCPs) in surface water, sediments and vegetation collected from seven locations along the South Riyadh and six locations along the Al-Jubail industrial city (Saudi Arabia) were reported. The median of the concentrations of ΣOPFRs, ΣPesticides, ΣPFASs and ΣPPCPs in water was 297, 231, 29.7 and 3794 ng L^{-1}, respectively, in sediments 56.2, 40.4, 5.66 and 419 ng g^{-1} d.w., in crops for human consumption of 45.6, 42.0, 0.46 and 42.0 ng g^{-1}, in farm crops of 13.4, 57.5, 3.2 and 637 ng g^{-1}, and in natural vegetation of 51.7, 10.3, 1.88 and 1580 ng g^{-1}. Predominant compounds in all matrices were tris-(1,3-dichloro-2-propyl)phosphate (TClPP), acetamiprid, imidacloprid, caffeine, bisphenol A (BPA), diclofenac and ibuprofen. Tris(2-butoxyethyl) phosphate (TBEP), tris-(2-ethylhexyl)phosphate (TPhP), perfluoroctanoic acid (PFOA), perfluoroalkyl sulfonate (PFOS) and paracetamol were also in many samples but at low concentrations. The contaminants' levels showed similar values in both cities. However, pesticide levels were significantly higher in surface water ($p < 0.05$) and lower in natural vegetation ($p < 0.05$) of Riyadh than those of Al-Jubail. The risk assessment for the aquatic biota showed that abamectin, diazinon (pesticides), bisphenol A and caffeine (PPCPs) had the highest risk levels. The cumulative risk assessment showed that the contaminant mixture in all water samples is of concern. As far as the risk to human health is concerned, individual contaminants did not show a significant hazard for the population. However, OPFRs and pesticide requires a closed monitoring since % of

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admissible daily intakes (ADIs) or reference doses (RfD) are high. This is one of the most comprehensive study covering environmental and human risk assessment of emerging contaminants carried out in Saudi Arabia.

1. Introduction

The presence of emerging contaminants (ECs) including pharmaceutical and personal care products (PPCPs), pesticides, perfluoroalkyl substances (PFASs) or flame retardants (FRs) among others is one of the most important indicators of the anthropic pressure on the environment (Gogoi et al., 2018; Ramírez-Malule et al., 2020; Snow et al., 2019; Vazquez-Roig et al., 2011). The concern regarding these contaminants has risen because of the exacerbate growth in the population that increased by three billion in just 50 years (Roka, 2019). Several review papers show that over the past two decades there was a rather rapid progress in scientific research devoted to establish the environmental occurrence of ECs (Carmona and Picó, 2018; Lorenzo et al., 2018; Nilsen et al., 2019; Ramírez-Malule et al., 2020; Vazquez-Roig et al., 2011). An important number of studies demonstrated their presence in Africa (Fekadu et al., 2019; K'Oreje et al., 2020), America (Conn et al., 2020; Llorca et al., 2017; Vélez et al., 2019), Asia (Sacdal et al., 2020), Europe (Aminot et al., 2019; Schulze et al., 2019; Vandermeersch et al., 2015) and Oceania (Kroon et al., 2020; McKenzie et al., 2020). Furthermore, these ECs have been found in all the environmental compartments including water, soils, sediments, and biota (Fekadu et al., 2019; McKenzie et al., 2020; Sacdal et al., 2020; Vandermeersch et al., 2015). This impact has encouraged the development of studies on their sources, transport, toxicity, stability and environmental degradation and fate (Conn et al., 2020; K'Oreje et al., 2020; Kroon et al., 2020; Nilsen et al., 2019).

Nowadays, the water pollution by ECs is facing a new challenge due to the added effect of climate change (Burri et al., 2019; Jarsjö et al., 2020; Libera et al., 2019; Picó et al., 2013). In these circumstances, hyper-arid zones already highly affected by climate change, such as the Middle East, have become a study cases (Álvarez-Ruiz et al., 2020; Razack et al., 2019). Saudi Arabia presents many issues related to water quality and population pressures due to the combination of an above-average annual population growth rate (2.5%), 8.8% annual increase in water demand and changes caused by climate change (temperature can reach 50 °C and average long-term rainfall throughout the country is 114 mm per year) (DeNicola et al., 2015). One of the solutions adopted is a greater recycling of wastewater for irrigation of crops and other vegetables (Mu'azu et al., 2020; Picó et al., 2019). However, wastewater (treated or not) is a source of ECs for the environment and human being (Álvarez-Ruiz et al., 2020; Picó et al., 2019; Picó et al., 2020). Thus, the global situation of this country deserves attention. Although, some previous studies focus on the prevalence of PPCPs and pesticides (Picó et al., 2020), these constitute only one piece of a much larger puzzle. The spectrum of contaminants studied needs to be expanded to get more pieces of the puzzle and once complete, to advance in the assessment of the additional risk that ECs mixtures pose to biota and humans. Thus, the main objective of this study was to assess the environmental risk due to occurrence of ECs in urban areas of Saudi Arabia as well as their implications to aquatic ecosystems and human health. This assessment involves to (i) measure the concentrations of 131 ECs belonging mainly to four chemical classes [PPCPs, pesticides, PFASs and organophosphorus flame retardants (OFRs)] in different types of environmental samples (water, sediment, wild flora and vegetables intended for human consumption) of two Saudi cities (Riyadh and Al-Jubail); (ii) assess the potential risk to the aquatic biota and its association with the contaminants' levels, and (iii) evaluate the health risk for the human population due to exposure to these contaminants through the vegetables consumption. The mixture of contaminants include the most relevant classes of ECs (Richardson and Kimura, 2017), and the compounds were selected based on their occurrence and levels in the aquatic environments. Bisphenol A, caffeine and salicylic acids, compounds of difficult classification were included within PPCPs. Bisphenol A (industrial origin and as plasticizer) has already been reported in Saudi Arabia at high concentrations (Picó et al., 2020). Caffeine is considered a tracer for the contamination of the water compartments with untreated wastewater (Patel et al., 2019). Finally, salicylic acid is the active metabolite of acetylsalicylic acid but also a natural compound in some plants related to water stress (Nunes, 2019). This is one of the most comprehensive study on the simultaneous presence of several types of contaminants including the environmental and human cumulative risk assessment carried out in Saudi Arabia.

2. Experimental

2.1. Research area and sampling

The location of the sampling stations is illustrated in Fig. 1. The part of Riyadh covered is the area of influence of the south wastewater treatment plant (WWTP) including the artificial pond that receives the effluent (through a channel). The detailed description of the Riyadh area was given in a previous study (Picó et al., 2019). In Al-Jubail, samples were taken following the water run-off canal system that transports treated water discharged from different industries, water from occasional rainfall and flooding, and overflow water from the Arabian Gulf (El-Sorogy et al., 2018). In February 2019, water, sediment, natural vegetation and crops intended for human consumption (77 samples in total) were taken from six stations located in Al-Jubail ($n = 40$) and seven located in Riyadh (Saudi Arabia) ($n = 37$), according to the information detailed in supplementary material Table S1 for each sampling point. Water ($n = 11$), sediment ($n = 11$), natural vegetation ($n = 8$) or food crops ($n = 47$) from both, markets ($n = 22$) and farms ($n = 25$), were sampled according to NEIC (1985) to ensure proper cleaning of the material and quality control. Water samples were collected at points (ca. 2 L), in the middle of rivers and channels at a depth of approximately 30–40 cm. Sediment samples were collected as much as possible at the same point as water samples with a Van Veen grab sampler (0.5 L capacity) at up to 15 cm depth. Natural vegetation and vegetables procured directly from the field were taken as composite samples (10 plants randomly distributed) in a square of 16 m^2 in thick quality polyethylene bags. Fruits and vegetables from the markets were sampled according to the EU guidelines (EU, 2002) at various places distributed through the lot (size ≈50 kg). Samples were collected at random using net bags. Each sample weighed a minimum of 2 kg and contained at least 10 pieces.

2.2. Extraction, determination and quality assurance

Once at the laboratory, surface water samples were filtered through glass microfiber filters (90 mm Ø) and stored at −20 °C until the analysis that was performed by solid-phase extraction (SPE) with STRATA-X Polymeric Reversed Phase cartridges and liquid chromatography tandem mass spectrometry (LC-MS/MS) following a previously described method (Picó et al., 2019). Lyophilized sediments, soil and plant were sieved (2 mm Ø) and extracted by ultrasound assisted extraction using methanol, distilled water and McIlvaine–EDTA buffer (pH = 4.5) in the proportion (1:1:1) followed by the same SPE clean-up procedure as used for water samples. Natural vegetation and crops for human

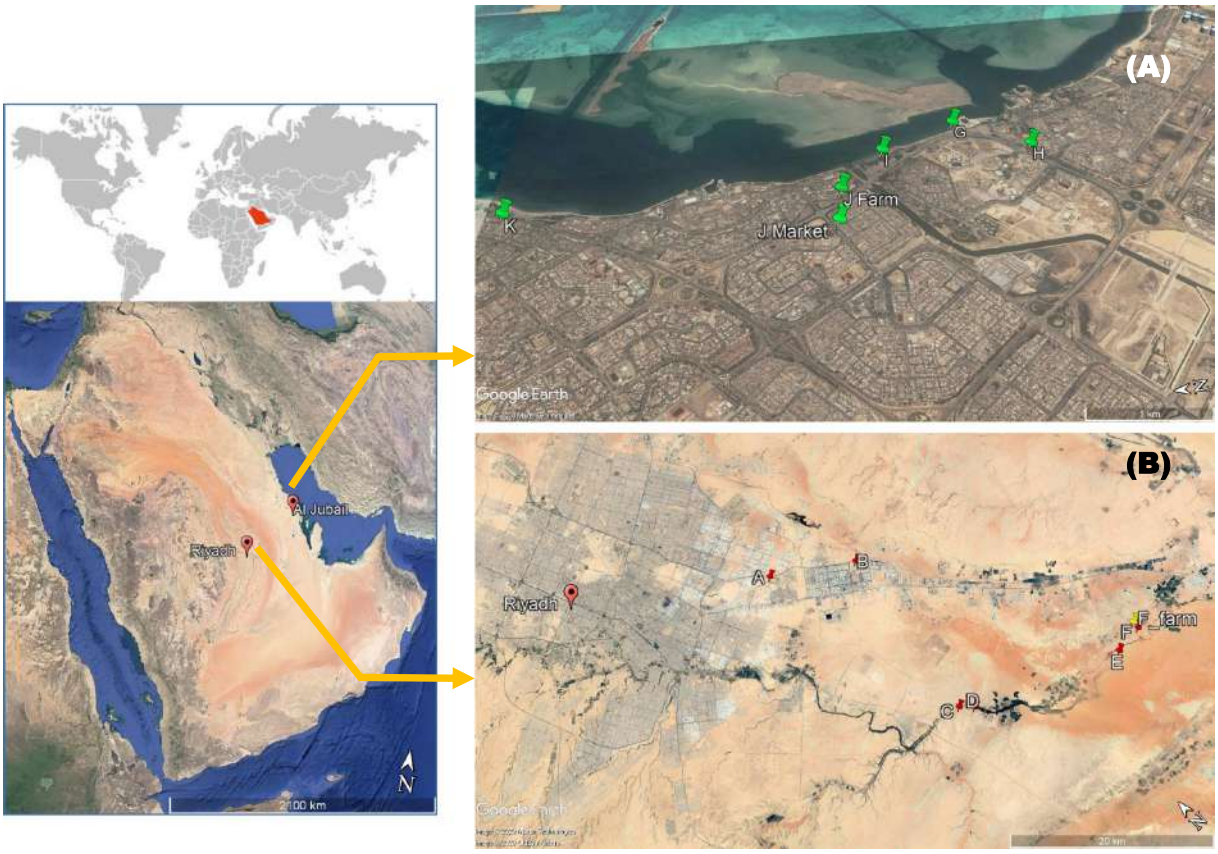

Fig. 1. Maps of the study areas showing the sampling points in (A) Al-Jubail (from G to K) and (B) Riyadh South (from A to F).

consumption were cleaned with distilled water, air dried and chopped using a food processor and extracted using the same method as for sediments (Picó et al., 2020).

The LC-MS/MS system was a 1260 Infinity Ultra-High-Performance Liquid Chromatograph (UHPLC) combined with an Agilent 6410 Triple Quadrupole (QqQ) Mass Spectrometer (MS/MS) with an electrospray ionization (ESI) source (Agilent Technologies, Santa Clara, CA, USA). Compounds were separated using conventional reverse-phase chromatography and determined in either positive (pesticides, some PPCPs and OPFRs) and negative (PFASs and some PPCPs) ionization as previously detailed (Lorenzo et al., 2019; Picó et al., 2020). Validation of these methods was also reported in those articles and a summary for the representative matrices of this study is included in the supplementary material (Table S2).

In order to minimize laboratory contamination, only glass and metal equipment was used. All glassware was cleaned by ultrasonic agitation in water containing detergent and, then, rinsed with ultrapure water and high-purity methanol. The solvents were purchased from VWR, Germany. One procedural blank and one spiked sample were performed with each batch of samples (ca. 25 samples) to avoid background contamination or variations in the recovery. Only trace amounts of PFOS and TClPP were detected in procedural blanks and the recovery was within the RSDs. The analytical standards of the target compounds (21 PFASs, 12 OPFRs, 60 pesticides, 40 PPCPs) were purchased from Sigma-Aldrich (Steinheim, Germany), Wellington Laboratories (Guelph, Ontario, Canada) and LCG standards (Barcelona, Spain) (see Table S3 for a detailed list and structures).

2.3. Risk assessment for the aquatic biota

The ecological risks assessment was based on the risk quotient (RQ) method for three trophic levels (green algae, *Daphnia magna* and fish). For each individual contaminant detected in water, the RQ value was calculated using the ratio of the mean or maximum concentrations measured for each compounds to the predicted no-effect concentration (PNEC), as shown in Eq. (1). Most of PNEC values derived from the Ecological Structure Activity Relationships (ECOSAR)™ database (a QSAR tool to predict a chemical's acute (short-term) toxicity and chronic (long-term or delayed) toxicity) that worked out according to the US Guideline on the Environmental Risk Assessment of Medicinal Products for Human use (EMEA) (Table S4). In this program, chronic aquatic toxicity (ChV) is estimated in mg/L as the geometric mean of the no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC). When using this theoretical approach some values may be higher than the experimental ones. However, the advantage of this system is that the values for all compounds are obtained in the same way. The PNEC (predicted no effect concentration) was determined applying an assessment factor (AF) of 10 to take into account the intra-species variability and the impact of the extrapolation of the laboratory data to field (since the inter-species variability was already taken into account using three trophic levels) (ECHA, 2008; US-EPA, 2012) (Eq. (2)).

For individual contaminants, RQ was calculated using the following equation:

$$RQ_{(CONTAMINANT)} = EC/PNEC \quad (1)$$

where, EC is the mean or maximum concentration of PPCPs detected in the water samples.

$$PNEC = ChV/AF \quad (2)$$

For the mixture of contaminants found at each sample point, the risk was evaluated following the concentration addition (CA) concept

recently proposed by Backhaus and Faust (2012) and modified to examine specific cases as suggested by Riva et al. (2019) (Eq. (3)). In our study, the same criteria used in the evaluation of individual compounds was followed.

$$RQ_{(SITE)} = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i} \quad (3)$$

The CA concept applies two RQs for each mixture: (i) one results from summing the RQ of each compound at each trophic level providing three RQs (for algae, daphnia and fish), and selecting the highest one, and (ii) the other is calculated summing the RQ for each compound calculated using the lowest PNEC of the three trophic levels.

RQ > 1 suggests high ecological risk and the environmental risk posed by the individual compound or the mixture could not be excluded, 0.1 ≤ RQ ≤ 1 suggests medium ecological risk and RQ < 0.1 suggests low ecological risk.

2.4. Human health risk assessment

The chronic exposure assessment for the individual compounds was carried by calculating the % of the admissible daily intake (ADI) that is ingested. To this, the estimated daily intake (EDI) was quantitatively derived using a deterministic approach based on a predefined level of consumption and a fixed value from the distribution of occurrence/concentration in food (multiplying average residue concentrations by average daily per capita consumption). This consumption was estimated for each commodity on the basis of the GEMS/Food Consumption cluster diets (G4 for Saudi Arabia) (WHO, 2013).

The estimated daily intake (EDI) of ECs was calculated as follows:

$$EDI = \sum \frac{Fi \times RLi}{mean\ body\ weight}$$

where EDI is the estimated daily intake, Fi is the food consumption data, and RLi is the residue level for the commodity.

EDIs are then, expressed as a percentage of the ADI for a 60 kg person.

$$\%EDI = \frac{EDI}{ADI} \times 100$$

where ADI represents the ADI or tolerable daily intake (TDI) as they are established for pesticides, PFOS and PFOA or the reference dose (RfD) for OPFRs divided for a factor of 10 (to consider at least intra-specie variation) or the highest therapeutic dose (NOAEL) for most PPCPs also divided for 10 for the same reason.

The cumulative risk arising from the co-exposure to all ECs measured in vegetable samples was assessed by summing up the individual % of ADIs of all the substances measured. To ensure safety of population the % of ADI must be below the threshold of 100%.

2.5. Statistical analysis

Data were analyzed by parametric or non-parametric tests depending upon whether data satisfied normality and homogeneity of variances assumptions. Normality was tested using Kolmogorov-Smirnov ($n > 50$) or Shapiro-Wilk's ($n < 50$) tests and homogeneity of variances by means of Levene's test. For the parametric analysis, differences in concentrations were established through one factor ANOVA, and confirmed a posteriori with the Tukey's or student's *t*-tests, considering city (Riyadh, Al-Jubail) and compound's family (OPFRs, Pesticides, PFASs, PPCPs) as factors. For non-parametric analysis, differences were determined by the tests of Mann–Whitney U (M-W) or Kruskal-Wallis (K-W). In all the cases, results were considered to be statistically significant at $p < 0.05$. All statistical analyses were carried out using IBM SPSS Statistics 26®.

3. Results and discussion

3.1. Occurrence and distribution of ECs

The concentrations of OPFRs, pesticides, PFASs and PPCPs are presented in Table 1 for water and sediments and in Table 2 for crops for human consumption, crops in farm and natural vegetation. In both tables, a total of 87 different contaminants belonging to all kinds were identified. According to the matrix, in water samples 70 different contaminants were detected, in sediments 60, in food crops 63 and in natural vegetation 37. For ΣOPFRs, the median of the concentrations in water, sediments, crops for consumption, crops in farm and natural vegetation were 297 ng L^{-1}, 56.2 ng g^{-1} d.w., 45.6 ng g^{-1}, 13.4 ng $g^{-1}$and 51.7 ng g^{-1}, respectively. TClPP was the most abundant presenting a high frequency in water (91% of the samples), sediments (73%), crops in farm (73%) and natural vegetation (45%). TBEP, TPhP and TDClPP appeared also frequently in water (91%, 91% and 82%, respectively), CDP in all types of vegetation (>54%) and TBEP and TClDPP in vegetables for consumption (78% and 70%, respectively). Concentrations and OPFR congeners profile are within the range reported elsewhere (Chokwe et al., 2020; Lorenzo et al., 2019). Some OPFRs are suspected to be mutagenic, carcinogenic, neurotoxic or embryotoxic (Mo et al., 2019). Although these contaminants have been widely detected in environmental media and human samples (Lorenzo et al., 2019; Mo et al., 2019; Zhu et al., 2020), their presence in the environment have not been regulated through Environmental Quality Standards (EQS) (Decision(EU)2018/840, 2018; Directive2013/39/EU, 2013).

The concentrations for Σpesticides in water ranged from 4.01 to 1754 ng L^{-1} with a median of 231 ng L^{-1} and in sediments from 8.73 to 142 ng g^{-1} d.w. with a median of 40.4 ng g^{-1} d.w. Abamectin, diazinon, imidacloprid and pyridaben were found in both matrices. The sediments also contained non-polar pyrethroids (acrinathrin, bifenthrin, cyhalothrin, etofenprox, and flumethrin), azinphos methyl, dichlofenthion, dimethoate, spinosad A and tolclofos methyl and the water more polar pesticides (neonicotinoids, herbicides such as triazines, ureas and carbamates). The median concentration of Σpesticides in crops for human consumption, crops in farm and natural vegetation were 42.0, 57.5 and 10.3 ng g^{-1}, respectively. Our previous studies (Picó et al., 2019; Picó et al., 2018) also reported high frequency of fungicides and insecticides in samples intended for human consumption at concentrations below the maximum residue limits (MRLs). Azinphos methyl and ethyl, bifenthrin, carbendazim, carbofuran, clothianidin, diazinon, dichlofenthion, dimethoate, diuron, imidacloprid, propazine, thiametoxan are not approved in the EU and in many other countries. These pesticides could come from runoff of the residues of previous applications. The EQS includes diuron with an annual average (AA) of 300 ng L^{-1} (Directive2013/39/EU, 2013) Neonicotinoids (acetamiprid, chlotianidin, imidacloprid and thiometoxan) have been added very recently to the watching list of the European Union but without limit values yet (Decision(EU)2018/840, 2018). Regarding, pesticide residues found in food crops, only carbendazim in Okra overpassed the MRLs established both, in Europe and in Saudi Arabia (EC, 2020; SFDA, 2018).

For ΣPFASs, the median of the concentrations in water, sediments, crops for consumption, crops in farm and natural vegetation were 29.7 ng L^{-1}, 5.66 ng g_{-1} d.w., 0.46 ng g^{-1}, 3.2 ng g^{-1} and 1.88 ng g^{-1}, respectively. Perfluoroalkyl butanoic acid (PFBA), perfluoroalkyl butane sulfonate (PFBS), perfluoroalkyl hexanoic acid (PFHxA) and perfluoroalkyl octane sulfonate (PFOS) were the most frequent. There was no previous data on PFASs in the environment of Saudi Arabia. However, similarly Pérez et al. (2014) reported concentrations of ΣPFASs for the global diet of Saudi Arabia in the pg/g or pg/mL levels and PFOS, PFOA and PFBA as the most abundant congeners. More recently, Banjabi et al. (2020) also found PFASs in >80% samples of serum of the population of Jedda (Saudi Arabia)

Table 1
Maximum, mean and median concentrations of OPFR, Pesticides, PFASs and PPCPs as well as frequency of detection in water and sediment.

Contaminants	Water ($n = 11$)				Sediment ($n = 11$)			
	Concentration (ng L^{-1})			Freq[a]	Concentration (ng g^{-1} d.w.)			Freq[a]
	Max	Mean	Median		Max	Mean	Median	
ΣOPFRs[b]	498	278	297	11	612	11.2	56.2	11
CDP	45.6	9.05	0	3	6.86	1.41	0.00	4
TBEP	121	21.7	3.33	11	5.60	0.94	0.51	10
TCEP	23.0	9.93	11.1	8	32.0	10.6	6.47	8
TClPP	387	198	231	10	562	94.8	37.4	8
TDBPP	5.58	1.33	0	4	6.03	0.55	0.00	1
TDClPP	27.7	12.2	8.64	9	3.52	0.81	0.16	7
TMPP	0.97	0.08	0	1	1.03	0.39	0.35	9
TnBP	77.0	9.79	3.47	10	8.45	1.08	0.00	5
TPhP	33.0	9.25	8.82	11	4.47	1.81	1.67	11
TPP	0.37	0.03	0	1	–	–	–	–
ΣPesticides	1754	363	231	11	142	45.1	40.4	10
Abamectin	125	13.6	0.00	2	18.0	3.18	0.00	3
Acetamiprid	1408	136	3.25	7	6.17	0.56	0.00	1
Acrinathrin	–	–	–	–	25.7	6.06	0.00	3
Azinphos-ethyl	–	–	–	–	38.0	3.45	0.00	1
Bifentrhin	–	–	–	–	25.3	3.64	0.00	5
Buprofezine	1.00	0.10	0.00	1	–	–	–	–
Carbendazim	32.8	14.6	12.08	9	–	–	–	–
Carbofuran	51.8	7.42	0.00	5	–	–	–	–
Carbofuran 3-OH	26.5	4.48	0.00	2	–	–	–	–
Clothianidin	38.2	6.56	0.00	5	–	–	–	–
Cyhalothrin	–	–	–	–	25.0	6.34	0.00	5
Diazinon	36.8	8.60	0.00	3	2.63	0.24	0.00	1
Dichlofenthion	–	–	–	–	3.04	0.28	0.00	1
Dimethoate	–	–	–	–	35.2	3.78	0.00	2
Diuron	30.2	2.75	0.00	1	–	–	–	–
DMA	–	–	–	–	113	10.2	0.00	1
Etofenproph	–	–	–	–	10.2	1.80	0.00	5
Flumethrin	–	–	–	–	5.16	0.47	0.00	1
Imidacloprid	308	115	103	10	23.1	2.10	0.00	1
Malathion	28.9	2.62	0.00	1	–	–	–	–
Pyridaben	46.0	6.45	0.00	2	10.1	1.46	0.00	2
Propazine	12.8	1.16	0.00	1	–	–		–
Spinosad A	–	–	–	–	11.0	1.00	0.00	1
Terbuthylazinedeethyl	21.2	7.21	0.00	4	–	–	–	–
Terbutylazine	15.9	4.78	0.00	4	–	–	–	–
Terbutylazine-2-OH	40.5	9.79	3.20	6	–	–	–	–
Thiametoxan	212	22.0	2.40	7	–	–	–	–
Tolclofos-methyl	–	–	0.00	–	5.55	0.50	0.00	1
ΣPFASs	108	55	29.7	11	116	25.0	5.66	11
ipPFNA	1.72	0.63	0.35	6	0.25	0.04	0.00	2
ipPFNS	–	–	–	–	0.10	0.01	0.00	1
PFBA	9.54	1.34	0.00	2	110	20.3	0.00	4
PFBS	57.5	6.21	0.00	4	2.55	0.28	0.00	2
PFDA	0.30	0.03	0.00	1	0.19	0.03	0.00	2
PFDS	0.15	0.01	0.00	1	0.48	0.14	0.00	5
PFHpA	30.6	7.53	4.56	9	–	–	–	–
PFHpS	2.13	0.40	0.00	4	3.05	0.40	0.00	4
PFHxA	42.8	12.2	5.03	9	3.86	0.35	0.00	1
PFHxS	7.89	1.66	0.89	8	–	–	–	–
PFNA	6.09	1.16	0.60	7	0.50	0.06	0.00	2
PFOA	14.2	2.74	1.38	11	1.86	0.35	0.17	7
PFODA	1.36	0.12	0.00	1	1.30	0.12	0.00	1
PFOS	88.4	15.1	9.54	11	10.6	2.95	2.18	11
PFPa	39.2	5.81	0.00	5	–	–	–	–
PFTrDA	–	–	–	–	0.12	0.01	0.00	1
ΣPPCPs	32,016	6767	3794	11	3630	1277	419	11
Alprazolam	5.71	1.28	0.63	9	28.5	2.59	0.00	1
Amoxicillin	87.98	22.28	7.15	6	59.9	9.23	5.15	6
Atenolol	1851	465	227	8	17.4	1.58	0.00	1
Atorvastatin	13.6	1.24	0.00	1	57.6	8.67	0.00	3
Benzafibrate	11.15	4.04	0.00	4	11.1	2.02	0.00	2
BPA	5108	854	97.3	7	3208	833	84.0	8
Butylparaben	0.90	0.08	0.00	1	2.38	0.42	0.00	3
Caffeine	12,374	1814	318	10	28.0	11.5	9.24	11
Chlofibric acid	15.9	5.72	0	4	16.2	1.48	0.00	1
Codeine	65.9	21.7	13.0	7	–	–	–	–
Diclofenac	4992	1188	204	7	65.7	24.6	22.8	7
Etoricoxib	3.32	0.76	0.00	4	8.92	0.81	0.00	1
Ibuprofen	9747	976	0.00	3	–	–	–	–

(continued on next page)

Table 1 (*continued*)

Contaminants	Water ($n = 11$)				Sediment ($n = 11$)			
	Concentration (ng L^{-1})			Freq[a]	Concentration (ng g^{-1} d.w.)			Freq[a]
	Max	Mean	Median		Max	Mean	Median	
Indomethacine	0.90	0.08	0.00	1	–	–	–	–
Lorazepam	792	87.7	19.2	8	11.4	1.42	0.00	2
Metformin	12.5	2.50	0.52	9	1.15	0.23	0.00	5
Methylparaben	29.2	2.65	0.00	1	–	–	–	–
Naproxen	25.8	4.36	0.00	4	20.3	6.16	0.00	4
Norfloxacin	2763	537.4	0.00	4	3323	338	0.00	3
Ofloxacin	2198	393	0.00	4	–	–	–	–
Omeprazol	52.5	13.2	2.57	7	41.0	8.35	0.00	5
Paracetamol	158	29.4	7.77	10	57.1	8.60	2.13	7
Propylparaben	7.48	0.73	0.00	2	3.44	0.87	0.67	9
Salicylic acid	144	24.7	12.6	10	28.4	9.74	7.02	8
Simvastatin	6.34	2.20	2.05	8	4.65	0.55	0.00	2
Thiamphenicol	4.69	1.68	0.00	5	4.21	0.69	0.00	2
Tramadol	1035	312	248	8	55.4	7.73	0.00	3
Triclocarban	0.90	0.08	0.00	1	0.48	0.07	0.00	2
Triclosan	0.90	0.08	0.00	1	–	–	–	–

[a] Freq. = Frequency of detection as number of occurrences in the samples.
[b] TEHP was not detected in any sample and it was considered as zero.

with high levels of PFBA. The maximum concentration of PFOS in our study (88 ng L^{-1}) was well below of the maximum allowable concentration (MAC) established in EQS for inland water of 36 10^3 ng L^{-1}. However, its average concentration (15.1 ng L^{-1}) is 23 times higher than the value of the AA (6.5 10^{-4} ng L^{-1}) (Directive2013/39/EU, 2013).

The median of the concentration of ΣPPCPs in water, sediments, crops for consumption, crops in farm and natural vegetation were 3794 ng L^{-1}, 419 ng g^{-1} d.w.,42 ng g^{-1}, 637 ng $g^{-1}$and 1580 ng g^{-1}, respectively. Most relevant compounds in water and sediment were BPA, caffeine, diclofenac and paracetamol. These results were comparable to those found in other areas of Saudi Arabia (Picó et al., 2020). The abundance of caffeine and paracetamol (extensively transformed in WWTPs) in surface water indicates an abundant discharge of poorly treated wastewater (Gogoi et al., 2018; Patel et al., 2019). Although nowadays eliminated, diclofenac was once included in the EQS, with an AA of 100 ng L^{-1} (Directive2013/39/EU, 2013). The average value obtained in this study (Table 1) is 10 times higher. Salicylic acid and warfarin that could be produced by plants were present at high concentration in all types of vegetables. Thiamphenicol often used in veterinary medicine occurred at high concentrations in both types of crops. Unlike chloramphenicol, thiamphenicol is predominantly excreted unchanged in cattle, poultry, sheep, or humans. Cross contamination from food of animal origin can explain its presence.

Overall, no significant differences between Riyadh and Al-Jubail ($p > 0.05$) were observed for the sum of all contaminants or for the sum of each kind of contaminants. Statistically significant differences ($p < 0.05$) were observed for each city between the sum of the concentrations for each kind of contaminants (following in both the pattern PPCPs>pesticides>OPFRs>PFASs). Regarding the different sample matrices, Figs. 2 and 3 compared the sum of concentrations of each type of contaminant between the different cities for the same matrix. Significant differences were observed in the values of Σpesticides for water and natural vegetation between Riyadh and Al-Jubail ($p < 0.05$), with no significant differences found between ΣOPFRs, ΣPFASs and ΣPPCPs ($p > 0.05$). The concentration of pesticides in water was higher in Riyadh, while, in natural vegetation, was higher in Al-Jubail. No significant differences for the sum of any type of contaminants were observed in sediments and vegetables for consumption or on farm. This could suggest that contaminants coming from diffuse sources present higher variability.

3.2. Environmental risk assessment for aquatic biota

The ecological risk of the detected contaminants to three typical freshwater organisms (fish, daphnia and algae) was assessed based on the mean and maximum concentrations found in the water samples (Table S5). For most OPFRs, pesticides, PFASs and PPCPs, their ecological risks to algae were generally higher than to daphnia and fish. The risk for most of the compounds was low. However, this risk assessment possess several limitations, such as the use of PNEC values derived from QSAR approach instead of experimental ones. In addition, the ECs were considered individually while in the samples, a mixture of compounds is present that can add up or even potentiate their effects, so care must be taken before ensuring that they do not pose a risk to aquatic biota.

Diazinon (pesticide) and bisphenol A and caffeine (PPCPs) showed the highest risk levels, with the largest RQs of 4.5 (mean concentrations) and 31 (maximum concentration) of caffeine. At the average concentration levels, caffeine for green algae and diazinon for daphnia posed a high risk (>1), and the RQs of the other compounds and organisms were at low level whereas at the maximum concentration levels, also bisphenol A for green algae and caffeine for fish possess a medium risk (0.1–1). Our previous study also showed that caffeine and diazinon had significant ecological risk for green algae and daphnia, respectively (Picó et al., 2020). Caffeine as well as several pesticides have pointed out to pose an environmental risk in a variety of fresh water ecosystems (Dafouz et al., 2018; Di Lorenzo et al., 2019; Kandie et al., 2020; Szymczycha et al., 2020).

The risk for the entire mixture of ECs in surface water was also assessed. Table 3 reports the ΣRQs calculated for each trophic level at each sampling point and the ΣRQs based on the MEC/lower PNEC ratios for all compounds detected and only for those that provide RQs < 1. Fig. 4 shows the spatial distribution of these RQs in the different sampling points. Fortunately, water used in the areas where there are crops showed much lower RQs. If all the compounds are considered, the RQs for all sampling points were > 1 for the mixture, as expected, as contaminants as caffeine that have RQs > 1 were found in almost all sampling points. However if only those compounds with RQs < 1 were taken into account, the individual compounds provided RQs<<<0.01 that indicated a negligible ecological risk, but, the mixture gave RQs around 0.1 that suggest a medium ecological risk. Riva et al. (2019) also conducted a cumulative risk assessment of ECs that by themselves did not represent any hazard to biota and concluded that instead the mixtures are of concern. This emphasizes the significance of

Table 2
Máximum, mean and median concentration as well as frequency of occurrence for OPFRs, Pesticides, PFASs and PPCPs in crops for human consumption, crops in farm and natural vegetation.

Contaminants	Crop for consumption ($n = 22$)				Crop in farm ($n = 25$)				Natural vegetation ($n = 8$)			
	Concentration (ng g^{-1})			Freq[a]	Concentration (ng g^{-1})			Freq[a]	Concentration (ng g^{-1})			Freq[a]
	Max	Mean	Median		Max	Mean	Median		Max	Mean	Median	
ΣOPFRs[b]	113	50.0	45.6	20	177	26.9	13.4	20	177	74.8	51.7	8
CDP	85.1	33.1	29.7	16	46.3	10.6	4.2	13	37.0	17.0	15.5	5
TBEP	2.29	0.82	0.83	18	2.43	0.20	0.00	4	1.92	0.55	0.55	6
TCEP	1.44	0.39	0.00	10	22.6	2.55	0.00	6	27.0	9.25	3.21	6
TClPP	23.9	1.10	0.00	2	87.2	12.8	0.00	8	134	40.2	3.14	5
TDBPP	1.03	0.1	0.00	4	—	—	—	—	—	—	—	—
TDClPP	50.7	6.83	3.20	16	0.53	0.04	0.00	2	—	—	—	—
TMPP	41.8	10.0	6.42	13	5.52	0.44	0.00	2	—	—	—	—
TnBP	0.34	0.15	0.00	2	0.84	0.09	0.00	4	3.29	1.18	0.12	5
TPhP	2.06	0.1	0.00	1	1.76	0.26	0.00	8	1.90	0.66	0.59	5
TPP	0.53	0.1	0.00	7	—	—	—	—	2.02	0.25	0.00	1
ΣPesticides	3906	323	42	19	789	140	575	22	70.2	31.7	10.3	8
Abamectin	40.0	2.72	0.00	2	482	64.6	11.1	16	—	—	—	—
Acetamiprid	39.7	5.06	0.00	7	141	13.0	0.00	7	—	—	—	—
Acrinathrin	16.1	1.37	0.00	1	15.3	1.07	0.00	2	—	—	—	—
Azinphos-ethyl	26.63	1.21	0.00	2	97.8	5.20	0.00	2	—	—	—	—
Bifentrhin	21.92	1.14	0.00	2	4.26	0.72	0.00	5	3.68	1.28	0.00	3
Buprofezine	7.07	0.37	0.00	8	1.15	0.05	0.00	1	—	—	—	—
Carbendazim	3446	197.82	0.00	1	—	—	—	—	—	—	—	—
Carbofuran 3-OH	15.57	0.71	0.00	2	23.1	0.96	0.00	1	—	—	—	—
Clothianidin	283.85	12.94	0.00	5	—	—	—	—	—	—	—	—
Cyhalothrin	9.86	1.75	0.00	1	9.50	2.76	3.00	10	24.2	3.85	0.00	2
Dichlofenthion	—	—	—	—	—	—	—	—		0.59	0.00	1
Dimethoate	—	—	—	—	7.77	0.60	0.00	2	8.17	1.02	0.00	1
DMF	8.01	0.36	0.00	3	8.54	0.36	0.00	1	—	—	—	—
DMPF	541.03	25.62	0.00	3	40.7	7.33	0.00	8	44.6	5.58	0.00	1
Ethion	35.52	1.61	0.00	1	—	—	—	—	7.50	0.94	0.00	1
Etofenprox	2.46	0.31	0.00	3	2.56	0.19	0.00	2	2.61	0.63	0.00	1
Fipronil	77.07	3.62	0.00	2	—	—	—	—	—	—	—	—
Flumehrin	3.85	0.17	0.00	1	6.43	0.51	0.00	2	—	—	—	—
Hexythiazox	2.58	0.12	0.00	1	—	—	—	—	—	—	—	—
Imazalil	608	27.7	0.00	2	4.15	0.23	0.00	2	—	—	—	—
Imidacloprid	68.70	9.24	0.00	11	20.5	1.22	0.00	2	—	—	—	—
Piridaben	–	–	–	–	301	37.0	5.42	15	—	—	—	—
Prochloraz	28.69	1.30	0.00	2	—	—	—	—	—	—	—	—
Pyriproxyfen	–	–	–	–	69.9	3.06	0.00	2	—	—	—	—
Spinosad A	8.49	0.64	0.00	3	31.7	1.94	0.00	2	23.4	5.86	3.95	3
Spinosad C	12.99	1.67	0.00	2	—	—	—	—	—	—	—	—
Spinosad D	2.18	0.20	0.00	2	—	—	—	—	—	—	—	—
Tebuconazole	15.93	0.77	0.00	22	—	—	—	—	—	—	—	—
Thiabendazole	434.37	19.74	0.00	1	—	—	—	—	—	—	—	—
Thiametoxan	73.37	3.33	0.00	1	—	—	—	—	—	—	—	—
Tolclofos-methyl	—	—	–	—	—	—	—	—	5.69	1.37	0.00	2
ΣPFASs	398	20.0	0.46	16	90.2	20.5	3.2	13	47.7	9.12	1.88	7
ipPFNA	—	—	—	—	1.22	0.05	0.00	1	—	—	—	—
PFBA	—	—	—	—	56.6	3.47	0.00	5	10.3	1.29	0.00	1
PFBS	209	9.49	0.00	3	85.6	13.8	0.00	8	—	—	—	—
PFHxA	191	8.31	0.00	1	16.84	1.05	0.00	3	47.7	6.34	0.00	2
PFNA	—	—	—	—	1.52	0.06	0.00	1	—	—	—	—
PFOA	11.8	0.77	0.32	14	1.15	0.22	0.13	12	0.61	0.34	0.31	6
PFOS	5.19	0.58	0.00	7	22.2	1.80	0.00	8	3.26	0.59	0.00	2
∑PPCPs	3906	323	42.0	22	6625	1368	637	25	4778	1571	1580	8
Alprazolam	3.09	0.15	0.00	1	—	—	—	—	—	—	—	—
Amoxicillin	89.4	4.26	0.00	1	—	—	—	—	—	—	—	—
Benzafibrate	158	12.83	0.00	5	594	37.2	1.00	8	40.7	5.09	0.00	1
BPA	158	7.20	0.00	1	1188	53.7	0.00	5	26.2	6.40	0.00	2
Butylparaben	86.3	3.92	0.00	1	298	15.3	0.00	3	808	116	0.00	2
Caffeine	7.47	1.47	0.00	21	2.93	1.11	0.00	23	2.80	1.78	1.69	8
Chlofibric acid	26.3	7.16	0.00	7	63.3	9.30	0.00	7	779	194	0.00	1
Codeine	21.1	1.00	0.00	1	—	—	—	—	—	—	—	—
Diclofenac	25.1	2.25	0.00	2	49.4	7.64	0.00	6	—	—	—	—
Ethylparaben	—	—	—	—	69.1	8.47	0.00	6	—	—	—	—
Etoricoxib	1.05	0.05	0.00	1	—	—	—	—	—	—	—	—
Ibuprofen	126	7.74	0.00	2	313	22.3	0.00	4	112	14.0	0.00	1
Indomethacine	16.5	1.94	0.00	4	368	33.2	0.00	7	74.7	15.7	0.00	2
Metformin	0.66	0.17	0.00	10	2.52	0.53	0.30	19	2.9	0.85	0.76	5
Methylparaben	218	16.9	0.00	3	194	27.5	15.58	13	166	54.1	23.2	7
Naproxen	17.2	1.54	0.00	2	16.9	2.60	0.00	4	—	—	—	—
Ofloxacin	94.1	4.48	0.00	1	—	—	—	—	—	—	—	—
Omeprazol	330	15.7	0.00	1	—	—	—	—	—	—	—	—

(continued on next page)

Table 2 (*continued*)

Contaminants	Crop for consumption ($n = 22$)				Crop in farm ($n = 25$)				Natural vegetation ($n = 8$)			
	Concentration (ng g^{-1})			Freq[a]	Concentration (ng g^{-1})			Freq[a]	Concentration (ng g^{-1})			Freq[a]
	Max	Mean	Median		Max	Mean	Median		Max	Mean	Median	
Paracetamol	12.1	2.40	1.69	20	23.1	8.23	7.0	24	17.4	7.7	4.36	8
Propylparaben	59.6	2.71	0.00	1	71.4	3.54	0.00	2	858	107	0.00	1
Salicylic acid	—	—	—	—	6496	485	94.2	18	3264	893	615	8
Simvastatin	—	—	—	—	—	—	—	—	0.12	0.01	0.00	1
Thiamphenicol	1193	244	70.1	21	2571	271	6.96	9	107	13.3	0.00	1
Tramadol	18.9	0.90	0.00	1	—	—	—	—	—	—	—	—
Triclocarban	2.98	0.14	0.00	1	128	12.8	0.00	5	124	29.6	0.00	2
Triclosan	—	—	—	—	631	36.7	0.00	5	—	—	—	—
Warfarin	248	15.4	0.00	2	5685	353	0.00	4	910	113	0.00	1

[a] Freq. = Frequency of detection as number of occurrences.
[b] TEHP was not detected in any sample and it was considered as zero.

the environmental risk assessment for mixtures of contaminants and the need to refine the approaches used.

3.3. Risk assessment for the human being

Table 4 shows EDIs and the % ADI that represents for the food consumed in Riyadh and in Al-Jubail and the total diet. This is the first time that the intake of the Saudi Arabia population has been calculated for so many different contaminants. The items selected cover about 3% of all the food intake. Then, these results should be considered with some caution. The ADIs are not available for all types of contaminants, RfDs for OPFRs, TDI for PFASs and maximum therapeutic dose for PPCPs were used. Values used are reported in the supplementary material (Table S6). Data on contaminant concentrations reported correspond to the average EDIs for Riyadh and Al-Jubail and for both. Regarding the OPFRs, TClPP, TDClP and TPMPP are relevant in both cities (the average daily intake is 14, 28 and 14% of the ADI, respectively). Furthermore, TDClPP and TMPP were also present in a considerable amount in food from Al-Jubail (27 and 13% of the ADI, respectively). This could be explained due to the industrial character of Al-Jubail. Regarding pesticides, only abamectin, carbendazim and carbofuran-3-hydoxy have

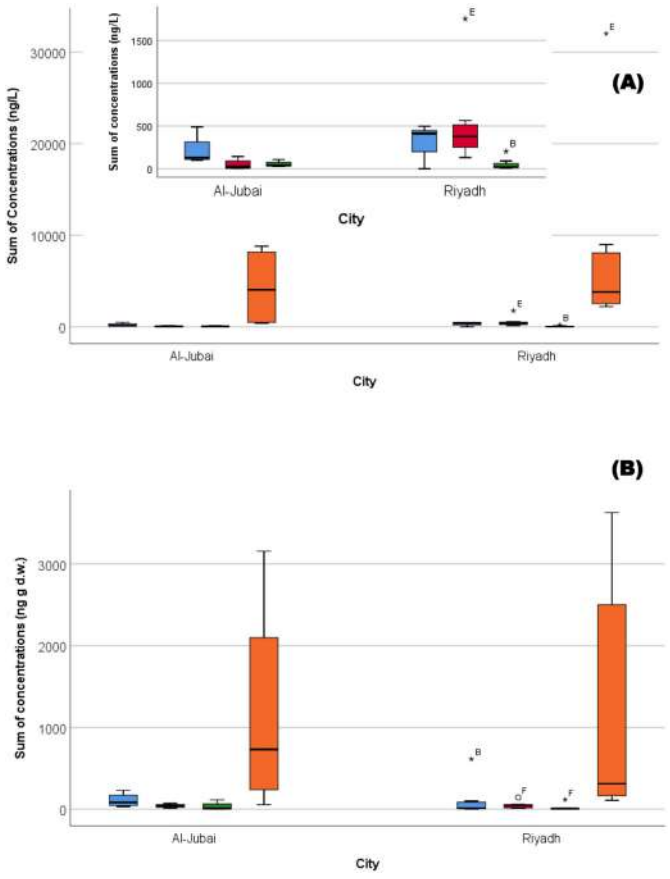

Fig. 2. Comparison of the sum of concentrations of each type of contaminants found in Riyadh and Al-Jubail in (A) water and (B) sediments. A smaller scale on the insert of the figure (A) to visualize ∑OPFRs, pesticides and PFASs in water. Box colours indicate the type of contaminants ■ ∑OPFRs, ■ ∑Pesticides, ■ ∑PFASs and ■ ∑PPCPs. * indicates outliers and the letter the sampling point (see Fig. 1).

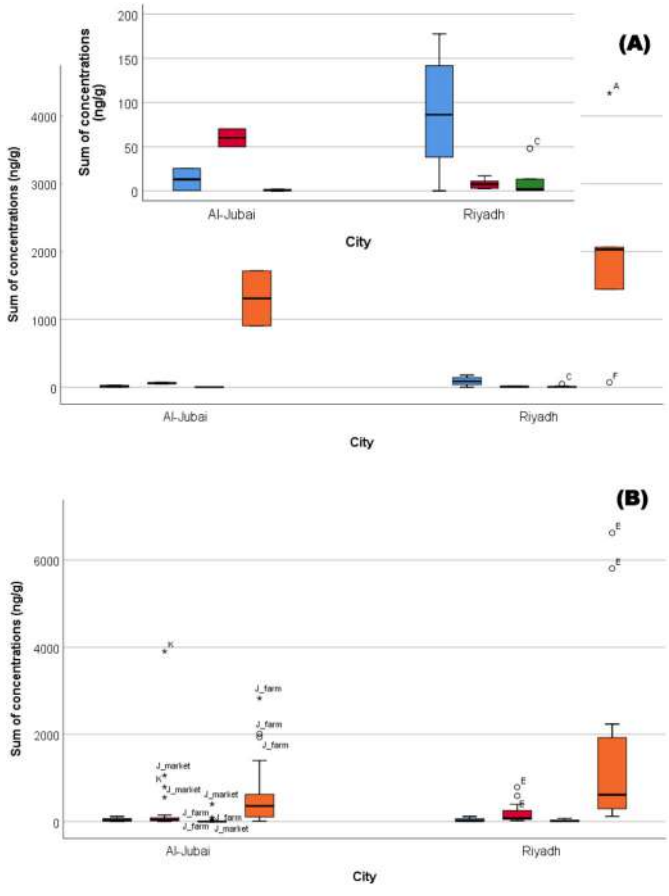

Fig. 3. Comparison of the sum of concentrations of each type of contaminants found in Riyadh and Al-Jubail in (A) natural vegetation and (B) crops intended for human consumption. A smaller scale on the insert of the fig. (A) to visualize ∑OPFRs, ∑pesticides and ∑PFASs in natural vegetation. Box colours indicate the type of contaminants ■ ∑OPFRs, ■ ∑pesticides, ■ ∑PFASs and ■ ∑PPCPs. * indicates outliers and the letter the sampling point (see Fig. 1).

Table 3
Environmental Risk Assessment of mixtures found at each sampling point.

		Riyadh							Al-Jubail			
		A	B	C	D	E	F	F_farm	G	H	I	J_farm
All contaminants found												
ΣRQ	Green algae	4.49	0.83	4.24	7.08	31.03	0.38	0.42	0.61	0.42	1.04	0.01
	Daphnia	0.07	0.06	2.93	4.45	125.20	4.64	25.03	0.05	0.01	0.04	0.01
	Fish	0.04	0.07	0.07	0.09	0.24	0.03	0.03	0.09	0.01	0.12	0.01
Higher ΣRQ		4.49	0.83	4.24	7.09	125.03	4.64	0.42	0.61	0.42	1.04	0.01
ΣRQ using lower PNEC		4.54	0.91	7.16	11.51	156.14	5.01	25.44	0.63	0.43	1.06	0.02
Contaminants with RQs < 1												
ΣRQ	Green algae	0.01	0.03	0.03	0.03	0.09	0.02	0.02	0.16	0.01	0.23	0.01
	Daphnia	0.07	0.06	0.07	0.09	0.20	0.04	0.03	0.05	0.01	0.04	0.01
	Fish	0.02	0.07	0.05	0.05	0.11	0.02	0.03	0.08	0.01	0.12	0.01
Higher ΣRQ		0.07	0.07	0.07	0.09	0.20	0.04	0.03	0.16	0.01	0.23	0.01
ΣRQ using lower PNEC		0.07	0.12	0.09	0.11	0.20	0.05	0.03	0.18	0.02	0.26	0.02

some relevant contribution to the total intake. PFOS and PFOA and PPCPs are all well below the ADI. The results show that even through there are many contaminants in fruits and vegetables of Saudi Arabia, they cannot be considered as dangerous. However, the presence of pesticides and OPFRs needs to be monitored because values determined are high. This is the first study of the occurrence of several ECs in the fruits and vegetables consumed in Saudi Arabia. Pesticides concentrations in both cities were similar to those reported previously for South Riyadh. The most relevant PFASs were PFOS and PFOA but their intake is not of concern and still remain similar to that reported in previous studies. Regarding PPCPs the results are also well below the EDIs even through a very conservative approach of divide per 10 the therapeutic dose was chosen. The sum of all the EDIs pointed out that the Saudi Arabian population intakes about 292 μg/person and day of the different contaminants. This is a small amount but it requires study and monitoring in order to ensure a proper health of the population.

4. Conclusions

The results filled the data gap on ECs occurrence and distribution in two important urban areas in the center and eastern Saudi Arabia. Of the 131 target ECs analyzed, 70 were detected in surface waters, 60 in sediments, 63 in vegetables for human consumption and 37 in wild vegetation. In water, the predominant contaminants were TBEP, TClPP. acetamiprid, imidacloprid, atenolol, BPA, caffeine and diclofenac. In sediments, vegetables and wild vegetation, the predominant contaminants were TClPP and BPA, thiamphenicol and salicylic acid, and this last one and methyl paraben, respectively. Overall, PPCPs were more frequently detected than the other compounds. In addition, polar pesticides (kow < 3) were more abundant in water and non-polar ones (Kow > 3) were more prevalent in sediments. No differences in the ECs abundance were observed between cities, except for pesticides in water and natural vegetation.

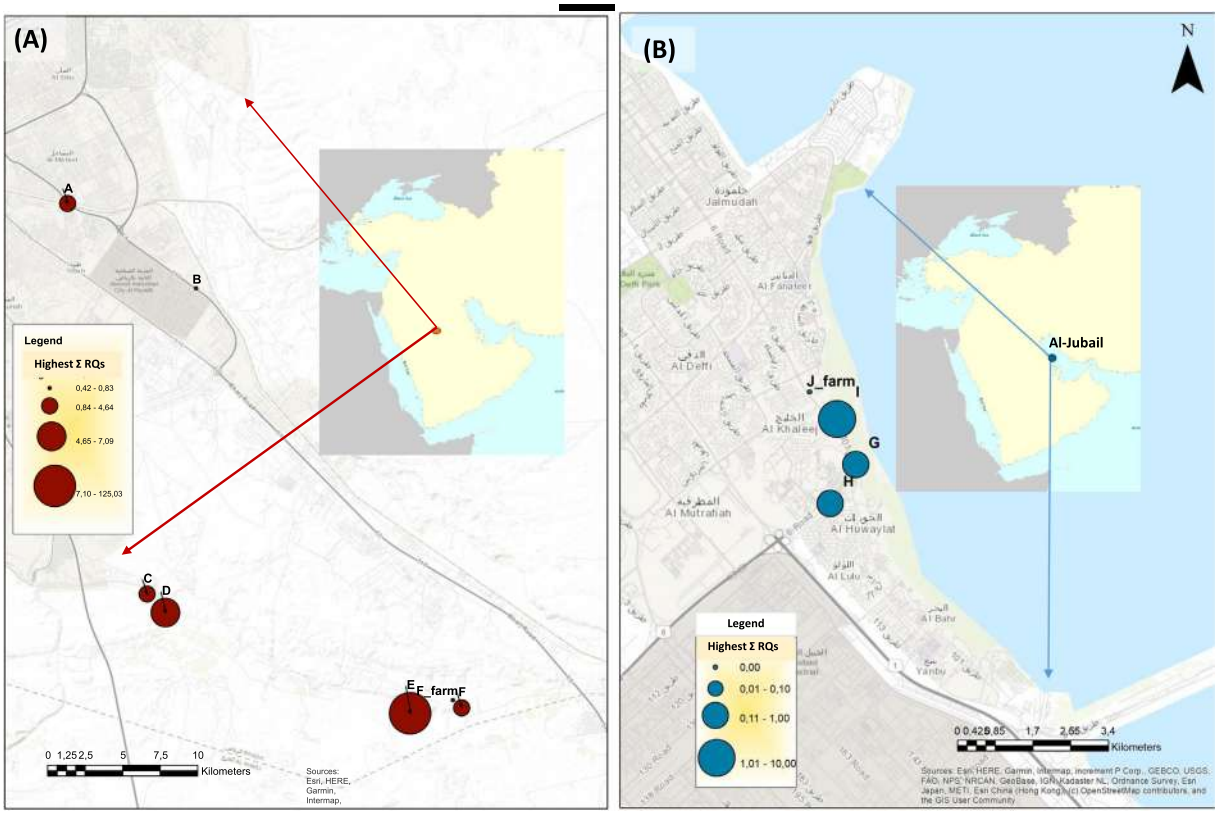

Fig. 4. ΣRQs at each sampling point showing the differences between the different sampling points in (A) Riyadh and (B) Al-Jubail (both maps are not in the same scale).

Table 4
Estimated daily intakes as EDI (μg/person/day) and % ADI in Riyadh, Al-Jubail and Total.

	Riyadh		Al-Jubail		Total (average values)	
	EDI (μg/person/day)	% ADI	EDI (μg/person/day)	% ADI	EDI (μg/person/day)	% ADI
OPFR	4.97	13.31	16.66	55.28	13.57	61.22
CDP	2.25	–	9.64	–	6.44	–
TBEP	0.01	0.11	0.28	3.12	0.17	1.90
TCEP	0.22	1.69	0.35	2.69	0.44	3.55
TClPP	2.44	11.28	2.17	10.03	2.99	14.14
TDBPP	–	–	4×10^{3}	0.01	4×10^{-3}	0.01
TDClPP	0.01	0.08	2.14	27.45	2.14	27.50
TMPP	4×10^{-3}	0.06	1.82	23.29	1.06	13.53
TnBP	4×10^{-3}	0.03	0.02	0.14	0.02	0.16
TPhP	0.04	0.11	0.21	0.50	0.18	0.44
TPP	2.25	–	0.03	–	0.02	–
Pesticide	11.88	4.31	112	17.93	115	20.14
Abamectin	3.99	2.66	0.15	0.10	2.39	1.59
Acetamiprid	1.41	0.09	2.11	0.14	2.06	0.14
Acrinathrin	0.63	0.11	1.05	0.18	1.31	0.22
Azinphos-ethyl	–	–	4.75	–	4.75	–
Bifentrhin	0.23	0.03	1.42	0.16	1.54	0.17
Buprofezine	–	–	0.07	0.01	0.03	0.01
Carbendazim	–	–	52.12	4.34	52.23	4.35
Carbofuran 3-OH	–	–	0.60	6.69	0.60	6.69
Clothianidin	–	–	0.80	0.01	0.47	0.01
Cyhalothrin	0.70	0.46	0.54	0.36	0.65	0.43
Dimethoate	0.02	0.01	–	–	0.01	0.01
DMF	0.08	0.04	0.01	4×10^{-3}	0.09	0.05
DMPF	0.46	0.25	1.33	0.74	1.77	0.99
Ethion	–	–	2.29	1.91	2.29	1.91
Etofenprox	0.02	10^{-3}	0.10	0.01	0.12	0.01
Fipronil	–	–	0.13	1.07	0.13	1.11
Flumehrin	0.27	0.11	0.26	0.11	0.37	0.15
Hexythiazox	–	–	0.17	0.01	0.17	0.01
Imazalil	–	–	23.24	1.55	23.24	1.55
Imidacloprid	0.85	0.02	0.71	0.02	0.87	0.02
Piridaben	3.93	0.66	–	–	0.92	0.15
Prochloraz	–	–	0.07	0.01	0.03	0.01
Pyriproxyfen	0.79	0.13	–	–	0.70	0.12
Spinosad	–	–	0.07	5×10^{-3}	0.07	5×10^{-3}
Tebuconazole	–	–	0.66	0.04	0.66	0.04
Thiabendazole	–	–	16.46	0.27	16.46	0.27
Thiametoxan	–	–	3.04	0.18	3.04	0.18
PFASs	0.42	1.19	0.87	0.38	1.09	1.03
PFBA	0.54	–	0.01	–	0.55	–
PFBS	0.06	–	0.45	–	0.50	–
PFHxA	0.07	–	0.31	–	0.39	–
PFOA	0.03	0.03	0.08	0.84	0.11	0.08
PFOS	0.14	1.55	0.03	–	0.15	0.59
PPCP	59	1.69	283	4.15	162	4.32
Alprazolam	–	–	0.20	0.02	0.20	0.02
Amoxicillin	–	–	5.77	0.07	5.77	0.07
Benzafibrate	4.37	0.01	5.50	0.01	7.74	0.02
BPA	1.34	4×10^{-3}	0.16	10^{-3}	0.74	4×10^{-3}
Butylparaben	2.66	0.02×10^{-3}	4.38	0.14×10^{-3}	1.95	0.3×10^{-3}
Caffeine	0.12	0.6×10^{-3}	1.02	0.02	0.95	5×10^{-3}
Chlofibric acid	0.16	3×10^{-3}	3.83	0.07	1.89	0.04
Codeine	–	–	1.36	0.02	1.36	0.02
Diclofenac	0.50	0.01	0.05	10^{-3}	0.53	0.01
Ethylparaben	0.21	4×10^{-3}	–	–	0.11	2×10^{-3}
Etoricoxib	–	–	0.07	10^{-3}	0.07	10^{-3}
Ibuprofen	0.02	0.03×10^{-3}	5.26	0.01	2.13	3×10^{-3}
Indomethacin	4.93	0.10	1.44	0.03	3.00	0.06
Metformin	0.02	0.02×10^{-3}	0.04	0.04×10^{-3}	0.06	0.1×10^{-3}
Methylparaben	0.37	0.01	16.04	0.03	11.76	0.19
Naproxen	0.04	0.1×10^{-3}	0.71	10^{-3}	0.73	10^{-3}
Ofloxacin	–	–	6.07	0.30	6.07	0.02
Omeprazol	–	–	21.32	0.04	21.32	1.07
Paracetamol	0.74	10^{-3}	1.58	3×10^{-3}	1.54	3×10^{-3}
Propylparaben	0.17	3×10^{-3}	0.54	0.01	0.62	0.01
Salicylic acid	27.63	–	–	–	17.86	–
Thiamphenicol	0.68	–	180.81	–	64.19	–
Tramadol	–	–	1.22	4×10^{-3}	1.22	4×10^{-3}
Triclocarban	1.24	10^{-3}	10^{-3}	0.001×10^{-3}	0.95	10^{-3}
Triclosan	0.54	0.3×10^{-3}	0.23	0.02	0.39	0.3×10^{-3}
Warfarin	15.35	1.55	25.23	2.55	27.57	2.79
∑	73	20.5	413	78.6	292	87

The risk assessment for the individuals compounds to aquatic biota showed that only abamectin, diazinon, caffeine and tramadol might be of environmental concern while for the other contaminants the risk is negligible (<0.01). However, the exposure to all the ECs that were present in each sample makes that all samples were also of environmental concern. These results highlight the importance of examining the whole mixture of pollutants to assess the environmental risk. The risk assessment for human health makes it possible to rule out the possibility that the contaminants found, alone or in mixtures, pose a palpable risk to human health, even though concentrations of BPA in the environment are high and needs a closed monitoring. However, further research on ECs occurrence, behavior, fate and potential risks in water, sediment and vegetables are needed.

CRediT authorship contribution statement

Yolanda Picó: Methodology, Conceptualization, Resources, Investigation, Writing – original draft, Visualization. **Julian Campo:** Conceptualization, Methodology, Validation, Formal analysis, Writing – review & editing. **Ahmed H. Alfarhan:** Writing – review & editing, Supervision, Project administration. **Mohamed A. El-Sheikh:** Methodology, Validation, Resources, Writing – review & editing. **Damià Barceló:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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