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## Accumulation, sources, and health risks of phthalic acid esters (PAEs) in road dust from heavily industrialized, urban and rural areas in southern Iran

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#### ABSTRACT

In this research, a total of 51 road dust samples were collected from three districts (Asaluveh, Bushehr, and Goshoui) in the south of Iran from April to June 2022 and analyzed for the concentration of 7 phthalic acid esters (PAEs) compounds. Asaluyeh was considered as an industrial area (near gas and petrochemical industries), Bushehr as an urban area, and Goshoui as a rural area (far from pollution sources). The PAEs concentration of the street dust samples was determined using a mass detection gas chromatography (GC/MS). The mean  $\pm$  SD levels of  $\Sigma$ PAEs in samples from industrial, urban, and rural sources were 56.9  $\pm$  11.5, 18.3  $\pm$  9.64, and 5.68  $\pm$ 1.85  $\mu$ g/g, respectively. The mean concentration levels of  $\Sigma$ PAEs was significantly (P < 0.05) higher in samples from the industrial area than urban and rural areas. The mean levels of di(2-Ethylhexyl) phthalate (DEHP) in industrial, urban, and rural areas were 20.3  $\pm$  8.76, 4.59  $\pm$ 1.71, and 2.35  $\pm$  0.98 µg/g, respectively. The results of the PCA analysis indicate that the likely major sources of PAEs in the road dust in the studied areas are the application of various plasticizers in industry, solvents, chemical fertilizers, waste disposal, wastewater (e.g., agricultural, domestic, and industrial), and the use of plastic films and plastic-based irrigation pipes in greenhouses. As well as, it was found that the non-cancer risk of exposure to dust-bound PAEs was higher for children than for adults. These values were <1 for both age groups (children and adults) and the exposure of inhabitants to PAEs in road dust did not pose a notable non-cancer risk. The cancer risk from exposure to DEHP in road dust was below the standard range of

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 $10^{-6}$  in all three areas. Further studies that consider different routes of exposure to these contaminants are needed for an accurate risk assessment. Moreover, since higher PAEs level was found in industrial area, decision-makers should adopt strict strategies to control the discharging of pollution from industries to the environment and human societies.



Fig. 1. The location of study area (A) and sampling station's (B).

#### 1. Introduction

Phthalate esters (PAEs) are a group of organic pollutants mainly used in the synthesis of commercial plastic-based products as plasticizers/additives to soften plastics and improve their durability, elasticity, and flexibility [1,2]. PAEs leak into the environment during the production, use, and disposal of plastic products, considering that a strong chemical reaction is not established between these molecules and plastic polymers [3]. Toxicological studies have indicated that PAEs (as endocrine disrupting chemicals (EDCs)) have adverse effects and pose a significant risk for physiological function of endocrine hormones in living organisms [4]. For example, it has been reported that exposure to di(2-Ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and butyl benzyl phthalate (BBP) are substances that can affect the body's endocrine/metabolic system [5]. Phthalate compounds may also interact with  $\beta$ 17-estradiol by binding to the estrogen receptor and disrupting the endocrine system in women [6]. Moreover, it has been hypothesized that prolonged exposure to these toxic substances may play a role in some endocrine-related cancers, including prostate and breast cancer [7,8]. Therefore, PAEs as most ubiquitous and dangerous organic pollutants, their distribution, fate, and potential hazard to humans and the environment in various matrices is an important subject for monitoring researches around the world.

Fugitive road dust is a complex matrix with dynamic interactions with soil dust, house dust, airborne particles, and vehicle exhaust [9–12]. In Iran, a developing country, road dust has recently become a considerable environmental problem [13,14]. Fugitive road dust is a major accumulation reservoir for numerous hazardous pollutants including PAHs, heavy metals, and PAEs [15–18].

Asaluyeh represents an industrial area in the southwest of Iran, which is known worldwide as the energy capital of Iran due to its large industrial projects [19]. The Asaluyeh region is dedicated to a series of gas refineries, various petrochemical industries, petrochemical processing and packaging, rubber industries, machine repair shops, and the cement industry [20] [21]. The spread and accretion of pollutants in the environment of this region and their transport have led to a serious and permanent threat to the biodiversity cycle in this area [22]. Bushehr is also a port city located 100 km from Asaluyeh and has large agricultural land. The usage of agricultural equipment including plastics for greenhouses, application of pesticides, irrigation systems, plastic packaging/cartons, etc. can be one of the main sources of phthalic acid ester released to the environment in this region [23]. Gashouei is a rural area far from pollution sources and selected as background area. A limited number of studies have been conducted in recent years to examine toxic metals and petroleum compounds associated with road dust in the area [24,25]. PAEs pollution researches in this area focused on seawater [26], sediment [27], organic solid waste [28], landfill leachate [29] or urban runoff [30] but neglects street dust, which is also a significant pollution marker as humans are at risk through direct/indirect exposure to street dust. To the best of the authors' knowledge, there is no report on the distribution of PAEs in the street dust of Asaluyeh and Bushehr and information about the levels, possible sources, and health risk assessments of the desired contaminants is still rare and unclear. Our survey is the first record of PAEs in road dust in the south of Iran with the objectives of (I) determining the levels and spatial distribution of PAEs in the street dust in the south of Iran, (II) investigating the possible source and human health effects of the street dust in the south of Iran, and (III) evaluating the effect of different landuses (Asaluyeh, Bushehr, and Goshoui represent the industrial zone, urban area and rural district, respectively) in the distribution of PAEs in the street dust in the south of Iran.

#### 2. Materials and method

#### 2.1. Study area and sampling

The current study was carried out in the cities of Asaluyeh (27.4721°N, 52.6146°E) and Bushehr (28.9234°N, 50.8203°E) in the south of Iran, on the northern side of the Persian Gulf. It should be pointed out that in recent decades, the rapid and explosive growth of the industry in the Asaluyeh region has led to the creation of a number of large and small industrial enterprises and supporting units including industrial plants and associated warehouses [31-33]. Since there are a variety of position jobs for different groups, including graduates of different fields and other people in the Asaluyeh region, many people from different cities of Iran and other countries migrate to this city every year, which leads to overpopulation in this industrial area [33]. As a result, many problems may appear in this area, including the release of various pollutants from industries to the environment. In Bushehr City, extensive urban and agricultural operations have resulted in high production of municipal waste, excessive usage of plastics, and dumping of plastic waste in various environment (e.g., parks, and recreational areas) [34-36]. Goshoui, a rural area without traffic and highways, and is far from industrial or urban zones, was selected as control area. In this research, a total of 21 sites in the industrial city of Asaluyeh were chosen for road dust sampling. For comparison, 20 and 10 sampling sites were also selected in Bushehr City and Goshoui village (control area), respectively. One sample was collected from each selected sampling site in three districts (Asaluyeh (n = 21), Bushehr (n = 20), and Goshoui (n = 10). The spatial location of the sampling points in the defined regions is depicted in Fig. 1. The road dust samples were collected from April to June 2022 at the specified stations. Dust samples were collected by sweeping 1 m<sup>2</sup> of the road with a clean broom and non-plastic dustpan. If 1.00  $m^2$  of dust appeared insufficient for analysis, a larger area was selected for sampling. The collected dust samples were transferred to amber glass containers (pre-washed with n-hexane) and transported to the laboratory with dry ice at a temperature of 4.00 °C and stored at -20.0 °C until analysis. To reduce the possibility of contamination, no plastic instruments were utilized during the sampling and processing. All the glass instruments were submerged in a solution of H<sub>2</sub>SO<sub>4</sub> and subsequently cleaned with sodium hydroxide solution, deionized water, and acetone, respectively.

#### 2.2. Physicochemical properties of dust samples

The pH value of street dust samples was determined by the calcium chloride method by means of a pH meter (PHS–3C, China). The Olsen technique was used for measuring the total phosphorus in the dust samples [37,38]. Also, for the measurement of chloride content in the dust samples, Mohr's procedure was applied [31,39]. Details regarding measuring the total phosphorus and chloride content in the dust samples are provided in Supplementary Materials. The difference between the weight before and after drying the sample at 103–105 °C for 2.00 h was used to determine the moisture content of collected dust samples. A carbon, hydrogen, and nitrogen (CHN) analyzer (PerkinElmer, model 2400 CHN) was used for total organic carbon measurement. A particle analyzer (Mastersizer 2000 model, Malvern, United Kingdom) with particle size analysis from 0.02 to 2000  $\mu$ m was utilized to analyze the particle distribution of the dust samples. The percentage of clay and silt (<0.063 mm), the percentage of sand (particles between 0.063 and 2.00 mm), and the percentage of gravel (>2.00 mm) were then identified.

## 2.3. Preparation of samples for analysis of PAEs

The method recommended by Wang et al., was used to extract PAEs compounds from dust samples with a slight modification [40]. In the first step, 2.00 g of the dried and homogenized dust sample was weighed and placed in a clean glass centrifuge tube. Then, 6 mL of acetone/n-hexane solution in a volume ratio of 1:1 and a specified amount of a surrogate standard mixture solution (diphenyl phthalate, di-n-phenyl phthalate, and di-n-benzyl phthalate) were added. Finally, the centrifuge tubes were sealed with Teflon. The method-blank samples were also prepared using a similar methodology without the addition of dust samples. To prepare standard samples for the quality control, firstly, a mixture of acetone/n-hexane at a ratio of 1:1 v/v was procured and then a specific amount of standard solution was added. Moreover, spiked samples were made by the addition of a certain volume of the standard solution to the samples. All samples were agitated for 1 min, then the obtained mixture was sonicated for 15.0 min and centrifuged at 2000 rpm for 10.0 min to extract the PAEs. After the above steps, the organic layer that contained the target compounds was extracted with the Pasteur pipette, and the dust was extracted two additional times with 6.00 mL of acetone/n-hexane solution in a volume ratio of 1:1 v/v. Finally, all extracts were combined and activated copper was added to desulfurize the samples. The resulting mixture was dried over anhydrous sodium sulfate and concentrated under a stream of 0.6 mL nitrogen. Mass detection gas chromatography (GC/MS) was then used to analyze the PAEs value of the samples by adding an internal standard solution (phenanthrene-d10 and chrysene-d12) to the resulting mixture.

#### 2.4. Instrumental analysis

All samples were analyzed by GC/MS (Agilent 7890 GC - 5975MSD) in electron impact mode and selective ion monitoring mode using a capillary column (DB-5 (30 m  $\times$  0.25 mm  $\times$  0.25 mm fused-silica capillary column) for chromatographic separation. Detailed GC/MS parameters are provided in Table S1. High-purity helium (99.9999 %) was used as the carrier gas with a constant flow rate of 1.20 mL/min. The temperature program included several steps. The column temperature was reached at 50.0 °C for 1.00 min, then increased to 200 °C at a ramp of 15.0°/min and maintained at this temperature for 1.00 min. The temperature was then increased to 280 °C at a rate of 8.00°/min and held at this temperature for 3 min. A 2  $\mu$ L sample was injected into the system at an injection point temperature of 250 °C without pulsing or splitting. The temperature of the transfer line in the column was set at 280 °C. The PAEs concentration in the dust was calculated based on the dry weight.

## 2.5. Quality control and quality assurance

Due to the fact that PAEs are ubiquitous contaminants in the laboratory (found in solvents, plastic consumables, suspended particles/settled dust), great attempts were performed to minimize the background levels of these pollutants, which was also in agreement with the points given by other valid researches [41,42]. To avoid possible contamination, plastic materials were not used in sample preparation and processing. Instead, glassware was submerged in a prepared potassium chromate/sulfuric acid solution (K<sub>2</sub>CrO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>) and rinsed with deionized water, NaOH, and acetone. Then it was baked at 400 °C (for 24 h) and kept sealed with glass stoppers and wrapped in aluminum foil in a furnace (to avoid any organic pollution by indoor air, known to be a main source of PAEs in glassware). Finally, the glassware was rinsed with dichloromethane before utilize. The equipment' was calibrated every day with calibration standards. The method-blank samples without street dust, were processed in every 10 samples to determine if the process was contaminated. Five-point standard calibration curves were utilized with the regression coefficients ( $R^2$ ) > 0.999. Moreover, spike samples with concentrations ranging from 20 ng mL $^{-1}$  to 1000 ng mL $^{-1}$  were analyzed with internal standards to assess the effects of the matrix. The recoveries for the diisophenyl phthalate standard were 84.7  $\pm$  8.70 %, for di-n-phenyl phthalate 76.3  $\pm$  4.10 %, and for di-n-benzyl phthalate  $103 \pm 9.40$  %. The limit of detection (LOD), the limit of quantitation (LOQ), and the mean recoveries of the target PAEs are listed in Table S2. The recoveries for the phthalate composition in spike samples were 66.4–109 %, with a standard deviation of less than 10.0 %. For some compounds, very low values were detected in the blank samples, which were accordingly subtracted from the values recorded in the samples. About 10 % of the gathered dust samples were repeated, and the relative standard deviation (RSD) obtained to reflect the repeatability of analysis was <10 %.

#### 2.6. Human health risk assessment

Human exposure to PAEs bonded-road dusts occurs via three main pathways including direct ingestion of dust particles ( $DI_{ing}$ ), inhalation of dust particles through the mouth and nose ( $DI_{inh}$ ), and dermal absorption ( $DI_{dermal}$ ). Daily intake (DI, mg/kg-day) for each intake pathway can be computed using Eqs. (1)–(3). For carcinogenic compounds, the lifetime average daily dose (LADD) was also used to assess cancer risk (Eq. (4)) [40]:

$$DI_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times CF$$
<sup>(1)</sup>

$$DI_{inh} = C \times \frac{InhR \times EF \times ED}{BW \times AT \times PEF}$$
(2)

$$DI_{der} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF$$
(3)

$$LADD = C \times \frac{EF}{AT} \times \left(\frac{CR_{Children} \times ED_{Children}}{BW_{Children}} + \frac{CR_{Adults} \times ED_{Adults}}{BW_{Adults}}\right)$$
(4)

The parameters used in these equations are listed in Table 1. The values for concentration (C) and exposure factor (EF) are used for estimating the maximum acceptable exposure. The upper limit is the 95.0 % confidence interval for the average. Since the concentration of PAEs in dust samples is approximated to the log-normal distribution, 95.0 % UCL is calculated by Eq. (5)) [40].

$$C_{95\%UCL} = \left\{ \overline{X} + 0.5 + s^2 + \frac{s \times H}{\sqrt{n-1}} \right\}$$
(5)

Where x is the arithmetic mean of the log-transformed data, s is the standard deviation of the log-transformed data, H is the H statistic, and n is the number of samples.

The computed dose of each PAEs and each exposure pathway were divided by the associated reference dose (RfD, mg/kg/day) [40], and a non-cancer risk factor (HQ) was calculated. The LADD calculated dose was multiplied by its slope factor (SF,  $(mg/kg/day)^{-1}$ ) to estimate the cancer risk. The hazard index was also determined by totaling the HQs obtained for each combination of PAEs (Eq. (6)). If the HI value was >1.00, there is a possibility of non-carcinogenic effects, which if the HI value for cancer risk is within the threshold range (10<sup>-4</sup>-10<sup>-6</sup>), the cancer risk is acceptable [40]:

$$HQ = \frac{DI}{RfD}, HI = \sum HQ$$
(6)

#### 2.7. Possible sources of PAEs

The determination of different PAEs congeners in peripheral matrices can identify possible PAEs contamination sources. In this context, principal component analysis (PCA) was applied as a statistical technique to investigate the possible sources of PAEs in the dust of the defined study areas. This mathematical analysis examined the association of observed variables by reducing the dimensions of the original datasets and principal components. In our previous study, this methodology was used to identify possible sources of PAEs and polychlorinated biphenyls (PCBs) in the coastal sediments of Asaluyeh [48]. Moreover, several researchers have made use of the PCA technique to analyze the content of various pollutants including bisphenol A, PAHs, etc. [49,50]. In this study, varimax normalized rotation was used to maximize the values of loading factors to minimize ambiguity for each component concerning each rotated principal component. Given that, in PCA analysis, the number of samples should be n > 30 + (V + 3)/2 (n number of samples and V number of variables), the results of all samples were combined.

## Table 1

ment.
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Parameters	Unit	Children	Adults	References
Ingestion rate (IngR)	mg/day	200	100	[43,44]
Exposure frequency (EF)	day/year	180		[45]
Exposure duration (ED)	Year	6	24	[43]
Body weight (BW)	Kg	15	58.6	[43,44,46]
Average time (AT)				
Non-carcinogen	Day	$ED \times 365$		[45]
Carcinogen	Day	70  imes 365		[45]
Inhalation rate (InhR)	m <sup>3</sup> /day	7.6	12.8	[46]
Particle emission factor (PEF)	m <sup>3</sup> /day	$1.36 imes10^9$		[43,44]
Skin surface area (SA)	cm <sup>2</sup>	1150	2145	[46]
Skin adherence factor (AF)	mg/Cm <sup>2</sup>	0.2	0.7	[43,44]
Adsorption factor (ABS)	Unitless	1		[47]

#### 2.8. Statistical analysis

The normality of the data was checked with the Shapiro-Wilk test before analyzing the samples. The significance of the association between the variables was evaluated with Fisher F-test. The significance of the correlation between PAEs compounds was also tested by Pearson correlation analysis. The level of significance of the statistical tests was considered as 0.05 and 0.01 (confidence levels of 95 and 99 %). These analyses were conducted using the statistical package SPSS version 19.0 (SPSS Inc.). GIS software was used as a suitable tool for mapping the dispersion of pollutants. ArcMap (version 10.2) also was used to interrogate contaminants in the area between sampling locations. Details regarding the spatial distribution of PAEs in street dust using GIS-ArcMAP are provided in Supplementary Materials.

## 3. Results and discussion

## 3.1. Physicochemical properties of dust samples

The physicochemical characteristics results of street dust samples that were collected in Asaluyeh, Bushehr, and Goshoui are presented in Fig. S1 and Table S3. As can be seen from Fig. S1, the silt fraction (particle sizes <0.063 mm) in the industrial, urban, and rural areas ranged from 12.2 to 27.3 % (mean  $\pm$  standard deviation (SD) = 19.3  $\pm$  3.70 %), 5.48–18.3 % (mean  $\pm$  SD = 11.6  $\pm$  3.60 %), and 2.78–8.34 % (mean  $\pm$  SD = 5.60  $\pm$  2.24 %), respectively. The proportion of sand (0.063–2 mm) in the industrial, urban, and rural areas was 63.2–82.1 % (mean  $\pm$  SD = 69.8  $\pm$  4.50 %), 64.5–86.3 % (mean  $\pm$  SD = 74.9  $\pm$  5.40 %), and 60.1–89.1 % (mean  $\pm$  SD = 75.8  $\pm$  6.9 %), respectively. Gravel fractions (particle size >2 mm) in industrial, urban, and rural areas ranged from 2.62 to 18.5 % (mean  $\pm$  SD = 10.7  $\pm$  4.60 %), 5.49–22.2 % (mean  $\pm$  SD = 13.3  $\pm$  4.70 %), and 7.3–29.7 % (mean  $\pm$  SD = 18.4  $\pm$  5.60 %), respectively. These data indicate that the most predominant dust texture in all defined study areas was sand. In a study in Ostrava, it was also found that the road dust collected in urban areas is predominantly sand [51].

Table S3 shows that the pH value of the road dust samples in the industrial area, urban and rural areas were 5.68-7.66 (mean  $\pm$  SD =  $6.90 \pm 0.70$ ), 6.78-7.89 (mean  $\pm$  SD =  $7.19 \pm 0.26$ ), and 7.09-8.39 (mean  $\pm$  SD =  $7.70 \pm 0.41$ ), respectively. The pH of the dust samples in the industrial area was in the slightly to neutrally acidic category and in the weak to neutral range in the urban and rural areas. The lower pH in industrial areas can be explained by the fact that the waste contains high concentrations of organic matter [52]. The decomposition of organic matter produces humic acids and the pH value is decreased [32]. Indeed, decomposition of organic matter in soil/dust is primarily carried out by microorganisms like bacteria and fungi and they release various byproducts, including organic acids [53]. These organic acids are formed as a result of the breakdown of complex organic compounds into simpler molecules. Common organic acids produced in this process include acetic acid, citric acid, and humic acids [54]. Also, the higher pH in dust samples from rural areas compared to other areas suggests that human activities including discharge of acidic industrial wastes, usage of fertilizers and chemical modifiers in agricultural fields and urban parks, use of insecticides against pests, fish farming, etc. may cause acidification of soil environment in these areas [32,55]. The moisture content results in the dust samples gathered in areas with different land uses are also given in Table S3. The moisture content in the industrial, urban, and rural areas was 4.00-8.00 % (mean  $\pm$  SD =  $6.30 \pm 0.90$  %), 6.00-9.00 % (mean  $\pm$  SD =  $7.35 \pm 0.85$  %), and 4.00-7.00 % (mean  $\pm$  SD =  $6.00 \pm 0.89$  %), respectively.

The TOC level in the dust samples collected from defined areas is also displayed in Table S3. The TOC content in the industrial, urban, and rural areas was 1.24-3.76 % (mean  $\pm$  SD =  $2.50 \pm 0.92$  %), 0.73-2.93 % (mean  $\pm$  SD =  $1.60 \pm 0.61$  %), and 0.23-1.41 % (mean  $\pm$  SD =  $0.53 \pm 0.42$  %), respectively. Accordingly, the order of TOC content in the regions was including the following: Industrial area » Urban area » Rural area. Among the studied sites, the maximum TOC content was detected at the stations located in the industrial area. Such stations received a high quantity of industrial waste, which is enriched in organic matter [32]. The results illustrate that human activities are the main source of dust carbon and can have a significant impact on the carbon cycling processes in the environment, which strongly affecting the ecology of the Earth [56,57].

The electrical conductivity (EC) value in the industrial, urban, and rural areas ranged from 1.66 to 3.74 ds/m (mean  $\pm$  SD = 2.06  $\pm$  0.41 ds/m), 1.29–2.32 ds/m (mean  $\pm$  SD = 1.81  $\pm$  0.23 ds/m), and 0.14–0.58 ds/m (mean  $\pm$  SD = 0.41  $\pm$  0.15 ds/m), respectively (Table S3). The EC values determined show that the road dust from the cities of Asalouye and Bushehr is considered non-saline. Moreover, the EC content was higher in dust samples from industrial and urban areas than in rural areas. This difference may be attributed to chemical compounds and salts in industrial and urban wastes and the use of chemical fertilizers on agricultural land [55, 58].

The amount of phosphorus in road dust in industrial, urban and rural areas ranged from 96.0 to 404  $\mu$ g/g (mean  $\pm$  SD = 234  $\pm$  93.0  $\mu$ g/g), 338–681  $\mu$ g/g (mean  $\pm$  SD = 412  $\pm$  84.5  $\mu$ g/g) and 63.0–135  $\mu$ g/g (mean  $\pm$  SD = 82.9  $\pm$  25.5  $\mu$ g/g), respectively (Table S3). Also, the phosphorus levels in street dust in defined areas was as follows: urban > industrial > rural. High phosphorus concentrations in dust samples from urban areas can be related to the application of organic phosphorus pesticides in urban park soils and agricultural land [59]. Moreover, salinity is a major factor in the dispersion of phosphorus in environmental samples, and as salinity increases, the amount of phosphorus absorbed by the surface of dust particles rises, thereby decreasing the quantity of phosphorus in the dust [60]. One of the factors responsible for the increased desorption is that as the salt content increases, the ionic strength also increases. As a consequence, other anions including hydroxyl, fluoride, sulfate, and tetrahydroxyborate are in competition with phosphorus for active sites on the surface of the dust particles and release phosphorus [61]. In addition, sulfide ions also play an important role in releasing phosphorus from street dust, causing the dissolution of the FeP complex, and the formation of the mineral FeS<sub>2</sub> [62]. With these explanations, lower phosphorus amounts in the samples collected from industrial areas than urban areas can be related to the high salinity of dust in industrial areas compared to urban areas.

Table 2	
Individual level ( $\mu g/g$ ) of PAEs in street dust collected from studied regions.	

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-	IndS						UrbS							RurS				
Parameters	Min	Max	Med	$\begin{array}{l} \text{Mean} \pm \\ \text{SD} \end{array}$	DF	Comparison with UrbS	Comparison with RurS	Min	Max	Med	$\begin{array}{l} \text{Mean} \pm \\ \text{SD} \end{array}$	DF	Comparison with RurS	Min	Max	Med	$\begin{array}{l} \text{Mean} \pm \\ \text{SD} \end{array}$	DF
DMP	3.02	7.91	4.15	$\begin{array}{c} \textbf{4.42} \pm \\ \textbf{1.18} \end{array}$	100	P < 0.05	P < 0.05	< LOD	3.90	1.23	$\begin{array}{c} 1.23 \pm \\ 0.79 \end{array}$	95.0	P < 0.05	< LOD	0.40	0.17	$\begin{array}{c} \textbf{0.20} \pm \\ \textbf{0.13} \end{array}$	80.0
DEP	< LOD	6.65	5.28	$\begin{array}{c} 5.21 \\ \pm \\ 0.93 \end{array}$	90.5	P < 0.05	P < 0.05	< LOD	6.14	1.97	$\begin{array}{c} 1.94 \pm \\ 1.21 \end{array}$	95.0	P < 0.05	< LOD	1.35	0.51	$\begin{array}{c} \textbf{0.57} \pm \\ \textbf{0.28} \end{array}$	90.0
DBP	< LOD	12.8	10.97	$\begin{array}{c} 10.4 \pm \\ 1.78 \end{array}$	95.2	P < 0.05	P < 0.05	< LOD	12.5	3.56	$\begin{array}{c} 3.65 \pm \\ 2.35 \end{array}$	90.0	P < 0.05	< LOD	1.93	0.97	$\begin{array}{c} 1.04 \pm \\ 0.35 \end{array}$	90.0
BBP	5.55	10.2	8.73	$\begin{array}{c} \textbf{8.19} \pm \\ \textbf{1.52} \end{array}$	100	P < 0.05	P < 0.05	< LOD	8.79	3.25	$\begin{array}{c} 3.08 \pm \\ 1.67 \end{array}$	95.0	P < 0.05	< LOD	2.42	0.73	$\begin{array}{c} \textbf{1.24} \pm \\ \textbf{0.77} \end{array}$	70.0
DEHP	8.57	37.6	18.64	$\begin{array}{c} 20.3 \pm \\ 8.76 \end{array}$	100	P < 0.05	P < 0.05	3.31	11.5	4.17	$\begin{array}{c} \textbf{4.59} \pm \\ \textbf{1.71} \end{array}$	100	P < 0.05	1.29	4.11	1.95	$\begin{array}{c}\textbf{2.35} \pm \\ \textbf{0.98} \end{array}$	100
DnOP	< LOD	9.10	5.97	$6.21~\pm$ 1.54	95.2	P < 0.05	P < 0.05	< LOD	7.73	2.61	$\begin{array}{c} \textbf{2.67} \pm \\ \textbf{1.45} \end{array}$	90.0	P < 0.05	< LOD	1.22	0.92	$\begin{array}{c} \textbf{0.93} \pm \\ \textbf{0.18} \end{array}$	90.0
DiBP	< LOD	4.14	2.42	$\begin{array}{c}\textbf{2.67} \pm \\ \textbf{0.85} \end{array}$	90.5	P < 0.05	P < 0.05	< LOD	3.65	1.28	$\begin{array}{c} 1.18 \ \pm \\ 0.77 \end{array}$	90.0	P < 0.05	< LOD	0.40	0.35	$\begin{array}{c}\textbf{0.35} \pm \\ \textbf{0.04} \end{array}$	40.0
∑7PAEs	37.8	82.5	54.01	$\begin{array}{c} 56.9 \pm \\ 11.5 \end{array}$	-	P < 0.05	P < 0.05	9.00	54.2	17.94	$\begin{array}{c} 18.3 \pm \\ 9.64 \end{array}$	-	P < 0.05	3.72	9.24	4.55	$\begin{array}{c} \textbf{5.68} \pm \\ \textbf{1.85} \end{array}$	-

#### 3.2. Concentrations of PAEs in street dust samples

The corresponding PAEs concentration <u>levels</u> in the road dust samples from the three areas are listed in Table 2, and the spatial distribution of total PAEs values is presented in Fig. 2. As shown, PAEs were identified in all samples, indicating that these chemicals are the widespread pollutants in the study areas. The  $\Sigma$ PAEs concentration levels in the industrial, urban, and rural areas were 37.8–82.5 µg/g (56.9 ± 11.5 µg/g), 9.00–54.2 µg/g (18.3 ± 9.64 µg/g), and 3.72–9.24 µg/g (5.68 ± 1.85 µg/g), respectively. Most PAEs pollution researches focused on soil, sediment, or indoors but neglects street dust, which is also a significant pollution marker as humans, particularly in megacities, are at risk through direct/indirect exposure to street dust [63,64].

The mean concentrations level of  $\Sigma$ PAEs in dust samples from industrial and urban areas was significantly (P < 0.05) higher than rural areas. This implies that PAEs levels are strongly affected by human activities and the continuous release of waste, industrial effluents, and atmospheric emissions from defined areas [65]. The numerous human activities increase the release of PAEs during the stages of synthesis, use, and disposal of plastic waste into street dust PAEs concentrations in dust from these areas [3] [64]. Elevated PAEs levels in samples from industrial environments can be induced by wastes and industrial effluents discharged from large and small industries including petrochemical, gas refining, electronic/electrical component factories, chemical plants, plastic pipe manufacturing, packaging industries, etc. [66,67]. Wang et al. [68] reported that the PAEs content in industrial areas are greater than that in urban environments, which was consistent with the results of the present study.

The high PAEs levels in urban locations can also be attributed to the various urban activities including construction, building greenhouses for vegetables, fruit packing, and pesticide application [69]. The urban environments also receive pollution from the discharge of wastewater from municipal sewage treatment plants [70]. Irrigation of the soil by contaminated water with municipal and industrial wastewater leads to a significant increase in toxic pollutants including heavy metals, PAEs, and polychlorinated biphenyls (PCBs) even after treatment [71]. Confirming these findings, a study conducted in China reported that plastic film usage, irrigation with wastewater, and chemical fertilizers were the major sources of PAEs in agricultural soils [72]. High concentrations of PAEs in a street dust sample collected from urban areas could also be attributed to the commercial activity in intense areas in the vicinity of the Bushehr traditional market [73]. The obtained results demonstrate that PAEs have a similar transport pathway including other pollutants, including heavy metals, PCBs, pesticides, and polycyclic aromatic hydrocarbons (PAHs) generated by human activities. Eventually, they are transferred and accumulate in soils, beach sediments, and road dust in the form of atmospheric emissions, effluents, and wastes [74–77]. Over the past few years, various industries such as the agricultural packing industry, fish and shrimp farming, textile industry, chemical industry, cement and stone factory, electronics production, and shipping have been established in this area. Wastes and effluents leaching from these industries could be potential sources for the emission of various environmental



Fig. 2. The spatial distribution of  $\sum$ PAEs in Asaluyeh (A), Bushehr (B) and Gashoei (C) areas.

contaminants including PAEs [75]. Analysis of the composition (ester-phthalate species profiles) and individual concentrations of PAEs compounds can help determine the source, fate, and transport of PAEs in the environment.

Of the seven phthalate compounds examined, DEHP had the highest detection frequency (DF) and levels in all regions (Table 2). The DF of this compound was 100 %, which means that it was detected in the samples of all locations. The mean concentrations of this compound in industrial, urban, and rural areas were  $20.32 \pm 8.78$ ,  $4.59 \pm 1.71$ , and  $2.35 \pm 0.98 \,\mu\text{g/g}$ , respectively. DEHP contributes 35.4, 25.1 and 35.2 % of PAEs in street dust samples collected from industrial, urban, and rural areas, respectively (Fig. S2). After this compound, the highest concentrations are corresponded to di-n-butyl phthalate (DnBP) and BBP. The DF of DnBP in industrial, urban, and rural sampling sites was 95.23 %, 90 %, and 90 %, and BBP composition was 100 %, 70 %, and 90 %, respectively. The DnBP content in the industrial, urban, and rural areas was  $10.41 \pm 1.78$ ,  $3.65 \pm 2.35$ , and  $1.04 \pm 0.35 \mu g/g$ , respectively. Also, the BBP level in the industrial, urban, and rural areas was  $8.19 \pm 1.52$ ,  $3.08 \pm 1.67$ , and  $1.24 \pm 0.77 \mu$ g/g, respectively. This distribution pattern is in accordance with previous studies reporting the predominant PAEs compounds distributed in various environmental matrices [78, 79]. DEHP was the most abundant PAEs congener and represents about 50 % of PAEs production in various countries including Canada, China, Malaysia, and Europe [79-82]. The high levels of these compounds can be associated with their high consumption and usage as plastic additives, their strong absorption by dust particles, and their low degradability [83]. Compounds containing long alkylene or branched structures (e.g., DEHP, BBP, and di-n-octyl phthalate (DnOP)) are widely utilized as plasticizers in the polymer industry to improve the flexibility and handling properties of plastic products [84]. DEHP constitutes about 40 % of PVC products, including building products, automotive parts, food packaging, etc., and is therefore widely used in industry, commerce, and even households [68,85].

The PAEs concentration detected in present study was compared with the levels reported in other locations in the literature (Table 3). DEHP had the maximum level among the quantified PAEs compounds for all the researches. The level of DEHP was observed as  $0.15-22.47 \ \mu g/g$  in Kocaeli city in Turkey [86],  $6.00-363 \ \mu g/g$  in Kaohsiung city in Taiwan [87],  $0.432-451 \ \mu g/g$  across China [88],  $0.66-163 \ \mu g/g$  in Xi'an city in China [44],  $7.88-372 \ \mu g/g$  across Hong Kong [89],  $125-779 \ \mu g/g$  in Guangzhou city in China [90], and  $0.128-4.82 \ \mu g/g$  in Novi Sad city in Serbia [91]. The DEHP concentrations in China, Taiwan and Hong Kong were much higher than 37.6  $\ \mu g/g$  measured in our study. The DEHP concentration in current study was higher than level reported for Kocaeli city in Turkey [86] and far higher that level found in Novi Sad in Serbia [91]. These differences can be explained by differences in population intensity and sources contributing to PAEs compounds, therfore geographical/cultural dependent pollution control strategies are needed.

## 3.3. Correlation between PAEs and physicochemical properties of street dust

The results of the correlation between the content of PAEs compounds and the physicochemical features of the dust, including particle size (clay, silt, and sand), moisture, TOC, pH, EC, and total phosphorus, were calculated using the Spearman correlation test and are listed in Table 4. The analytical data presented that the fine fraction of dust particles have a significant positive relationship with TOC, moisture content, and  $\Sigma$ PAEs. In contrast, there was a negative association between the coarse fraction of road dust and TOC, moisture content, and  $\Sigma$ PAEs. These observations may be attributable to the high specific surface area of the fine particles, resulting in more adsorption sites on the surface of the particles [27,92,93]. Consequently, organic pollutant molecules are more easily and more strongly absorbed by the surface of these particles, so their concentration in the dust increases [36]. In addition, the compounds of DEHP, DnBP, BBP, and DniP were significantly associated with  $\Sigma$ PAEs content. This implies that these compounds are the most important congeners and representative PAEs in the dust samples of the studied areas. However, DEHP showed the strongest association with  $\Sigma$ PAEs, suggesting that this compound could be used as a convenient marker for  $\Sigma$ PAEs in dust samples [32,94]. Spearman analyses indicated that road dust features (e.g., particle size, TOC, and moisture) were not significantly correlated with concentrations of low molecular weight PAEs (such as dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DiBP), and DnBP). A significant correlation, however, was observed between high molecular weight species of PAEs and a branched structure like DEHP. Moreover, the association of  $\Sigma$ PAEs with TOC values was more significant than the association of  $\Sigma$ PAEs with particle size, suggesting that the distribution of PAEs compounds is more influenced by the organic content of the dust samples than by

## Table 3

The concentration ranges of PAEs	(µg/g)	in the street	dust reported	in studies
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Location	Sample size	DMP	DEP	DBP	BBP	DEHP	DnOP	DiBP	∑7PAEs
Iran (this study)	51	< LOD -7.91	< LOD $-$ 6.65	< LOD – 12.8	< LOD $-$ 10.2	< LOD - 37.6	< LOD $-$ 9.10	< LOD - 4.14	9.00-82.5
Turkey [86]	90	< LOD $-$ 0.48	< LOD $-$ 0.21	0.02-0.93	< LOD $-$ 9.65	0.15-22.47	0.03-1.33	-	0.16-36.8
Taiwan [87]	52	< LOD	< LOD $-1.00$	4.00-22.0	< LOD - 2.00	6.00–363	< LOD $-$ 7.00	-	13.0-394
China [88]	203	0.12 - 12.8	0.12-3.47	0.18-239	0.003-6.13	0.432-451	< LOD $-10.7$	0.55-78.4	0.47-499
China [40]	58	< LOD $-$ 4.76	< LOD $-$ 9.17	0.03-183	< LOD - 5.92	0.66-163	0.02-5.41	-	0.87-253
Hong Kong	30	0.01 - 2.28	0.05 - 13.6	< LOD $-$	0.37-19.7	7.88-372	0.04-3.67	< LOD $-$	1.70-303
[89]				5.63				1.36	
China [89]	90	< LOD $-$ 5.62	0.02 - 3.88	0.09-29.3	< LOD - 21.8	0.96-833	0.01-10.5	0.09-13.0	1.75-869
China [90]	60	0.04 - 0.122	0.027-0.117	7.77–59.5	1.14-10.7	125-779	0.914-3.73	-	135-853
Serbia [91]	30	0.004-0.021	0.003-0.017	0.02-0.213	0.0002 - 0.351	0.128 - 4.82	0.001 - 0.035	-	0.156-5.46

Table 4 Spearman correlation analysis between the physiochemical parameters and phthalate esters in street dust samples collected from studied areas.

Parameters	pН	EC	Moisture	TOC	TP	Gravel	Clay + silt	DMP	DEP	DBP	BBP	DEHP	DnOP	DiBP	ΣPAEs
pН	1.00														
EC	0.21	1.00													
Moisture	-0.35*	0.21	1.00												
TOC	-0.53**	0.19	0.71**	1.00											
TP	-0.65**	0.11	0.18	0.27*	1.00										
Gravel	-0.13	0.23	-0.32*	-0.53**	0.16	1.00									
Clay + silt	0.13	-0.23	0.32*	0.53**	-0.16	-1.00	1.00								
DMP	0.09	0.18	0.11	0.23	0.08	-0.09	0.09	1.00							
DEP	0.11	0.11	0.19	0.26	0.23	0.13	-0.13	0.65**	1.00						
DBP	-0.17	0.09	0.26	0.15	-0.08	0.11	-0.11	0.42**	0.32*	1.00					
BBP	0.13	-0.07	0.18	0.24	0.06	-0.34*	0.34*	0.40**	0.19	0.12	1.00				
DEHP	0.09	0.12	0.59**	0.79**	0.16	-0.44**	0.44**	0.77**	-0.11	-0.13	0.31*	1.00			
DnOP	0.11	0.10	0.32*	0.51**	0.15	-0.33*	0.33*	0.59**	0.13	0.29**	0.43**	0.31*	1.00		
DiBP	-0.13	0.07	0.14	0.18	0.22	0.09	-0.09	0.34*	0.41**	0.12	0.35*	0.51**	-0.05	1.00	
ΣPAEs	0.08	-0.12	0.42**	0.67**	0.21	-0.25*	0.26*	0.56**	0.46**	0.67**	0.64**	0.87**	0.24	0.14	1.00

\* Correlation is significant at p < 0.05 (two-tailed). \*\* Correlation is significant at p < 0.01 (two-tailed).

particle size. A reasonable reason for this finding is that PAEs are a group of hydrophobic compounds that are quickly absorbed and accumulate in the organic part of environmental samples [68]. But a negative significant relationship was found between pH and total phosphorus and TOC, which indicates that low pH reduces anoxic decomposition rates and; thus promotes the accumulation of total phosphorus and organic phosphorus in environmental samples [95]. Moreover, no significant relationship was observed between pH, EC and ΣPAEs, indicating that pH and EC are not crucial parameters for the distribution of PAEs compounds in road dust [96].

#### 3.4. Determining the possible sources of PAEs

The principal component analysis (PCA) has been applied as a statistical method to identify the possible sources of PAEs in road dust samples in the studied areas. Two principal components were extracted to simplify the observations. Their total variance was 38.2 and 7.21 %, respectively (Fig. 3). The first component (C1) is mostly related to DEHP, BBP, and DnOP, implying that these PAEs compounds may have a common source. The other component (C<sub>2</sub>) is related to DnBP, DiBP, DMP, and DEP, which may have a common origin. The compounds in C<sub>1</sub> are a range of long-chain compounds, suggesting that they are originated from plasticizers that are utilized in various chemical industries [97,98]. C<sub>2</sub> compounds also comprised low molecular weight compounds. These compounds originate mainly from the usage of pesticides, chemical fertilizers, and irrigation of agricultural fields with municipal wastewater and industrial effluents [75,99]. As mentioned earlier, many large and small industries exist in the study areas, which use a variety of solvents and plasticizers in the manufacture of their products [100]. Various plastic films, polymeric irrigation pipes, nylons for greenhouses, etc. are also increasing usage in agricultural fields in this area. These may be PAEs sources in the road dust in Asaluyeh and Bushehr ports. The results of the current study agree well with the literature that reported that PAEs levels in agricultural soils are significantly related to the consumption of plastic films in agriculture [67,72]. Today, direct release of industrial wastes and effluents into the environment has been decreased by a number of official laws and regulations issued by responsible organizations. However, PAEs compounds contained in plastic products and other phthalate-containing materials can reach into the air, soil, water, and other environmental media, and then enter the environment through industrial and municipal wastewater, surface flooding, and dust deposits in industry and agricultural land. Surface and municipal runoff are the primary sources of PAEs leaching into the environment of some areas and street dust [101]. Therefore, in order to control the spread of PAEs in these areas, local authorities should take effective measures to protect environmental quality and reduce PAEs pollution.

#### 3.5. Risk assessment for PAEs exposure bonded with street dust particles

The results of the risk assessment of exposure to PAEs compounds bonded to road dust in the studied industrial, urban and rural areas are shown in Table 5. The daily intake (DI) of these contaminants is reported for both age groups (adults and children) through the three pathways including ingestion, inhalation, and dermal exposure. As shown in Table 5, the main ways of human exposure to PAEs bound to road dust are ingestion and dermal route of the dust particles, while exposure to these pollutants by inhalation was neglected. Similar results were reported for exposure to heavy metals and polycyclic aromatic hydrocarbons (PAHs) bound in road/ urban dust [102,103]. Both ingested and inhaled DI levels were higher in children than in adults, possibly related to the fact that children engage in more hand-to-mouth activities than adults. Absorption of PAEs through the skin was lower in children than in adults, possibly due to the larger skin surface area of adults compared with children [104]. Ingestion of pathogenic DIE PAEs for children and adults was lower than the U.S. EPA-recommended oral reference dose (RfD). The U.S.EPA recommended oral reference dose for daily ingestion of DEHP, BBP, DnBP, and DEP is 0.02, 0.2, 0.1, and 0.8 mg/kg-day, respectively [105]. Since there are no inhalation reference doses and dermal absorption for PAEs compounds and no oral reference doses for DMP and DnOP, the non-cancer risk for DEP, BBP, DnBP, and DEHP was analyzed by dust particle ingestion only [32]. According to the HI values in Table 5, the non-cancer risk declined in the order DEHP > DnBP » BBP > DEP, which is in agreement with the fact that DnBP and DEHP were the



Fig. 3. Factor loadings of PAEs congeners on two principal components.

	PAEs	95 %	RfD	SF oral	DI <sub>ing</sub>		DI <sub>inh</sub>		DI <sub>der</sub>		LADD	HI		Cancer
Areas		UCL	oral		Children	Adults	Children	Adults	Children	Adults	-	Children	Adults	Risk
Industrial Area	DMP	4.19	-	-	$2.79  imes 10^{-5}$	$3.57  imes 10^{-6}$	$7.81  imes 10^{-10}$	$3.37  imes 10^{-10}$	$3.21 \times 10^{-5}$	$5.36 imes$ $10^{-5}$	-	-	-	-
	DEP	4.95	0.8	-	$3.23 \times 10^{-5}$	$4.15  imes 10^{-6}$	$9.08 imes$ $10^{-10}$	$3.91 \times 10^{-10}$	$3.73 \times 10^{-5}$	$6.23  imes 10^{-5}$	_	$8.71 \times 10^{-5}$	$8.31 imes$ $10^{-5}$	-
	BBP-noncancer	7.78	0.2	-	$\begin{array}{c} 5.12 \times \\ 10^{-5} \end{array}$	$6.54 imes$ $10^{-6}$	$1.42\times10^{-9}$	$6.16  imes 10^{-10}$	$5.88 \times 10^{-5}$	$9.84 imes$ $10^{-5}$	-	$\frac{5.50}{10^{-4}}\times$	$\frac{5.25}{10^{-4}}\times$	-
	BBP-cancer	7.78	-	-	_	-	-	_	-	-	-	-	_	-
	DBP	9.88	0.1	-	$6.55  imes 10^{-5}$	$\frac{8.40}{10^{-6}}\times$	$\textbf{1.83}\times \textbf{10}^{-9}$	$7.90\times \\ 10^{-10}$	$7.55 \times 10^{-5}$	$\frac{1.26}{10^{-4}}\times$	-	$1.41 imes$ $10^{-3}$	$\frac{1.34}{10^{-3}}\times$	-
	DEHP- noncancer	19.30	0.02	-	$1.30 imes$ $10^{-4}$	$1.66 \times 10^{-5}$	$\textbf{3.62}\times 10^{-9}$	$1.56 \times 10^{-9}$	$1.49 \times 10^{-5}$	$2.48  imes 10^{-5}$	_	$1.39 \times 10^{-2}$	$1.32 imes$ $10^{-2}$	-
	DEHP-cancer	19.30	-	0.014	-	-	-	-	-	-	$rac{1.64}{10^{-5}} imes$	-	-	$2.31 imes 10^{-7}$
	DnOP	5.89	-	-	$3.87 \times 10^{-5}$	$4.95 imes$ $10^{-6}$	$1.08\times10^{-9}$	$4.66 \times 10^{-10}$	$4.45 \times 10^{-5}$	$7.44 \times 10^{-5}$	-	-	-	-
	DiBP	2.54	-	-	$4.73 \times 10^{-5}$	$6.05 \times 10^{-6}$	$1.57\times10^{-9}$	$6.75 \times 10^{-10}$	5.44 × 10 <sup>-5</sup>	$9.08 \times 10^{-5}$	-	-	-	-
Urban Area	DMP	1.17	-	-	$7.80 \times 10^{-5}$	$9.98 \times 10^{-7}$	$2.18  imes 10^{-10}$	$9.39 \times 10^{-11}$	8.96 × 10 <sup>-5</sup>	$1.50 \times 10^{-5}$	-	-	-	-
	DEP	1.84	0.8	-	$1.23 \times 10^{-5}$	$1.57 \times 10^{-6}$	$3.44 \times 10^{-10}$	$1.48 \times 10^{-10}$	$1.41 \times 10^{-5}$	$2.36 \times 10^{-5}$	-	$9.68 \times 10^{-6}$	$9.23 \times 10^{-6}$	-
	BBP-noncancer	2.79	0.2	-	$1.93 \times 10^{-5}$	$2.47 \times 10^{-6}$	$5.37 \times 10^{-10}$	$2.32 \times 10^{-10}$	$2.22 \times 10^{-5}$	$3.71 \times 10^{-5}$	-	$8.33 \times 10^{-5}$	$7.95 \times 10^{-5}$	-
	BBP-cancer	2.79	_	_	_	_	_	_	_	_	_	_	_	_
	DBP	3.46	0.1	-	$2.30  imes 10^{-5}$	$2.95 imes$ $10^{-6}$	$6.43 imes 10^{-10}$	$2.78 imes 10^{-10}$	$2.65 \times 10^{-5}$	$4.43  imes 10^{-5}$	-	1.42 imes 10 <sup>-4</sup>	$1.34 imes$ $10^{-4}$	-
	DEHP- noncancer	4.37	0.02	-	$2.93 \times 10^{-5}$	$3.74 \times 10^{-6}$	$8.18 \times 10^{-10}$	$3.52 \times 10^{-10}$	$3.36 \times 10^{-5}$	$5.61 \times 10^{-5}$	-	$1.61 \times 10^{-3}$	$1.54 \times 10^{-3}$	-
	DEHP-cancer	4.37	-	0.014	_	-	_	-	-	-	$rac{2.01 imes}{10^{-6}} imes$	_	-	$rac{2.87 imes}{10^{-8}} imes$
	DnOP	2.54	-	-	$1.66 \times 10^{-5}$	$2.13 imes 10^{-6}$	$4.65  imes 10^{-10}$	$2.00 imes$ $10^{-10}$	$1.91 \times 10^{-5}$	$3.20 \times 10^{-5}$	_	-	-	-
	DiBP	1.12	-	-	$2.10  imes 10^{-5}$	$2.69 imes$ $10^{-6}$	$6.95 imes$ $10^{-10}$	$3.00 imes$ $10^{-10}$	$2.42 \times 10^{-5}$	$4.03 imes$ $10^{-5}$	-	-	-	-
Rural Area	DMP	0.19	-	-	1.27 imes 10 <sup>-6</sup>	$rac{1.62 imes}{10^{-7}} imes$	$\begin{array}{c} 3.55 \times \\ 10^{-11} \end{array}$	$1.53 imes 10^{-11}$	$1.46 \times 10^{-6}$	$2.44 imes$ $10^{-6}$	-	-	-	-
	DEP	0.54	0.8	-	$1.50  imes 10^{-5}$	$1.92 imes$ $10^{-6}$	$\begin{array}{c} \textbf{4.19}\times\\\textbf{10}^{-10}\end{array}$	$1.81 \times 10^{-10}$	$1.72 \times 10^{-5}$	$2.88 imes$ $10^{-5}$	_	$3.30 \times 10^{-5}$	$3.15  imes 10^{-5}$	-
	BBP-noncancer	1.17	0.2	-	$7.75  imes 10^{-6}$	$9.91 \times 10^{-7}$	$2.16  imes 10^{-10}$	$9.33  imes 10^{-11}$	$8.92 \times 10^{-6}$	$1.49 \times 10^{-5}$	-	4.95 imes 10 <sup>-4</sup>	$4.72 imes$ $10^{-4}$	-
	BBP-cancer	1.17	_	_	_	_	_	_	_	_	_	_	_	_
	DBP	0.99	0.1	-	$6.58  imes 10^{-6}$	$8.43 imes 10^{-7}$	$1.84 imes$ $10^{-10}$	$7.93 imes$ $10^{-11}$	$7.58 \times 10^{-6}$	$1.27 imes$ 10 $^{-5}$	-	$rac{2.08}{10^{-4}} imes$	$rac{1.98 imes}{10^{-4}} imes$	-
	DEHP- noncancer	2.34	0.02	-	$1.50 \times 10^{-6}$	$1.92 imes$ $10^{-6}$	$4.19  imes 10^{-10}$	$1.81 \times 10^{-10}$	$1.72 \times 10^{-5}$	$2.88 \times 10^{-5}$	-	$3.15 \times 10^{-3}$	$2.92  imes 10^{-3}$	-
	DEHP-cancer	2.34	-	0.014	-	-	-	-	-	-	$3.71 imes$ 10 $^{-5}$	-	-	$\begin{array}{c} 5.21 \times \\ 10^{-8} \end{array}$
	DnOP	0.88	-	-	$\begin{array}{c} 5.80 \times \\ 10^{-6} \end{array}$	$7.42 imes$ $10^{-7}$	$\begin{array}{c} 1.62 \times \\ 10^{-10} \end{array}$	$6.98 imes$ $10^{-11}$	$6.67 \times 10^{-6}$	$1.11 imes$ $10^{-5}$	_	-	-	-
	DiBP	0.33	-	-	$\begin{array}{c} \textbf{6.18}\times\\ \textbf{10}^{-6} \end{array}$	$\begin{array}{c} \textbf{7.90}\times\\ \textbf{10}^{-7} \end{array}$	$\begin{array}{c} \textbf{2.04}\times\\ \textbf{10}^{-10} \end{array}$	$\begin{array}{c} \textbf{8.82}\times\\ \textbf{10}^{-11}\end{array}$	$7.10 \times 10^{-6}$	$\begin{array}{c} 1.19 \times \\ 10^{-5} \end{array}$	-	-	-	-

Table 5Health risk of human exposure to PAEs in street dust.

most commonly used plasticizers in these areas. The non-cancer risk values for children exposed to PAEs bound to road dust were higher than those for adults. This value, however, was less than 1 for both groups (children and adults), indicating that exposure of residents to PAEs in road dust does not pose a significant non-cancer risk. Among the 7 examined phthalate substances, DEHP and BBP belong to categories C and B<sub>2</sub>, respectively, according to the U.S. EPA Comprehensive Hazard Information System. However, the slope risk factor for oral cancer was only available for the compound DEHP, which is 0.014 mg/kg day. Thus, the cancer risk due to human exposure to DEHP in road dust was only analyzed for dust particle ingestion in this study. The obtained results indicated that the cancer risk from exposure to DEHP in road dust in industrial, urban, and rural areas by ingesting route was  $2.3 \times 10^{-7}$ ,  $5.21 \times 10^{-8}$ , and  $2.87 \times 10^{-8}$ , respectively, and the value was lower than the standard value in defined study areas.

#### 4. Study limitations and ideas for future researches

Our study have had some shortcomings which should be considered when utilizing its findings in a wider context and for other regions of the world. First of all, it is recommended that future researches be carried out in a wider area (with a larger number of sampling stations) and across different seasons. Moreover, several industrial activities in this area could cause the entrance of large amounts of xenobiotic contaminants alongside PAEs to aquatic and terrestrial environments. Therefore, it is recommended to investigate other emerging pollutants as well. Eventually, in this study, only the concentration of parent molecules has been determined while other metabolites including mono-methyl phthalate (MMP), mono-ethyl phthalate (MEP), mono-benzyl phthalate (MBZP), mono-iso-butyl phthalate (MiBP), mono-hydroxy-n-butyl phthalate (OH–MnBP), mono(2-ethylhexyl) phthalate (MEHP), etc. were ignored. Since most of these PAEs compounds are transformed into their metabolites in the environment, it is expected that PAEs concentration is twice as large as the amount reported in this research. At the end, further research is recommended to investigate effective and practical strategies to limit the release of waste containing phthalates in the environments of these areas.

### 5. Conclusion

This study presented the first data on the phthalate acid esters levels in the road dust of the Asaluyeh industrial area, Bushehr City, and Goshoui village. The data of this study showed that PAEs compounds are a widespread environmental contaminants in these areas, and the most predominant compounds were DEHP, DnBP, and BBP. As well as, the mean levels of  $\sum$ PAEs were significantly higher in industrial area compared to urban and rural areas. The phthalic ester compound content had a positive and significant association with TOC, suggesting that the dispersion of PAEs compounds in road dust is strongly influenced by the organic content of the dust. The strongest association between  $\sum$ PAEs and different compounds was found with DEHP, so this compound may be a suitable marker substance to be used for the identification of  $\sum$ PAEs in road dust in the evaluated areas. The plasticizers and solvents utilized in various chemical industries, pesticides and fertilizers applied in agriculture activities, various plastic films and polymer pipes in greenhouses were the predominant sources of PAEs in road dust of the defined areas. The non-cancer risk of exposure of children to PAEs bound to road dust was found to be higher than that of adults. However, this value was <1 for both children and adults, demonstrating that exposure to PAEs bound in road dust did not pose a significant non-cancer risk. Also, the cancer risk of exposure to DEHP in street dust in all defined area (industrial, urban, and rural areas) was less than the standard value of  $10^{-6}$ . However, the results of health risk assessment depicted that PAEs compounds' bioavailability and bio-accessibility were not considered. Separate and more detailed researches on the bioaccumulation of PAEs in organisms and plants in the food chain are necessary to evaluate the hazard of these dangerous pollutants, as a key to environmental and health protection.

#### Ethics approval and consent to participate

"Not applicable".

#### Availability of data and materials

Additional data from the study are available by request to the corresponding author by email.

## CRediT authorship contribution statement

Javid Karamianpour: Data curation, Formal analysis, Investigation, Writing – original draft. Hossein Arfaeinia: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing. Dariush Ranjbar Vakilabadi: Conceptualization, Investigation, Project administration, Writing – review & editing. Bahman Ramavandi: Methodology, Writing – review & editing. Sina Dobaradaran: Investigation, Methodology, Writing – review & editing. Mehdi Fazlzadeh: Methodology, Software, Writing – review & editing. Zahra Torkshavand: Methodology, Software, Writing – original draft. Sara Banafshehafshan: Writing – original draft. Hanyeh Shekarizadeh: Software. Sami Ahmadi: Software. Ahmad Badeenezhad: Software, Validation.

#### 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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e23129.

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