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The Investigation of Volatile and Semi-volatile Organic Contaminations in Houjing River, Kaohsiung City, Southern Taiwan

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Having long been a victim of organic contamination, Houjing River (Kaohsiung City, Southern Taiwan) has been a subject of interest to both citizens and the city government. In fact, along with progressively negative concerns from local residents, the city government has tried to identify the contamination sources and mitigate adverse effects on human health and the well-being of local residents who have dwelled along the river for decades. In this study, related industrial plants that were specific contamination sourceshave been identified after a series of samplings and analyses. Water and sediment samples were analysed employing Gas Chromatography and Mass Spectrometry (GC-MS) techniques. The analytical results were then used to discuss the impact of riverside industrial plants in worsening the contaminationof the river. Comparisons between different river basins in terms of contamination have also beendiscussed for a more comprehensive studyof the Houjing River. Hopefully, the results of this study would be able to provide scientific andtangible evidence for the city government in order to take immediate and more forceful actions on the aggravating contaminationof the river as the well-being of more than 100,000 lives depend on it.

INTRODUCTION

Houjing River is one of the three major river watersheds in Kaohsiung City, Taiwan. Houjing River passes through four major industrial parks, including the Dashe Industrial Park, Renwu Industrial Park, the Kaohsiung Oil Refinery of the Chinese Petroleum Corporation, and the Nanzih Export Processing Zone. Residents in this area have often complained about the foul odours released from the Houjing River, and often domestic solid wastes and debris have been observed in this area. In the past decades, residents of this area have suffered from accidental industrial spills and illegal discharges into the river.

Based on the recent water quality analysis, the Houjing River is heavily polluted. Both point and non-point source pollutants have been identified as the major causes of poor water quality in the Houjing River. Investigations have demonstrated that the main point pollution sources included municipal (domestic), agricultural, and industrial wastewaters (Lin *et al.,* 2010).

The national major river water quality monitoring network operated by Taiwan Environmental Protection Agency has determined Houjing River to be one of the most polluted rivers in the country. However, this network only monitors general parameters, such as odour, pH, turbidity, total suspended solids, dissolved oxygen, biological oxygen demand (BOD), chemical oxygen demand (COD) and total coliforms. In recent years, the Houjing River passed through four major petroleum-related industrial parks and has become highly susceptible to VOC, SVOCs, and heavy metal contamination which were not (systematically) monitored by the network. Lin *et al.* (2009) reported that the highest concentration of DEHP was recorded at the Jhongsing Bridge (20.22 $mg.kg^{-1}$ dry wt.) near the Dashe

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Industrial Park, followed by the Renwu Bridge (8.93 mg.kg^{-1} dry wt.) near the Renwu Industrial Park. Lin *et al.* (2007) also reported that unusually high levels of BTEX concentrations were found at the Jingjian Bridge sampling location of the Houjing River. The world's leading provider of semiconductor packaging and testing services, Advanced Semiconductor Engineering (ASE) was found to illegally discharge large amounts of toxic wastewater into the nearby Houjing River in Kaohsiung City Taiwan in Dec 2013. The investigations conducted by the Kaohsiung City government indicated that the toxic wastewater discharged into Houjing River contained nickel and highly acidic toxic substances, which in turn,polluted about 1,390 hectares of farmland downstream. In follow-up investigations, the local governments also found that the K5 and K11 Plant of the ASE in Kaohsiung and the Chungli Plant in Taoyuan County illegally discharged untreated wastewater. After the investigations, the Kaohsiung City government suspended some production lines of theK7 plant of ASE related to the discharge of toxic waste water.

Hence, this study hasinvestigates VOCs and SVOCs contamination in surface water and sediment samples of the Houjing River. The main objectives of this research were (1) to assess whether the Houjing River was contaminated by these contaminants, (2) to assess the hot zones of contamination, if they existed, (3) to identify and reprimand the pollution dumper and (4) to discuss possible negative health effects, and resolve related problems by engineering and social measures.

MATERIALS AND METHODS

Location

Houjing River is located in the north-west of Kaohsiung City, southern Taiwan. It has two different upstream origins, Dashe and Renwu, which then meet at the Si-Chingpu Landfill. The river then flows directly into the ocean. In the past, the Houjing River used to be a major water source for irrigation and fish farming in the area. However, the rapid economic development with the building of industrial areas has turned the river into a seriously contaminated area.

Sampling

A total of 10 sampling sites depicted in Figure 1 (VOC) and 9 sites depicted in Figure 2 (SVOC) were considered in this study. Water samples were collected following astandard method of the National Institute of Environmental Analysis (NIEA) W104.51C while sediment samples were collected as per NIEA W104.31B indications.

Instrumental Analysis

For VOCs analyses, we employed the NIEA W785.53B method. An OI-model 4552 autosampler and OI-model 4660 Eclipse purge and trap sample concentrator were employed for the sample pretreatment. An HP 6890 gas chromatography (GC) coupled with a 5973N mass spectrometer (MS) system was then used for VOC analysis. The established method included 61 compounds.

For the SVOCs analyses, the NIEA M731.01C and NIEA M167.01C methods were adopted to extract and analyse SVOCs from sediment samples.

All chemicals used were of reagent grade, all standards were ofre NIST traceable quality and deionised water was used in all analyses involved.

RESULTS

Spatial Characterisation of VOC Contamination

As shown in Figure 1, there was no total VOC contamination at the upstream area of the northern and southern distributaries of the river: Sannaitan Bridge, Xinggong Bridge (Dashe Branch) and Bakong Bridge (Renwu Branch). However, the observed concentrations of Total VOCs in water samples at Jingjian Bridge (Dashe Branch) and

Renwu Bridge (Renwu Branch) were unusually high (values please, respectively). The concentrations became exponentially lower when it came to the next two sampling sites near the two river junctions, CingPu and Huifeng Bridge. Henceforth, the concentrations of total VOCs showed gradually decreasing tendency in the stations (Dehuei and Youchangda bridges) near the ocean mouth. Thus, it could be concluded that the significant potential VOC contamination sources must have been in the vicinity of the Jingjian and Renwu Bridges. Subsequently, there was no other dramatically obvious contribution to the total VOC content in the Houjing River. These findings agreed well with the location of the Dashe Industrial Park and Renwu Industrial Park, both petrochemical and plastic manufacturers that dominated the area releasing wastewaters containing high amounts of total VOCs around the Jingjian and Renwu bridges, respectively. Progressively decreasing total VOC concentrations at other sampling sites such as CingPu, the Huifeng and Demin Bridges could be due to the natural dilution effect of the river. Similarly, the Dehuei and Youchangda Bridges had significantly lower total VOC concentrations, indicating the possibility of continuous contamination dilutions.

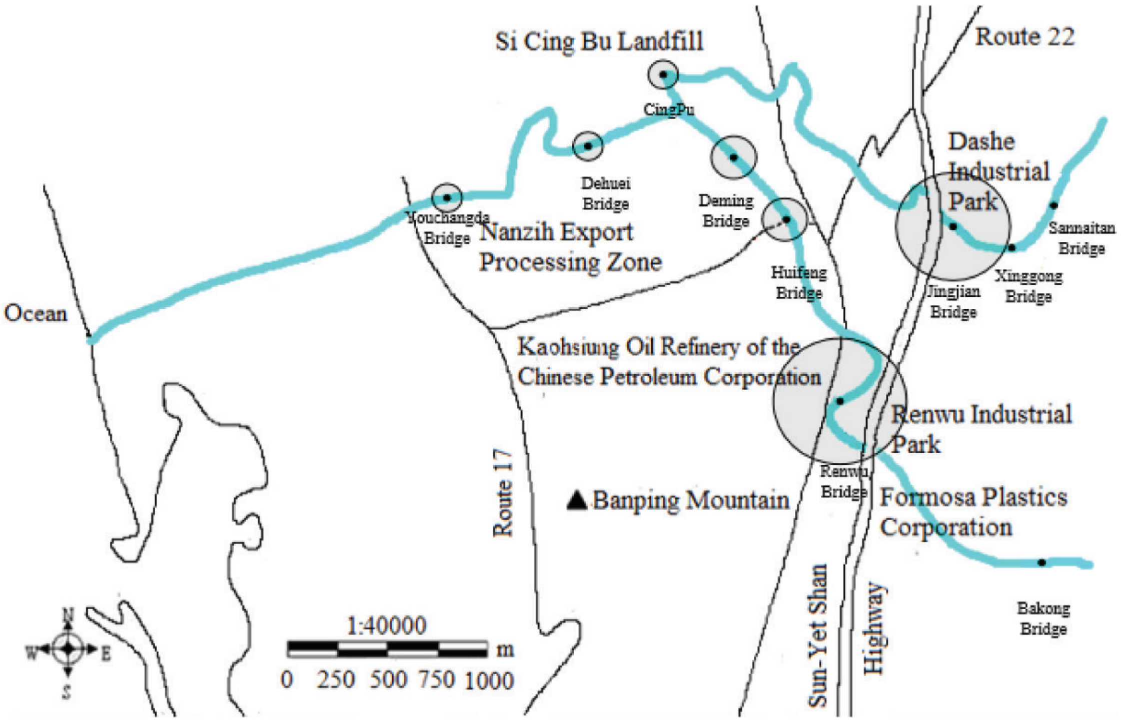

Figure 1. Spatial distribution of total VOC contamination in the waters ofHoujing River. The size of the grey circle indicates the relative concentration of VOC contamination per station studied.

Identification of SVOC-discharged Sources

Similar to total VOCs, total SVOC identification in this study was also conducted through a series of field sampling, instrumental analysis, data processing and finally constructing a contamination map of potential discharge sources (Figure 2). For the southern distributary, it was apparent that the Renwu Industrial Park and Kaohsiung Oil Refinery of Chinese Petroleum Corporation were less involved in the total SVOC contamination since the concentrations at Bakong Bridge, Renwu Bridge and Hueifeng Bridge exhibited no significant changes. When it came to the Deming Bridge, the contamination concentration inflated, which indicated a discharge of SVOCs into the river. In this case, the Nanzih Export Processing Zone, which is a semiconductor testing and packaging area was considered the contamination source. For the Dashe distributary, the situation was more complicated as the SVOC concentrations were already high at the beginning of the upstream area (Sannaitan Bridge). The contamination concentrations decreased at the Jingjian Bridge which could be due to a dilution effect. However, at the CingPu Bridge station, an exponential rise in total SVOC concentrations was observed again. At this site, there was no possibility of industrial discharges occurring and it was assumed that the commercial and residential activities of the area were the main cause of contamination. Again, contamination levels decreased in the stations (Dehuei and Youchangda Bridges) near the ocean mouth and coulf be due to the ocean outflow dilution effect.

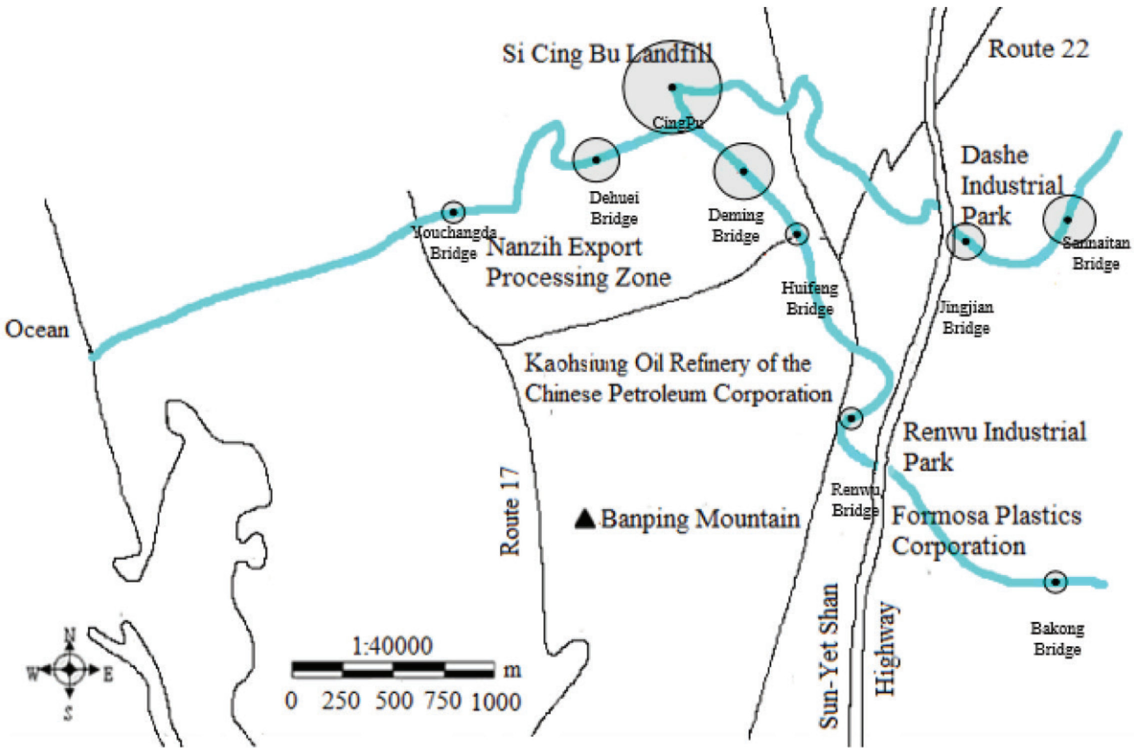

Figure 2. Spatial distribution of Total SVOC contamination in the sediment of the Houjing River. The size of the grey circles indicates the relative concentrations of SVOCper station.

Comparisons with similar studies

It was remarkable to note that when compared to other similar studies around the world (Table 1), the Houjing River seemed to be the most serious case. This was especially the case when the maximum concentrations of benzene, toluene and ethylbenzene were considered. Table 1 shows that these organic chemical compounds constituted most of the total VOC in the Houjing River, overshadowing concentrations observed in other ecosystems. The comparisons with other similar studies also showed that, in relation to chlorinated-VOCs, Houjing River was vastly more contaminated than monitoring studies conducted in the US (Phelan *et al.* 2001) and the Southern North Sea (Huybrechts *et al.* 2005), but less contaminated than that in Italy (Pecoraino *et al.* 2008). This clearly indicated that the concentrations of the chlorinated-VOCs at the Houjing River were alarming and wereto be taken seriously. Such values were of much concern and there was a considerable need for pollution prevention or environmental protection strategies in the industrial areas involved. For Di (2-ethylhexyl) phthalate (DEHP) - the major SVOC found in the contaminants of the Houjing River, the Houjing River's DEHP concentrations were significantly higher than other ecosystems apart from the study done by Gao *et al.* (2014). This inferred that the DEHP contamination of Houjing River was at a very serious level and should receive wider attention, and is thus required immediate action and management from the government and related industries.

DISCUSSION

Effects of VOC on Health

Volatile organic compounds (VOCs) are one of the chief issues in environment contamination and their wide distribution has raised major concerns, in particular with environmental sciences. VOCs correspond to a class of organics that are characterised by their highly volatile nature under existing environmental conditions. The chemical characteristics (e.g. low water solubility, high lipid solubility, semi-volatility and ability to pass through biological membranes and accumulation in fatty tissues) make them of great concern to the environment. The main subgroups of VOCs include halogenated organics, monocyclic aromatic hydrocarbons, organic sulphides and sulphoxides, BTEXs, THMs, acetone, and esters.

Table 1. Comparison of BTEX, chlorinated-VOC and DEHP contaminations in similar studies

Geographical areas	Types of water bodies	BTEX (µg/L)					Chlorinated-VOCs (µg/L)	DEHP (mg/kg dry weight)	Reference
		Benzene	Toluene	Ethylbenzene	m+p - Xylene	o - Xylene			
Greece	Rivers, lakes and ocean	ND	ND - 6.7	ND	ND	ND			Lekkas *et al.* (2004)
North Sea	Ocean	ND	0.060^{b}	0.009^{b}	0.021^{b}	0.013^{b}			Huybrechts *et al.* (2005)
Portugal	Rivers	0.01 - 0.70	0.01 - 4.77	0.09 - 4.75	0.01 - 27.61	0.02 - 2.16			Moliner-Martínez *et al.* (2013)
India	Groundwater	0.55 - 0.85	-	-	-	-			Senthil kumar *et al.* (2013)
US	Creek	-	-	-	-	-	6.52^{b}		Phelan *et al.* (2001)
Southern North Sea	Ocean	-	-	-	-	-	$0.12^{a} – 0.37^{b} – 4.18^{c}$		Huybrechts *et al.* (2005)
Italy	Groundwater	-	-	-	-	-	947.82^{c}		Pecoraino *et al.* (2008)
India	River	-	-	-	-	-	-	ND – 0.324	Srivastava *et al.* (2009)
Nigeria	River	-	-	-	-	-	-	0.020 – 0.820	Adeniyi *et al.* (2010)
China	River	-	-	-	-	-	-	0.365 – 6.239	Sun *et al.* (2013)
China	River	-	-	-	-	-	-	0.415 – 29.5	Liu *et al.* (2014)
China	River	-	-	-	-	-	-	227.08 – 566.54	Gao *et al.* (2014)
Iran	Lagoon	-	-	-	-	-	-	0.25 – 43.12	Hassanzadeh *et al.* (2014)
Taiwan	River	0.89 - 157.95	ND - 16.96	ND - 270.57	ND	ND	$100.65^{a} – 131.21^{b} – 331.64^{c}$	0.46 – 120.28	This study

Concentrations are expressed as (min - max) except for a few cases as noted
a median
b mean
c maximum

VOCs have been found to be a major contributing factor to the production of ozone, a common air pollutant that has been proven to be a public health hazard. VOCs react with stratospheric ozone thusdestroying the stratosphere and increasing the hole in the ozone layer that protects us from ultra violet rays. Some organic contaminants have been linked to cancer cases in animals; some are suspected or known to cause cancer in humans. Key signs or symptoms associated with exposure to VOCs include conjunctive irritations, nose and throat discomfort, headaches, allergic skin reactions, dyspnea, decline in serum cholinesterase levels, nausea, emesis, epistaxis, fatigue, dizziness.

Effects of SVOC on Health

Semi-volatile organic compounds (SVOCs) are a group of compounds that include some pesticides, ingredients in cleaning agents and personal care products, and additives to materials such as vinyl flooring, furniture, clothing, cookware, food packaging and electronics. Reflecting their extensive use in commercial and domestic chemical products, many SVOCs are ubiquitous contaminants of the indoor environment {Wang, 2010 #11921}(Kanazawa *et al* 2009; Wang *et al*. 2010), and over a hundred are among the chemicals frequently detected in the CDC's bio monitoring program. Exposure typically comes from direct product use as well as from contaminated indoor environments where occidental societies spend over 87% of their time. The USEPA lists more than a thousand SVOCs as high-production-volume chemicals (produced or used at more than 1 million lbs/yr). SVOCs are generally identified as organic molecules that can be abundant in both the gas phase and condensed phase represented by vapour pressures between 10-14 and 10-4 atm. Because of their slow release rate from sources and their propensity to partition into sorb states, SVOCs can persist for several years indoors, akin to persistent organic pollutants in the outdoor environment (Weschler and Nazaroff 2010).

Many SVOCs are considered as endocrine-disrupting chemicals that alter human and wildlife hormones (Wang *et al.* 2010). They are suspected to contribute to the occurrence of neurodevelopmental and behavioural problems (e.g., mental retardation or attention deficit disorders), reproductive abnormalities (e.g., decreased fertility or hypospadias), metabolic disorders (e.g., obesity, diabetes), and cancer (e.g., breast, prostate, and testicular cancers) (Zhang and Smith 2003).

Solutions for Houjing River – Future work

The contamination in Houjing River requires synergistic efforts. The industries should apply business ethics when disposing or treating their wastes properly and thus, conserving the environment. However, this is, by all means, hardly feasible and, often not systematically applied, as the main concern of most industries is increasing profits. This has become a challenge to the government as economic values contributed by the industries can, often, outweigh societal well-being and protection. The local society should be informed of any environmental risks and impacts that they are most likely are exposed to. The government should provideearly alerts so that people can take appropriate actions when pollution levels exceed acceptable limits. The government should also takee actions like banning direct access (e.g., swimming or fishing)in contaminated waters. Local populations should also be sensitive to water degradation signals such as foul odours, massive fish deaths, floating debris, unusual water colour, etc., and they should report such cases immediately to the government or responsible bodies. The government should launch rapid monitoring assessments to confirm any anomalies and once validated, should immediately investigate and enforce firm regulations on any illegal industrial discharging behaviours and supply the society with right-to-know acts. In some cases, the international community can also play important roles. For example, with the term 'Green supply chain', customers can boycottproducts from environmentally harmful production systems (Srivastava 2007). By implementing this management plan, industries would pay more attention as they would be under huge pressure if their products could not be sold. The government should facilitate this by inviting the participation of the media.

Aside from the government and local population, another important sector that can provide solutions is the scientific community. With the heavy pollution of the Houjing River, multiple scientific works and research needs to be carried out in the future. It remains unclear if the river is only polluted with organic compounds as the industries and the wastes occupying the riverside vary widely, not to mention additional and potential contaminant imports from agricultural, commercial and residential sources. Further studies should be conducted to assess whether the river is polluted with other kinds of pollutants such as heavy metals, hydrophobic organic compounds, etc. In addition, bioaccumulation or the pathways and mechanisms on how these pollutants are transferred from water to sediments to aquatic species and potentially, to humans need to be studied and understood. That can be done by a variety of modelling studies (i.e., Arnot and Gobas 2004). The assessment of toxicity, ecological impacts and health risks arising fromthe pollution is also important. Continuous monitoring plans should be devised to regularly reflect major changes in the river's pollution. In future, the pollution of the Houjing River should be mapped and the improvement of water and sediment quality should be communicated to the residents along the riverside, whih arearound 100,000 people. We hope that we would be able to address the multiple and complicated challenges mentioned above. Our work intends to provide scientific proof of the actual state of the river and we hope that these observations can be useful to the government and local bodies in identifying priorities and applicable goals that may help resolve, mitigate and/or alleviate the aggravating river pollution in the country.

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