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Validating the effect of trace metals levels in wastewater discharges, sediment and *Euchelus asper*, mollusc in the marine environment

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Abstract
This study describes the investigation on the major trace metals levels in wastewater discharges and sediment from twenty four permanent and five semi-permanent wastewater drain outlets into the Kuwait coast. *Euchelus asper*, gastropod, abundantly inhabiting near the rocks and the surrounding edges of the drain outlets was also investigated to determine the trace metals levels released from untreated wastewater discharges. Results showed high trace metal levels in *E. asper* tissues, followed by sediment and in wastewater during winter than in summer irrespectively of the sampled areas. Regionally, distributed wastewater drain outlets in six Kuwait Governorates (GI-GVI) revealed high trace metal levels in GI due to industrialization and occasional untreated wastewater discharges into the marine environment. High Zn and Cr in the gastropod, sediment and wastewater samples indicated the effect of oil spills and untreated wastewater discharged into the sea. Results of our study exceeding the standards pollution limits could be validated as a tool to undertake precautionary measures to similar polluted areas elsewhere in the globe.

Keywords: Trace metals, drainagewater, sediment, mollusc, Kuwait Coast

1. Introduction
Wastewater generated from various anthropogenic activities forms as a natural sink in the sea. Wastes from urban, industrial, and agricultural sources have been disposed into the sea. Wastes from urban areas are classified to municipal wastes, a combination of residential, institutional, commercial establishments and storm water [1-2]. FAO anticipates the total volume of 40 bcm.yr^{-1} of domestic wastewater by the year 2015 [3]. Toxic heavy metals were found associated with industrial and domestic effluents [4-5]. Metals found in wastewater are commonly elevated because of its anthropogenic use. Therefore, metals are used as tracers of wastewater in the ocean [6]. Marine organisms that live near the wastewater discharge points are food source for other organisms, birds, and humans. They are found elevated with high inorganic and organic constituents and thus, bioaccumulation in flora and fauna is common [7-10].

In the Gulf region, 40% of wastewater is discharged into the sea without treatment. In Kuwait, the estimated annual volume of wastewater ranges between 206 and 254 Mm^3. Out of the total wastewater treated (208,000cu.m d^{-1}), approximately 62% is reused for agriculture, landscape and roadside irrigation and the rest is discharged into the sea [11]. The recent increase in population, urban development and rapid industrialization

has led, not only in the voluminous discharge of domestic and industrial wastewater, but also frequent discharge of untreated wastewater into the marine environment [12]. Wastewater containing inorganic and organic pollutants, fluctuating seawater variables (temperature, D.O., salinity) and compounded by global warming are some factors nurturing algal blooms, some species of molluscs and 'fish kill' that led to the environmental stress in Kuwait marine ecosystem. Marine gastropods are found to accumulate high metal concentrations in their body tissues. *Euchelus asper*, is a genus of top shells, marine gastropod molluscs inhabiting the lower rocky shores. They graze on algal films. They are tolerant to trace metals exposures. Although a large volume of wastewater is let out into the sea, only few publications exists concerning their synergistic effect upon water, sediment, hydrological and physical variables. Therefore the present study was undertaken to study: (1) trace metals levels in the wastewater discharged into the Kuwait Coast, (2) trace metals levels in sediment deposited near the mouth of the drain outlets, (3) trace metals levels in the abundantly available gastropod mollusc, *E. asper* and (4) the relationship between the seasonal trace metals levels in samples collected from the drain outlets of Kuwait Governorates and the hydrological variables that is suspected to pollute the Kuwait marine ecosystem.

2. Experimental method

2.1 Sampling sites

Our study chose twenty four functional and permanent concrete drain outlets along the Kuwait Coast that are constructed and spread across six Kuwait Governorates. These drains let the major domestic and industrial wastewater into the Kuwait's marine environment throughout the year (***Fig. 1***). During the years 2009-2011, we suspected an increase in the trace metals levels in four major concrete drain outlets (DT1-DT4) that discharged wastewater from the respective Kuwait Governorates (GI-GVI) during summer and winter seasons. Besides the twenty four drains, five semi-permanent drains (SD) located especially in the southern region of Kuwait were also investigated in the present study (***Fig. 1***).

2.2 Wastewater sample collection

A horizontal polycarbonate point water sampler (2.2 L) was employed to collect wastewater samples from three loci at the entry point of each drain outlet. Water from the sampler was allowed to settle in a sediment settleometer. Wastewater was filtered using a 0.45µm membrane filter and processed for trace metals analysis. The settled deposits and filtrate were separately weighed and analyzed for residual trace metals.

The average wastewater velocity ($ft.sec^{-1}$) discharged from each drain outlet (DT1-DT4) of the respective Kuwait Governorates (GI-GVI) was measured by using a (5-15ft) digitalized open channel flow probe (FP211, Global water, US).

Wastewater physical variables such as temperature, salinity, pH and dissolved oxygen from each drain outlet (DT1-DT4) were measured at discharge outlets by using a portable multi-parameter water checker (Hach Inc., USA).

2.3 Sediment sample collection

Using a Van Veen Grab sampler (5Kg capacity), three sediment replicates (50g) near the surrounding mouth of the each DT bed was collected and stored in polyethylene container. Samples were dried in an oven (GallenKamp II, USA) at $45^{o}C$ until dryness, ground to obtain a homogenized powder and sieved using a 1mm mesh. Powdered sediment (0.2g) was used to analyze trace metals levels.

2.4 Gastropod, Euchelus asper collection

Gastropod, *Euchelus asper* was found abundantly on either sides of the low water level zone rocky embankment near the drain outlets. They were handpicked and transported in sterile plastic bags to the lab. They were cleaned in deionized distilled water and the tissues were removed from the shell. Ten replicates of the whole tissues (10g) from each drain outlets were processed for trace metals analysis.

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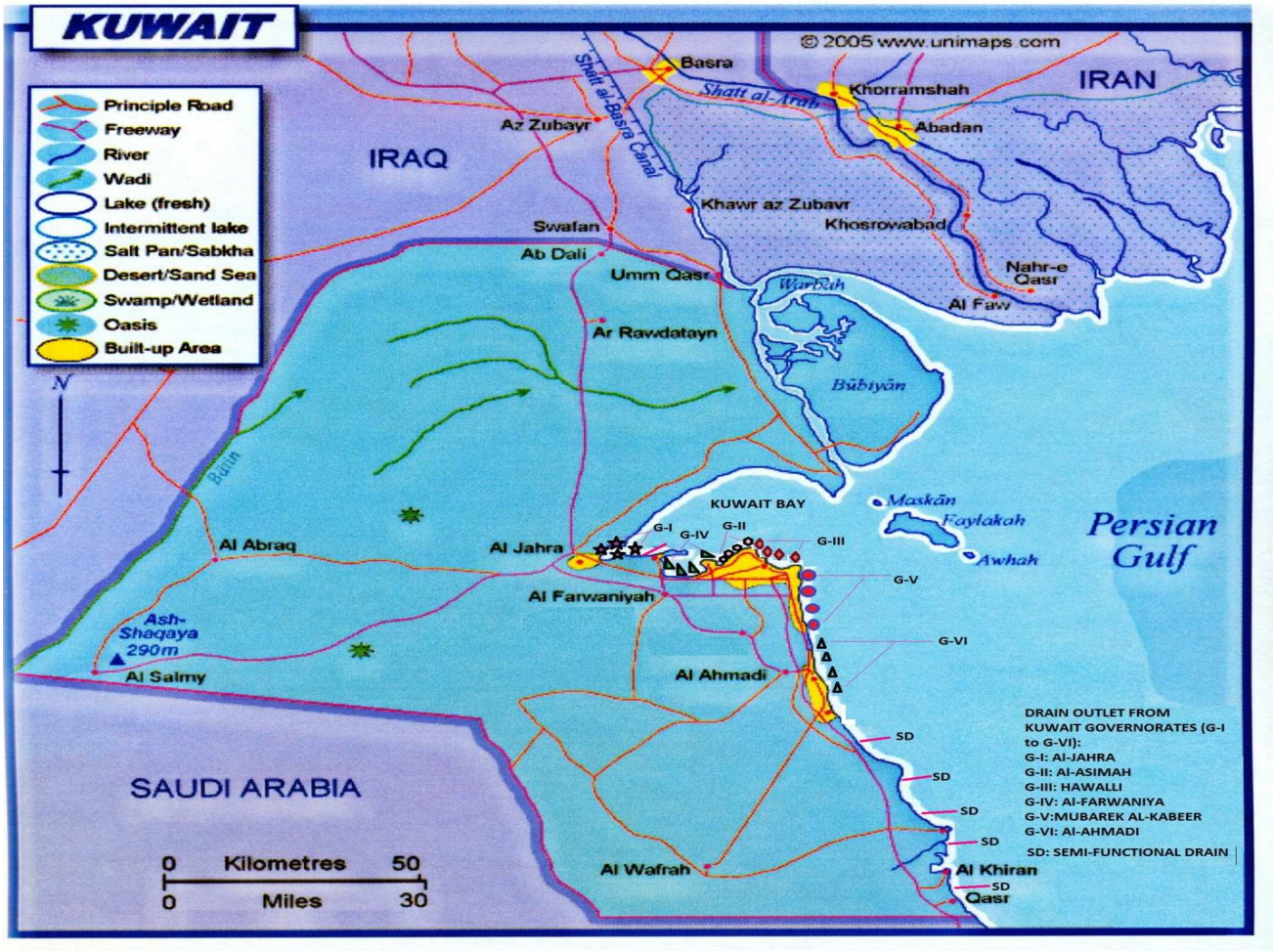

Figure 1. Wastewater discharges from drain outlets of Kuwait Governorates

2.5 Determination of trace metals in wastewater

To one-liter filtered wastewater, 25 ml ammonium-pyrrolidine-dithiocarbonate (2% v/v), 10ml HCl and 35ml methyl isobutyl ketone was added in a separatory funnel, shaken for 2 minutes and left undisturbed for 15-20 minutes. Two separate phases, namely, upper organic and lower aqueous solutions were obtained. One liter of seawater was added to the organic solution with the above chemicals and the process repeated. The lower aqueous solution was eluted in another separatory funnel. The upper solutions were collected in a 50 ml volumetric flask and the lower solutions discarded. The upper solutions were analyzed in Atomic Spectrophotometer (Analytik Jena, graphite system) and the concentration of trace metals measured following the quality control and assurance method described earlier [13] were carried out by using the respective trace metals standards (ICP grade), blanks, Certified and Standard Reference Materials (CRM-403 and SRM-2702: marine water and sediment respectively).

2.6 Trace metals analysis in sediment and Euchelus asper

Dried sediment and whole tissues of *E. asper* samples (0.2g) were digested with 5ml HNO_3 (v/v, Aristar grade) in a Microwave digester (Ethos1, Milestone, Italy). The resultant samples were diluted and analyzed for trace metals analysis in the ICP-MS. Mercury levels in wastewater, sediment and *E. asper* tissues were directly analyzed using DMA-80 direct mercury analyzer (Milestone, Italy).

3. Results and discussion

Trace metals concentrations in wastewater, sediment and gastropod, *E. asper* collected from the drain outlets of the six Kuwait Governorates (Fig.1) during summer and winter seasons correlating the water velocity are presented (Fig. 2). The data were logarithmically transformed to correct unequal variation, varied units and express consistency. Five semi-permanent drains (SD) located in the southern region of Kuwait (Fig.1) were found dry during most part of the year and was observed functional only during the event of major sewer blockade and hence, not investigated in the present study.

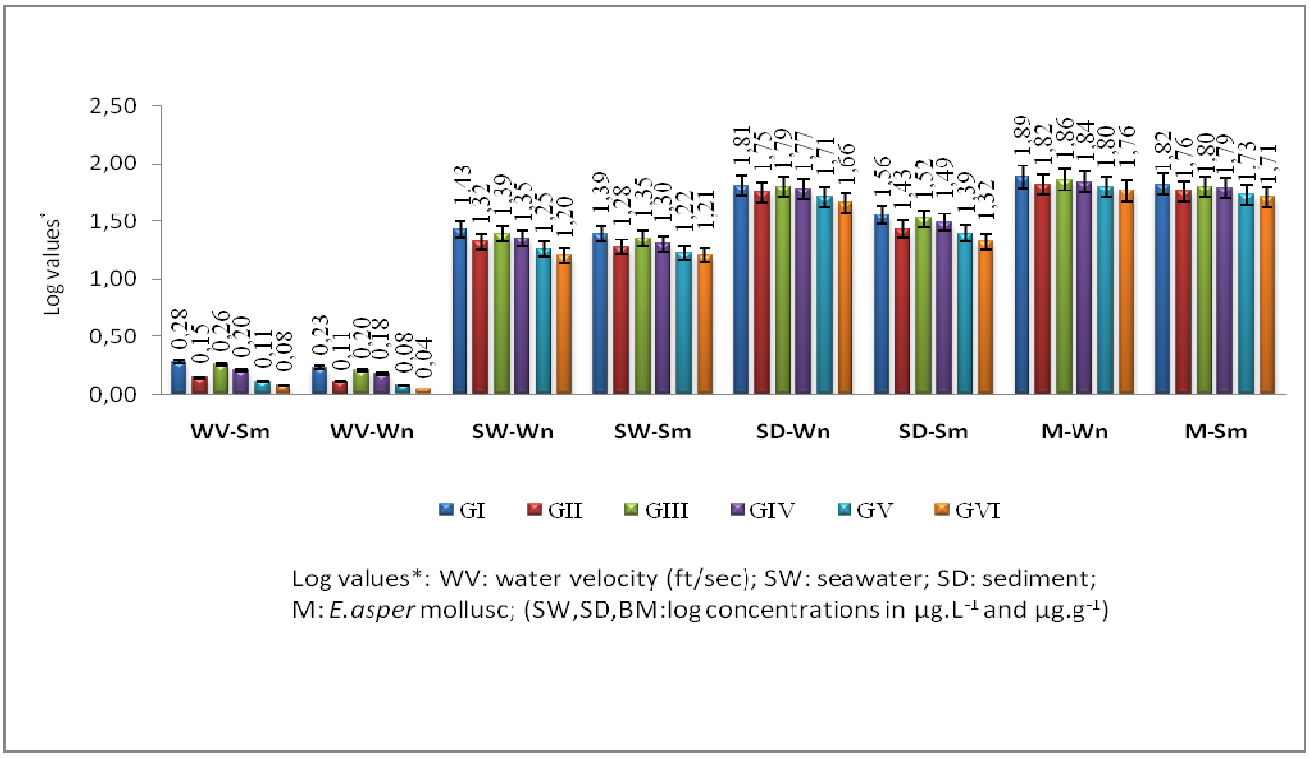

Figure 2. Logarithmic data on the season-wise water velocity, trace metals concentrations in wastewater, sediment and *E.asper*

Observations showed high trace metals concentrations in *E. asper* followed by sediment and in wastewater (Fig.2) indicating the high accumulation of metals from sediment and wastewater, primarily due to low water current and flushing of wastes in the Kuwait Bay, and secondarily as a result of different waste resources. This phenomenon was found in line with the earlier findings [1-2, 8, 10]. Seasonally, high trace metals levels were observed during winter than in summer in all the samples (Fig.2). This observation was found similar to that of the earlier investigators [2, 5]. Governorate wise analysis (GI-GVI) showed high trace metals levels in the sequence of GI>GIII>GIV>GII>GV>GVI irrespective of seasons in *E. asper*, sediment and wastewater (Fig.2). Wastewater discharges from thermal, desalination and power plants besides the discharges from construction activities, automobile wash centers, public utility services and few recreational activities attributes to very high trace metals levels in samples collected from GI and GIII. Trace metals levels in GIV and GII were also found moderately high due to the domestic waste discharges into the Kuwait coast. The northern coastal area in GV has moderately populated residential areas with more recreational activities and business centers. However, the southern part of GV and northern part of GVI comprises of small scale industries and thus, wastewater analysis revealed low trace metals levels in GVI than in GV. In an overall view, trace metals levels in GV and GVI was comparatively lower than trace metals in samples collected from the other Kuwait Governorates. Reasons could be attributed to the lesser number of drain outlets, influence of open sea that rapidly flushes wastewater to the

southern Persian Gulf, regular transport and treatment facilities of domestic wastewater from residential areas besides the low density of human population in the GVI areas.

Four drain outlets (DT) each, from six Kuwait Governorates that discharged wastewater revealed high trace metals in the sequence of Zn>Cr>Ni>Cu>Fe>Pb>Hg irrespective of both the summer and winter seasons. Accidental oil spills, automobile wastes, untreated domestic wastewater discharges, plastic wastes, constructional and e-wastes attributes to the high Zn, Cr and Ni levels in both the analyzed samples. Such phenomenon was not uncommon, globally [4, 6, 9, 11-12]. Trace metals sequence in sediment samples was found similar to that of the trace metals sequence observed in wastewater analyzed during summer and winter. However, variation was observed in the trace metals sequence in the gastropod, *E. asper*. These changes may be attributed to efficacy of *E. asper* to accumulate essential trace metals from the sediment deposition, besides the factors governing the trace metals absorption from food and environmental variables such as temperature, salinity, dissolved oxygen (DO), and tidal effects. Such changes were found in agreement with the earlier findings [7]. Statistical analysis (ANOVA) revealed significance between the velocity of water, trace metals in wastewater, sediment, *E. asper* and hydrological variables from the six Kuwait Governorates during summer and winter (Table 1). Correlation coefficient (SPSS, v.19) revealed significant relationship between the samples collected from the six Kuwait Governorates and the two seasons (Fig.3).

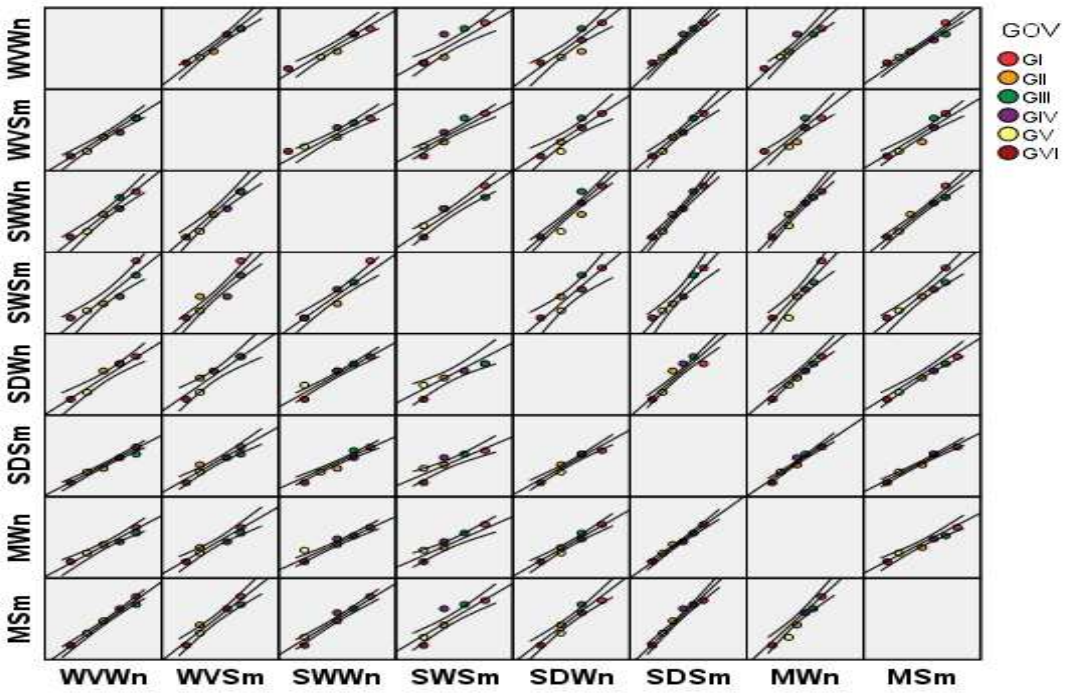

Figure 3. Governorates -wise correlation coefficient between water velocity, wastewater, sediment and *E. asper* tissue.

Table 1. ANOVA between water velocity, wastewater, sediment, *E. asper* and hydrological variables during summer and winter

Variation	df	F	P-Value	F critical	Significance
Governorate-wise	5	15.55	<0.004	2.35	*
Season-wise	13	1318.04	<0.0001	1.87	*
Error	65				
Total	83				

Table 2. Mean hydrological variables in Kuwait's wastewater drain outlets

Gov.	DO. Sm (mg/L)	S. Sm (‰)	T. Sm °C	DO. Wn (mg/L)	S. Wn (‰)	T. Wn °C
G-I	5.3	44	42	6.4	36	20
G-II	5.2	41	40	6.4	38	22
G-III	5.4	43	42	6.2	38	25
G-IV	5.3	42	41	6.3	39	27
G-V	5.1	41	40	6.5	39	23
G-VI	5.0	41	40	6.6	37	22

Gov.: Kuwait Governorates (GI-GVI); DO: dissolved oxygen; S: salinity;
T: temperature; Sm: summer; Wn: winter; (‰): parts per thousand

Conclusion

Based on the present investigation, we found that *E.asper* could be characterized as an indicator to trace metals, different kinds of wastes influences the level of trace metals contamination, in addition to the water current, flushing rate of wastewater into the marine environment. Furthermore, we suggest meticulous monitoring of treated water that is accidently or clandestinely mixed with untreated wastewater and appropriate treatment of untreated wastewater prior to its release into the marine environment.

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