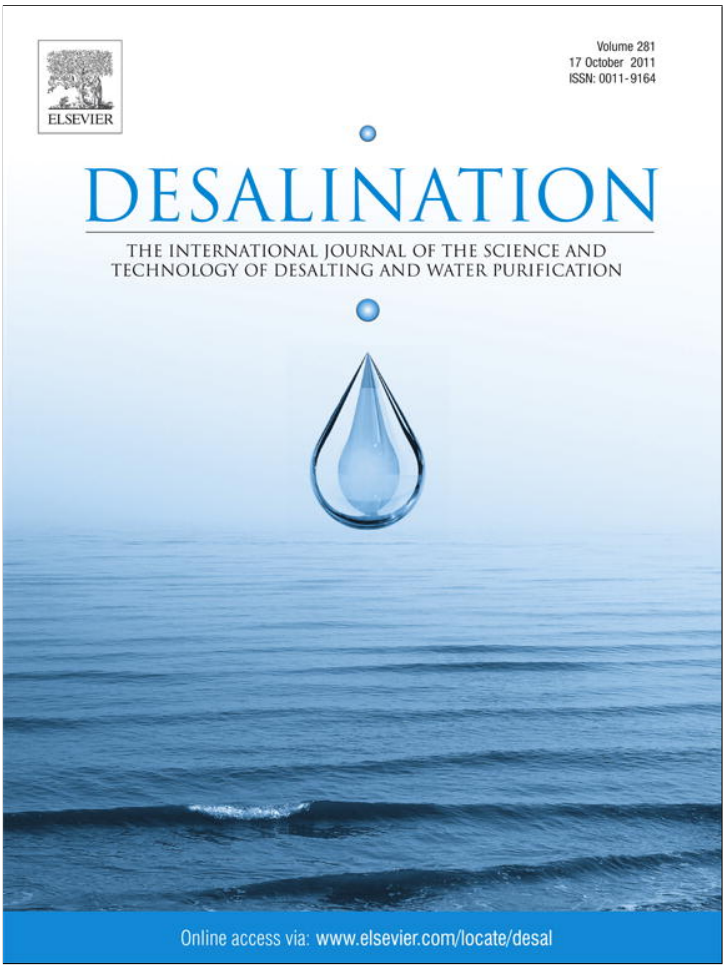

Desalination 281 (2011) 159–164

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Pollutant trends and hazard ranking in the desalination area of the Penghu Islands, Taiwan

Yung-Chang Lin [a], Cheng-Haw Lee [b], Kuo-Hsin Yang [c,*], Ming-Hsun Lin [b], Ku-Fan Chen [d], Chien-Pang Pan [b]

[a] Dept. of Electrical Engineering, Cheng Shiu University, Taiwan, No. 840, Chengcing Rd., Niaosong Township, Kaohsiung County 833, Taiwan
[b] Dept. of Resources Engineering, National Cheng Kung University, Taiwan, No. 1, University Rd., Tainan City 701, Taiwan
[c] Dept. of Construction Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei City 106, Taiwan
[d] Dept. of Civil Engineering, National Chi Nan University. No. 1, University Rd, Puli, Nantou County, 54561, Taiwan

ARTICLE INFO

Article history:
Received 2 October 2010
Received in revised form 22 July 2011
Accepted 25 July 2011
Available online 9 September 2011

Keywords:
Desalination plant
Sediment
Seawater
Hazard ranking

ABSTRACT

This work examines the distributions of potentially toxic trace elements (*e.g.*, Cu, Zn and As) and assesses the potential hazards of contaminants to environment. Trace elements are released from seawater desalination facility in the Penghu Islands, Taiwan. Temporal trends of trace element concentrations are investigated by comparing biannual concentrations for a 2-year period (2006–2007). Analytical results demonstrate that only As in seawater had an increasing trend after 2006. Further, a hazard index (HI) is applied to assess the potential hazard of contaminants to the environment. The HI ($HI = C_{95\%}/C_{allowable}$) is defined as the ratio of the 95th percentile for a pollutant concentration ($C_{95\%}$) to an allowable concentration for each pollutant ($C_{allowable}$). The hazard index is used to establish a pollutant priority ranking and, then, serves as a useful screening tool for developing strategies for desalination pollution control. In this study, if the priority is to improve water quality, focus should be placed on Cu ($HI = 0.32$). On the other hand, if the priority is sediment quality, the As concentration ($HI = 0.51$) should be reduced. If the two HIs (seawater and sediment) are considered together, As ($HI = 0.56$) becomes the highest-ranking trace element, followed by Zn ($HI = 0.54$).

1. Introduction

Penghu County, Taiwan, is an offshore island located in the Taiwan Strait. The marine environment around Penghu is home to diverse fish and shellfish species which are important natural and tourist resources for Penghu Island residents. However, due to the geography of Penghu Islands, precipitation is rare and potable water is generally generated by seawater desalination. The use of desalinated seawater as drinking water has increased significantly; however, many desalination plants release high amounts of concentrated brine containing trace elements into the marine environment. As a result, the marine environment is polluted with potentially toxic trace elements (PTTEs), which are frequently detected in desalination plant effluent outfall areas [1]. These PTTEs have been recognized as the most deleterious contaminants to biota in marine and estuarine environments. These PTTEs discharged from desalination plants are mainly from the following three sources: scale inhibitors, brines, the corrosion of permeate tubes and other utility pipes [2].

Desalinated activity in Penghu has added sizeable volumes of waste to desalination effluence water and sediments for several years. Therefore, the desalination effluent area was recognized as a major environmental issue for the marine environment around Penghu. Consequently, interest in studying the contaminant distribution and environmental impact of effluent has been significant. As reported by previous studies [3–7], sediments and organisms (Pacific oyster—*Crassostrea gigas*) have been sampled from an offshore area near the Penghu Islands during 1991–1998. Lin et al. [14] found that concentrations of copper (Cu), zinc (Zn) and arsenic (As) are detectable in bivalves. However, the possible relationship between seafood consumption and human exposure to many contaminants has not been extensively investigated. This may require a comprehensive analysis of chemical, toxicological and ecological data [8–10]. These high PTTE concentrations may not affect organisms directly but rather may transfer toxicity to humans through the food chain and accumulate in human bodies. Moreover, an increase in environmental stress of the Penghu Island ecosystem from added pollution may reduce seafood resources and adversely affect human health.

In this study, total 54 sediment samples and 170 water samples, collected from each season during 2006–2007 in the desalination area of the Penghu Islands, Taiwan, are used for the analysis. Different from the aforementioned researches which mainly focused on the PTTE concentrations in sediment and bivalves, the importance of this work and novelty are highlighted as follows. This paper presents a study to investigate the temporal and spatial trends of the PTTE concentrations in both seawater and sediment. The correlation of PTTE concentrations between different seawater depths and sediment is analyzed by a statistic correlation method. In addition, the PTTE concentrations

* Corresponding author. Tel.: +886 2 2730 1227.
E-mail address: khy@mail.ntust.edu.tw (K.-H. Yang).

0011-9164/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2011.07.059

measured in the desalination plant effluent are compared with the PTTE concentrations obtained in seawater and sediments to prove that the desalination discharge is the point source of PTTEs. Further, a hazard index, defined as the ratio of the 95th percentile of a pollutant concentration to an allowable concentration, is applied to assess the potential hazard of contaminants to the environment. In the hazard assessment, a pollutant priority ranking is established, and then, serve as a useful screening tool for developing strategies for desalination pollution control.

2. Materials and methods

2.1. Sample collection

The effluent area of the seawater desalination plant in this work is located on southeastern side of Penghu County, Taiwan. As the desalination effluent discharge outfall was the point source in the study area, analyzed PTTE concentrations from sediment samples are expected to detect directly from desalination plant effluent as well. Fig. 1 shows a map of the study area. Sediment and water were sampled from a sector area and a radius of approximately of 3 km. Three sediment and water samples were collected at each distance of 50, 100, 200, 400, 600, 1000, 1500, 2000 and 3000 m from the coast near the desalination plant outfall area. Sediment samples were collected from the seabed at target locations at a depth of 25–50 m below the water surface. Sampling depths for water samples were 1, 25 and 50 m (close to the deepest point), respectively. In total, 54 (6×9) sediment samples and 170($6\times9\times3$) water samples were collected. Fig. 1 shows sampling locations of the location of desalination plant outfall. Season samplings were taken from June 2006 to December 2007.

2.2. Sample processing

Sediment samples were collected by diving into the surface layer of the seabed at target locations. Sediment was collected by gently pushing a bottle to surface layer with a depth of approximately of 5 cm and then slowly moving the bottle forward until it was loaded. The filled bottles were then sealed with lids. Sediment and water samples were maintained fresh by storing them inside an ice box before being transported back to laboratory for sample preparation and analysis.

2.3. Sample analysis

2.3.1. Sediment analysis

In the laboratory, excess seawater in bottles was decanted and sediment samples were then air-dried at room temperature. The dried sediment samples were first screened through a 1 mm sieve to remove large particles. The screened sediment was then washed with deionized water to remove any remaining salts before drying in an oven at 65 °C for at least 24 h. Dried sediment was ground to a powder using an agate mortar and pestle. The particles sized less than 63 μm were collected and roughly 1 g dry weight sediment was digested using a mixture of concentrated acids (HNO_3:HCl = 1:3). The digestion procedure was described by Rauret et al. [11]. The digested samples were then ready for analysis of trace elements (*e.g.*, Cu, Zn and As). Samples were prepared according to the procedure by Hung and Hsu [12] and Chen et al. [13].

PTTEs in digested sediment samples were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent-7500a) according to the U.S. Environmental Protection Agency (USEPA) Method 6020. Blanks were included in each test batch for quality assurance (QA) and quality control (QC). The standard calibration procedure was followed to ensure the accuracy of the analytical method. A certified reference standard sediment, PACS-1, from the National Research Council of Canada was utilized to test analytical method and instrument accuracy. The difference between the certified and measured results was <10% for samples in this study. The minimum detection limits (MDL) were 0.118, 0.404, and 0.179 mg kg^{-1} for Cu, Zn, and As, respectively.

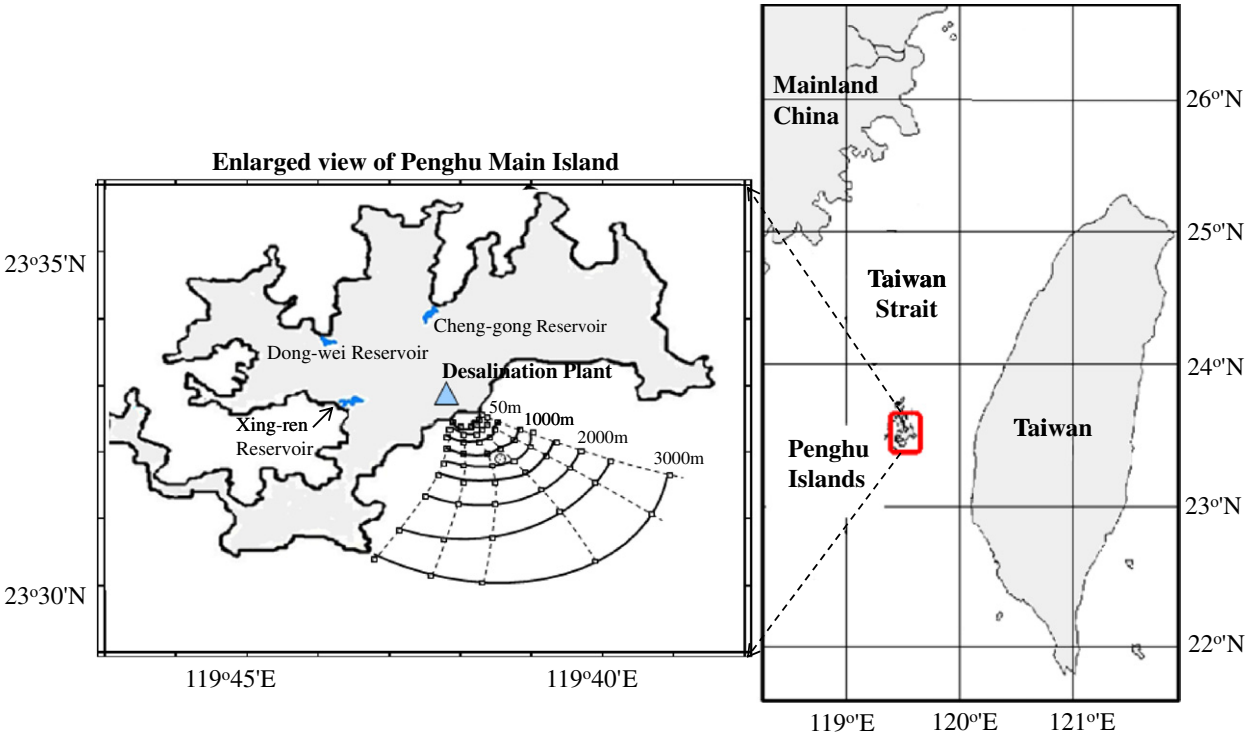

Fig. 1. Study area and location of sampling points (⊠).

2.3.2. Effluent and seawater analysis

The volumetric flow rate of the desalination plant effluent was 30,000 m^3 day^{-1}. The seawater samples and effluent samples were taken to the laboratory and digested using a microwave digester with a mixture of nitric and sulfuric acid (1/1, v/v) solution. Both Cu and Zn were measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin Elmer-2000DV) according to the USEPA Method 6020. The As concentration was determined by graphite atomic absorption spectrometry (Perkin Elmer AA700). Standard addition procedures were employed to calculate analytical concentrations. A certified reference standard material, NIST 1640, representing a mine-impacted creek was utilized to test method and instrument accuracy. The difference between the certified and measured results was insignificant. The MDL were 0.03, 0.19, and 0.14 mg kg^{-1} for Cu, Zn, and As, respectively.

2.4. Statistical analysis

Data analysis utilized statistical methods. To assess the strength of the relationship of PTTE concentrations between sediment and water, Spearman's rank correlation instead of a simple linear correlation, such as the Pearson technique analysis, was used. To test for significant differences between PTTE distributions within 1000 m and those outside the effluence from 1000 to 3000 m, the One-Way analysis of variance (ANOVA) statistic method was used. Spearman's correlation analysis and the One-Way ANOVA were performed using PAWS Statistics 18 for Windows [17]. Spearman correlation analysis was employed to study the relationship among sediment characteristics [13].

3. Results and discussion

3.1. Temporal trends and relationships

Variations in concentrations of Cu, Zn, and As over time were determined using plotted sector diagrams of the mean biannual concentration values (average of several sampling rounds) for seawater at three depths and sediment samples. Fig. 2 shows a systematic trend of decreasing concentrations, as was the case for Cu. Copper concentration peaks were observed from high (0.77–0.82 μg/L) to low (0.08–0.05 μg/L) in seawater since the fourth quarter of 2006 (Fig. 2a). Sediment also exhibited a moderate decreasing trend (Fig. 2d). Consequently, fluctuations in Cu concentrations from the discharge may lead to definitive conclusion (Fig. 2a). Conversely, peaks of Zn concentrations were observed from non-detectable to the

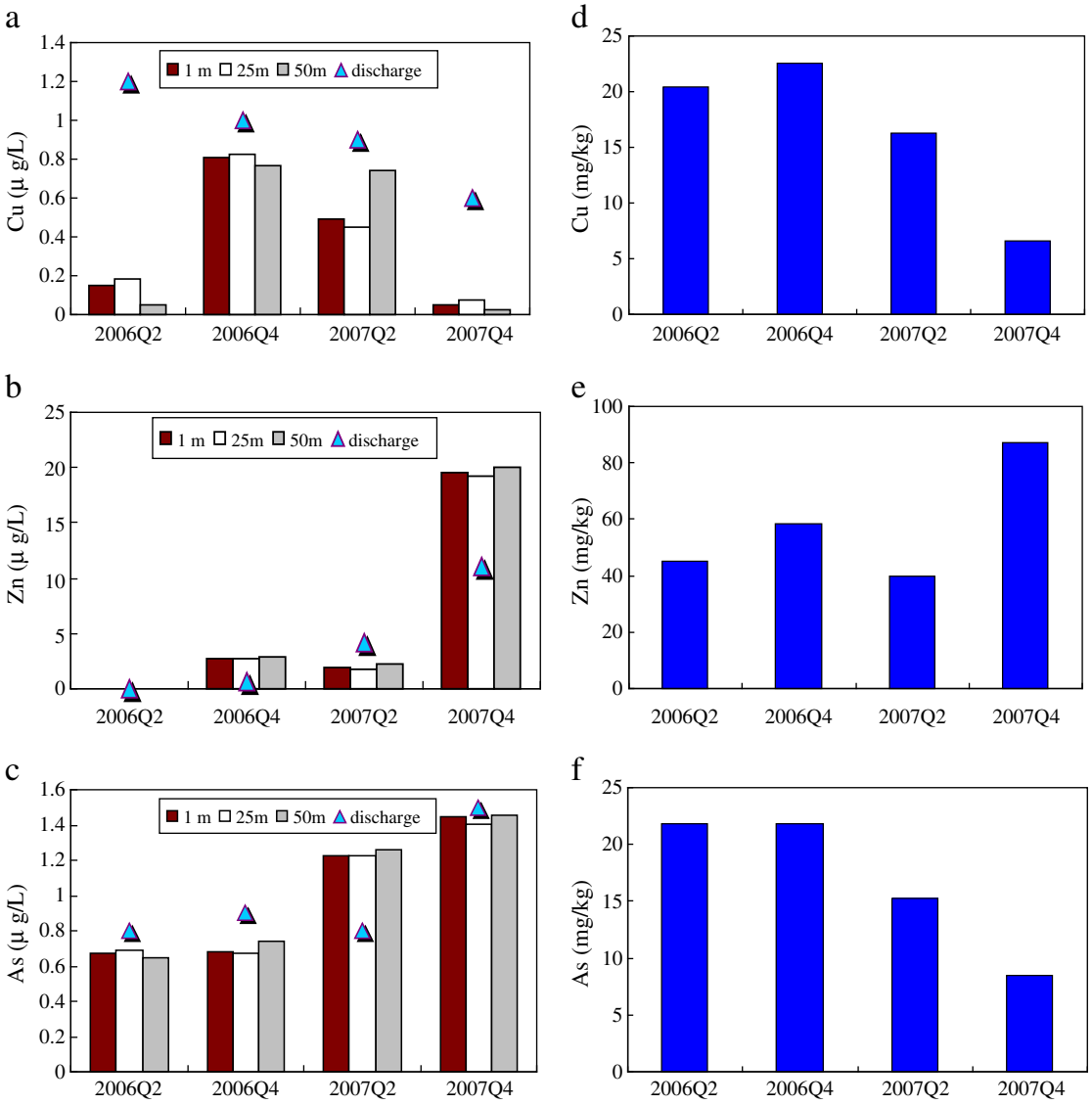

Fig. 2. Mean biannual PTTE concentrations of Cu, Zn, and As collected in seawater ((a), (b), and (c)) and in sediment ((d), (e), and (f)), for a 2-year period (2006–2007).

highest concentration (19.29–20.02 μg/L) in seawater since the second quarter of 2006 (Fig. 2b). Similarly, the highest Zn concentration in sediment was also detected in the fourth quarter of 2007 (Fig. 2e). Comparatively speaking that the circumstance of the fluctuations of Cu and Zn in the desalination effluent area may be proved using discharge concentrations (Fig. 2b). The temporal trends of As concentrations between seawater and sediment were differed from those of Cu and Zn. Fig. 2c shows that the As concentration increased in seawater, and decreased in sediment (Fig. 2f). The fluctuations in seawater may be influenced by discharge concentrations, but may not those in sediment.

To discuss the correlation between the three depths seawater and sediment in three PTTEs (Cu, Zn, and As), Chen et al. [13] applied Spearman correlation analysis to test the relationship among sediment characteristics between the six trace PTTEs (*i.e.*, Cu, Zn, Cr, Cd, Hg and Pb), and Lin et al. [14] reported that the trace element concentrations of Cu, Zn, and As in organisms exhibit an apparent variation compare to Cr, Cd, Hg and Pb. Therefore, this work applied Spearman correlation analysis to test the relationship among sediment and seawater at depths of 1, 25, and 50 m respectively in the three trace elements (Cu, Zn, and As) is showed in Table 1. Table 1(b) shown a correlation coefficient of 0.913 and confidence level of 99% (or $r=0.913$, $p<0.01$), indicating that high Zn concentration existed at a depth of 25 m and was usually accompanied a high concentration at a depth of 50 m. The correlations among concentrations of seawater at depths of 1, 25 and 50 m indicate that seawater received pollutant input from desalination effluent and contaminants accumulated in the vicinity of the desalination effluent area. Second, Spearman correlation analysis was applied to test the relationship between trace element concentrations (Cu, Zn, and As) in seawater and sediment (Table 1(a), (b) and (c)). The correlation coefficients for Cu and Zn were not significant at $p>0.05$, but the correlation coefficients of As was significant at $p>0.01$ (Table 1(c)). The high As concentration in sediment accompanied a low concentration at a depth of 50 m in seawater with a negative correlation coefficient of 0.544 and confidence level of 99% (or $r=-0.544$, $p<0.01$). Most studies a presented strong negative correlation between sediment grain sizes and trace metal concentrations in sediment [18,19]. Another, organic matter content was important factor affecting the trace metal concentration in sediment [13]. In this study, the result of As concentration at a depth of 50 m in seawater may be another factor affecting the trace metal concentration in sediment.

Conversely, results of this study indicated that such correlations for Cu and Zn were anticipated, due to the differences between physical, chemical and biological processes at work in seawater and sediment matrices.

Table 1
Spearman correlation coefficients for (a)Cu, (b)Zn, and (c)As concentrations in water at a depth of 1 m, 25 m, 50 m, and in sediment.

(a) Cu	n	1 m	25 m	50 m
1 m	216			
25 m	216	0.759*		
50 m	216	0.740*	0.740*	
Sediment	216	–	–	–
(b) Zn	n	1 m	25 m	50 m
1 m	216			
25 m	216	0.900*		
50 m	216	0.884*	0.913*	
Sediment	216	–	–	–
(c) As	n	1 m	25 m	50 m
1 m	216			
25 m	216	0.832*		
50 m	216	0.795*	0.828*	
Sediment	216	−0.527*	−0.535*	−0.544*

(–: not significant at $p>0.05$; others are significant).
* Significant at $p<0.01$.

3.2. Spatial trends and sediment characteristics

In terms of temporal trends, trace As concentrations from effluent increased (Fig. 2c) and were influenced in the spatial trends of seawater and sediment. As concentrations presented negative correlation between sediment and seawater (Table 1(c)). In the references, the concentrations of As were researched by Hsueh et al. [15] have shown multiple risk factors of the Black-Foot Disease (BFD) from fishing communities in Taiwanese; therefore, in spatial trends, there was the first detail investigation of As trace element concentrations about seawater and sediment in the desalination effluence area. The selected sampling locations are closed to the outfall of the seawater desalination, where waste by-products have been discharged. Hence, it is of interest to explore the relationship between the known industrial activities and observed peak values in the concentration records of the trace elements. The spatial trends of As concentrations were concerned with this topic.

The spatial trends of As concentrations were investigated in seawater and sediment. First, concentrations of As trace element in seawater ranged from 0.4 to 1.1 μg/L for 1 meter depth, from 0.4 to 1.3 μg/L for 25 meter depth, and from 0 to 1.0 μg/L for 50 meter depth as shown in Fig. 3a–c; furthermore, the results were showed that there were generally lower in the desalination effluence station than within surrounding stations except for the distance range from 1000 to 3000 m from the coast near the desalination plant outfall area. Second, concentrations of As trace element in sediment ranged from 0.67 to 5.67 mg/kg, as shown in Fig. 3d; in addition, the results were showed that the higher concentration of As trace element was located on areas near the distance of 600 m, as well as within the desalination effluence. Hence, the elevated trace element may be discharged from non-specific coastal land, lagoon and the desalination. On the other hand, the elevated trace element of As distribution within the desalination plant outfall area was apparently derived mainly from the desalination plant, and the coastal area wasn't significantly polluted from plants except for the desalination plant. It has been suggested that the desalination plant effluent increases PTTE concentrations in the sediment in the outfall area [14].

3.3. Pollutant priority ranking

Addressing diffused pollution in the desalination discharge area requires identification of priorities. Pantazidou et al. [10] developed an approach for ranking contaminants based on toxicity reflected by allowable limits. The main idea was to identify each contaminant, and for each matrix identify a conservative measure for the high end of detected concentrations and compare this value with concentration limits in water and sediment. In the proposed approach for the desalination discharge area, all concentrations of trace elements in a matrix are pooled together (*e.g.*, all measured Cu concentrations from sediment samples between the second quarter of 2006 and the fourth quarter of 2007 are combined for 648 Cu concentration values). Then, the 95th-percentile concentration value ($C_{95\%}$) is exceeding 95% of all measured concentration values. The ratio of the 95th-percentile concentration value ($C_{95\%}$) to the concentration limit (C_{limit}) is a measure of the hazard associated with each trace element. As mentioned the C_{limit} for water and sediment samples was considered equal to the limit concentration specified by the EPA for saltwater (USEPA, 2006) and the intervention value for sediment in Dutch regulations (Netherlands Ministry of Housing, 2000), respectively.

Table 2 shows the hazard indices for the three PTTEs in seawater and sediment, and when both matrices are considered together. These analytical results demonstrate that to improve water quality, measures are necessary to decrease Cu concentrations. Additionally,

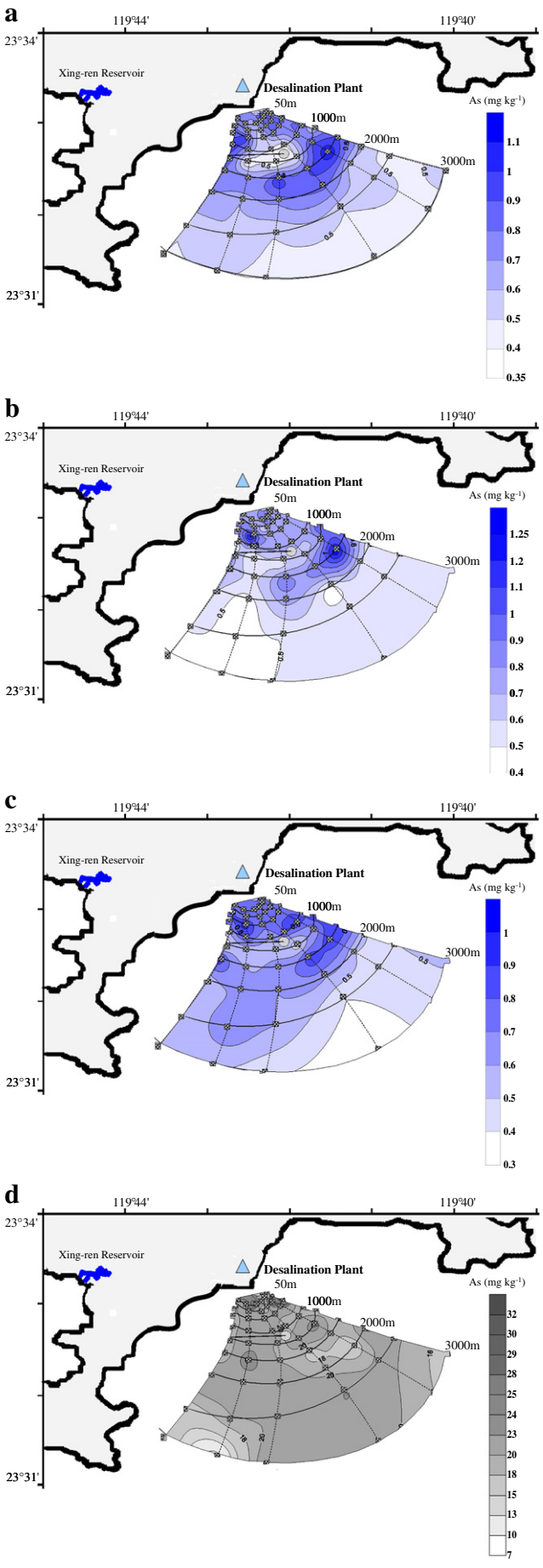

Fig. 3. Contour map of As concentrations (mg kg^{-1}) in seawater at a depth of 1 m (a), 25 m (b), 50 m (c) respectively, and in sediment (d).

Table 2
Hazard indices for three PTTE pollutants in the desalination area.

PTTE	Hazard index = $C_{95\%}/C_{limit}$		
	Water	Sediment	Water + sediment
Copper (Cu)	1.20/3.70 = 0.32	23.5/190.0 = 0.12	0.45
Zinc (Zn)	23.00/85.60 = 0.27	197.75/720.00 = 0.28	0.54
Arsenic (As)	1.80/36.00 = 0.05	28.10/55.00 = 0.51	0.56

Concentration units are in (μg/L) for water samples and (μg/g) for sediment samples.

to improve sediment quality, measures are necessary to decrease As concentrations. Miri et al. [16] claimed the impact of PTTEs on organisms, specifically for some commercially important fish and shrimp species, has also been evaluated for potential human health impacts. In Taiwan, epidemiological studies of residents from fishing communities in the Black-Foot Disease (BFD) area identified multiple risk factors associated with As-induced skin cancer [15]. The As concentration in sediment may be a potential risk factor for human health in the desalination discharge environment. Finally, the two matrices are of equal interest, as As had the highest-ranking PTTE, followed by Zn.

4. Conclusions and recommendations

Analysis of a 2-year-long record of Cu, Zn, and As concentrations in water and sediment samples from Penghu Island shows a strong negative correlation between seawater and sediment for As only. The As concentration at a depth of 50 m in seawater may be a factor affecting the trace metal concentration in sediment. Analysis of the spatial variation along the coast also clearly shows the relationship between desalination effluent and elevated As concentrations as no other point source existed in the sampling area. The hazard indices developed to characterize desalination discharge show that As was the contaminant with the highest concentration. If, on the other hand, locations are ranked the priority area is the desalination effluence area within 1000 m, where most As concentrations exceeded allowable limits. Once these priority areas have been established, sediment quality should then be assessed in detail using both ecotoxicological and chemical data. Finally, analytical results will prove helpful when developing effective watershed and coast management strategies to control PTTEs discharged from desalination plants.

References

[1] M. Sadiq, Metal contamination in sediments from a desalination plant effluent outfall area, Sci. Total Environ. 287 (2002) 37–44.
[2] F.S. Al-Ketbi, E.Z. Isnasious, A.M. Al-Mahyas, Practical observations on reverse osmosis plants including raw water contamination problems, different intake stations and permeator performance, Desalination 93 (1993) 259–272.
[3] B.C. Han, T.C. Hung, Green oysters caused by copper pollution on the Taiwan coast, Environ. Pollut. 65 (1990) 347–362.
[4] B.C. Han, W.L. Jeng, T.C. Hung, M.S. Jeng, Copper intake and health threat by consuming seafood from copper-contaminated coastal environments in Taiwan, Environ. Toxicol. Chem. 13 (1994) 775–780.
[5] B.C. Han, W.L. Jeng, T.C. Hung, M.Y. Wen, Relationship between copper speciation in sediments and bioaccumulation by marine bivalves of Taiwan, Environ. Pollut. 91 (1996) 35–39.
[6] B.C. Han, W.L. Jeng, M.S. Jeng, L.T. Kao, P.J. Meng, Y.L. Huang, Rock-shells (*Thais clavigera*) as an indicator of As, Cu and Zn contamination on the Putai coast of the Black-Foot Disease area in Taiwan, Arch. Environ. Contam. Toxicol. 32 (1997) 456–461.
[7] B.C. Han, W.L. Jeng, T.C. Hung, Y.C. Ling, M.J. Shieh, L.C. Chien, Estimation of metal and organochlorine pesticide exposures and potential health threat by consumption of oysters in Taiwan, Environ. Pollut. 109 (2000) 147–156.
[8] P.M. Chapman, The sediment quality triad approach to determining pollution-induced degradation, Sci. Total Environ. 97/98 (1990) 815–825.

[9] W. Ahlf, H. Hollert, H. Neumann-Hensel, M. Ricking, A guidance for the assessment and evaluation of sediment quality: a German approach based on ecotoxicological and chemical measurements, J. Soils Sediments 1 (2002) 37–42.
[10] M. Pantazidou, S. Kapniaris, A. Katsiri, A. Christidis, Pollutant trends and hazard ranking in Elefsis Bay, Greece, Desalination 210 (2007) 69–82.
[11] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit. 1 (1999) 57–61.
[12] J.J. Hung, C.L. Hsu, Present state and historical changes of trace metal pollution in Kaoping coastal sediments, southwestern Taiwan, Mar. Pollut. Bull. 49 (2004) 986–998.
[13] C.W. Chen, C.M. Kao, C.F. Chen, C.D. Dong, Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan, Chemosphere 66 (2007) 1431–1440.
[14] M.H. Lin, C.H. Lee, Y.C. Lin, K.H. Yang, Potentially toxic trace elements accumulating in marine sediment and bivalves in the outfall area of a desalination plant, Desalin. Water Treat. 25 (2011) 106–112.
[15] Y.M. Hsueh, G.S. Cheng, M.M. Wu, H.S. Yu, T.L. Kuo, C.J. Chen, Multiple risk factors associated with arsenic-induced skin cancer: effects of chronic liver disease and malnutritional status, Br. J. Cancer 71 (1995) 109–114.
[16] R. Miri, A. Chouikhi, Ecotoxicological marine impacts from seawater desalination plants, Desalination 182 (2005) 403–410.
[17] SPSS, PAWS Statistics 18 for Window, SPSS Inc., 233 S. Wacker Dr., Chicago, IL 60606, USA, 2009. www.spss.com.
[18] F. Wang, J. Chen, Relation of sediment characteristics to trace metal concentrations: a statistical study, Water Res. 1 (4) (2000) 694–698.
[19] K.M. Huang, S. Lin, Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan, Chemosphere 53 (2003) 1113–1121.