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The Impacts of Environmental Characteristics to Groundwater Quality and Influencing Toxicity in Seashore Area

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Abstract. Groundwater is an important substitute water source in seashore zone of Taiwan owing to its accessibility and stability. However, the potential toxicity derived from inorganic metal, organic contaminant leaking from industrial area, soil salinity and disinfection by-products (DBPs) has attracted governors' attention to the health risk in groundwater usage. To figure out the impacts of environmental factors to the patterns of pollutant as well as to bio-toxicity in groundwater, Redundancy analysis (RDA) technology is utilized to assess their causalities in this study. Results pointed out that inorganic arsenite concentration is highly related to biological toxicity. The main species of HAAs is bromodichloroacetic acids and dichloroacetic acids, they was dominated by bromide (Br^-) concentration and humic substances, respectively. The existence of bromide in groundwater is resulted from soil salinity due to seawater incursion. For water safety, the removal of HAAs and arsenite are necessary, and effective limit of HAAs generation should devote to limit the increase of Br^- and humic substances. Thus, RDA was demonstrated a useful tool to investigate the causal relationship among the environment variables, pollution and toxicity in environmental studies.

Introduction

The safety of groundwater is always an important issue in most developing countries as groundwater is dispensable in agricultural and industrial sectors. In some areas such as the seashore area in central Taiwan, groundwater for non-drink usage will be purified by simple water treatment procedures. For past decades, population and industrial areas are crowded into seashore area because of lower land cost. Intensive human actives have increased the possibility of pollutants leakage and lead to higher health risk in groundwater usage. For such concerns, many researches have survey the environmental toxicants and their negative impacts to various groundwater usages. It is believed that inorganic arsenic contamination in groundwater is enriched in sediments and weathered rocks [1-2]. High arsenate (As^{3+}) and arsenite (As^{5+}) concentration can cause blackfoot disease and various cancers[3-5]. Some organic pollutants such including trihalomethanes (THMs) and haloacetic acids (HAAs), produced disinfection procedure, are identified to be a carcinogen. If humic substances, the precursor of DBPs, appeared in groundwater, the DBPs would be stimulated the formulation of DBPs. Many researches also indicated that bromide will active the halogen from chlorine to bromine, so that natural organic matters turned into bromine more faster with the help of bromide [7]. Teksoy (2008) reported that the specie patterns in DBPs are relative to pH, temperature, dissolved organic matter, bromide concentration, and operation factors [7]. To quantify the impacts of toxic substances to organisms, biological toxicity tests are concerned as a useful index in revealing the comprehensive impacts of toxic substances for water bodies. However, it is difficult for decision makers to distinguish the contributions of inorganic metal, organic contaminant and it by-product to biological toxicity[8]. Thus, researches attempted to investigate the predominant factors in biological toxicity by using the data mining technologies. For example, Belkhiri et al.,(2010) used multivariate statistical analysis to evaluate the species distributions in groundwater [9]. Redundancy analysis (RDA) is a multivariate analysis method that capable of determining the correlations between two sets of variables [10-13].

To reveal the causality among environmental variables, toxic substances and bio- toxicity, this study used RDA approach to (1) explore the relationship between contaminant and biological toxicity from their spatial concentration distributions and (2) investigate the existence of clear causality between physico-chemical environment parameters and the generation of HAAs after simple drinking water treatment for reducing the HAAs product, by using RDA methods which enabled the interpretation of species product inside these disinfection processes. In which environment parameters included dissolved organic carbon (DOC), chlorine (Cl^-), dissolved oxygen (DO), turbidity, conductivity, H.S., pH, bromide concentration (Br^-).

METHODOLOGY

Background and Study Area.

The study area, the seashore area of Taichung city, was located in central Taiwan and next to the coast line of the Taiwan Strait. In this area, groundwater is one of main drinking water source after simple drinking water treatment. A conventional industry complex is heavily operated for about 30 years and a lot of plants tend to relocate there due to the rapid growing in population density in Taiwan. Here is possibly facing the threats the unexpected leakages from industrial waste. It would influence the groundwater quality and increase the health risk of drinking water. Hence, lots of sampling sites as shown in Fig. 1(A) to monitor groundwater quality were collected using standard sampling procedures [14] during the dry season in 2011. The monitored parameters in sampling site included environmental parameter, contaminants, biological toxicity and derived DBPs that refer to HAAs. In which the Microtox test was conducted to evaluate the biological toxicity of groundwater after simple drinking water treatment. Microtox uses a decrease in the luminescence of the bacterium Vibrio fischeri to calculate an effective concentrations (EC50) at which luminescence is decreased by 50 %. HAAs concentration was sum of various species that monochloro- (MCAA), dichloro- (DCAA), trichloro- (TCAA), monobromo- (MBAA), bromochloro- (BCAA), bromodichloroacetic acids (BDCAA) and Tribromoacetic acid (TBAA). All monitored results of groundwater quality and HAAs were present in spatial concentration distributions using the geographic information system integrated with Kriging method.

Redundancy analysis

To reduce the HAAs product, the RDA was conducted to identify the causality between environmental parameter and the generation of HAAs species. It also could understand the dominant species of HAAs. RDA is a linear, direct gradient constrained ordination method by which response variables are constrained to be linear combinations of explanatory variables [15].Each canonical ordination axis in RDA biplot corresponds to a direction, in the multivariate scatter of objects (response variables), which is maximally related to a linear combination of the explanatory variables. RDA preserves the Euclidean distance among objects in matrix containing values of response variables fitted by regression to the explanatory variables. The eigenanalysis equation for RDA may be derived through multiple linear regressions, followed by principal component decomposition. Detail calculation steps of RDA referred to the Legendre et. al. reference [17]. The sum of canonical eigenvalues in RDA equals the amount of variance in the response variable explained by the explanatory variables [18]. In this study, RDA was carried out with the software Canoco for Windows 4.5 and their graphics were created with CanoDraw for Windows 4.1. This software distinguishes

Table 1. The environment parameters and HAAs components in sampling site

Site	Environment parameters (explanatory variables)								Speciation composition of HAAs (response variables)*						
	DOC	Cl^-	pH	DO	**Turbidity**	**Conductivity**	H.S.	Br^-	MCAA	DCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA
L-2	2.85	33.47	7.52	4.71	0.72	611.00	1.81	0.16	10.42	36.93	14.52	6.57	4.67	4.71	9.00
L-4	0.55	19.50	7.19	6.05	0.32	389.00	0.16	0.09	1.78	4.35	1.17	7.16	1.62	1.32	1.15
L-6	0.68	21.49	6.14	3.85	0.28	351.00	0.38	0.10	2.85	5.13	2.43	2.66	1.70	1.05	6.33
L-11	1.10	14.08	6.79	2.34	8.27	427.00	0.14	0.00	10.34	20.58	2.31	0.00	0.00	0.00	0.00
S-3	3.67	18.20	6.93	6.36	0.37	412.00	1.26	0.28	22.48	15.35	2.71	29.07	3.09	3.09	4.49
S-5	0.80	23.60	5.90	3.87	0.97	352.00	0.51	0.11	6.36	11.62	3.57	1.02	0.80	0.60	2.98
S-10	4.78	20.60	6.19	2.86	1.05	451.00	0.38	0.37	19.64	6.46	7.73	26.61	1.13	2.13	4.78
W-2	1.02	20.50	8.07	6.18	0.59	482.00	0.31	0.31	9.80	15.59	5.02	7.16	1.59	2.59	6.97
W-6	1.03	15.76	7.71	3.50	0.95	495.00	0.40	0.24	8.20	11.64	3.07	4.73	1.64	2.24	4.64
W-10	1.75	243.04	7.57	4.57	0.35	1320.00	0.57	0.48	22.88	3.87	2.87	36.41	0.97	2.17	2.95
W-14	2.42	55.40	7.57	4.43	4.88	1263.00	0.99	0.67	6.25	27.90	3.53	28.05	2.45	2.29	4.42
W-16	2.23	81.21	7.92	5.37	0.38	1012.00	0.94	0.00	10.20	25.97	9.78	0.00	0.00	0.00	0.00

HAAs = MCAA+ MBAA+ DCAA+TCAA+BDCAA+DBAA+CDBAA+TBAA, MCAA: $CH_2ClCOOH$, DCAA: $CHCl_2COOH$, TCAA: CCl_3COOH, MBAA: $CH_2BrCOOH$, DBAA: $CHBr_2COOH$, TBAA: CBr_3COOH , BCAA: $CHClBrCOOH$, BDCAA: $CHClBr_2COOH$; * Unit= μg/L

among response variables, explanatory variables in this study, and the input variable of RDA and site data was shown in Table 1 for identifying the causality between environmental parameter and the generation of HAAs. Further, two case was conducted that first case is the response variables consisted of "HAA-with Br" and "HAA-with Br", response variables in second case is each species of HAAs. In which the named "HAA-with Br" concentration was sum of MBAA, BCAA, BDCAA and TBAA. The named "HAA-without-Br" concentration was sum of MCAA, DCAA, and TCAA. The output of RDA is a biplot ordination diagram that will be illustrated the correlations between response and explanatory variables in the first two major axes.

RESULT AND DISCUSSION

Relationship between contaminant and biological toxicity distribution

Fig. 1(B)-(F) show the spatial concentration distribution of monitored parameter that included Cl^-, As^{3+}, As^{5+}, biological toxicity and HAAs, respectively. From the monitored Cl- concentration in Fig 1(B), it is believed that seawater intrusion then soil salinization is happening in this area. In Fig. 1(C)-(D), the highest concentration of As^{3+} and As^{5+} appeared in W-7 and W-10 site, respectively. The salinization, geochemical conditions, and pollutants leakage may be the reasons that leading to the difference in spatial distribution between of As^{3+} and As^{5+}. The highest biological toxicity site appeared in location of about W-10 mention site and the trend of biological toxicity was decreased as distance far from seashore as Fig.1(E). In which this distribution was approximately consistent with the concentration distribution of Cl^- and As^{+5} in Fig. 1(B)-(E) and implied the biological toxicity possibly correlative with the effect of salinization and inorganic contaminant As^{+5}. However, As^{3+} was regularly more toxic than As^{5+}, but the site of highest biological toxicity and As^{5+} appeared in same location. It indicated that the dosage of contaminant in geochemical conditions of study area is possible main contribution of affecting the biological toxicity.

In addition, the spatial concentration distribution of HAAs was shown in Fig. 1(F) and higher concentration of HAAs present in W-8, S-3 and S-10 site. Though this HAAs distribution is not consistent with biological toxicity, HAAs is still the possible enhanced contribution to biological toxicity. Due to that the HAAs is a group of compounds concentration and the generation of specie in

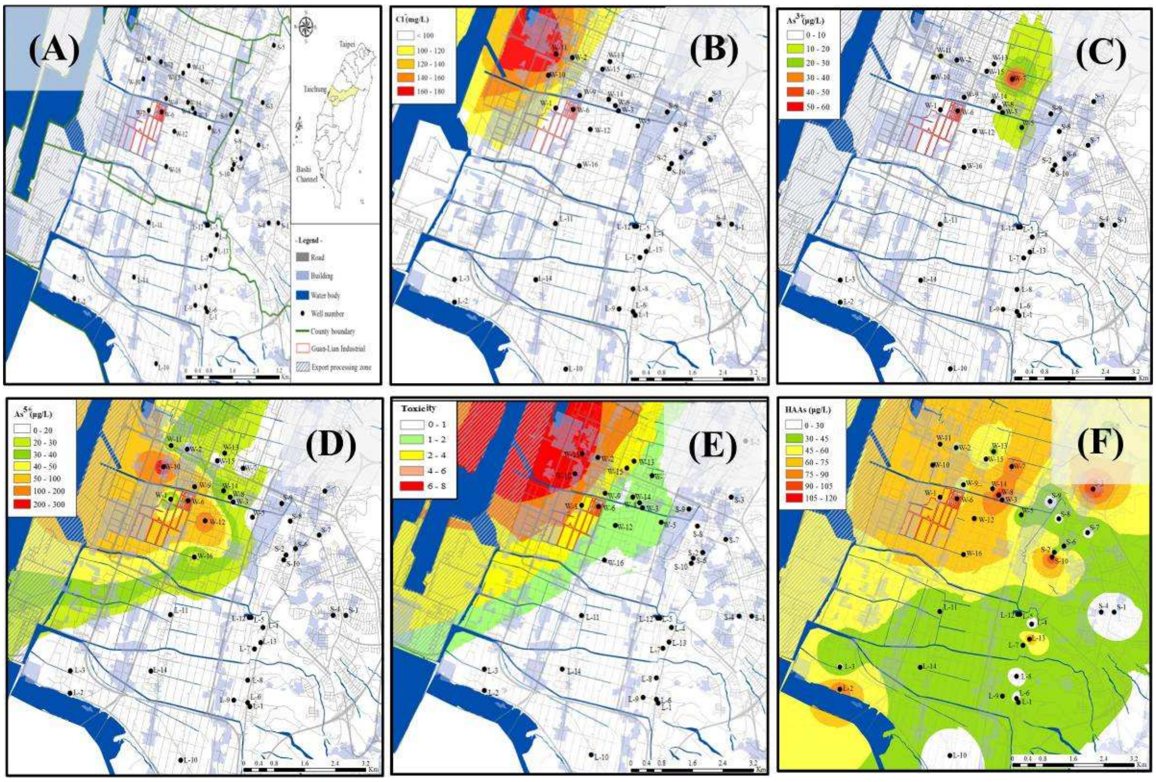

Fig. 1 (A) Study area and spatial distribution of groundwater quality parameter that (B) Cl^-, (C) As^{3+}, (D) As^{5+}, (E) biological toxicity, (F) HAAs.

HAAs is depend on environmental condition, it would be difficult to interpret the contribution to biological toxicity from the spatial concentration distributions. How to explore the dominant specie in HAAs that would possibly increase the biological toxicity is requested for reducing the DBPs concentration and biological toxicity. Further, identifying the main environment parameter that lead to the generation of dominant specie in HAA is also assist the removal of DBPs. For this reason, the development of technology to explore the main contribution resulted in biological toxicity or generation of DBPs from the complicated contributions and environment parameters is necessary.

Causality between environmental parameter and DBPs speciation.

RDA analysis was conducted to investigate the influence of groundwater environmental parameter on species composition of HAAs and identify the main species in HAAs for reducing the DBPs concentration and biological toxicity, the input variable of RDA and site date shown in Table 1 and two cases was test. First, Fig.2 (A) revealed that the red arrows of environmental variables that Br^-, Cl^- DOC and conductivity point in the same direction implied these parameters are existence of positive correlation. On the contrary, turbidity point opposite directions indicated the correlation between turbidity and other parameter as conductivity is negative. It also implied the turbidity seems to be composed by nonorganic substances. The angles between red arrows of environmental variables indicated correlations between individual environmental variables, and the appearance of high correlation between the Br^- and Cl^- concentration depicted that the Br^- also resulted from salinization. The arrow points of environmental parameter in the direction of the steepest increase of values of environmental parameter, for example the higher DOC concentration appeared in S-3sample site. Similarly, the length of the arrow of contaminant variable is associated to the importance of the variable and the two type HAAs that “HAA-with Br” and “HAA-with Br” revealed similar importance for HAAs distribution in study area. The result we concerned that possible causality between production of two type HAAs and environmental parameter indicated that the generation of “HAA-with Br” and “HAA-with Br” were dominated by the environment parameter that Br^- and H.S. ,respectively. It implied that reducing the concentration of Br^- and H.S. would limit the generation of “HAA-with Br” and “HAA-with Br”. But this RDA biplot in Fig. 2(A) only explain 79% of the total variation in the HAAs data (dependent variables) by the chosen environmental variables and it could not point out the dominant species of HAAs in study area as well.

Hence, this study also identified the influence of groundwater environmental parameter on each species generation of HAAs. The RDA biplot result in Fig. 2(B) could demonstrate that 91.3% of the total variation in the HAAs data (dependent variables) could be explained by the chosen environmental variables. The red arrow of Br^- in Fig. 2(B) pointed out the higher Br- concentration present in S-3 and W-10 sample site. The interests we concerned are that possible causality between production of HAAs speciation and environmental parameter. These closed arrows among BDCAA, MCAA, Cl^- and Br^- indicated the production of BDCAA and MCAA could be dominated by Cl^- and Br^-, respectively. The longer blue arrows of BDCAA that projected on first axes denoted that BDCAA is dominant species of HAAs in study area. It also implied that removing the Br^- concentration would reduce efficiently the most of HAAs. Reducing the DOC concentration to limit the production of BDCAA and MCA is effective than reducing the H.S. concentration. Moreover, another dominant speciation of HAAs, DCAA, in study area groundwater is correlation with H.S and slight related to pH and turbidity. It also suggested remove the dominated H.S. contaminant would prevent the generation of DCAA. Other product of HAAs speciation including BCAA, DBAA, TBAA and CDBAA all were dominated by H.S. despite they were not the dominant species. Based on the RDA results of Fig.2, it revealed that the environmental variable including Br^-, Cl^-, DOC and H.S. would be the dominant factors for explaining DBPs groups. In which demonstrated that RDA is a useful tool to investigate the causal relationship among the environment variables, pollution and toxicity in environmental studies as well.

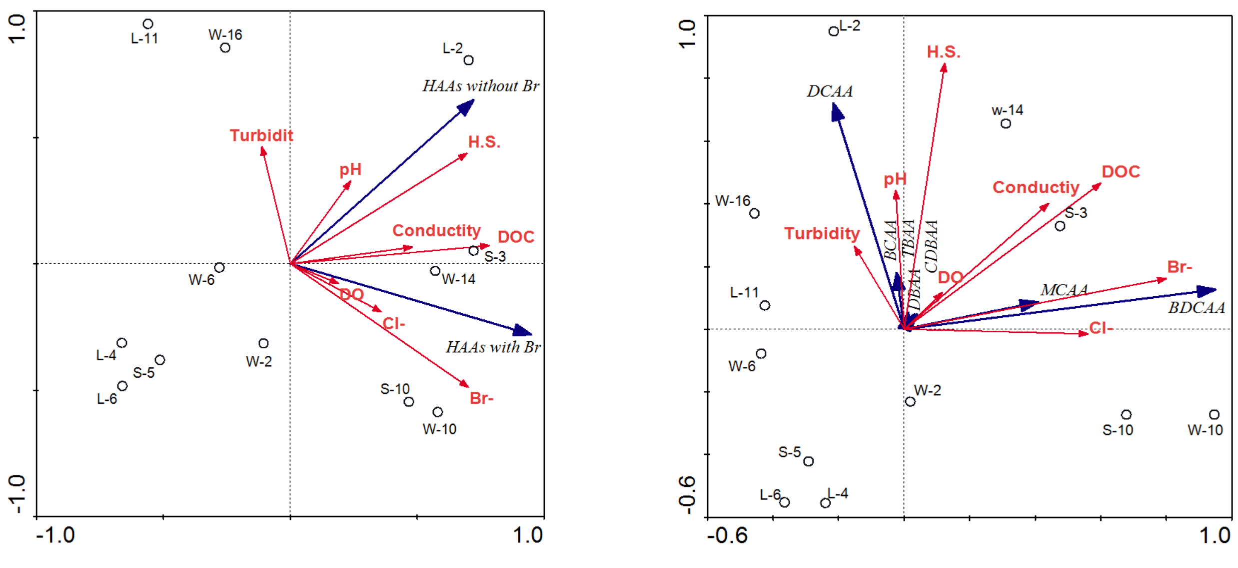

Fig. 2. RDA biplot result that environment parameters (red solid lines with arrowhead), sampling sites (circle point), and (A) two type specie of HAAs (blue solid lines with arrowhead) and (B) each species of THMs (blue solid lines with arrowhead).

CONCLUSION

Groundwater is one of possible source for drinking water in our study area after simple drinking water treatment, then attempt to explore the dominated environmental contaminant and DBPs that resulting in toxicity is necessary for water management. Hence, the spatial analysis and RDA technology were conducted to analysis monitored groundwater data in study area. The result point out that the dominated factor lead to bio-toxicity was possible As^{5+} contaminant using the analysis of spatial concentration distributions. However, using the spatial concentration distributions of contaminant, DBPs and biological toxicity could not interpret clearly the correlation among them and not identify their contribution. The RDA biplot results reported that avoiding to the generation of dominant speciation in HAAs, it could eliminate the Br^- concentration in groundwater to reduce efficiently the BDCAA and MCAA. Removal of DCAA should devote to limit the H.S. concentration. In conclusion, RDA method can serve as a powerful tool for assessing the correlation between environment contribution and DBPs. In which it could obtain the dominant factors for removal efficiencies of hazardous material. The seawater intrusion and soil salinization increased the Br^- concentration and it lead to the generation of HAAs after simple drinking water treatment then possibly enhanced the biological toxicity in study area.

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