Bulgarian Chemical Communications, Volume 49, Number 1, (pp. 157 – 160) 2017

Environmental safety assessment on chlorination by-products in brine discharged from desalination plant

Jing Liu [*], Xingyu Zeng, Dongxing Zhou, Yunrong Zhao, Xianhui Pan

The Institute of Seawater Desalination and Multipurpose Utilization(SOA), Tianjin ,China

Received October 10, 2016; Revised February 10, 2017

Concentration analysis was performed on five chlorination by-products (chloral, dichloroacetic acid, trichloroacetic acid, 2,4,6-trichlorophenol, and pentachloro-phenol) present in the brine discharged from desalination project of Dagang New Spring Co., Ltd. Moreover, toxic effects ($L(E)C_{50}$) analysis was performed on three basic levels of aquatic organisms, namely, *Scenedesmus vacuolatus*, *Daphnia magna*, and *Oncorhynchus mykiss*. Based on the analysis, the quotient method from the technical guidance document on safety assessment of chemical substances by the European Union was adopted to assess the ecological risks of five chlorination by-products in the brine discharged from desalination plant. The results showed that the rates of detection of five chlorination by-products were 100%. The quotients of PEC/PNEC of chloral, dichloroacetic acid, trichloroacetic acid and pentachlorophenol were higher than 1. Among the four pollutants, we must pay more attention to chloral which environmental concentration in the brine discharged from desalination plant is 17 times higher than the no effect concentrations.

Key words: by-products, brine, chlorination, desalination, discharged, safe assessment.

INTRODUCTION

The global water production by desalination will exceed 38 billion cubic meters per year, nearly twice the rate of global water production in 2008[1]. According to the 12th Five-Year (2010–2015) Plan for the scientific and technological development of seawater desalinization [2], an innovative system would be established during the period, and desalinization technology should reach an advanced level [3]. But brine discharge from desalination plants contains pollutants such as chemical additives and heavy metals, resulting in serious impacts on the offshore seawater environment and the ecological system. This discharge also includes anticorrosion products used in the plants and has to be treated to acceptable levels of each chemical before discharge; however, acceptable levels vary depending on certain factors such as receiving waters and state regulations. Furthermore, the extent of impact intensifies with the increasing capacity of desalination [4-6].

In order to prevent biofouling and corrosion caused by bacteria, algae, and other marine organisms during the process of desalination, bactericides such as chlorine or hypochlorite are commonly used with a regular dosage of 2–5 mg/L and a maximum of 8 mg/L [7]. These chlorine-based bactericides may react with organic compounds in seawaters to form chlorination by-products such as chloral. Although concentration of chloral declines due to continuous degradation and dilution, even very low level could harm the aquatic organisms [8-9]. These chlorinated and halogenated organic byproducts are toxic, carcinogenic, or otherwise harmful to aquatic life. Therefore, monitoring of chlorination by-products in the discharged brine to study their environment effects has attracted significant attention which remarkably facilitates the sustainable development of the desalination industry.

In this study, concentration analysis was performed on five chlorination by-products (chloral, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), 2,4,6–trichlorophenol (2,4,6-TCP) and pentachlorophenol(PCP)) present in the brine discharged from desalination project of Dagang New Spring Co., Ltd. The vulnerability of marine ecosystems is likely to be influenced by the chlorination by-products present in brine. Therefore, preliminary environmental safety assessment on chlorination by-products in the brine discharged from desalination plant was introduced in this study.

EXPERIMENTAL

Materials Analytical methods

Nine surface water samples were collected from three sections of the hydrological station in the immediate vicinity of the brine discharge of Tianjin Dagang Newspring Co., Ltd. in July 2015 (Figure 1. Sampling points: S1-S9). Samples were collected in chemically cleaned glass sampling bottles, refrigerated, and sealed for laboratory detection. An Agilent 7890 gas chromatography system was used for analysis.

To whom all correspondence should be sent:
E-mail: g.kashi11@yahoo.com

Fig 1. Sampling locations map of 5 chlorination by-products in the brine discharged of Tianjin Dagang Newspring Co. Ltd

Analysis of chloral

The head space and gas chromatography used to determine chloral. The method has many advantages such as wide linear range, high precision, accuracy and sensitivity. The minimum detection limit can reach 0. 05μg/L, the water sample determination is simple and rapid, and the result is satisfactory. The peak with retention time of 4.28min was chloral, respectively (Fig. 2)

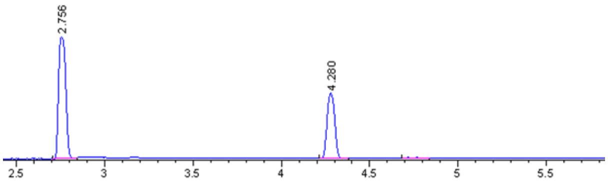

Fig.2. Chromatogram of standard solutions of chloral

Analysis of DCAA and TCAA

The purge and trap/gas chromatography used to determine DCAA and TCAA. The analyte was esterified by acidic methanol, preconcentrated by purge and trap, determined by gas chromatograph (GC) with an electron capture detector (ECD). The factors of acidic methanol were discussed. The linear correlation coefficients at concentrations ranging from 0.0 to 120.0 μg/L were 0.998 and 0.996.The detection limits of this method were 0.15 and 0.84μg/L.

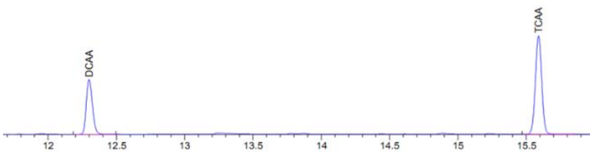

Fig. 3. Chromatograms of standard solutions of DCAA and TCAA

The relative standard deviations (RSD %) for the determination of DCAA and TCAA in water were 1.01 and 2.68%, and the recovery was 87.2-112.4%.The feasibility of this method was sensitive and precise for determination of DCAA and TCAA. The peaks with retention time of 12.32min and 15.62min were DCAA and TCAA, respectively (Fig. 3)

Analysis of chloral

The automated headspace solid phase micro extraction (HS-SPME) and gas chromatography used to determine TCP and PCP. Through automated sample pre-treatment to improve the detection efficiency and results accuracy. The linearity in the detecting range is good (> 0.999) with the detection limits of 0.148 and 0.126μg/L, and the RSD (n =7) were 4.89 and 7.31%.Test for recovery was made by standard addition method, giving results in the range of 90.0 % - 112.8 %. The peaks with retention time of 7.65min and 9.51min were TCP and PCP, respectively (Fig. 4)

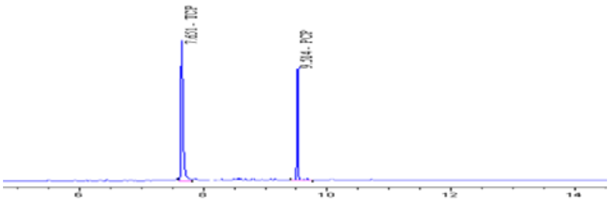

Fig. 4. Chromatograms of standard solutions of TCP and PCP

Method of Environmental Risk Assessment

An ecological risk assessment method was adopted for the environmental safety assessment, which roughly included both the qualitative and quantitative analysis. Qualitative methods were designed to assess the effects with minor quantitative information, providing the decision-making process involving deep-level information. However, quantitative methods mainly consisted of quotient methods, probability risk assessment methods, and statistical analysis methods, with quotient methods representing the most commonly and extensively used risk characterization approaches. The hazard quotient is calculated through comparison between actual environmental exposure concentrations and toxicity data characterizing the substance's harm extent, thus assessing the ecological risk of the pollutant [10-12]. Referring to Guidelines for Risk Assessment of Chemical Substances [13], the acute toxicity effects of algae, fleas, and fish could be considered as the initial assessment index in the environmental safety assessment of the pollutant, in order to preliminarily determine the range of safe concentration. Therefore, the results indicated that safety analysis and assessment could be conveniently conducted through a quotient method on five chlorination by-products in the brine discharged from desalination plant.

RESULTS AND DISCUSSION

Concentrations of chlorination by-products in the brine discharged from desalination

The statistical data of concentrations of individual chlorination by-products in the brine discharged from desalination plant are listed in Table 1. The rates of detection of five chlorination by-products were 100%.

Table 1. Concentrations of chlorination by-products in the brine discharged from desalination plant (μg/L)

	S1	S2	S3	S4	S5
Chloral	15.4	18.5	22.2	13.3	9.65
DCAA	21.9	1.37	1.37	0.36	3.3
TCAA	10.1	4.27	4.27	4.26	4.3
TCP	0.51	0.47	0.47	0.41	0.44
PCP	0.20	0.43	0.43	0.18	0.20

	S6	S7	S8	S9
Chloral	30.6	10.7	21.0	14.6
DCAA	3.56	0.36	0.36	2.69
TCAA	4.26	4.26	4.26	4.47
2,4,6-TCP	0.37	0.36	0.31	0.42
PCP	0.08	0.07	0.06	0.20

Safety Analysis

The Predicted No Effect Concentration (PNEC) is an estimate of the highest concentration of a chemical in a particular environment at which no adverse effects are expected and is an estimate of the sensitivity of the ecosystem to a chemical. A dose-effect assessment was adopted with the objective of determining the PNEC which could be predicted through the acute toxicity data of five chlorination by-products on algae, fleas, and fish. Dose-effect assessment primarily requires species laboratory toxicological test to obtain toxicological data before considering adequate assessment factors, which is applied to toxicological data extrapolation to calculate the PNEC, the highest concentration offering the least possible unacceptable effects. On account of several uncertainties of the extrapolation process, the assessment coefficient has been considered 1000 as extrapolating PNEC through the acute toxicity effects ($L(E)C_{50}$) of the three basic nutrition levels (algae, fleas, and fish) [14].

Referring to the concentrations based on aquatic life protection from Canadian Water Quality Guidelines for the Protection of Aquatic Life [15], this study provided the preliminarily prediction of the PNEC (Tab. 2).

The Predicted Environmental Concentration (PEC) represents the exposure situation of a chemical substance in the evaluated environment. PEC is obtained through model prediction or environmental monitoring. This study conducted the exposure assessment based on the field measurement. Adhering to the "worst situation" principle in risk assessment, the highest environmental detection concentration was selected as the PEC of exposure assessment in the analysis results of different batches of samples (Tab. 2).

Risk assessment is designed to supervise the possible risks and provides the guarantee of safety. The internationally accepted hazard quotient (HQ) represents the ratio of the PEC to PNEC. In this study, quotient method was adopted to assess risk characterization and risks are quantified by using the following formula:

$$HQ = PEC/PNEC \quad (1)$$

Where, HQ represents hazard quotient; PEC is Predicted Environmental Concentration, and PNEC is the abbreviation for Predicted No Effect Concentration. Following conclusions were derived, conclusion A:for HQ <0.1, environmental risks were negligible and implementation of the management measures over target substances was not required; conclusion B: when HQ was in the range of 0.1–1.0, environment was still considered to be in the safe level, however, required long-term observation of the environmental dynamics of target substances to avoid the occurrence of high risks; conclusion C: HQ >1.0 indicated possibility of environmental risks under the existing pollution conditions; therefore, long-term monitoring was necessary and the predictability should be improved through conscientiously analyzing all links of risk assessment. The HQs of five chlorination by-products in the brine discharged from desalination plant are listed in Table 2.

Table 2. Safety assessment of chlorination by-products in the brine discharged from desalination plant

	PEC	PNEC	HQ	Conclusion
Chloral	30.6	1.8	17.0	C
DCAA	21.9	8.7	2.51	C
TCAA	10.1	8.7	1.17	C
TCP	0.51	18.0	0.03	A
PCP	0.43	0.25	1.72	C

The HQ value of chloral, DCAA, TCAA, and PCP were higher than 1.0, in particular, the HQ value of chloral reaching a peak of 17.0. The results showed that potential ecological risk from chlorination by-products was presented in the brine discharged from desalination plant. Bactericides were used in seawater desalination pretreatment, which were tended to have chlorination reaction with humus in water. The chloral was the major product, leading to a relative high level in concentrate discharge. The risk of chloral has been proved by toxicology and biology. Based on the research, we concluded that monitoring should be conducted over chlorination by-products in brine discharged from desalination plant posing serious environmental risks. Moreover, an effective resolution program should be proposed and implemented through the study on the relationship between the ambient concentrations of chlorination by-products in concentrate and the types and amount of biocides in use.

CONCLUSION

In conducting ecological risk assessment, exposure concentration and toxicity data are represented either as single values or as distributions. Among the five chlorination by-products studied, the by-products of bactericides used in seawater desalination concentrate discharge posed serious risks on the ecology. We proposed intense monitoring of bactericide by-products, in particular, chloral. Moreover, a series of management measures should be considered to strengthen the control over concentrate discharge and the use of bactericides.

Acknowledgements: *This work was supported in part by a research grant (201305039) from the State Oceanic Administration People's Republic of China, and in part by a grant (2014BAB06B00) from the National Science Foundation. However, the manuscript has not been subjected to peer and policy review of the agency and therefore does not necessarily reflect its views*

REFERENCES

1. M. Elimelech, W. Phillip, *Science*, **333**, 712 (2011).
2. Ministry of Science and Technology of People's Republic of China & National Development and Reform Commission, 2012.
3. T. Chen, Q. Wang, Y. Qin, X. Chen, X. Yang, *PLOS ONE* , **13**, 1 (2015).
4. Y. Wang, J. Liu, J. Lan-Ying, Q. Zhou, X.Y. Zeng *Marine environmental science*, **32**, 456 (2013).
5. J. Sadhwani, J. Veza, C. Santana, *Desalination*, **185**, 1427 (2005).
6. C. Sommariva, H. Hogg, K. Callister, *Desalination* **167**, 439 (2004).
7. M.A. Xuehu, Z. Lan, S. Wang, L. Lu, *Chemical Industry and Engineering Progress* , **30**, 233 (2011).
8. A. David, L. Emma, *Water Reseach*, **44**, 5117 (2010).
9. M. Elabbar, F. Elmabrouk, *Desalination*, **185**, 31 (2005).
10. X.Y. Zeng, J. Liu, Y. Wang, X. Pan, *Journal of Safety and Environment*, **14**, 234 (2014).
11. Y. Wang, J. Liu, *The Administration and Technique of Environmental Monitoring*, **24**, 35 (2012).
12. Z. Pang, L. Feng, J. Zhou, Z. Liu, *Environmental Chemistry*, **3**, 430 (2011).
13. H. Wang, N.Y. Yang, R.Z. Yu, Z. Fang, J.L. Zhou, *Research of Environmental Sciences*, **22**, 805 (2009).
14. EU:Technical Guidance Document (TGD) on risk assessment of chemical substances following european regulations and directives, 2nd ed, Italy, 2003.
15. National Guidelines and Standards Office: Environment Canadian Water Quality Guidelines for the Protection of Aquatic Life, December 2007.

ЕКОЛОГИЧНА ОЦЕНКА НА БЕЗОПАСНОСТТА НА ВТОРИЧНИ ПРОДУКТИ НА ХЛОРИРАНЕ В САЛАМУРА, ИЗХВЪРЛЕНА ОТ ИНСТАЛАЦИЯ ЗА ОБЕЗСОЛЯВАНЕ

Джинг Лиу*, Ксингю Зенг, Донгксинг Жу, Юнронг Жао, Ксианхюй Пан

Институт за обезсоляване на морска вода и комплексно оползотворяване (SOA), Тиендзин, Китай

Получени 10 октомври 2016 г., ревизирана 10 февруари 2017 г.

(Резюме)

Извършен е анализ на концентрацията на пет вторични продукти на хлориране (хлорал, дихлорооцетна киселина, трихлороцетна киселина, 2,4,6-трихлорофенол, и пентахлоро-фенол), намиращи се в саламурата, изхвърлена от проект за обезсоляване на Dagang New Spring Co., Ltd. Освен това , анализа на токсичните ефекти (L (E) C50) се извършва на три основни нива за водни организми, а именно, *Scenedesmus vacuolatus*, водни бълхи, и дъгова пъстърва. Въз основа на анализа, методът от документа за технически насоки за оценка на безопасността на химичните вещества на Европейския съюз е приет, за да се направи оценка на екологичните рискове от петте странични продукти на хлориране в саламура, изхвърлена от инсталация за обезсоляване. Резултатите показват, че процентът на откриване на петте продукти на хлориране е 100%. Коефициентите на PEC/PNEC на хлорал, дихлорооцетна киселина, трихлороцетна киселина и пентахлорфенолът са по-високи от 1. Между четирите замърсители, трябва да се обърне повече внимание на хлорала, чиято концентрация в околната среда от саламурата, изхвърлена от инсталацията за обезсоляване е 17 пъти по-висока от безопасната концентрация.