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수산물가공산단 대기 중 황 및 질소 화합물의 분포

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Distributions of sulfur and nitrogen compounds in ambient air of a fishery industrial complex

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ABSTRACT

This study was performed to investigate the distributions of sulfur and nitrogen compounds in ambient air at the boundary area of a fishery industrial complex in Yeosu during May to November in 2007. Samples were collected from the total 8 sampling sites and analyzed by the air dilution olfactory method and instrumental analysis method. The sum of mean concentration of sulfur(hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) and nitrogen(ammonia and trimethylamine) compounds measured from all of the sampling sites were 0.6ppb and 87.0ppb, respectively. Among the odor compounds, the mean concentration of ammonia was 85.3ppb which was significantly higher than other odor compounds. Furthermore, the mean concentrations of each odor compound are much lower than the limits of the Odor Emission Standard regulated on the industrial area. However, the mean dilution to threshold (D/T) ratio at site O-6 is higher than the limit of the Odor Emission Standard 5 times. With the odor diffusion, it will cause the headaches or health risk on the people who worked or lived at this boundary area. In addition, from the correlation analysis results, we confirmed that the trimethylamine(TMA) is the primary odor compound in the boundary area of this fishery industrial complex.

Key words : Odor(악취), Boundary area(부지경계), Sulfur compounds(황 화합물), Nitrogen compounds (질소 화합물), Fishery(수산물가공)

1. Introduction

Nowadays, the large-scale of food industries have increased such as fishery and these operations usually generate more and more numerous types of odors. The residents who lived around such industrial area complain for odor nuisance whenever the odor leaks to the outside[1]. So the Offensive Odor Control Law is enacted for the purpose of preserving living environment and contributing to protection of the people's health by carrying out necessary regulations and by promoting other countermeasures to control offensive odors generated in the course of business activities at factories in many industrialized countries[2]. There are various measurement techniques, such as gas chromatography, open-path fourier transform infrared spectroscopy and human nose are used for odor measurement. In fishery, the composition of volatile compounds in fish contributing to the characteristic odors can be determined and related to quality and the odor of fish can be classified as species-related fresh fish odor, microbial spoilage odor, oxidized odor, processing odor, and environmentally derived odor[3), 4)]. In the case of microbial spoilage odor, the odor compounds generated from the microbial activity and oxidative degradation and the odor components included such as sulfur compounds, nitrogen compounds and other compounds which may cause malodor[5)~9)]. In this study, we attempted to investigate on the distributions of sulfur and nitrogen compounds in ambient air at the boundary area of a fishery industrial complex in Yeosu.

2. Materials and Methods

Samples were collected from the boundary area, including 6 boundary(O-1~O-6) sites and 2 complaint(O-7, O-8) sites, total of 8 sampling sites located at a fishery industrial complex in Yeosu during May to November in 2007. Fig 1 shows the specific locations of sampling sites. Sample items are selected such as ammonia, trimethylamine(TMA), hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide which are the typical odor compounds in fishery. Table 1 shows the Odor Emission Standard and the threshold limit values of the sulfur and nitrogen compounds. Two of the odor measurement methods are used including air dilution olfactory method and instrumental analysis method. In the case of air dilution olfactory method, samples are collected by the Tedlar bag When sampling, after placing a Tedlar bag into the sealed sampling vessel, sample air is drawn into the bag by the pressure difference between the inside and outside, and we use the Panel Method for calculating the dilution to threshold(D/T) ratio. In the case of nitrogen compounds collection, the ammonia is collected in the collecting solution(boric acid) by air suction for 5 minutes at the flow rate of 10 liters per minute and the ambient air based on impinger sampling in dilute 1N H_2SO_4 at flow rate of 10 liters per minute for 5 minutes are used for the collection of TMA. The Tedlar bag(5L, Tokyo Deodorant Inc. Japan) are used for the collection of sulfur compounds. Before the sampling, we used the high purity nitrogen gas(99.999%) to clean the sampling bag more than 3 times. All of the sampling methods are regulated in the Korean Odor Analysis Standards[10]. Table 2 shows the instrumental analysis and the operating conditions, all of the samples were analyzed within 24 hours.

In order to assessment the characteristic of odor and the interrelationship between each odor compound, the sum of odor concentration(SOC) and the sum of odor quotient(SOQ) were cited, the equation of this two factors can be described as follows:

$$SOC = \Sigma Odor\ Concentration = \Sigma OC \quad (1)$$

where OC is the concentration of each odor compound(ppb) measured by the instrumental analysis.

$$SOQ = \Sigma Odor\ Quotient = \Sigma OQ \quad (2)$$

where OQ is the quotient between the concentration(ppb) and the odor threshold value of each odor compound(ppb).

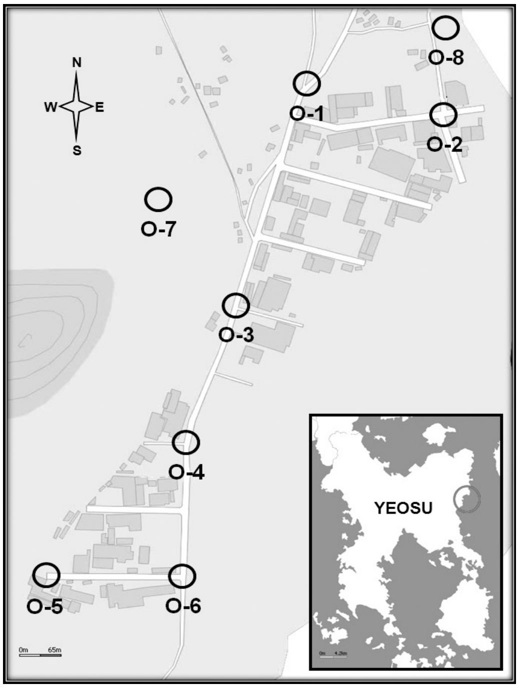

Fig 1. The specific locations of sampling sites.

3. Results and Discussion

Figs. 2 and 3 show the comparison of sulfur and nitrogen compound concentrations from the boundary area, respectively. The sum of mean concentration of total compounds was 87.6ppb and the ammonia mean concentration was 85.26ppb in the proportion of 95%, followed by TMA, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide with the mean concentrations of 1.75, 0.25, 0.18, 0.07, 0.06ppb, respectively. The mean concentrations of each odor compound are much lower than the limits of the Odor

Table 1. Odor Emission Standard and the threshold limit values of the sulfur and nitrogen compounds

Category	Compounds	Chemical formula	Odor Emission Standard(ppb)		Threshold limit values (ppb)[11]
			Industrial area	Other area	
Sulfur compounds	Hydrogen sulfide	H_2S	60	20	0.5
	Methyl mercaptan	CH_3SH	4	2	0.1
	Dimethyl sulfide	C_2H_6S	50	10	0.1
	Dimethyl disulfide	$C_2H_6S_2$	30	9	0.3
Nitrogen compounds	Ammonia	NH_3	2000	1000	100
	TMA	$(CH_3)_3N$	20	5	0.1

Table 2. Instrumental analysis and the operating conditions

Category	Compounds	Instrumental analysis and the operating conditions
Sulfur compounds	Hydrogen sulfide Methyl mercaptan Dimethyl sulfide Dimethyl disulfide	GC: GC-17A, Shimadzu Detector: FPD Column: GS-Q(30m×0.53mm×2.65um) Column temperature: 110℃(1min)→15℃/min→210℃ Injector temperature: 200℃ Detector temperature: 200℃ Carrier gas: He(99.999%), 20ml/min
Nitrogen compounds	Ammonia	UV-1201, Shimadzu
	TMA	GC: GC-17A, Shimadzu Detector: NPD Column: Volamine capillary column(60m×0.32㎜) Column temperature: 50℃(3min)→10℃/min→190℃ Injector temperature: 240℃ Detector temperature: 240℃ Carrier gas: He(99.999%), 2ml/min

Emission Standard regulated on the industrial area. Furthermore, it is important to note that the difference is at least 10 times between the maximum and the minimum concentrations of all odor compounds. It is suspected that this phenomenon was attributed to the operation hours of factories, wind direction and some direct and indirect factors. It also certified the randomicity and instantaneity of odors.

The concentration distribution of the sulfur compounds are shown in Fig 4. The OQ of TMA is the highest at all of the sampling sites and the mean of OQ distribution can be described as TMA (81%) > methyl mercaptan (9%) > ammonia (4%) > dimethyl sulfide (3%) > hydrogen sulfide (2%) > dimethyl disulfide (1%). Fig 5 shows the comparison of the (D/T) ratio and the SOQ. As we know, the major facilities belong to neither the outlet nor the boundary area, so the limit of the (D/T) ratio was not regulated by the Odor Emission Standard. The mean (D/T) ratio at site O−6 is near 100 which is higher than the limit of the Odor Emission Standard 5 times while others are lower than the limit value. In addition, to the accompaniment of odor diffusion, it will affect people's normal life and be the cause for complaint around site O−6. In the case of OQ, the result shows the similar trend to the (D/T) ratio. Actually, the value of (D/T) ratio should be higher than the SOQ at the same sampling site. However, some of the data are opposites. Under the influence of temperature, humidity and wind speed, it will lead to the departure from what is expected.

Correlation coefficients were performed in order to determine if there was any discernible statistical relationship between the (D/T) ratio, the concentrations of nitrogen and sulfur compounds, the SOC and the SOQ at the boundary area(Table 3). From the table we can find that the ammonia has a strong correlation with the SOC(r=0.997, n=48) and this analysis supported that the ammonia concentration is significantly higher than any other odor compounds at the boundary area. However, it is absolute no correlation between the (DT) ratio and the OQ of ammonia(r=−0.045, n=48, Fig 6). Furthermore, the highest correlation between the (D/T) ratio and the OQ of TMA(r=0.872, n=48, Fig 7) is appeared and it indicated that the TMA was the major odor compound at this boundary area.

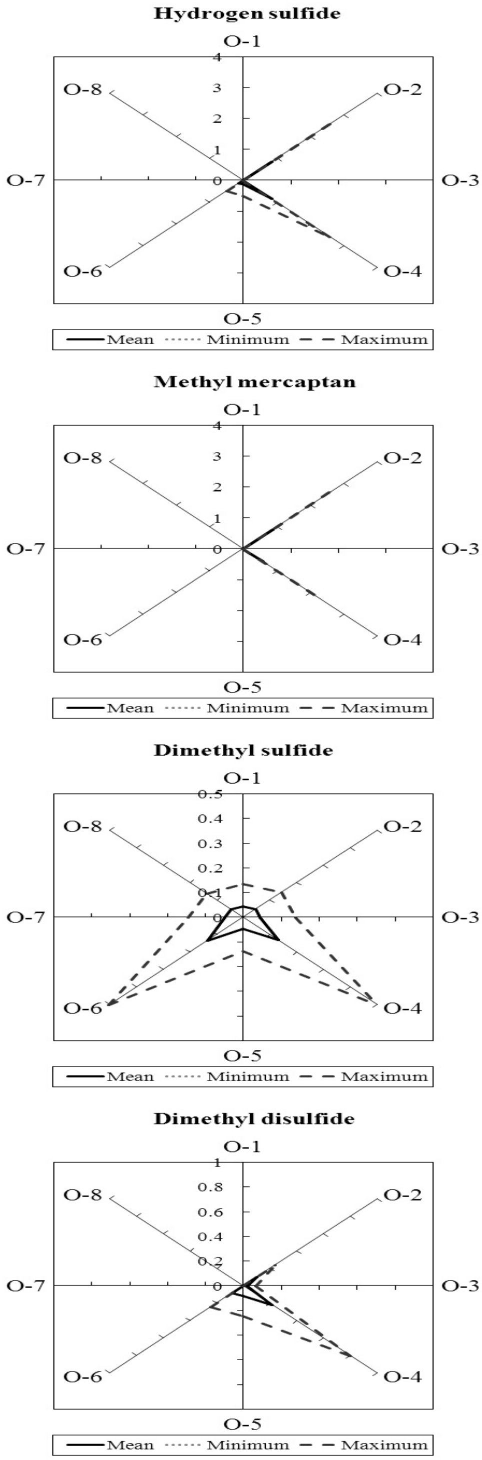

Fig 2. Concentration distribution of the sulfur compounds(unit: ppb).

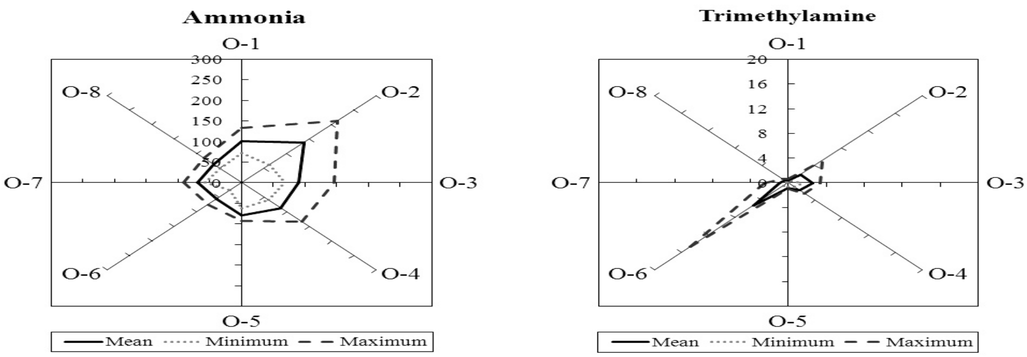

Fig 3. Concentration distribution of the nitrogen compounds(unit: ppb).

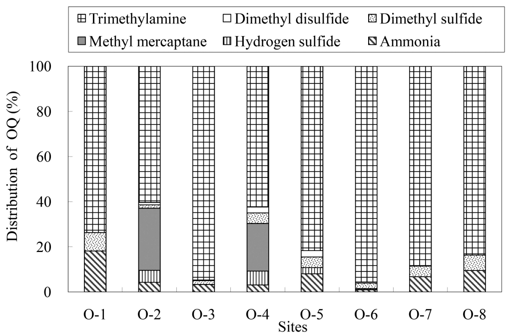

Fig 4. Distribution of the OQ of all odor compounds.

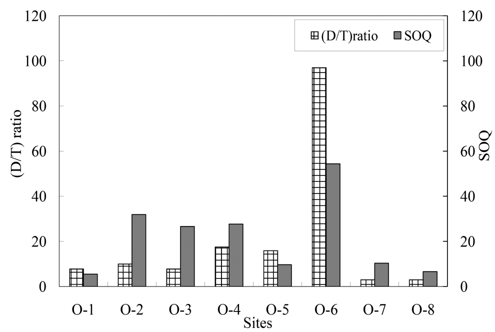

Fig 5. Comparison of the (D/T) ratio and the SOQ.

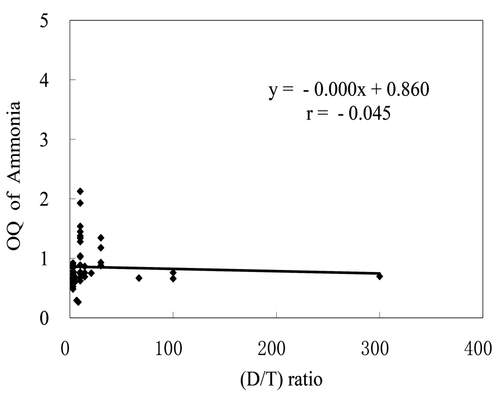

Fig 6. Correlation analysis between the (DT) ratio and the OQ of ammonia.

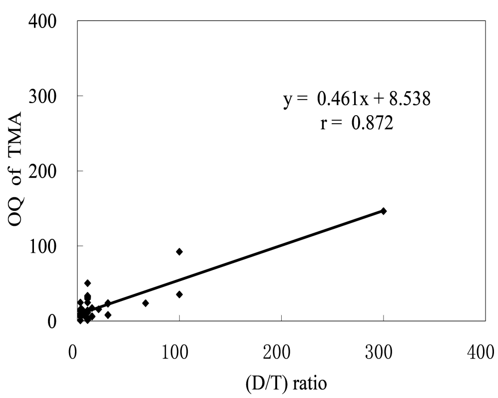

Fig 7. Correlation analysis between the (DT) ratio and the OQ of TMA.

Table 3. Results of correlation analysis between the different analysis items(n=48)

	(D/T)ratio	Ammonia	Hydrogen sulfide	Methyl mercaptan	Dimethyl sulfide	Dimethyl disulfide	TMA	SOC	SOQ
(D/T)ratio	1.000								
Ammonia	−0.048	1.000							
Hydrogen sulfide	0.043	−0.142	1.000						
Methyl mercaptan	−0.015	0.025	0.531	1.000					
Dimethyl sulfide	0.176	0.005	0.046	0.151	1.000				
Dimethyl disulfide	0.082	0.107	0.095	0.696	0.382	1.000			
TMA	0.872	0.164	−0.008	−0.070	0.257	0.026	1.000		
SOC	0.011	0.997	−0.112	0.050	0.029	0.126	0.228	1.000	
SOQ	0.842	0.172	0.179	0.228	0.336	0.238	0.954	0.242	1.000

4. Conclusions

In this work, the distributions of sulfur and nitrogen compounds in ambient air at the boundary area of a fishery industrial complex have been investigated. The results of this study indicate that the ammonia concentration is significantly higher than other odor compounds and all of the mean concentrations of sulfur and nitrogen compounds are much lower than the limits of the Odor Emission Standard regulated on the industrial area. The mean (D/T) ratio at site O−6 is higher than the limit of the Odor Emission Standard [(D/T) ratio: 20] 5 times while others are lower than this limit value. Furthermore, from the correlation analysis, it confirms that the TMA is the primary odor compounds in this fishery industrial complex.

5. Acknowledgement

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