

Surface microlayer enrichment of volatile organic compounds and semi-volatile organic compounds in drinking water source

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Abstract: Enrichment of volatile organic compounds(VOC) and semi-volatility organic compounds(SVOC) in surface microlayer(SM) of three drinking water sources were studied. The enrichment factor(*EFs*) were 0.67 to 13.37 and 0.16 to 136, respectively. The results showed some VOC and most SVOC could enrich in SM. Some *EFs* of SVOC was quite high. Suspension and temperature could affect *EFs* of SVOC, slim wind and water movement do not destroy enrichment of organic in SM.

Keywords: surface microlayer; enrichment; GC-MS; SPE

Introduction

Surface microlayer(SM), is usually defined as the top several microns of the air-water interface. Three decades ago, people noticed the special properties of the surface microlayer differ from the subsurface water(SW). It is only in recent two decades that attempts have made to study this microlayer. Much research showed many kinds of active-material enrich in the layer; for instance, polysaccharide and polypeptide(Williams, 1986), lipids, carbohydrates, and proteins have high enrichment in SM. It is reported that concentration of polychlorinated biphenyls and hexachlorobenzene in SM of sea were 2 and 10 times higher than in SW of sea water(Booij, 2001). Some researches showed quite a few metals, Fe, Zn, Cd, Cu and Pb(Hardy, 1985) were enriched in the surface film by up to 10^4 times relative to the seawater. Compare with surface microlayer plays important role in the materials exchange between water and air, the much research on the properties of the surface microlayer of sea water has been studied(Yang, 1999) and many attempts have been to measure the concentration various about natural and anthropogenic materials in the layer, there is a few studies on SM of fresh in China(Sun, 1999), especially. Enrichment property of organic in fresh has not been studied deeply. There are not enough reports on enrichment of volatile organic compounds(VOC) and semi-volatile organic compounds(SVOC) in SM of fresh up to now.

The purpose of this work is to analyze the composition of organic chemicals in several large drinking water sources, measure enrichment factors(*EFs*) of volatility organic compounds and semi-volatility organic compounds in the surface microlayer in these water source and attempt to realize the affecting factors about *EFs* of these compounds between air and the SM of the fresh.

1 Materials and methods

1.1 Reagents and materials

Dichloromethane, methanol, hexane and acetone (HPLC grade) were purchased from Surpeco Ltd., USA. 4-chloro-nitrobenzene, nitrobenzene, 1, 2-dichloro-3-iodo-benzene, 1, 2, 3-trichlorobenzene, were analytical grade. Sodium sulfate(analytical grade) was rinsed with dichloromethane, baked at 400°C for 4 h. The other materials such as SPE-filtration device with a vacuum pump and connectors, SPE units,

C₁₈ cartridges and 0.7 μm glass-fiber filters were supplied by Technical University of Graz. Suspension (come from Changjiang River) was grinded to pass 100-mesh sieve.

A total of 3 surface microlayer and 3 subsurface water samples of SVOC were collected from three drinking water sources during December 2001 in Huangqiao, Taixing and Jintan towns, which locate in Jiangsu Province of China. VOC samples of surface microlayer and subsurface water were collected from Jintan town. Drinking water source locates near center of Huangqiao Town is a big lake and the other sources are rivers about three kilometers from the center of related towns. It is known that these areas have quite a few automobile, textile, chemical and electronic plants. Wind power was two to three-grade during sampling process.

Surface microlayer samples were collected by the glass plate technique(Hardy, 1985) from the boat. The thickness of SM film was from 40 μm to 80 μm. The collecting method is introduced as follow simply. Briefly, the clean glass plate(20 × 40 cm and 0.5 cm thick) is immersed vertically through the surface and then withdraw vertically at a rate of 20 cm/s. The water remaining on the plate is removed into a clean glass bottle by two blades both sides fixing a silicon rubber until sample is 500 ml. Subsurface water samples(4 L) were collected at 1.0 m below the water surface with a specially designed iron bucket. The water samples for VOC were collected in two 25 ml vials and fixing agent(HCl and ascorbic acid) was added into the bottles. All sample bottles were kept in an ice-salt bath until analyzed. The parameters of the three water samples are shown in Table 1.

Table 1 Parameters of water samples

	Huangqiao	Jintan	Taixing
pH	7.5	8.32	7.6
Conductivity, μs/cm	568	428	378
Temperature, °C	9.5	6.6	10.5
Suspension, g/L	0.0343	0.0404	0.0927

To examine affecting of organic concentration and total suspension (TSP) on *EFs*, about 15 L distilled water was added into a 40 L aquarium to simulate micro-environment in laboratory. Solutions of nitrobenzene, 4-chloro-nitrobenzene, 1, 2, 3-trichlorobenzene and 1, 2-dichloro-3-iodo-benzene were added into the aquarium. The aquarium was sealed by sheet film. After 12 h, SW and SM samples were

collected by glass plate as above described. Volume of SW and SM were 100 ml and 30 ml, respectively. Results of GC-FID showed that blank samples only containing suspension did not contain above four organics compounds.

1.2 Analytical determination

Samples were pretreated by SPE according to method 625 of United States Environmental Protection Agency (USEPA) for analysis of SVOC. Before used, SPE cartridge was filled with 15 ml dichloromethane and 15 ml methanol twice, respectively. The vacuum was adjusted by the valve to control the water sample at the flow of max 1 L/h. 15 ml dichloromethane was drawn through the solid phase twice at flow max 1 ml/min. The elution was added 2.0 g anhydrous Na_2SO_4 then was concentrated by means of a rotary evaporator to near 0.50 ml.

A Tekmar 3000 purge and trap apparatus coupled to a gas chromatograph-mass spectrometer was used to analyze VOC of SM and SW. The operation conditions were as follows: The column is a DB-624 75 m \times 0.53 mm ID \times 3 μm (J & W Scientific, Folsom, CA). 40 ml/min flow of ultra pure nitrogen was used as the purge gas. Purged under the following conditions: 40 ml/min flow of ultra pure nitrogen was used as the purge gas, purge was 11 min at room temperature. The compounds concentrated in the non-cold trap were desorbed at 225 $^\circ\text{C}$ for 3 min; after adsorptions, the trap was washed by purging at 230 $^\circ\text{C}$ for 10 min. For mass spectrometry, highly pure helium was the carrier gas, ion source temperature was set at 200 $^\circ\text{C}$, ionizing voltage was 70 eV and the transfer line temperature was set at 250 $^\circ\text{C}$. The mass range 26.0—450.0 m/z, the scan speed 0.45 s/scan. Fluorine benzene was as internal standards.

Saturn 2200 MS equipped with a Varian gas chromatograph system (model cp-3800, DB-5MS capillary column with a film thickness of 0.25 μm ; 30 m \times 0.25 mm i. d.) was used to carry out qualitative and quantitative of SVOC of three drinking sources in the splitless mode. In each case, quantification was done with external standards using the most intensive and characteristic fragment ions of the respective compounds. The operation conditions were as follows: injector, 250 $^\circ\text{C}$, oven temperature: 40 $^\circ\text{C}$ (5.0 min) to 280 $^\circ\text{C}$ (11 min) at a rate of 8 $^\circ\text{C}$ per minute. Highly pure helium was the carrier gas. Transfer line to the MS was set at 240 $^\circ\text{C}$, ionizing voltage 70 eV and the temperature of the source was 180 $^\circ\text{C}$.

SW and SM samples collecting from the aquarium were extracted three times with 10 ml dichloromethane. After adsorbing residential water with anhydrous Na_2SO_4 , the extractions were concentrated to 0.50 ml. The four organic compounds were dissolved in dichloromethane to be as standard solution.

A gas chromatograph (HP-6890, DB-1 capillary column with a film thickness of 0.25 μm ; 30 m \times 0.25 mm i. d.) equipped with Flame Ionization Detector (FID) was used to analyze the four compounds. Correlation coefficient (R) of standard curve of every standard solution was beyond 0.991. The operation conditions were as follows: H_2 30 ml/min, air 300 ml/min, N_2 1.5 ml/min. Injector: 240 $^\circ\text{C}$, oven temperature: 45 $^\circ\text{C}$ (2.0 min) to 280 $^\circ\text{C}$ (10 min) at a rate of 8 $^\circ\text{C}$ per minute.

Quantitative and quantification of SVOC was according to standards 625 of USEPA methods. Percentage recovery of standards distribute from 31.4% to 79.5%. As far as the analytical quality control is concerned, blank runs revealed no impurities.

The enrichment factor (EF_s) was calculated as follows:

$$EF_s = C_{SM} / C_{SW}$$

C_{SM} and C_{SW} are the concentration of compounds in surface microlayer and in subsurface water, respectively.

2 Results and discussion

The VOC data of SM and SW are presented in Table 2. There are 16 kinds of VOC were detected from the surface water and subsurface water sample. Data showed that ten kinds of concentration of VOC were higher in SM than that in SW and six kinds of concentration of VOC were lower in SM than that in SW. The max and min EF_s (chloroform and xylene) reached 13.37 and 0.65, respectively. Some kinds of VOC (1,4-dichlorobenzene and 4-isopropyl toluene) had not detected in subsurface water but had been detected in SM. Most EF_s ranged from 1.0 to 2.0. The enrichment results showed substantial enrichment of VOC in the SM of the drinking water.

Table 2 EF_s of VOC in SM of Jintan water drinking source

VOC	Conc. in SM, $\mu\text{g/L}$	Conc. in SW, $\mu\text{g/L}$	EF_s
Dichloromethane	0.070	0.021	3.33
Chloroform	0.254	0.019	13.37
Benzene	0.032	0.029	1.10
1,2-dichloroethane	0.029	0.041	0.71
Trichlorethylene	0.007	0.008	0.88
1,2-dichloropropane	0.011	0.012	0.92
Toluene	0.030	0.029	1.03
Chlorobenzene	0.003	0.001	3.0
Ethylbenzene	0.012	0.007	1.71
Xylene	0.011	0.017	0.65
Orthoxylene	0.005	0.007	0.71
Styrene	0.003	0.003	1.0
1,2,4-trimethylbenzene	0.002	0.003	0.67
1,3-dichlorobenzene	0.001	0.001	1.0
4-isopropyl toluene	0.001	ND	—
1,4-dichlorobenzene	0.001	ND	—

* ND = not detectable

Enrichment of VOC has not been studied deeply and the enrichment mechanism has not been comprehended completely. It is known that VOC is easy transfer from water to air for their volatility, especially exist effecting of wind. But results showed that there is an accumulation trend in SM for the VOC. Some researches showed organics (polypeptide, polycyclic aromatic hydrocarbon and phthalic ester, etc.) will produce very substantial enrichment while lots of bacteria and microorganism is in the surface of sea, however, there are a few reports about affecting factors of VOC in SM. The above results showed although wind and wave movement may play negative role, quite many kinds of VOC could enrich in SM of fresh.

Concentration and EF_s of SVOC in three drinking water sources are shown in Table 3. About 39 compounds were detected from these water samples according to standard sample EPA-625. Concentration of 28, 21 and 29 compounds were higher in SM of Huangqiao source, Jintan water source and Taixing water source than in SW of above three water sources, respectively. Mostly, the EF_s of the three sources were from 1.0 to 10.0. Max EF_s reach 136, 28.9 and 20.5 in three SM of drinking water source, respectively. There were several organic

compounds(hexachloroethane, hexachlorobutadiene and dibenzo(*a, h*) anthracene etc.) had not been detected in SW but found in three SM

samples. These showed substantial enrichment of SVOC in SM of the three drinking water samples.

Table 3 *EFs* of SVOC in SM of three water-drinking sources

SVOC	Huangqiao bridge source			Jintan source			Taixing source		
	Conc. in SM,	Conc. in SW,	<i>EF_s</i>	Conc. in SM,	Conc. in SW,	<i>EF_s</i>	Conc. in SM,	Conc. in SW,	<i>EF_s</i>
	$\mu\text{g/L}$	$\mu\text{g/L}$		$\mu\text{g/L}$	$\mu\text{g/L}$		$\mu\text{g/L}$	$\mu\text{g/L}$	
Phenol	0.0080	0.0487	0.16	0.0992	0.0948	1.04	0.1192	0.0959	1.24
Bis(2-chloroethyl)ether	ND	ND	—	ND	ND	—	0.0040	ND	—
2-chlorophenol	0.0144	ND	—	ND	0.0012	0.0	0.0040	ND	—
<i>p</i> -dichlorobenzene	0.0272	0.0093	2.92	0.0288	0.0164	1.76	0.0584	0.0422	1.39
<i>o</i> -dichlorobenzene	0.0088	0.0063	1.40	0.0112	0.0168	0.67	0.0176	0.0215	0.82
Bis(2-chloroisopropyl) ether	0.0200	0.0283	0.71	0.0072	0.1338	0.054	—	—	—
N-nitrosodi- <i>n</i> -propylamine	0.0064	0.0086	0.74	0.0360	0.0030	12.0	0.0072	0.0097	0.74
Hexachloroethane	0.0008	ND	—	ND	0.0050	0.0	0.0128	ND	—
Nitrobenzene	0.0152	0.0485	0.31	0.0064	0.0600	0.11	0.0320	0.0784	0.16
2-nitrophenol	0.2416	0.1040	2.32	1.2448	1.3352	0.98	0.9120	0.2516	3.62
Bis(2-chloroethoxy) methane	0.0096	0.0100	0.96	0.0520	0.0154	3.46	0.0208	ND	—
2,4-dichlorophenol	0.0288	0.0700	0.41	0.0136	ND	—	0.0200	0.0401	0.50
1,2,4-trichlorobenzene	0.0080	0.0053	1.51	0.0072	0.0054	1.33	0.0064	0.0030	2.13
Naphthalene	0.0336	0.0215	1.56	0.0648	0.2338	0.28	0.0336	0.0356	0.94
Hexachlorobutadiene	0.0184	ND	—	0.0008	0.0036	0.22	0.0104	0.0030	3.47
4-chloro-3-methylphenol	0.0004	ND	—	ND	0.0004	0.0	0.0944	ND	—
2,4,6-trichlorophenol	0.1040	0.0620	1.68	0.0832	0.072	1.16	0.1808	0.1224	1.48
Dimethyl phthalate	2.6360	0.0846	31.2	1.6808	0.9806	1.71	1.2768	0.6246	2.04
Acenaphthylene	0.0112	0.0500	0.23	0.0232	0.0098	2.37	0.0112	0.0022	5.10
Acenaphthene	0.0520	0.0106	4.91	0.0432	0.0190	2.26	0.0608	0.0054	11.2
Diethyl phthalate	0.4216	0.0820	5.14	0.7944	0.0716	11.1	0.9048	0.5186	1.74
Fluorene	0.0256	0.0094	2.72	0.0368	0.0158	2.33	0.044	0.0444	1.0
Azobenzene	0.0200	0.0004	50.0	0.0392	0.0170	2.30	0.0128	0.0081	1.58
4-bromophenyl phenyl ether	0.0040	ND	—	0.0016	0.0004	4.0	0.0016	0.0007	2.3
Hexachlorobenzene	0.0024	ND	—	ND	0.0006	0.0	ND	ND	—
Phenanthrene	0.1008	0.0146	6.9	0.0744	0.0278	2.66	0.0584	0.0146	4.0
Anthracene	0.0336	0.0407	0.83	0.0056	0.0104	0.55	0.0384	0.0069	5.57
Carbazole	0.6344	0.0217	29.2	0.7752	0.0268	28.9	0.8456	0.0766	11.1
Di- <i>n</i> -butyl phthalate	17.3288	1.3789	12.6	26.334	2.8772	9.15	24.49	1.1947	20.5
Fluoranthene	0.0408	0.0121	3.38	0.0448	0.0150	2.99	0.0552	0.0066	8.36
Pyrene	0.0464	0.0147	3.16	0.0448	0.0112	4.0	0.0616	0.0113	5.45
Butyl benzyl phthalate	0.0160	ND	—	0.1312	ND	—	0.2688	ND	—
Chrysene	0.0136	0.0001	136	0.0104	ND	—	0.0224	ND	—
Bis(2-ethylhexyl)phthalate	2.4968	1.6601	1.50	3.0408	0.8578	3.54	2.1344	2.7978	0.76
Benzo(<i>b</i>)fluoranthene	0.0088	ND	—	ND	0.0008	0.0	0.0008	0.0005	1.6
Benzo(<i>k</i>)fluoranthene	ND	ND	—	ND	ND	—	0.0024	ND	—
Benzo(<i>a</i>)pyrene	ND	ND	—	ND	ND	—	0.0032	0.0004	8.0
Indeno(1,2,3- <i>cd</i>)pyrene	0.0056	ND	—	ND	ND	—	0.0000	0.0025	0.0
Dibenzo(<i>a, h</i>)anthracene	0.0040	ND	—	ND	ND	—	0.0040	ND	—

* ND = not detectable

The results showed similar *EFs* of the same SVOC in the different drinking water sources when concentrations of SVOC were similar in SW. For instance, 1, 2, 4-trichlorobenzene, nitrobenzene, 2, 4, 6-trichlorophenol, N-nitrosodi-*n*-propylamine, etc., have similar *EFs* in different sources.

Many factors were found to influence enrichment of organic compounds in SM of water, suspension, bacteria, microorganism, wind and wave action were deemed to possibly important influential factors of organic enrichment in SM. Some studies showed bacteria and many types of microorganism occur enrichment at the sea surface; there is an enhancement of both dissolved and particulate organic matter. However, in our study, it was found that concentration of organic compounds in SW

obviously affected *EFs*. Fig. 1 described relationship between organic compounds concentrations in SW and *EFs* in three sources. In general, *EFs* of most organic compounds trend higher while their concentrations became lower in SW. For instance, the *EFs* of SM was no more than 3 when the concentration of organic matter was about 0.020 $\mu\text{g/L}$ in SW; while the concentrations of organic matters were lower, the *EFs* were up. Some compounds, bis(2-chloroethoxy) methane butyl benzyl phthalate, 4-bromophenyl phenyl ether etc., had not been detected in SW, but had been detected in SM of water.

Some researches reported the relation of concentration and *EFs*. Williams(Williams, 1967) found that when concentration of NH_3 were 0.4, 0.4, 0.5, 0.6, 1.7 and 2.2 $\mu\text{g/L}$ in sea bulk water, the *EFs*

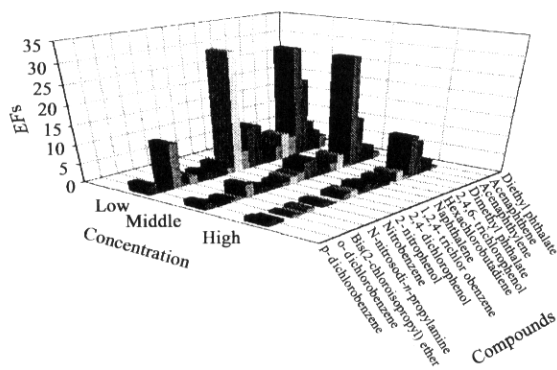


Fig.1 Relationship between concentration and EFs

were 25, 24, 29, 15, 6 and 5, respectively. Concentration of particle organic nitrogen (PON) were 0.4, 0.9, 1.3, 1.7 and $3.7 \mu\text{g/L}$ in sea bulk water, the EFs were 50, 12, 7, 9 and 4, respectively. In the main, EFs of a compound increased with its concentration decreased in bulk water. Knulst *et al.* (Knulst, 1997) also found EFs of DOC and POC increased when concentration of dissolve organic carbon (DOC) and particle organic carbon (POC) decreased in SW in two lakes. Study on enrichment of DOC in sea surface microlayer (Carlson, 1972), the results showed DOC enrichments in SM diminished with increasing bulk water DOC concentrations in coastal water. It showed the organic matters might enrich in SM while their concentration trend to lower.

According to the enrichment mechanism, the lower concentration of a compound in SM, the higher absorbed rate in SM, therefore, EFs was higher trend when concentration of compound was lower.

The suspension in water was considered having affection on the enrichment of organic matter. The suspensions filtered by $0.45 \mu\text{m}$ glass-filter membranes were 0.03435 g/L , 0.04045 g/L and 0.09270 g/L in the three samples of subsurface water of Huangqiao, Jintan and Taixing drinking waters, respectively. Fig. 2 shows that relationship between EFs of some compounds and TSP in different sources. When concentration of SVOC was similar in different drinking sources, it was found that most EFs of SVOC in Fig. 2 have higher EFs when water samples contained more TSP.

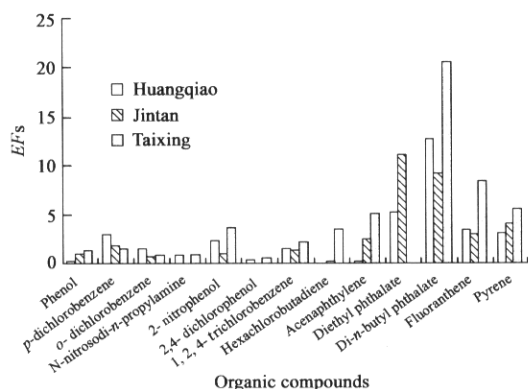


Fig. 2 Relationship between TSP and EFs

Analysis results of micro-environment in laboratory (Fig. 3) also approved EFs of compounds varied with suspension in bulk water. All the EFs of four compounds trended to higher when the suspension increased. Except 1,2-dichloro-3-iodobenzene, EFs of the other three compounds in bulk water containing 1.5 g were not the highest. It could

be explained that small particles of TSP reached maximum enrichment in SM before the TSP was 1.5 g in bulk water. Yu studied the enrichment of suspension particles in SM of a natural lake (Yu, 1997). In their study, it was found that EFs of suspended particulate varied from 0.82 to 3.46. The EFs increased with decreasing of suspended particulate in bulk water. Liu also found particulate polycyclic aromatic hydrocarbons (PAHs) concentration increased nonlinearly with total suspension (TSP) even if the particulate PAHs are not uniformly distributed on the TSP accumulating at the air-water interface (Liu, 1997). Their research showed these small particles act as nucleus for the growth of particles during the bubbling so that the particles to harvest organic matter and transport it to the microlayer. This being so, it was possible to confirm that enrichment of the compounds had been contributed by the smaller particles. Because of specific area and electric charge, particulate could adsorb the organic matter and carry them to SM.

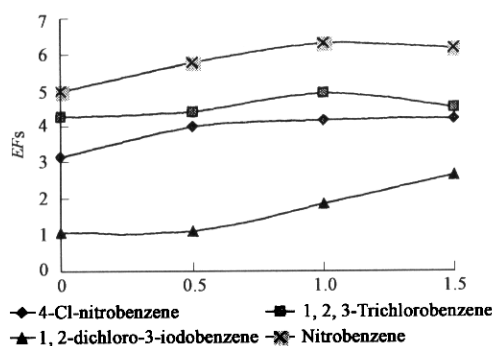


Fig. 3 Relationship between EFs and TSP

It is noted that wind and wave movement may be an important reason for enrichment of the organic matter in SM. Much rising bubbles in water produced by wind and wave action scavenge the organic matter from subsurface water up to microlayer. In general, wind and wave movement could destroy the SM, but some researches (Knulst, 1997) found SM seem to exist on all bodies of water even if SM is strained by the force of wind and water movement, sunlight and biological activity. Carlson (Carlson, 1983) also found DOC concentration in SM was not influenced obviously by the wave states from Beauford 0 to 4. During sampling the SM samples in the three water sources, wind power was 2 to 3 grade and there was small wave in the all three drinking resource, however, the analysis results showed that enrichment in SM was obvious in three drinking sources.

3 Conclusions

Most compounds of VOC and SVOC were found enriched in SM of drinking water and the foregoing results showed that the enrichment of organic matter in SM might be universal. In general, concentration of compounds in bulk water and small particles might play important role in enrichment of organic compounds in the surface microlayer. Although wind has negative influence on enrichment of VOC and SVOC, the organic materials were obviously enriched in SM of the three drinking water sources.

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