



Research Article

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Design of sampling method based on sampling comparative test of volatile organic components

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ABSTRACT

Effects on volatile and semi-volatile organic components (VOCs) in water have been studied by comparison of three sampling methods, which were applied in typical groundwater contaminated site. The results show that DS technique of sampling is stable and reliable, better than both bailer sampler and peristaltic pump in terms of collecting water samples to obtain content of VOCs in water. Factors with impact on loss of VOCs during sampling are negative pressure, contact with outside atmosphere and turbulent flow in order from strong to weak, where loss of VOCs caused by negative pressure is apparently higher than that caused by contact with outside atmosphere and turbulent flow; comparative analysis indicates that short-time sampling with sampler made of stainless steel, polyfluortetraethylene, and silica gel tube has no strong corrosion over water sample, and the effect on samples are negligible through analysis of chemical constituents. Based on that, DS sampling method is designed, applicable to sampling of underground water of open well, 110cm monitoring well, and shallow layer- 30cm shallower and 60cm shallower, and in the meanwhile, with introduction of automatic control circuit and sensors for water level, pressure, temperature, PH value and EC, the function of measuring and storing in-situ physical and chemical parameters accompanying sampling is achieved.

Keywords: sampling method; comparative trial; deep-set; in situ

INTRODUCTION

The fundamental guarantee for evaluating water quality and pollution level exactly is reliable analytical data, to which sampling process is the most critical. Different sampling methods can bring about different degrees of interferences to every component to be analyzed, especially to volatile and semi-volatile organic components that are everywhere but with very low contents, falling within trace analysis scope and with easy variation. At present, the maximum acceptable concentration of VOCs is from a few to several tens of microgram per liter, given in water quality standard for drinking water at home and abroad [1], and the limit for VOCs detected in laboratory is zero point some micrograms per liter or even lower [2]. The true concentration of VOCs in water may be changed in case of any minor impropriety in water sampling method. Therefore, the technological requirement for water sampling for organic component analysis is obviously higher than that for conventional analysis. As currently, there are only few comparisons regarding effects on volatile and semi-volatile organic components of analysis samples with different sampling approaches, comparison test of three sampling methods for typical underground contaminated site is carried out in this paper to research their effect on VOCs of water samples, and in addition, physical and chemical properties of sampler material are analyzed, especially degrees of disturbance to VOCs caused by negative pressure, turbulent flow, etc. generated during sampling processes.

EXPERIMENTAL SECTION

SAMPLE COLLECTION

The sampling site is located in living areas of platform marginal region of a delta where there is no significant industrial source of pollution, and 1.0m away from the site, there is a sewage ditch with width of approximately 2m, set by bricks and floated with much oil. The sampling site is an open well, a source of water for daily use of neighboring residents with occasional drinking purpose (Figure 1), with a diameter of 0.8m, of which the groundwater level depth is 1.8m. There is no significant air pollution source around the sampling site and the air quality there is good.

Two sets of groundwater sample had been collected with interval of five months respectively in March and August of 2008 by stainless steel deep-set in-situ sampler (DS sampler) and sent to Hong Kong ALS laboratory for testing, stored under the temperature of 4°C. The four VOCs, namely carbon disulfide, cis-1,2-dichloroethene, trichloroethene and tetrachloroethene through sample analysis are detected as shown in Table 1.

Three months later, i.e. November, 2008, comparison test is carried out at above stated sampling site with sampling depth 50cm under water surface, atmospheric temperature detected as 25.2°C and the water temperature of 25.0°C. German WTW Multi 340i portable multi-parameter water quality tester was used to test the in-situ chemical indicators, of which the results are similar to those of two previous sampling (refer to Table II). And there is no abnormalities in sampling environment and groundwater environment. Three sampling methods employed are as shown below:

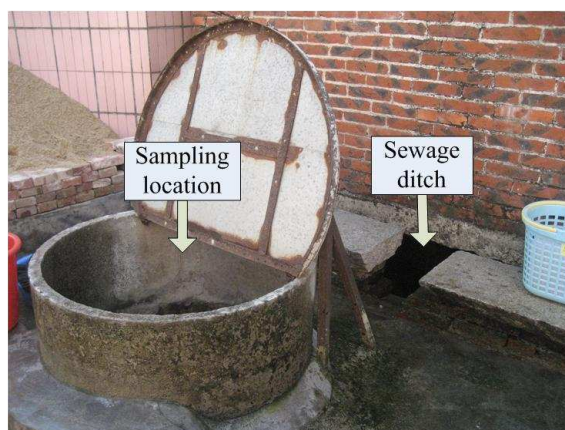


Fig.1 Overview of sampling site

Table.1 Detetable result of organic pollutants (Mg/L)

Analysis Description	LOR	First Sampling	Second Sampling
Carbon disulfide	0.5	<0.5	1.2
cis-1,2-Dichloroethene	0.5	7	9.8
Trichloroethene	0.5	0.9	1.3
Tetrachloroethene	0.5	1.4	1.7

Table.2 Results of physical and chemical characteristics of groundwater on-site test in three times

Sampling Date	EC (μs/cm)	DO (mg/L)	pH
First Sampling	189	No detection	5.19
Second Sampling	210	1.84	5.37
Sampling Comparison Test	201	2.20	5.63

Stainless steel DS sampler: As shown in Figure 2, there are three sampling bottles in the sampling tube (1), where the bigger sampling bottle (9) is assembled at the bottom of the sampling tube. The bottom of internal hold clip (8) is connected with the sampling bottle (9) so the sampling bottle is fixed. The two smaller sampling bottles (2) are assembled on the holders (3). For collection of water samples, sampler is lowered into water, and in case of insufficient length of sampling rod (5), it may be extended with bolts at its end. When the sampling tube reaches a preset depth, pull the rope tied on bottle lid to open it. Water goes into the sampling bottle along the water inlet which is at its bottom. When the water level is higher than the water inlet (7), the overflow water will enter the big sampling bottle and then overflow into the sampling bottle via water inlet (13) at bottom of tube. When water level

is higher than water inlet (7), water sample spills into large sampling bottle and then into small sampling bottle. After sampling is finished, lift the sampling rod, which will cause sensor get actuated to close electromagnetic valve, draw out sampler, fasten bottle lid underground, to which the whole sampling process is completed.

This kind of sampler is made of stainless steel which can collect on-site water sample of set depth. In the process of sampling, the period of water sample contacting with outside air is almost zero, however the turbulent flow is generated when water goes through the sampling bottle.

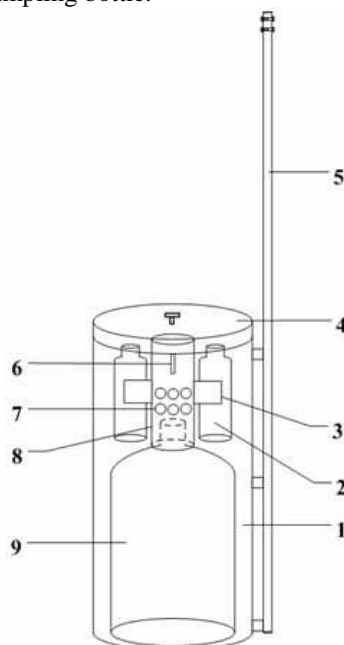


Fig.2 Structural scheme of DS sampler

Bailer Sampler: Bailer sampler is composed of two parts, namely tube body and check valve (refer to Figure 3) [3]. Lower the sampler when sampling and the check valve will be opened when the sampler reaches the water surface; Stop lowering when the predetermined depth is reached and then lift the sampler; after sampler is drawn out, water sample is led into the sample bottle through sampler releaser.

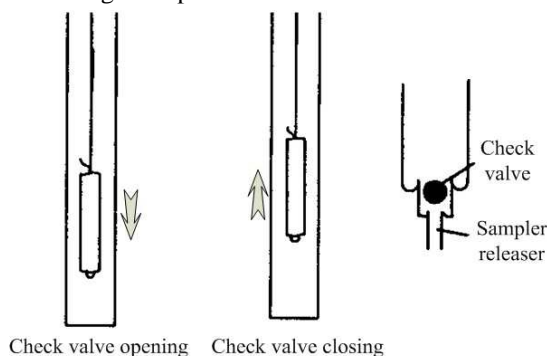


Fig.3 Bailer sampler

This sampling employs bail sampler made of poly-tetrachloroethylene that is able to collect water samples of predetermined depth but passing through of upper layer by sampler may cause cross pollution in case the upper water has polluted layer. What's more, after the collection, there must be a releaser delivering the sample into the sampling bottle, during which contact with outside air is available.

Sampling with Peristaltic Pump: Peristaltic pump is a kind of suction and emission sampling pump, as shown in Figure 4: putting the suction side of the pipeline into a desired depth of the well and the emission side into the sample container. Then vacuum is generated in the pipeline through electric rotation of three rollers to extract the well water to the ground.

The flowing rate of peristaltic pump is adjustable. It can collect water samples of predetermined depth. The pipeline is a kind of silicone tube. In the process of sampling, samples collected will not contact with sampling pump parts

but vacuum state generated in the sampling process may lead to volatile and sensitive air foaming. Besides, sampling pipeline may absorb organic components.



Fig.4 Peristaltic Pump

From 2005 to 2008, 937 groundwater samples were collected in the Zhujiang Delta. The samples were from the civil wells and manual excavated pits. The depths of the wells were below 10 meters, so the samples belong to shallow groundwater. Before taking samples from the civil wells, the well water was drained as much as possible. Till the next day, after the recovery of the water level, samples were taken from the fixed place below 50cm from the surface. As for the area with no wells, pits were excavated manually. Samples were taken after the water level was stable and the water was clear. All samples were filtrated through 0.45 μ m membranes and acidified on the spot, then were detected by the Guangzhou Mineral Resources Supervision Inspection Center of the Ministry of Land and Resources of China.

Determinations of Be, Al in all samples were performed using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). PH value was tested on the spot by applying the potentiometric method with the WTW Multi 340i portable tester made by Germany.

RESULTS AND DISCUSSION

After collection, samples were numbered as 1 to 3 and preserved at 4°C. An extra set of field blank samples was taken along together. In that afternoon, they were sent to Hong Kong ALS laboratory for test under the same condition. There were 57 items for volatile organic components test and 83 items for semi-volatiles organic components. The detection was limited in the scope of 0.05-5 μ g/L. The specific analysis methods and number of analyzing items are shown in Table 3 and Table 4.

The blank sample had no detection; the three sets of water samples were all detected with three kinds of VOCs: cis-1,2-dichloroethene, trichloroethene and tetrachloroethene. The test results are shown in Table 5.

Table.3 Analytical procedures and indexes of VOCs

Method	Analysis description	Numbers
EP-074A:	Monocyclic aromatics	14
EP-074B:	Oxygenated compounds	4
EP-074C:	Sulfonated compounds	1
EP-074D:	Fumigants	5
EP-074E:	Halogenated aliphatics	19
EP-074F:	Halogenated aromatics	9
EP-074G:	Trihalomethanes	4
EP-074H:	Naphthalene	1

Table.4 Analytical procedures and indexes of svocs

Method	Analysis description	Numbers
EP-075A:	Phenols	11
EP-075B:	Polyaromatic hydrocarbons	17
EP-075C:	Phthalate esters	6
EP-075C:	Nitrosamines	10
EP-075E:	Nitroaromatics and ketones	17
EP-075F:	Haloethers	4
EP-075G:	Chlorinated hydrocarbons	10
EP-075H:	Anilines and benzidines	8

Influence of Sampler Material on Sample Components: Stainless Steel: the main chemical components are iron. It also contains chromium, nickel, carbon, manganese, silicon, phosphorus, sulfur and other components. Different series of stainless steel have different strength, ductility, temperature and corrosion resistance and its surface adsorption force is not strong.

Table.5 Detection of organic contaminants with different sampling processes (µg/L)

Analysis Description	DS Sampler	Bailer Sampler	Peristaltic Pump
cis-1,2-Dichloroethene	9.4	8.5	5.6
Trichloroethene	1.1	1.1	0.6
Tetrachloroethene	1.3	1.2	0.6

Polytetrafluoroethylene: the basic structure: $-(CF_2)_n-$, CF_2 unit arranged by the saw-tooth shape and form a spiral distorted chain. It has a strong chemical, biological inertia, high and low temperature resistance, corrosion resistance and the surface tension is of low adhesion.

Silica: the main chemical components are $mSiO_2 \cdot nH_2O$. Except addition to alkali and hydrofluoric acid, it does not react with other substances. Different types of silica have different micro porous structure because of their different manufacturing methods. It is of strong adsorption, thermal stability, mechanical strength and chemical stability.

Phthalic ester organics shall to be added as plasticizers during manufacturer of polytetrafluoroethylen, a major material for the short cables of stainless steel DS sampler and bailer sampler. For the three sampling methods, contact time between water samples and sampling materials is within 1min and actually no phthalic ester was detected. In addition, no abnormality is detected in 140 items of organics. It is revealed that sampling with the three samplers, in short time has no strong corrosion over water sample, and the effect on samples is negligible.

The three kinds of sampling materials cannot precipitate the three detected organic components, the surrounding environment has no source of secondary pollution that causes three detected organics detected in water samples, and sampling is in strict accordance with defined sampler and sampling bottle. That is to say there is only the possibility of loss as a result of volatilization and adsorption of the three detected organic components during sampling, namely the larger the test result of samples sampled by three samplers, the close it is to true value. Therefore, maximum values of each test items are taken as true values. The losses of volatile components caused by different sampling methods are shown in Table 6. It is obvious to see that DS sampler causes the least loss, followed by bailer sampler, of which the loss is within 10% relative to DS sampler. Loss caused by peristaltic pump is the largest, up to 34%-50% compared with DS sampler. It is deemed that the strong adsorption capability of silica gel, material for sampling of peristaltic pump, is one of the reasons for the loss of volatile components.

Table.6 Contrast of loss of VOCs Caused by THE THREE sampling methods (%)

Analysis description	DS Sampler	Bailer Sampler	Peristaltic Pump
cis-1,2-Dichloroethene	0.00	9.57	34.12
Trichloroethene	0.00	0.00	45.45
Tetrachloroethene	0.00	7.69	50.00
Average	0.00	5.76	43.19

Influence of Sampling Style on Sample ComponentsAs stated above, all three sampling approaches can be used to get samples from desired depth, but with different turbulent flow, negative pressure and contact time with outside atmosphere generated during sampling: Through comparison between Table 6 and Table 7 that sampling with DS sampler, features turbulent flow, almost no contact with atmosphere and no negative pressure. Sampling with bailer sampler features no negative pressure and slight turbulent flow, but sample water has to lead into sampling bottle with releaser, which requires contact with outside atmosphere. Through comparison test, loss of volatile component caused by contact with outside atmosphere is higher than that caused by turbulent flow;

sampling with peristaltic pump features turbulent flow, negative pressure and contact with outside atmosphere. On the basis of maximum value as standard, the average loss of volatile component caused by turbulent flow and contact with atmosphere is totaled around 6%, and that caused by peristaltic pump is 43%, namely, solos of volatile component caused by negative pressure is 37% approximately, much higher than both turbulent flow and contact with atmosphere.

Table.7 Contrast of loss of VOCs through different sampling methods

Sampler	Turbulent Flow	Contact with Atmosphere	Negative Pressure
DS Sampler	√		
Bailer Sampler		√	
Peristaltic Pump	√	√	√

DESIGN OF SAMPLING METHODS

Based on above stated conclusions, different DS sampling methods are designed to cater to different sampling demands:

DS sampling method with electric control : To avoid aeration caused by DS sampler pulling out tube lid, DS sampling method with electric control is designed (Figure 5). When sampler is lowered to predefined depth, liquid level sensor (10) sends out signal, microscopic power supply (11) switches to bottom electromagnetic valve (14) to make the latter open, thus water sample flows from electromagnetic valve (14) into tube body (1), gas discharges from exhaust port (12), and after sampling is finished, lift sampler, liquid level sensor (10) sends out signal to close electromagnetic valve (14), to which the entire sampling process is accomplished. This method is applicable to collect samples of open well underground water and shallow ground water.

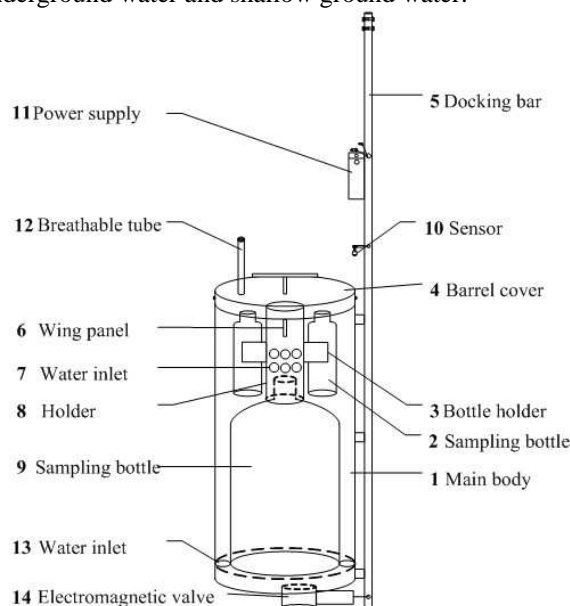


Fig.5 Structural Scheme of the DS Sampler

DS sampling method with small diameter and sampling depth of 30m: As shown in Figure 6: inside the 1L sampling tube, there is holding bracket to fix 40ml sampling bottle for volatile organic water samples and electromagnetic valve is equipped at both tube bottom and lid, used as water inlet and exhaust port. For sampling depth over 5m, sealing strip shall be used to seal tube body and tube lid. Electromagnetic valve cable is connected to upper winch, boasting also load-bearing function and winch cable joint connects with battery set and manual switch. This sampler is able to collect both samples of 110cm monitoring well and of ground water in DS manner, with maximum sampling depth up to 30m.

DS sampling and analysis method with automatic control for deep water: Sampler (Figure 6) consists of sampler control circuit board(9), sensors (17-20), electromagnetic valve (10), lithium battery(11), airtight cabin combination (22) and sampler tube combination (6); Sampler control circuit is electrically connected to electromagnetic valve and sensor respectively; sampler control device and electromagnetic valve are installed within sealed interlayer at bottom of sampler, top of interlayer is sampling tube, and outside wall of sampling tube is equipped with fixation clip to fix sensor; Bottom of sampling tube is water partition, and top are 1L semi-volatile organic sampling bottle and 40ml volatile organic sampling bottle fixed with holder (5). Sampling tube lid are sealed

and connected with sampling tube body, and on the lid, there is check-valve exhaust hole; sensors include water level sensor (18), temperature sensor (19), PH value sensor (17) and conductivity sensor (20).

Open and close of water inlet of sampler water sample container are controlled by electromagnetic valve, of which drive command is sent out from control circuit on the sampler. Sampler is equipped with parameter (temperature, liquid level, PH value, and EC) sensors that can measure real-time in-situ water quality parameters and transmit to its control circuit for treatment so as to effectively collect water samples, guarantee water sample quality and realize automatic control of sampling process with maximum sampling depth up to 60m under water.

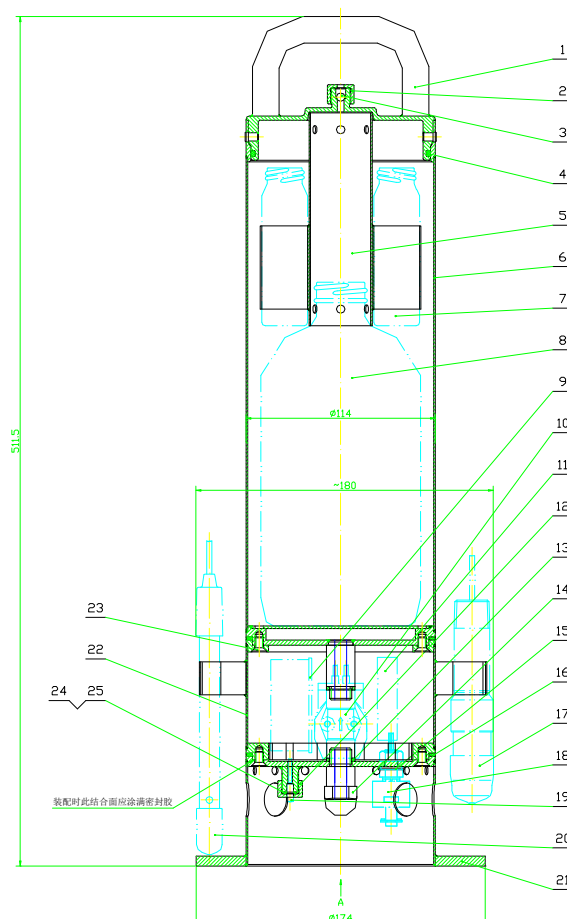


Fig.6 Structural Scheme of Sampler

CONCLUSION

Effects on volatile and semi-volatile organic components (VOCs) in water have been studied by comparison of three sampling methods, which were applied in typical groundwater contaminated site. The results show that DS technique of sampling is stable and reliable, better than both bailer sampler and peristaltic pump in terms of collecting water samples to obtain content of VOCs in water. Factors with impact on loss of VOCs during sampling are negative pressure, contact with outside atmosphere and turbulent flow in order from strong to weak, where loss of VOCs caused by negative pressure is apparently higher than that caused by contact with outside atmosphere and turbulent flow; comparative analysis indicates that short-time sampling with sampler made of stainless steel, polyfluortetraethylene, and silica gel tube has no strong corrosion over water sample, and the effect on samples are negligible through analysis of chemical constituents. Based on that, DS sampling method is designed, applicable to sampling of underground water of open well, 110cm monitoring well, and shallow layer- 30cm shallower and 60cm shallower, and in the meanwhile, with introduction of automatic control circuit and sensors for water level, pressure, temperature, PH value and EC, the function of measuring and storing in-situ physical and chemical parameters accompanying sampling is achieved.

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