

Design an Experiment Using Passive Sampling Technique for Monitoring Heavy Metals: A case study in Nhue river, Vietnam

Dao Duy Nam, Ton Thu Giang, Tran Thanh Chi*

Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam

Received: August 16, 2018; Accepted: June 24, 2019

Abstract

Passive sampling technique (Chemcatcher) was applied to monitor several heavy metals (Cd, Cu, Zn and Ni) in Nhue river (Vietnam). The components of sampler are sampler body (UK), Cellulose Acetate membrane (US) and Chelating Empore disk (UK). The effective sampling rate of the device (R_s , Lday⁻¹) is defined as the equivalent volume of water extracted per unit time and specific analyte. R_s can be determined experimentally in a flow-through tank. Impacts of water temperature and turbulence on the uptake rate of heavy metals were investigated under controlled laboratory conditions. The results of the sampling rate (R_s) are as follows 0.0092-0.0179 Lh⁻¹, 0.0042-0.0268 Lh⁻¹, 0.0063-0.0231 Lh⁻¹ and 0.0067-0.0205 Lh⁻¹ for Cd, Cu, Zn and Ni, respectively. Two sampling points on Nhue River were selected for sampling in parallel in 24- and 72-hours field deployment. In addition, spot samples were taken to evaluate data. The Time-weighted average (TWA) water concentration is 0.023-0.045 µg/L in two sampling points for Cadmium and 16.95-62.17 µg/L, 9.74-35.71 µg/L for sampling point NM1, NM2 of Zinc, respectively. Chemcatcher sampling measures only the labile fraction of heavy metals in water.

Keywords: Passive sampling, heavy metals monitoring, Chemcatcher monitoring

1. Introduction

According to study, sampling and sample preparation typically account for 70-90% of analysis time [1]. Certainly, sampling is one of the most important steps of any monitoring procedure. Any error taken place in this period will be very difficult to correct and can eventually cause irreversibly effects to analysis. Traditionally discrete grab spot or bottle sampling of water is the most common method of monitoring of heavy metals in surface water. However, this method has the following disadvantages: such as measuring total pollutants' concentration which maybe not assess accurately whether harmful or not; fee for sampling is high because need a lot of manpower and transportation; and provides only a 'snapshot' of pollution at the instant of sampling and may not be representative due to the fluctuation of pollutants' concentration. To overcome these difficulties, various techniques have been developed and applied internationally to complement spot sampling for heavy metals monitoring.

Passive sampling is capability to cover long sampling periods and indicate time average concentration values of contaminants. Generally, a passive sampler device will take only sample a fraction of the total analyte present; freely dissolved species and labile complexes as well as conjugated species. Most designs of passive sampler consist of a

receiving phase with a high affinity for the pollutants of interest separated from the external aquatic environment by a thin diffusion membrane. In most cases, uptake of analytes base on Fick's first law [2]. Passive samplers have several advantages over conventional water monitoring methods: (a) they enable the estimation of the time-weighted average (TWA) water concentration of a compound over the deployment period, (b) in some cases the amount of a chemical accumulated by the device reflects the concentration of the freely dissolved and labile fraction that is assumed to be the most readily bioavailable; compounds bound to suspended matter or dissolved organic carbon are generally not accumulated [3]. Although passive sample technique is very popular in European countries, but it is very new in Asian countries. Because of this, the study applied the technique to investigate the capacity of application in Vietnam or Asian countries. Besides, this study can also be considered as the first research conducted to closely investigate the presence of heavy metals in surface water in Nhue river (Vietnam) by passive sampling method. The performance of the Chemcatcher sampler was tested under controlled conditions of temperature, pH and turbulence of water to assess the effect of these parameters on the uptake kinetics which known sampling rate (R_s). The sampler was conducted at two places in Nhue river (Vietnam). The range of time-weighted average (TWA) concentrations of Cd, Cu, Zn and Ni using the sampler were compared with values of spot water samples taken during the trial to assess the utility of the device.

* Corresponding author: Tel.: (+84) 33 254 3001
Email: giang.tonthu@hust.edu.vn



Fig. 1. Chemcatcher sampler, Experiment setup and sampling

2. Material and Methods

2.1. Chemicals and reagents

Reagents were analytical grade or better purity. Ultrapure MilliQ water (waterPro PS Polishing systems US) was used throughout. A standard stock solution (Merck, Darmstadt, Germany) 1.0 gL⁻¹ as Cd, Cu, Zn and Ni was used for stock solution by dissolving appropriate amounts in 1% HNO₃ (65%, w/v Merck, Germany). A stock solution (10 mgL⁻¹) was prepared in 1% HNO₃ and stored in amber glass bottles at 4°C in the dark. Working solutions were prepared daily by appropriate dilution of the stock solution. Method US EPA Method 200.8 was applied for analysis Cd, Cu, Zn and Ni by using Perkin Elmer Elan DRC-E ICP Mass spectrometer (US).

2.2. Materials of construction and sampler design

Kingston et al.[4] and Persson et al.[5] developed a passive sampler, known as Chemcatcher, for the measurement of TWA concentrations of a range of organic compounds and metals in different aquatic environments. Chemcatcher sampler device includes three parts: Chemcatcher body, chelating empore disk (receiving phase) and cellulose acetate membrane.

2.2.1. Receiving phase

Chelating EmporeTM disk (47 mm diameter, 0.5 mm thickness) containing 90% iminodiacetate functionalized SDB and 10% PTFE (Polytetrafluoroethylene) were from 3M (United States) [6]. The disks were washed with 20 mL of 3.0 M nitric acid (ultrapure for trace metal analysis) followed by two washes with 50 mL ultrapure water. To convert the chelating EmporeTM disk into the active ammonium form add 100 mL of 0.1 M ammonium acetate buffer at pH 5.3 followed by several washes with ultrapure water [7]. Disks were stored in a Petri dish and kept damp until use.

2.2.2. Diffusion membranes

Cellulose acetate (CA) (47 μm diameter, 0.45 μm pore size, 152 μm thicknesses) was purchased from Portsmouth University, UK). To

remove any contamination by trace metals, immerse the diffusion-limiting cellulose acetate (CA) membrane in 1% HNO₃ for 30 minutes. Then thoroughly rinse the membrane with ultrapure water and store in a Petri dish [7].

2.2.3. ChemcatcherTM sampler

In the Chemcatcher sampler, sampler bodies retain both the receiving phase and diffusion membrane. For all configurations tested, the diffusion membrane was placed on the top of the conditioned Chemcatcher receiving phase disk avoiding formation of air bubbles between the two layers. The PTFE was shown to be free of contamination by heavy metals [8].

2.3. Flow-through exposure tank experiments

The flow-through exposure tank was described as Fig. 1. The stirring system was placed in a barrel tank (approx. 50-liters volume), which in turn was placed in a large external tank (approx. 180 liters). The external tank was filled with water and connecting a thermo-regulated-immersion heater (PolyScience SD07H170- US) to keep the temperature stable at the desired levels of 25 and 35°C controlled temperature. The ionic strength as regulated by adding 10 mL NaNO₃ and pH was adjusted to 6.5-7.0 using NaOH. to keep homogeneous conditions, the water was gently stirred (Heidolph overhead stirrer, type RZR-2000, Germany).

Besides, the four test solutions were prepared by mixing and diluting the standard metal solutions (Cd, Cu, Zn and Ni) with concentration 1000 mg/L (Merck, Germany) and de-ionized water for solution design.

At the beginning of the exposure the prepared passive sampler (5 samplers per calibration) were attached to the turntable as Figure 1 and immersed in the exposure tank. The turntable was the attached to an overhead stirring motor, which was keep turntable rotating at 40 and 60 rpm. The deployment of the Chemcatcher in the lab shown in Table 1.

Table 1. Calibration curve fits and estimated sampler uptake rate (R_s) for several heavy metals at different temperature and water turbulence in the flow-through tank. Four tests were retrieved after 4, 8, 24, 48 and 72 hours of exposure.

Parameters	Test 1	Test 2	Test 3	Test 4
Water temperature ($^{\circ}\text{C}$)	25	25	35	35
Rotation speed (rpm)	40	60	40	60
Flow rate (l/min)	0.275	0.275	0.275	0.275
Slope ($\mu\text{g/h}$) Cd	0.4664	0.568	0.2911	0.5166
Regression coefficient (R^2) Cd	0.991	0.9867	0.9643	0.9911
Sampling rate R_s (Lh-1) of Cd	0.0147 \pm 0.0031	0.0179 \pm 0.0022	0.0092 \pm 0.0021	0.0101 \pm 0.0002
Slope ($\mu\text{g/h}$) Cu	0.1515	0.1252	0.0722	0.1694
Regression coefficient (R^2) Cu	0.9397	0.9809	0.9708	0.9976
Sampling rate R_s (Lh-1) of Cu	0.0268 \pm 0.0155	0.0222 \pm 0.0057	0.0128 \pm 0.0033	0.0042 \pm 0.0011
Slope ($\mu\text{g/h}$) Zn	0.7564	0.6319	0.4274	0.401
Regression coefficient (R^2) Zn	0.991	0.981	0.7239	0.9662
Sampling rate R_s (Lh-1) of Zn	0.0231 \pm 0.0086	0.0193 \pm 0.0091	0.0130 \pm 0.0316	0.0063 \pm 0.0076
Slope ($\mu\text{g/h}$) Ni	0.4625	0.4422	0.23	0.4924
Regression coefficient (R^2) Ni	0.9896	0.9879	0.9541	0.9848
Sampling rate R_s (Lh-1) of Ni	0.0134 \pm 0.0027	0.0128 \pm 0.0017	0.0067 \pm 0.0023	0.0205 \pm 0.0035

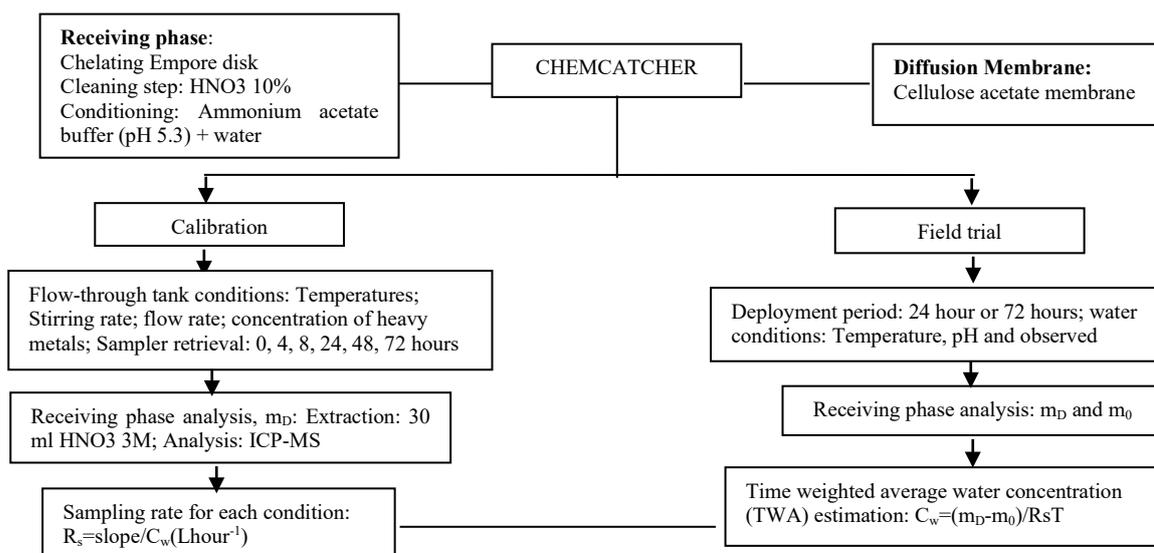


Fig. 2. Analytical protocol for calibration and field trial studies

2.4. Extraction Chemcatcher sampler

Extraction after exposure was conducted in vacuum filtration equipment, where the receiving phase disk was extracted using 30 mL 3M HNO₃. The extract was collected and analysis using ICP-MS equipment [7]. As a quality control measure procedure, field blanks were used. Procedural blank passive samplers were prepared and treated as described above. Field blanks were brought to and opened in the field at the sampling location.

2.5. Field trial location and analysis of water samples and extracts

A field trip was conducted in Nhue river consists of two sampling locations: First sample (NM1) at the intersection between To Huu street (Ha Dong) and Nhue river with coordinate (20.988678, 105.780493), second sample (NM2) at the White bridge Quang Trung street (Ha Dong) with coordinate (20.974233, 105.780424). The sampling locations were selected based on the influence of wastewater discharged from households and craft village

activities, so that concentration of metals could change over time. Chemcatcher devices were deployed at sampling sites in periods of 72 hours for NM1 and 24 hours for NM2 to monitor concentration of Cadmium, Copper, Zinc and Nickel in surface water. The deployment devices were suspended below surface of the river water at 20-40 cm, then removed out of river body at the end of sampling time. Samplers after deployment is retrieve as following: (a) retrieve samplers and take care not to touch the surface of the diffusion-limiting cellulose acetate membrane. Adding river water from the sampling site to the top of the diffusion-limiting cellulose acetate (CA) membrane, close the sampler by the transport lid and immediately seal the sampler back into the plastic zip-lock bag. (b) transport the samplers in a cooler, containing cooling bottles, to the processing laboratory, (c) store the Chemcatcher in a refrigerator at 4°C until processing [7].

Together with the Chemcatcher deployment, six and four spot water samples (200 mL) were collected from NM1 and NM2 at 0 hour, 4 hours, 8 hours, 24 hours 48 hours, 72 hours and 0 hour, 4 hours, 8 hours, 24 hours respectively. Samples were collected, preserved and transported to the laboratory for analysis.

3. Results and discussion

3.1. Results

3.1.1. Calibration of Chemcatcher in controlled tank

According to K.Booij et al [9] the uptake of a Chemcatcher into a sampler can be divided into three stages: Linear, curvilinear and finally equilibrium stage. During initial deployment accumulation is approximately linear. At this stage, the mass of analyte in the receiving phase is directly proportional to the concentration to which the system has been exposed, deployment time and effective sampling rate (R_s); following the equation: $M_D = m_0 + C_w R_s t$

Where m_D : Mass of target analyte accumulated in the receiving phase, m_0 : initial mass of the analyte in the receiving phase, C_w : TWA analyte concentration in water, R_s : Effective sampling rate of the device and t : deployment time.

To assess the effects of temperature and turbulence on the performance of Chemcatcher for the sampling of Cadmium, Copper, Zinc and Nickel, samplers were deployed in the calibration tank for up to 72 hours at two levels of water temperature (25°C and 35°C) and two levels of water turbulence (40 and 60 rpm) for combine Cadmium, Copper, Zinc and Nickel in the solution and flow rate of water at 0.275 L/min. After exposure, the amount of analyte (m_D) accumulated in the receiving phase was measured. Each calibration experiment yielded an uptake curve

from which the sampling rate (R_s) for heavy metals could be calculated. The table 1 summarizes the calibration data for each of the four experiments and the calculated sampling rates (R_s). The results show that for four experiments R_s value (Lh^{-1}) for cadmium, copper, zinc and nickel were $0.0092 \pm 0.0021 - 0.0179 \pm 0.0022$, $0.0042 \pm 0.0011 - 0.0268 \pm 0.0155$, $0.0063 \pm 0.0076 - 0.0231 \pm 0.0086$ and $0.0067 \pm 0.0023 - 0.0134 \pm 0.0027$ respectively.

3.1.2. Chemcatcher application for heavy metals monitoring in Nhue river

Two sampling sites (NM1 and NM2) in Nhue river were selected for deployment at 72 hours and 24 hours, respectively. Spot water samples were taken at 0, 4, 8, 24, 48 and 72 hours for NM1 and 0, 4, 8, 24 hours for NM2, preservation and transportation to the Lab for heavy metal analysis. The water temperature was 30, 28, 28.5, 27.5 and 25°C at NM1, 30, 28 and 28.5°C at NM2 and water pH around 6.8-7.2 for two sampling points.

At two sampling sites, spot water was taken and measured total Cd, Cu, Ni and Zn. However, the concentration of Cu and Ni were lower detection of analysis method (Cu concentration is lower 10 $\mu g/L$ and Ni concentration is lower 1 $\mu g/L$). For concentration of Cd and Zn are shown in Table 2. The results of spot samples are demonstrated that concentration of Cd is quite low and stable. However, concentration of Zn is higher and quite flexible. The results can be explained at the sampling sites where waste water (contained zinc) may be discharged by households or craft village activities

The mass of Cd and Zn found in the receiving phase of Chemcatcher after deployment at the two sampling points and the estimated TWA concentrations interval (C_w) are given in table 2. The temperature water was 25°C to 30°C and the turbulence of the river water during this season was assumed to be equivalent to the 40 - 60 rpm turbulence of the calibration tank experiments. Therefore, for TWA estimated concentration, R_s value in the range 0.0092- 0.0179 $L\ hour^{-1}$ for Cd and 0.0063- 0.0231 $L\ hour^{-1}$ for Zn was used.

Chemcatcher sampling technique was applied to measure the labile or free metals content while bottle sampling technique was used to measure the total metals content in surface water at Nhue river. That's why concentration of heavy metals measured by Chemcatcher was much lower than that found in spot samples collected over the same period. For the research, the results showed that Zn concentration obtained at NM1 and NM2 for Chemcatcher method was 11.05-40.09% and 10.52-38.60% compared to the spot sampler technique. In addition, the ratio of a

free metal ion content to a total concentration of the corresponding metal was used to assess the free and labile fraction of the total content of metal ions, and then, the one that response to the bioavailability and toxicity of presence of the metals in the water environment.

Table 2. Concentration of heavy metals in spot water samples collected at first and second sampling sites during passive sampling and mean concentration of Cadmium and Zinc;

DP (h)	SS	Spot water samples		Mean concentration of Cd and Zn was applied by Chemcatcher sampling	
		Cd ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)	Cd ($\mu\text{g/L}$) Rs (Lhour ⁻¹): 0.0092- 0.0179	Zn ($\mu\text{g/L}$) Rs (Lhour ⁻¹): 0.0063- 0.0231
0	NM10	1	110	Mass: 0.03 ($\mu\text{g/disk}$) TWA: 0.023-0.045 ($\mu\text{g/L}$)	Mass: 28.2 ($\mu\text{g/disk}$) TWA: 16.95-62.17 ($\mu\text{g/L}$)
4	NM11	<1	70		
8	NM12	<1	50		
24	NM13	<1	30		
48	NM14	<1	40		
72	NM15	7	620		
0	NM20	7	110	Mass: 0.03 ($\mu\text{g/disk}$) TWA: 0.023-0.045 ($\mu\text{g/L}$)	Mass: 16.2 ($\mu\text{g/disk}$) TWA: 9.74-35.71 ($\mu\text{g/L}$)
4	NM21	<1	70		
8	NM22	<1	140		
24	NM23	<1	50		

DP (h): Deployment Periods (hour), SS: Sampling sites

4. Conclusion

Passive sampling (Chemcatcher) method applied in Vietnam is the preliminary step for application of new sampling method to evaluate the feasibility of the implementation in Vietnam, especially for sampling for labile or free metals. In the research, four tests were done in the calibration tank with two levels of water temperature (25 and 35°C) and two levels of water turbulence (40 and 60 rpm) and the results show that the value of sampling rate (R_s) (Lh) for cadmium, copper, zinc and nickel were $0.0092 \pm 0.0021 - 0.0179 \pm 0.0022$, $0.0042 \pm 0.0011 - 0.0268 \pm 0.0155$, $0.0063 \pm 0.0076 - 0.0231 \pm 0.0086$ and $0.0067 \pm 0.0023 - 0.0134 \pm 0.0027$, respectively. Two sampling positions in Nhue river were chosen for applied Chemcatcher sampling and spot sampling. Two metals Cu and Ni for results lower detection of ICP-MS method. However, Zn concentration

obtained at NM1 and NM2 for Chemcatcher method was 11.05-40.09% and 10.52-38.60% compared to the spot sampler technique.

In summary, application of the method provides more data for reviving and assessment of water quality. However, it should be applied and expanded to supplement data of sampling rate of method (R_s value) and results in other water sources.

Acknowledgments

This research is funded by the Hanoi University of Science and Technology (HUST) under project number T2017-PC-013. The authors gratefully acknowledge Hanoi University of Science and Technology (HUST) for providing financial support for this research project.

References

- [1] Tadeusz Górecki, Jacek Namiński; Trends in analytical chemistry, 21, 4, (2002), 275 -291
- [2] R.Greenwood, G.Mills, B.Vrana; Passive sampling techniques in environmental monitoring; Wilson & Wilson's Volume 48, (2007)
- [3] Rocío Aguilar-Martínez, M. Milagros Gómez-Gómez, Richard Greenwood, Graham A. Mills, Branislav Vranab, María A. Palacios-Corvill., Talanta 77, (2009), 1483-1489
- [4] Kingston, Jenny K., Greenwood, Richard, Mills, Graham A., Morrison, Gregory M., Björklund Persson, Lena, Journal of Environmental Monitoring, Volume 2, 5, (2000), 487-495
- [5] Persson, Lena Björklund, Morrison, Gregory M., Friemann, Jens-Uwe, Kingston, Jenny; Mills, Graham; Greenwood, Richard, Volume 3, 6, (2001), 639-645
- [6] 3M Co-operation group., Empore extraction Disks, 1996
- [7] Graham A. Mills et al.; The Chemcatcher device for sampling metals, University of Portsmouth, 2012
- [8] R.Greenwood, G.Mills, B.Vrana.; Comprehensive analytical chemistry Volume 48, 2007.
- [9] K. Booij, B. Vrana, J.N. Huckins; in: R. Greenwood, G.A. Mills, B. Vrana, D. Barceló, Comprehensive Analytical Chemistry, volume. 48, Elsevier, Amsterdam, (2007), 251-278.