

Backward fugacity modeling for source load of PFOS in Huangpu River, Shanghai, China

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ABSTRACT

China is currently the only country to have documented continued production of perfluorooctane sulfonate (PFOS). To address the problem of insufficient emission data and utilizing available environmental concentration data of PFOS to estimate its emission, a Level III backward fugacity model was developed to calculate source loadings into a segment of Huangpu River, in Shanghai. The model was optimized for two decision variables and one objective function using Excel Solver[®], so that fugacity calculated from measured environmental concentrations were forced to equal output fugacity from the model. In this way, results based on available concentrations for both PFOS in river sediment and PFOS in surface water showed little differences between the observed concentration and the model output in the unoptimized phase. An approximation of emission load of 62–67 kg/year into the modeled segment of Huangpu River was verified. Wastewater treatment plant effluent was proven to be the major source. This backward fugacity model can serve as a preliminary estimation and a reference input to a further detailed emission inventory analysis in a region.

Key words | backward fugacity model, emission, Huangpu River, PFOS, WWT

INTRODUCTION

Perfluorooctane sulfonate (PFOS) along with its salts and perfluorooctane sulfonate fluorosulfonate (PFOSF), were listed in the Stockholm Convention as persistent organic pollutants (POPs) in 2001. Since the termination of 3 M's production of PFOS in 2002, the global PFOS application profile is expected to have changed dramatically (Armitage *et al.* 2009). China is currently the only country to have documented continued production of PFOS. According to the China Ministry of Environmental Protection (MEP), over 2000 tons of PFOS relative compounds were produced by Chinese enterprises, about half of which was used domestically (China MEP 2008a). Textile treatment, metal plating, semiconductor production, and fire-fighting foams are the main industries in China that utilize PFOS-based compounds, with PFOSF consumption amounts of 100 ton, 25 ton, 0.5 ton, and 80 ton, respectively (Liu *et al.* 2008). The reported environmental concentrations in surface water of most Chinese cities are comparable or lower than locations in other Asian countries and European/North American countries.

However, in cities such as Shanghai, Guangzhou, Tianjin, and the Taihu Lake, concentrations are much higher (Lim *et al.* 2011).

Mathematical modeling can be used to better understand the environmental behavior of a chemical pollutant in the environment. Among different types of mathematical models, the concept of fugacity was first applied to environmental modeling in 1979 as a way of reducing the complexity of the equations describing environmental behavior of a certain chemical (Mackay 1979). The fugacity approach is particularly suited to modeling POPs, because of their long half-lives, resilience to degradation, long-range transport potential and ability to partition into different environmental phases.

In the conventional use of the fugacity model, the key data inputs are the physical chemical properties of a pollutant, the emission amounts, and geographic data. Verification of the model would require observed environmental concentrations (Cahill *et al.* 2003). The emissions amount into the modeled environment is a key parameter

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in the fugacity model and dictates the amount of chemical that is allowed to partition between various phases. Generally, PFCs input into the aqueous environment occurs via various routes, including discharge from wastewater treatment plants (WWTPs), influx of nonpoint source runoff, as well as seepage and illegal discharge (Zhang et al. 2016). An ideal source emission calculation is to directly investigate all the potential pollution source in the field and then obtain the emission loads from all the sources. But this will cost massive manpower, material and financial resources. If emissions data is not available, it is impossible to proceed to calculate concentrations in various environmental media within the evaluative environment. The interpolation of very limited emissions data always would cause worst estimate of environmental concentration (Cahill et al. 2003).

However, in most areas, the environmental monitoring data are more available than emission load. In this study, a new methodology was developed based on the conventional fugacity model concept to be able to calculate approximate source loading from monitored environmental concentrations.

MATERIALS AND METHODS

As shown in Figure 1, in the conventional fugacity method, an estimate of the emissions inventory is required to calculate the environmental concentrations of the pollutant. In this study, a new methodology was developed to backward calculate source loading from monitored environmental concentrations based on the conventional fugacity model concept.

Backwards fugacity modeling for source load is an original application of the fugacity concept, which can be utilized under the following circumstances:

- (1) Emission data is nonexistent but there is existent environmental monitoring data;

- (2) There are unclear, ambiguous, or unreliable emissions data and more reliable environmental monitoring data;
- (3) Emissions data is incomplete and multi-phase environmental concentration data is available.

This method is particularly suited for preliminary assessment for a region in which a more comprehensive emission inventory investigation will be carried out. The results of the emissions inventory can be validated against the output emissions source loading from the carefully designed evaluative environment's fugacity calculations. It can serve as a tool for verification and quantification of uncertainty of emission inventory investigation.

The selection of the model for the estimation of source load must meet several conditions. Firstly, there must be existing environmental concentration data. For later optimization purposes, and to have greater confidence in the result, environmental concentrations should be available for at least two different environmental phases. Shanghai was chosen for study because there were data available in the phases of surface water and sediment (Huangpu River). A survey of available PFOS data for the Shanghai environment showed the majority of surface water monitoring data are clustered within the lower third reach of the Huangpu River (Figure 2). Since background concentrations are necessary to calculate the contribution of advective flow to the modeled environment, five data points upstream of the modeled environment were utilized to calculate the background concentration.

Level three fugacity model

In the Level III model, fugacities of each phase were calculated separately through the use of mathematical expressions of diffusive and nondiffusive processes. While these processes call for added algebraic complexity, it is still possible to back-calculate an emission load into the modeled area with the available data and appropriate

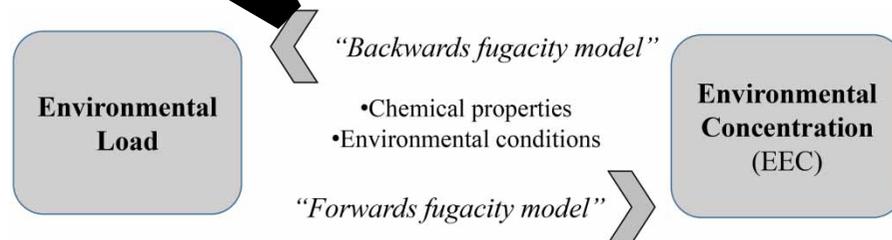


Figure 1 | Backwards and forwards fugacity methodologies schematic. Conventionally, 'Forwards Fugacity' is used to generate environmental concentrations. In 'Backwards Fugacity', observed environmental concentrations are used to estimate the modeled area's emissions amount.

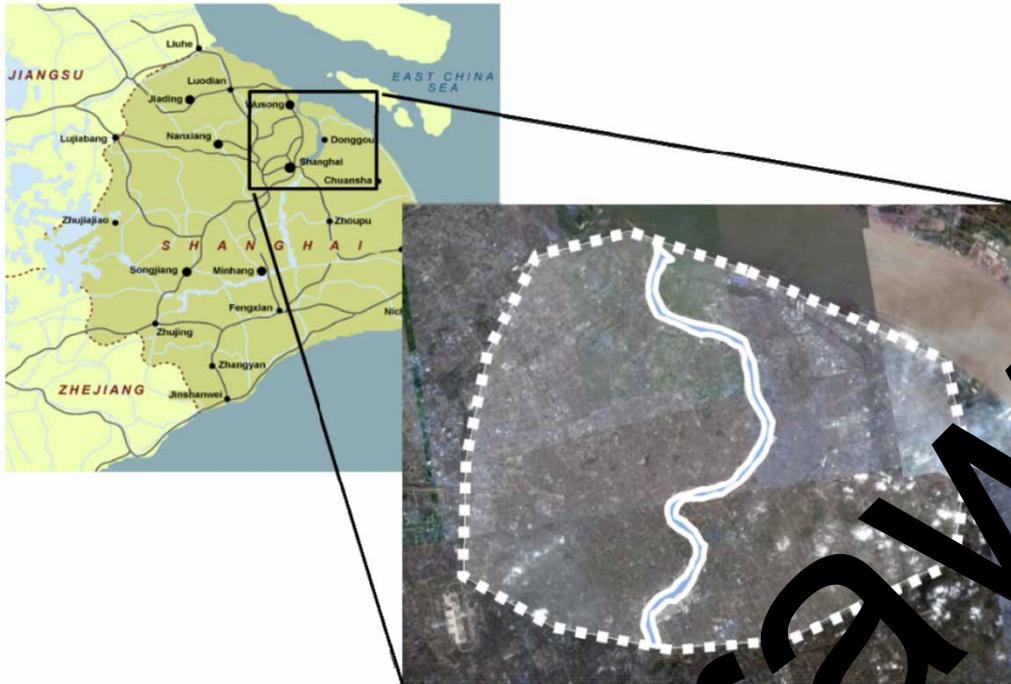


Figure 2 | Definition of the modeled area. The modeled area shown in dashed white, lower reaches of Huangpu River shown in solid white, black frame shows context within greater Shanghai region.

assumptions. Also, because the system is not assumed to be in an equilibrium state, the Level III fugacity model is able to distinguish between the phases receiving the emissions.

A Level III multimedia fugacity model was developed and applied to simulate the fate of PFOS based on an approach of Mackay (2001). For bulk phases including air (air and particulates), water (water suspended solids, and

$$E_i + A_i + \sum D_{ji}f_j - G_iZ_i f_i - V_iZ_iK_i f_i - \sum D_{ij}f_i = 0 \quad (1)$$

where, E_i is emission rate into the phase i ; A_i is advection input to the phase i ; D_{ji} is transfer coefficient from phase j to phase i ; f_i is fugacity of the phase i ; G_i is the volume velocity of phase i ; Z_i is fugacity capacity of the phase i ; V_i is the volume of the phase i ; K_i is reactive coefficient or the compound in the phase i . Phases air, water, soil, and sediment were indicated by 1, 2, 3, and 4, respectively. Equation (1) can be transformed into a matrix form (Wang et al. 2015):

$$Af + U = 0 \quad (2)$$

where, f is the solution matrix (fugacity matrix), A is the fate matrix, U is the emission rate matrix:

$$f = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{pmatrix}, \quad U = \begin{pmatrix} E_1 + G_1C_{B1} \\ E_2 + G_2C_{B2} \\ E_3 \\ E_4 \end{pmatrix}$$

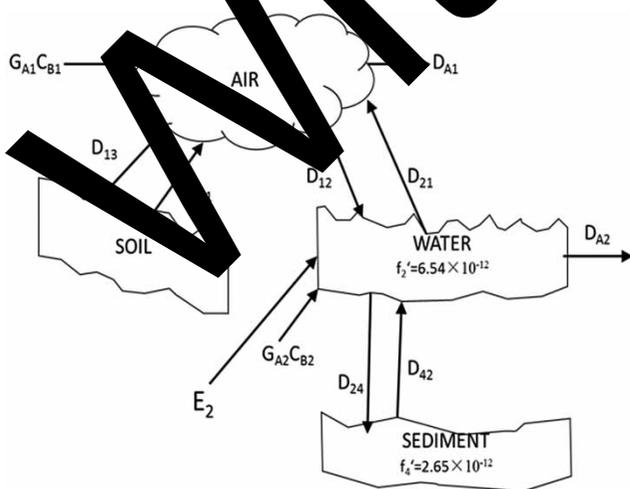


Figure 3 | Level III emissions scenario showing relationships between additional D values.

$$A = \begin{pmatrix} -(D_{12} + D_{13} + G_1 Z_1 + D_{R1}) & D_{21} & D_{31} & 0 \\ D_{12} & -(D_{21} + D_{24} + G_2 Z_2 + D_{R2}) & D_{32} & D_{42} \\ D_{13} & 0 & -(D_{31} + D_{32} + D_{R3}) & 0 \\ 0 & D_{24} & 0 & -(D_{42} + D_{A4} + D_{R4}) \end{pmatrix}$$

The above mass balance equations conventionally contain four unknowns, the fugacities in four phases. They can be solved directly by matrix computation. In the backward fugacity model, at least PFOS concentration in one phase is known, and the emissions scenario is the unknown parameter for which we will solve.

The environment-related properties of PFOS, environmental parameters and PFOS concentrations were acquired for the model calculation. The physico-chemical properties of PFOS mainly came from (USEPA 2012). The main physico-chemical properties included: molecular weight (MW) 538, water solubility 370 mg L^{-1} , vapor pressure (VP) 0.00033 Pa , Henry' Law constant (H) was $3.05 \times 10^{-9} \text{ atm m}^3/\text{mol}$. Organic-carbon partition coefficient ($\log K_{oc}$) was 2.57. Air-water partition coefficient ($\log K_{AW}$) were calculated from vapor pressure and solubility. Air-water partition coefficient ($\log K_{AW}$) were calculated from vapor pressure and solubility. PFOS is extremely stable and not expected to undergo physiochemical and biological degradation in the environment.

Atmosphere

Wind data for the Shanghai Pudong district indicates that the average wind speed in the region is 5.13 meters/second. The volume of atmosphere equals the product of the total area and a height of 500 m. Based on this volume and average wind speed, the advective flow of air through the modeled area is 4.26×10^{11} cubic meters per second, which translates to a residence time in this area of 0.75 hours. This residence time justifies the use of 500 m

for the atmosphere phase, since in such a short period of time, it is unlikely that PFOS would reach a greater height (Mackay 2001).

Water

The total volume of water equals to the product of water area and an average depth of 0.15 meters (Zhang 2007). Huangpu River's flow velocity is 5.13 cubic meters per second, which translates to 1,137,600 cubic meters per hour (Kuang et al. 2010). The average pH value is 7.4 for surface water in Huangpu River (Song et al. 2010).

Soil

The modeled environment concerns a largely urban area, therefore, an urban landscape was assumed to behave as 20% soil cover, which is within the acceptable range previously reported (Boyd et al. 1993; Diamond et al. 2001). This 20% represents not only the soil from urban parks and green areas, but also the 'urban film' described by (Diamond et al. 2001). Soil is active up to a depth of 15 centimeters, and the organic matter was defined to be 2%, which was less than those in suburban or rural areas.

Sediment

According to Wang (2005), a sediment depth of 20 centimeters was taken in Shanghai. The organic carbon fraction was set to be 4%. Information about the modeled environment is summarized in Table 1.

Table 1 | Modeled environmental properties

Parameter	Air	Water	Soil	Sediment
Area (m ²)	702,630,000	16,860,000	140,400,000	16,860,000
Depth (m)	500	9	0.15	0.2
Volume (m ³)	3.51×10^{11}	151,740,000	21,060,000	3,372,000
Density (kg/m ³)	1.206	1,000	1,500	1,500
Fraction Organic Carbon	0	0	0.02	0.04
Advective Flow G (m ³ /h)	4.63×10^{11}	1,137,600	NA	NA

It was assumed that all PFOS emissions occurred into water. Based on previous emissions inventories in which the overwhelming majority of PFOS emissions happened through wastewater streams, this is a reasonable assumption (3M Company 2000; Brooke et al. 2004). The valid environmental concentrations available for PFOS included water and sediment for the studied region in Shanghai (Table 2). Fugacity can be calculated as concentration divided by fugacity capacity (C/Z).

RESULTS AND DISCUSSION

As can be seen from Equation (2) matrix, the emissions term to be solved, is deeply embedded in the equations. This means that depending on the E terms, the fugacities in each phase will vary. Assuming that all PFOS emissions occurred into water, E_1 , E_3 and E_4 will be zero. Since the observed fugacity (f_i) values for water and sediment are known, we can vary E_2 until modeled fugacity (f'_i) equals f_i , or is as close to f as possible. To this end, an Excel worksheet was designed to handle the optimization. A third party add-on Solver[®] was selected as the optimization tool. The strategy was to alter a decision variable so that f and f' are equal for sediment or water. The Solver[®] optimization objectives and results are shown in Table 3.

Firstly, optimization of the water phase using Solver[®] resulted in an E_2 of 67.5 kg/yr. The difference

Table 2 | Measured environmental concentrations of PFOS in the study region

Phase	Mean	SD	n	Source
Surface water	11.30 ng/L	10.53	22	So et al. (2007) and Pan & You (2010)
Sediment	1.01 ng/g	2.71	22	Pan & You (2010) and Li et al. (2010)

Table 3 | The Solver[®] optimization objective and results

Solver [®] optimization objective		Optimization evaluation and validation			Results
Target variable	Error precision	Validation variable	Logarithmic error $\ln f' - \ln f$	Relative error $(f' - f)/f'$	Emission (kg/yr)
f_2	$<10^{-6}$	f_2	2.9×10^{-7}	6.8×10^{-7}	67
		f_4	1.8×10^{-2}	4.2×10^{-2}	
f_4	$<10^{-6}$	f_2	1.8×10^{-2}	4.2×10^{-2}	62
		f_4	4.0×10^{-7}	9.3×10^{-7}	
$f_2 + f_4$	<0.05	f_2	9.5×10^{-3}	2.0×10^{-2}	64
		f_4	8.8×10^{-3}	1.9×10^{-2}	

in modeled and observed logarithmic f values for the water phase was successfully minimized to a very low value, 2.9×10^{-7} , and the relative error $(f' - f)/f'$ was likewise minimized to be 6.8×10^{-7} . In the independent validation based on the unoptimized phase (sediment), the difference between the output f'_4 value and the observed f_4 value was as low as 0.02 for the logarithmic expression and 0.04 for the linear expression of $(f' - f)/f'$. Secondly, optimization of the sediment phase resulted in an approximate emission load of 62 kg/yr. In both cases, the difference of the common logarithms between the modeled and the observed fugacity value in the unoptimized phase was much less than 0.05, which verified the reliability of the model results. The above cross validations performed by optimizing f values in two separate phases (water and sediment) resulted not only a difference of only 5 kg/yr emissions, but also showed low differences between the observed concentration and the model output of the independent unoptimized phase. Lastly, the differences between the modeled and observed f values for water and sediment were combined by summing their absolute values (logarithmic error or relative error) and then were optimized to minimum. In this optimization, all the logarithmic errors and relative errors of both f_2 and f_4 were optimized to be less than 0.05, i.e. $f'_2 \approx f_2$ and $f'_4 \approx f_4$, and the emission amount of 64 kg/yr would be the value that most satisfies this condition.

The model results indicate that 70% of the chemical input into the modeled area was a result of direct emission into the water phase, and 30% of the chemical input is a result of advective flow of upstream concentrations. The very low f values for the air phase explain why PFOS is unlikely to be found in this phase.

According to the municipal WWTP data for Shanghai, there are 4 major WWTPs located within the modeled area (Table 4). Based on the average WWTP effluent

Table 4 | WWTP locations and estimated PFOS emission estimates

WWTP	Longitude	Latitude	Capacity (m ³ /d)	Calculated Yearly PFOS emission (kg/yr)
A	31°25'52.39"N	121°26'35.37"E	40,000	0.65
B	31°24'09.87"N	121°29'53.90"E	39,000	0.64
C	31°15'56.87"N	121°34'37.97"E	1,300,000	21.22
D	31°13'16.80"N	121°36'42.40"E	2,000,000	32.65
Total			3,379,000	55.15

PFOS concentration of 44.72 ng/L in this area (Chen et al. 2012; Zhang et al. 2013; Zhang et al. 2015), an estimate of the annual PFOS release into the modeled segment of Huangpu River was calculated as 55.15 kg/year. This is approximately 11%–18% less than current emission amount into water derived from the model. This could be explained by that about 15% of the total domestic wastewater was not treated and discharged directly into receiving surface water in Shanghai.

There is also some evidence that some industrial effluent was discharged directly into the environment following simple treatment processes with little removal of very recalcitrant PFOS in some areas in China (China MEP 2009; Guangdong Province 2008). In the modeled area, there were about 656 sources of industrial wastewater with an annual discharge of $1.4027 \times 10^8 \text{ m}^3$. Li et al. (2004) and Lin et al. (2010) indicated the high PFOS concentration in related industrial wastewater. However, in this area, industrial wastewater did not contribute much to the PFOS emission because there were few related industries, and also industrial wastewater was collected and treated by municipal sewage system in this area.

When verified emission information is available, forward fugacity model should be carefully put into application. In a previous study, forward fugacity model calculation in which emission inputs were based on a per capita emission rate of the United States, showed that estimated concentrations were more than 50 times higher than the observed environmental concentration (Cahill et al. 2003). Under such circumstances, it is very useful to firstly use backward model to estimate the source, and try to get a primary comprehension of the total emission.

In summary, Level III fugacity model was successfully calibrated to yield an approximation for emissions into the lower third portion of Huangpu River in the Shanghai region. Utilizing the optimization tool Excel Solver[®], fugacity values calculated from environmental concentrations

were forced to equal fugacity values that were the output from a Level III fugacity model. The water-only emissions scenario yielded a successful model optimization. The yearly emission into water was calculated to be 62–67 kg/year. Verification of this emission estimation showed its reasonableness according to an approximation of wastewater effluent discharge by WWTPs in this area. Thus, the backward fugacity model can serve as a preliminary estimation and a reference prior to a further detailed emission inventory analysis in a region.

CONCLUSIONS

A new methodology was developed based on the conventional fugacity model concept to be able to calculate approximate source loading from monitored environmental concentrations. An approximation of emission load of 62–67 kg/year into the modeled segment of Huangpu River was verified. WWTP effluent was proven to be the major source. This backward fugacity model can serve as a preliminary tool to further guide a more detailed emissions inventory analysis in a region.

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