Comparative Analysis of the Fugitive Model of Persistent Organic Pollutants in Soil Surface

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Abstract. As the constant perfection of the fugitive model of POPs in the soil surface, it is necessary to compare and analyze the fugacity model of POPs in soil. By comparing and analyzing the model of fugacity, which we can illustrate the escape of POPs in the soil surface, and demonstrate the influencing factors of POPs volatilization and infer the gas-soil exchange equilibrium state of regional soil POPs. The fugacity model can be used to express the exchange changes of POPs in the soil surface. It can also reveal the environmental behaviors such as migration of POPs in soil media, as well as providing basis of reference for the potential assessment of ecological risk in the area of POPs, and providing reference basis for the potential ecological risk assessment in the area of POPs and provide a reasonable explanation for POPs migration on a global scale, distribution and fate.

1. Introduction

Persistent Organic Pollutants (POPs), as a series of semi-volatile organic pollutants, can undergo long-range atmospheric transport (LRAT). In the course of the LRAT, the POPs experience the period of volatilization-transportation-sedimentation, which is taken into account the Grasshopper Effect[1] .Therefore, it's widespread environmental behavior that the POPs escape from the surface medium.

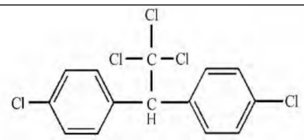
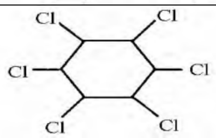
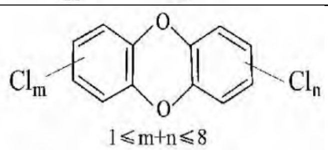
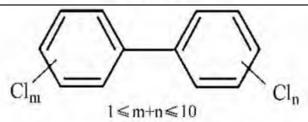
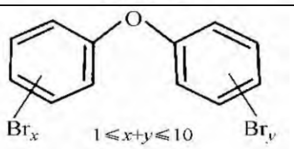
The former researches on the volatilization-sedimentation mostly attach great importance to applying fugacity to assume the trend of exchange and equilibrium state. Terzaghi [2] developed a new model of dynamic fugacity to discover the vital effect of surface soil on the process of air-soil exchange. Meanwhile, Liu[3] adopted the model of fugacity to evaluate the air-soil exchange equilibrium and explain the potential impact of soil on the sink and source of POPs, which is coincident with Harner's[4] results that concluded from utilizing the fugacity fraction(ff) to judge the air-soil exchange direction.

This paper firstly introduced several kinds of typical POPs in the polluted soil, as well as enumerating the corresponding representative POPs. Subsequently, it systematically explain the fugacity model of the organic pollutants in the soil medium and air-soil exchange in the surface soil. Furthermore, some newly model of the POPs in the soil medium are introduced in this paper. Lastly, the applying scale of the fugacity model is optimized in this paper .

2. Typical POPs causing soil pollution

Persistent organic pollutants(POPs) have the characteristics of semi-volatile and persistent. Therefore, they can better describe the comparative analysis of the fugacity model of gas in the soil surface. The POPs in the soil are broadly classified into: organochlorine pesticides such as DDT; waste combustion and industrial by-products such as dioxins; industrial chemicals such as polychlorinated biphenyls; and POPs afterwards added to the Stockholm Convention, such as Polybrominated diphenyl ethers, etc. Table 1. lists the molecular structure, saturation vapor pressure and physicochemical stability of several typical of soil POPs.

Table 1. lists the molecular structure, saturation vapor pressure and physicochemical stability of several typical of soil POPs.

POPs	Molecular structure	Saturated water vapor pressure.(kPa)	Physicochemical stability
DDT		2.53×10-8(20°C)	Undecomposable at room temperature; insoluble in water
HCH		1.25×10-6-3.30×10-6(20°C)	Undecomposable under high temperature and sunlight; insoluble in water
PCDD		~6.210×10-6(25°C)	Stable at room temperature; complicate to dissolve in water
PCBs		9.41×10-9-3.83×10-5(25°C)	Stable at room temperature; complicate to dissolve in water
PBDEs		9.049×10-9-1.66×10-5(25°C)	Very stable in normal environment, complicate to degrade; not easily soluble in water

3. Fugitive model

3.1. Analysis of fugitive model of dynamic multi-media organic pollutants

The dynamic multi-media fugacity model [5] can comprehensively and systematically analyze the migration and transformation of organic pollutants in environmental media. Its advantage can be simply summarized that it can be applied to the discharge of unstable pollution sources and can be applied to environmental media. Response time for pollutant emissions. Therefore, the fugacity model is applied to the soil medium to analyze the fugacity of organic pollutants on the soil surface. In accordance with the theory of fugacity model, the change of the fugacity f of organic pollutants in the soil surface combined with the fugacity model framework map, In this way the mass conservation equation of organic pollutants is established in the soil medium.

Mass conservation equation:
$$\frac{df_3}{dt}=\frac{I+f_1D_{13}-f_3D_{T3}}{V_3Z_3} \tag{1}$$

Mass transfer coefficient：
$$D_{13}=UA_1Z_1 \tag{2}$$

Reaction transfer coefficient：
$$D_{R3}=K_{R3}V_3Z_3 \tag{3}$$

Advection transfer coefficient：
$$D_{A3}=Q_3Z_3 \tag{4}$$

Transmission coefficient：
$$D_{T3}=D_{13}+D_{R3}+D_{A3} \tag{5}$$

Formula: I：emission rate of organic pollutants; f2、f3：the air and soil fugacity;DT3：the total reduction factor of organic pollutants in the soil medium;U：the mass transfer rate; the contact area of air and soil;A1：the contact area of air and soil;Z1、Z3 : the air and soil fugacity capacity; KR3: is the first-order rate constant of reaction;V3 :for studying the volume of soil; Q3:for volumetric flow.

3.2. Analysis of the fugacity model of organic pollutants on the gas-soil interface

As the majority of the organic pollutants evaporate from the volatilize of soil into the air, it's necessary to analyze the fugacity of organic pollutants on the gas-soil interface. The exchange flux of gaseous organic pollutants on the gas-soil interface determines that surface soil is the consequential process for 'source and sink', and the fugacity model is the powerful tool to estimate the exchange flux of gaseous organic pollutants in the gas-soil interface. By combined with Atmospheric fugacity, soil fugacity and gas-soil distribution coefficient, the formula to calculate fugacity of organic pollutants in fugacity model is established.

Atmospheric fugacity:
$$f_a = C_a RT \tag{6}$$

Soil fugacity:
$$f_s = \frac{C_s RT}{K_{SA}} \tag{7}$$

Gas-soil distribution coefficient:
$$K_{SA} = 0.411 \rho_s \varphi_{oc} K_{OA} \tag{8}$$

In the formula,Ca andCs are the concentrations of pollutants in atmosphere and soil ,respectively; R is the universal gas constant; T is the temperature; 0.411 is the conversion ratio; ρs is the soil density; φoc is the content of organic carbon in soil; KOA is the n-caprylic alcohol-air distribution coefficient of compound, which is related to temperature.

Gas-soil distribution coefficient (KSA) is defined as the ratio of soil and POPs concentration in the atmosphere with the equilibrium state. Higher the value of KSA is stronger the ability that soil adsorbs the compound is. The formula reflects that the value of KSA is in direct proportion to soil organic matter content, and the relation between the distribution coefficient of gas-soil increases with the decrease of temperature is pointed out. Moreover, the formula is much significant for simulating migration and return of POPs to the soil surface in gas-soil interface fugacity model[6].

The stronger the comparison process between the effects of gas deposition and desorption from soil to atmosphere determines the fugacity of POPs on the gas-soil interface. The fugacity and commutative direct of POPs on the gas-soil interface could be confirmed by the fugacity quotient and the fugacity fraction.

1）Fugacity quotient to confirm commutative direct of POPs on the gas-soil interface fugacity ratio/quotient：

$$f_{r/q} = \frac{f_s}{f_a} \tag{9}$$

When fr/q >1，it's net volatile；when fr/q<1，it's net sedimentation；when fr/q=1，it's the equilibrium state of gas-soil exchange.

2）Fugacity fraction to confirm commutative direct of POPs on the gas-soil interface fugacity fraction：

$$ff = \frac{f_s}{(f_s + f_a)} \tag{10}$$

When ff>0.5，it's net volatile；when ff<0.5，it's net sedimentation；when ff=0.5，it's the equilibrium state of gas-soil exchange.

3.3. Other fugacity model

The majority of the current fugacity models ignore the dynamic effects contributed to the constant changes of environmental factors, which will lead to prediction bias for the analysis of the fugacity for persistent organic pollutants in surface soil. In order to investigate the effects of dynamic changes in environmental factors on the fugacity of persistent organic pollutants in surface soil, Terzaghi [2]developed a new SoilPlusVegmodel to analyze the fugacity of air-litter-soil in forest systems and found out that the litters are associated with the accumulation or release of organic pollutants., affecting the concentration in air and soil and controlling the fugacity of POPs at the air-soil interface[7].

Additionally, there is a phase equilibrium fluency model in the soil[8], which indicates the fugacity of organic compounds in the organic phase of the soil in the course of phase equilibrium, as well as describing the balance of organic pollutants in various phases of the environment. There is also a three-degree fugacity model developed by the Canadian Centre for Environmental Modelling and Chemistry (CEMC), which is mainly applicable to steady-state, unbalanced systems. It also considers steady-state inputs and outputs of pollutants, and the various reaction processes occurring in each phase. Assuming that these processes are primary processes, they can help users study the migration and transformation of organic pollutants in different environments and environmental fate.

4. Prospect

(1) The environmental factors affecting the volatility of POPs from soil media are countless and the effects are more complex. The dynamic changes of different environmental factors affect the fugacity of POPs in the soil surface, while the current construction of fugacity model merely utilizes pops concentration, temperature and other factors. Therefore, the fugacity model requires to increase the research intensity and reinforce the adaptation range of the model.

(2) Given the difficulty in the actual measurement of POPs fugacity, there may be a lack of calibration basis when evaluating the fugacity model. Additionally, there are few studies on main parameters such as mass transfer coefficients in the fugacity model, and the parameters affected by various environmental factors cannot be measured in practice, which limits the application of the fugacity model.

(3) There are quite a few vegetations in the soil surface, and the surface layer of the forest soil is also covered with litter layer, which influences the soil surface evaporation and settling of POPs, thus affecting the accuracy of the fugacity (measured or simulated). The presence of surface vegetation such as surface vegetation and litter should be fully considered when making full use of the fugacity model to predict and evaluate the fugacity of POPs

References

[1] Gouin T, Mackay D, Jones K C, et al. (2004).Evidence for the "grasshopper" effect and fractionation during long-range atmospheric transport of organic contaminants[J]. Environmental Pollution, 128(1):139-148.

[2] Terzaghi E, Morselli M, Semplice M, et al. (2017).SoilPlusVeg: An integrated air-plant-litter-soil model to predict organic chemical fate and recycling in forests[J]. Science of the Total Environment, 595:169-169.

[3] Liu X, Wang S, Jiang Y, et al. (2017).Polychlorinated biphenyls and polybrominated diphenylethers in soils from planted forests and adjacent natural forests on a tropical island[J]. Environmental Pollution, 227:57-57.

[4] Harner T, Bidleman T F, Jantunen L M M, et al. (2007).Soil—air exchange model of persistent pesticides in the United States cotton belt[J]. Environmental Toxicology & Chemistry, 20(7):1612-1621.

[5] Mackay D. (2001).Multimedia environmental models :the fugacity approach[J]. Crc Press.

[6] Harner T, Bidleman T F, Jantunen L M, et al. (2010).Soil-air exchange model of persistent pesticides in the United States cotton belt.[J]. Environmental Toxicology & Chemistry, 20(7):1612-1621.

[7] Nizzetto L, Liu X, Zhang G, et al. (2014).Accumulation kinetics and equilibrium partitioning coefficients for semivolatile organic pollutants in forest litter[J]. Environmental Science & Technology, 48(1):420-428.
[8] Toro D. (1985).A particle interaction model of reversible organic chemical sorption[J].Chemosphere, 14(10):1503-1538.