Biophysical Viscosity: Thermodynamic Principles of Per Capita Chemical Potentials in Human Populations

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ABSTRACT: Dynamic viscosity has been used to describe molecular resistance to flow under an applied force. This study introduces the theory of biophysical viscosity, the resistance of a region to molecular flow under environmental force to define the rates of per capita anthropogenic chemical efflux into the environment. Biophysical viscosity is an important intermediate quantity, in that it can be used to calculate the chemical potentials of single molecules for individuals in a population. Nonhypothetical emission data was combined with chemical potentials of anthropogenic tracers, to demonstrate that thermodynamic quantities can be used as parameters to directly compare energies associated with individual chemical emissions across geographic regions. These results indicate that population density is not the only factor in the determination of population-level chemical efflux and that biophysical viscosity is a useful tool in determining the per capita chemical potentials of anthropogenic chemicals for environmental risk assessment.

INTRODUCTION

More than half of all accessible surface freshwater on Earth is allocated for human use.1 With unprecedented release of anthropogenic micropollutants and their subsequent transformation products (TPs) into depleting freshwater supplies, accurate monitoring of the remaining water resources is necessary to ensure future environmental and human health.2,3 The quantity and diversity of organic chemicals consumed on a global scale has resulted in complex TPs that conventional Water Resource Recovery Facilities (WRRFs) may not be designed to eliminate.4 Biologically active TPs may present toxicities greater than or equal to those of their precursors yet go undetected by traditional analytical approaches.5 As the physicochemical treatment of compounds in WRRFs is dependent on plant design, the removal efficiency of complex TPs from potable water sources will vary between sites.6,7 As increasingly complex TPs present a challenge to future WRRF designs, it is vital that analytical methodology be evolved to rapidly identify potential contamination with chemical lifecycle models.

Caffeine has been used as an anthropogenic marker for wastewater contamination and has also been used in ambient water quality monitoring as it frequently co-occurs with coliforms in contaminated surface waters.8,9 The concentrations of caffeine found in aqueous environments have been positively correlated with emerging contaminants that affect important hormonal physiological processes.10,11 Molecular modeling studies have confirmed the stability of caffeine complexes in aqueous solutions through purine stacking.12 Caffeine has been shown to influence the solubility of other aromatic contaminants through intermolecular π-stacking, which may influence the persistence of the TPs during WRRF processes and subsequent biological uptake from WRRF effluents in urban environments.13,14 Application of environmental risk assessment models that use aqueous caffeine concentrations can be used as a method to prioritize samples for biological assay.15

Pharmaceuticals, including caffeine, have been tracked through wastewater treatment processes with gas chromatography–mass spectrometry (GC–MS), and their potential molecular fates have been reviewed.16,17 GC–MS is limited in its capability to measure analytes that are heat-labile or distinguish between enantiomers that possess different biological half-lives. Liquid chromatography–mass spectrometry (LC–MS) has been used extensively to identify emerging anthropogenic contaminants of concern in sewage treatment plant effluents, surface water, and sea water.18 Environmental persistence of synthetic chemicals includes usage, disposal, and re-entry into nutrient cycles in the biosphere. A conceptual
basis to assess individual molecular emissions by populations to the aquatic environment is needed to actively monitor environmental and human health.

As a predictive tool in the environmental fate of chemical species, fugacity defines chemical potentials associated with the environmental partitioning of compounds with similar functionalities.\textsuperscript{19} Although fugacity is sufficient for predicting phase preferences of single molecules within an order of magnitude, it is limited by the uncertainty in the emission rates of the parent compounds in dynamic equilibrium with potentially more toxic TPs.\textsuperscript{20} Application of fugacity and thermodynamic activity models requires that a compound’s fugacity capacity and solubility be known.\textsuperscript{21} Fugacity ratios (a chemical’s fugacity in an organism relative to that in its environment) have been used in environmental risk assessment for commercial synthetic molecules, but no approach has utilized units of energy to model point-source chemical emissions of individuals that comprise a geographic area adjacent to water bodies.\textsuperscript{21}

Fugacity is based on chemical potential ($\mu$), which is defined as the tendency of chemicals to react, transform, and migrate.\textsuperscript{22} Chemical potential can describe equilibria in which two driving forces compensate for one other.\textsuperscript{22} An intrinsic dynamic equilibrium exists between human populations that synthesize or concentrate chemicals and the greater environment in which they are transformed or diluted (Figure 1).

Chemical potentials are temperature-dependent energies that can offer insight into conditions that affect emerging contaminant behavior in the face of climate change.\textsuperscript{23} The purpose of this article is to provide a conceptual basis for monitoring the changes in contaminants over time at the population level by coupling thermodynamic principles with nonhypothetical anthropogenic chemical concentrations in aquatic systems.

\section*{THEORY/CALCULATION}

Viscosity is a bulk property commonly used to describe a substance’s resistance to flow, with dimensions of mass, distance, and time.\textsuperscript{26} Internal molecular forces, temperature, pressure, and gravity are conditions that influence viscosity.\textsuperscript{26} The concept of viscosity is less applied to the diffusion of individual molecules through the biophysical environment, from a point source to an area of potential contamination.

Biophysical viscosity of a point source can be viewed as a measure of internal friction or resistance of molecular flow under environmental force that is determined by physicochemical properties, the degree of (a)biotic transformation, biological sequestration, and sorption processes. A low biophysical viscosity would indicate that a point source is able to disperse...
contaminants more readily than an area with a higher biophysical viscosity. An analogy of biophysical viscosity related to equilibrium systems is found in Gibb’s work, wherein “anything that restricts the free movement of a component substance is found to diminish the number of conditions necessary for equilibrium”.

Independent of environmental molecular path, the measured concentration of anthropogenic tracers can be used to compare the rates at which a given population deposits a molecular footprint on the surrounding environment.

A conceptual schematic is shown in Figure 2, wherein the population density of a geographic region (A) is viewed as the average concentration of a molecule that an individual is capable of releasing per unit area (B). (C) shows the biophysical viscosity of the molecule as it is transported from a given area of defined density to the aquatic environment. Biophysical viscosity, $\eta$, can be used as a metric to quantitatively compare the effect of population density on contaminant flow over time and is defined in eq 1

$$\eta = \frac{c}{\rho \Delta t} \quad (1)$$

where $c$ is the average measured analyte concentration (kg/m$^3$), $\rho$ is the population density of the associated geographic area (persons/m$^2$), and $\Delta t$ is the time (s) period over which the measured concentration of a chemical is averaged. Equation 2 gives SI units for biophysical viscosity in (kg/person m s).

$$\eta = \frac{\text{kg/m}^3}{(\text{person/m}^2)s} = \frac{\text{kg}}{\text{person m s}} \quad (2)$$

There are many mechanistic variables associated with molecular transport in the chemical lifecycle; however, biophysical viscosity can be used to derive chemical potentials associated with equilibria between human populations and the environment. Anthropogenic conditions placed on the environment have resulted in masses and concentrations of chemicals that are entirely different in composition from those of chemicals that have existed before. Calculating chemical potentials, or the tendency of a system to yield particles, can provide a conceptual framework to monitor the concentrations of anthropogenic contaminants in equilibrium with the environment by calculating the per capita energies associated with emission.

As there is a characteristic flow rate and resistance to flow for each molecule through the environment, flow rate $Q$ (eq 3) and biophysical viscosity $\eta$, can be used to derive the per capita chemical potential, $\mu$, in eq 4. The SI unit for per capita chemical potential is shown in eq 5 in J/person

$$Q = \frac{m^3}{s} \quad (3)$$

$$\mu = Q\eta \quad (4)$$

$$\mu = \frac{\left(\frac{m^3}{s}\right)\left(\frac{kg}{\text{person m s}}\right)}{\text{person}} = \frac{J}{\text{person}} \quad (5)$$

The per capita chemical potential can be viewed as the change in energy when one person is added/removed from a population or the energy associated with per capita usage/disposal of a substance. Quantitation of the energy associated with molecular movement from a higher chemical potential in anthropogenic sources to a lower chemical potential in the environment is a useful point of reference to simplify contaminant flow modeling to energy units per person. This can also be useful to objectively compare the chemical footprints of geographic regions for individual molecules of concern in environmental risk assessment.

### RESULTS AND DISCUSSION

Caffeine concentrations in the San Marcos River (San Marcos, TX) and rivers in Sao Paolo State, Brazil, were confirmed with LC–MS/MS. GC–MS/MS data was used to determine Lubbock caffeine concentrations at a water reclamation plant influent in a West Texas community, which was used as a pilot facility for the fate of pharmaceuticals and personal care products. The measured caffeine concentrations were initially in $\mu$g/L and converted to kg/m$^3$. The confidence limits of caffeine measurements over a 6 month period are reported in Table 1, except for the site at Campinas, BR (B), where caffeine was only detected once ($n = 1$) over the time course.

Population densities were used in conjunction with mean contaminant concentrations measured over a 6 month period, to evaluate per capita human contributions of chemical efflux to local aquatic systems. Caffeine was used here as a model compound to determine the viability of using biophysical viscosity as a factor for comparing molecular footprints of geographic regions of interest. Using eq 1, the biophysical viscosity was calculated for seven cities in Brazil and Texas. Locations, sampling times, mean caffeine concentrations, calculated biophysical viscosities, and associated rankings are summarized in Table 1.

This model found that Rio Preto had the lowest biophysical viscosity per capita, indicating that it has a relatively low resistance to biophysical flow of caffeine into the Rio Preto River. Campinas is a city geographically connected with two main aquatic sources, the Atibaia and Capiveri Rivers. In cases in which a single location is treated as a point source of chemical emission with effluent streams to various water bodies,

### Table 1. Comparison of Biophysical Viscosity Calculated for Eight Sampling Sites

| Location          | Time of Sampling    | $c$ (kg/m$^3$) $\times 10^{-6}$ | $\rho$ (persons/m$^2$) | $\eta$ (kg/person m s) | $\eta$ Rank | $\rho$ Rank |
|-------------------|---------------------|---------------------------------|------------------------|------------------------|-------------|-------------|
| Guarulhos, BR     | Jan 2010–June 2011 | 0.7 ± 0.6                       | 4.17 $\times 10^{-3}$  | 1.11 $\times 10^{-10}$ | 7           | 1           |
| Barueri, BR       | Jan 2010–June 2011 | 1.4 ± 0.9                       | 3.75 $\times 10^{-3}$  | 2.54 $\times 10^{-10}$ | 6           | 2           |
| Campinas, BR (A)  | Jan 2010–June 2011 | 0.20 ± 0.10                     | 1.36 $\times 10^{-3}$  | 1.04 $\times 10^{-10}$ | 8           | 3           |
| Campinas, BR (B)  | Jan 2010–June 2011 | 1.9                             | 1.36 $\times 10^{-3}$  | 8.87 $\times 10^{-10}$ | 3           | 3           |
| Rio Preto, BR     | Jan 2010–June 2011 | 0.03 ± 0.01                     | 9.47 $\times 10^{-4}$  | 2.01 $\times 10^{-11}$ | 9           | 4           |
| Lubbock, TX       | Dec 2008–Sept 2009 | 3.7 ± 1.1                       | 7.24 $\times 10^{-4}$  | 3.24 $\times 10^{-9}$  | 2           | 5           |
| Cerquilho, BR     | Jan 2010–June 2011 | 0.2 ± 0.1                       | 3.50 $\times 10^{-4}$  | 3.80 $\times 10^{-10}$ | 5           | 6           |
| Atibaia, BR       | Jan 2010–June 2011 | 0.21 ± 0.20                     | 2.90 $\times 10^{-4}$  | 4.59 $\times 10^{-10}$ | 4           | 7           |
| San Marcos, TX    | Oct 2006–Mar 2007  | 1.7 ± 0.9                       | 9.00 $\times 10^{-3}$  | 1.20 $\times 10^{-9}$  | 1           | 8           |
biophysical viscosity varies depending on the contaminant concentration within the water body.

Per capita biophysical viscosity focuses on the transport of molecules through the environment once it is emitted from a point source, it does not address the chemical potential or fundamental energy associated with the emission itself. Chemical potential is used here to define the emission energy for an individual molecule from a single person as an objective metric for comparing contaminants efflux across geographic regions.

Chemical potential is derived from per capita biophysical viscosity and the flow rate of an individual molecule through an environmental system (eq 5). Flow rates of the rivers associated with cities in Table 1 were used to calculate the per capita environmental system (eq 5). Flow rates of the rivers associated with cities in Table 1 were used to calculate the per capita environmental system (eq 5) and are summarized in Table 2.8

Calculations of the per capita chemical potentials for caffeine (eq 5) and are summarized in Table 2. The authors would like to thank FAPESP-SPRINT 2015/50458-9 (Sa Paulo Researcher in International Collaboration), George McMahan Development LLC, and the TTU Institute for Environmental and Human Health for providing funding for the initial phase of this international collaboration between researchers from the State of Sao Paulo and Texas Tech University to foster scientific and technological development.

### MATERIALS AND METHODS

Details of all geographic locations, analytical standards, reagents, sample collection methods, sampling sites, and instrumental analyses included in this study are discussed elsewhere.11,24,25 As a part of the Sao Paulo Researchers in International Collaboration, anthropogenic tracers were measured in both Texas and Brazil for evaluation of the criteria to prioritize sampling in international water quality programs. Caffeine was chosen as a representative anthropogenic tracer in all locations, as it has been shown to be a useful indicator in assessing estrogenic activity in both source and drinking water.13,15 LC–MS measurement of caffeine is used here as a proof of concept for other anthropogenic small molecules that may be used as biomarkers for modeling potential disease states in populations.

### CONCLUSIONS

It is known that there are many factors that influence molecular flow through the environment. However, a first approximation biophysical viscosity model calculates energies associated with individual contaminant emissions in populations over time on the basis of simple expressions and is non-data-intensive. These calculations demonstrate that biophysical viscosity and chemical potential can be used as parameters to directly compare energies associated with individual chemical emissions across geographic regions. This model can accommodate for changes in population, chemical concentration, speciation of metabolites, and environmental flow rates over time. It is also useful for city planning, in that there is a critical level of contaminant turnover that must be reached to determine appropriate WRRF designs for water resource management and reclamation. These thermodynamic parameters can be readily integrated with chemical lifecycle models to provide real-time epidemiologic data for application in environmental risk assessment.

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