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Two-dimensional gas chromatography/mass spectrometry, physical property modeling and automated production of component maps to assess the weathering of pollutants

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ABSTRACT

Local conditions influence how pollutants will weather in subsurface environments and sediment, and many of the processes that comprise environmental weathering are dependent upon these substances' physical and chemical properties. For example, the effects of dissolution, evaporation, and organic phase partitioning can be related to the aqueous solubility (S_W), vapor pressure (V_P), and octanol–water partition coefficient (K_{OW}), respectively. This study outlines a novel approach for estimating these physical properties from comprehensive two-dimensional gas chromatography–mass spectrometry (GC × GC/MS) retention index-based polyparameter linear free energy relationships (LFERs). Key to robust correlation between GC measurements and physical properties is the accurate and precise generation of retention indices. Our model, which employs isovolatility curves to calculate retention indices, provides improved retention measurement accuracy for families of homologous compounds and leads to better estimates of their physical properties. Results indicate that the physical property estimates produced from this approach have the same error on a logarithmic-linear scale as previous researchers' log–log estimates, yielding a markedly improved model. The model was embedded into a new software program, allowing for automated determination of these properties from a single GC × GC analysis with minimal model training and parameter input. This process produces component maps that can be used to discern the mechanism and progression of how a particular site weathers due to dissolution, organic phase partitioning, and evaporation into the surrounding environment.

1. Introduction

Fossil fuel pollution is the result of a number of factors, including naturally occurring and unintended seepages; collection, transport and storage activities; and incomplete combustion. When fossil fuels and their by-products are released into the environment, they are subject to a number of weathering factors. These weathering factors include physical (evaporation, adsorption, dissolution, and emulsification), biological (microbial degradation), and chemical (photo- and oxidative degradation) processes, all of which can significantly change the chemical composition of the substance over time. Understanding how local environments impact weathering is critical to determining whether the local ecosystem is capable of remediation, *i.e.*, the natural attenuation of pollution effects. Because site-specific weathering processes can dramatically change the chemical composition of fossil fuel mixtures, even at the isomer level [1], it is important to assess these changes as a function of each component's physical and chemical properties [2]. Once known, one can use this information to determine if natural attenuation is sufficient to reduce pollutant impact on the environment or if active remediation is required. To make this determination, the compositional effects of dissolution, organic phase partitioning, and evaporation must be known; each of which one can examine by studying the aqueous solubility (S_W), octanol–water partition coefficient (K_{OW}), and vapor pressure (V_P) of sample components, respectively [3,4].

The measurement of aqueous solubility and octanol–water partition coefficient of hydrophobic fossil fuel components such as benzene, polycyclic aromatic hydrocarbons (PAH) and sulfur heterocycles (PASH) and their substituted homologues is time-consuming, challenging, and susceptible to error [5]. For these reasons, gas chromatographic (GC) retention indices (RIs) are often used to estimate these properties [6,7]. GC provides the means to

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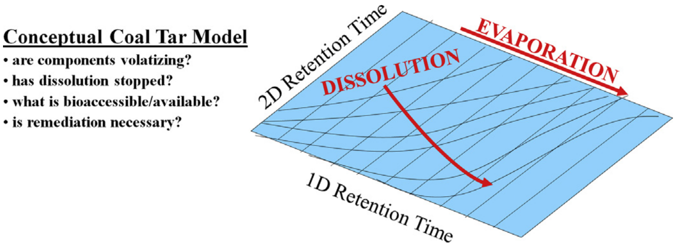

Fig. 1. Schematic representation of a component map; arrows correspond to weathering processes.

not only estimate these properties, but also to assess the extent to which natural attenuation has occurred, all without the need to identify each sample component or directly measure their properties. Both 1-dimensional GC and 2-dimensional GC × GC can be used to estimate S_W, K_{OW}, and V_P via linear or logarithmic free energy relationships (LFERs). GC × GC is often used in weathering studies because it provides a visual depiction of the differences between fresh and weathered sample chromatograms, and orthogonal column pairings provide the means to generate LFERs to estimate these properties simultaneously [4]. Arey and coworkers [8,9] derived an empirical expression for the isothermal partition coefficient (K), then used this information to estimate V_P, S_W, and the air–water and octanol–water partition coefficients from the 1st and 2nd dimension retention indices of diesel fuel. Based on the assumption that the partitioning of the solute is primarily controlled by size and polarizability, a two-component LFER, with the 1st dimension retention index (RI_{1D}) conveying information about size and the 2nd dimension polarizability, environmental researchers have used GC × GC to produce contour maps [10,11] and air and water mass transfer models [12], and estimate phase-transfer properties, phospholipid membrane–water partition coefficients and corresponding narcosis toxicity [13].

This line of research is not without its challenges – for example, the calculation of meaningful 2nd dimension retention indices, since either the 2nd dimension hold-up time ($t_{M,2D}$) or the retention of bracketing compounds at different temperatures across the separation space is required. Researchers have examined column bleed [14] and employed continuous injections of an unretained compound [15] to assess $t_{M,2D}$, and created “hypothetical” bracketing compounds [8,9] and isovolatility curves [16]. Isovolatility curves, the result of continuous solute elution over a prolonged period, can provide the means to obtain retention information at different elution temperatures by creating curved elution lines that cut across the 2nd dimension separation space. Unlike time-of-flight (TOF) mass filters, only recently have quadrupole mass spectrometers provided the scan speeds sufficient for invariant spectra across narrow 2nd dimension peaks and, in turn, accurate quantitative analysis of components of complex mixtures, such as PAH, PASH and their alkylated homologs in coal tar and crude oil [17].

Fig. 1 shows a weathering map that can be used to inform remedial decisions and to delineate site-specific weathering processes [10]. The axes correspond to volatility and solubility and provide important sample information. For example, sites that contain a large number of volatile and highly soluble compounds will continue to pose risk to the environment, as opposed to highly weathered sites in which only non-volatile and insoluble components remain. If these compounds are also biologically inaccessible, the pollution no longer poses risk to the environment. This is especially important since local weathering conditions, even at the same site, may attenuate pollution differently.

In this study, we report for the first time the use of isovolatility curves to generate retention indices in both GC × GC dimensions at every point in 2D space. In contrast with other studies that employed alkane standards to estimate the properties of aromatic targets, RIs are calculated and physical properties are estimated using 2-, 3-, 4-, and 5-ring PAH as bracketing compounds. Since PAH are mutagenic [18], carcinogenic [19], and persistent [20] organic pollutants, they serve as important model compounds for this study. We and others have shown that when target analytes, in this case alkylated PAH and PASH, are bracketed by structurally similar compounds, accurate measurement of their separation is obtained under linear temperature-programmed conditions [21–24]. This, in turn, leads to more robust linear free energy relationships and more accurate physical property estimates. This property estimation process has been encoded in a new software program, allowing for automated determination of physical properties from one analysis, with minimal model training and parameter input. Since coal tar is predominantly aromatic [25], it serves as an ideal model mixture to test this hypothesis, especially considering our experience with analysis of C_1- to C_4-alkylated PAH and PASH homologues [17,26–30].

2. Experimental

2.1. Standards and reagents

Airgas (Salem, NH, USA) supplied the ultra-high purity helium and nitrogen used in this study. Chromatography-grade toluene and dichloromethane were purchased from Sigma–Aldrich (St. Louis, MO, USA). The 16 EPA priority pollutant PAH, dibenzothiophene, and internal standards 1,4-dichlorobenzene-d_4, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} were obtained from Restek (Bellefonte, PA, USA). Supelco (Bellefonte, PA, USA) supplied the base/neutral surrogate spike mix (2-fluorobiphenyl, nitrobenzene-d_5, *p*-terphenyl-d_{14}) as well as a number of neat standards: anthracene, benzo(*b*)thiophene, fluorene, fluoranthene, hexylbenzene, pyrene, 1-phenyloctane, 1-methylnaphthalene, 2-methylnaphthalene, and 1,7-dimethylnaphthalene. Also purchased were neat standards of *n*-decylbenzene and 2,6-dimethylnaphthalene from Ultra Scientific (North Kingstown, RI, USA) and Crescent Chemical (Islandia, NY, USA), respectively.

2.2. Samples and sample preparation procedure

Pure coal tar and impacted soils were obtained from a utility in Illinois. We modified EPA method 3550C [30–32]: 15 g of sample was spiked with surrogate mix and sonicated for 10 min in 8 mL of 50% (v/v) toluene/dichloromethane (Branson Ultrasonics, Danbury, CT), and the procedure was repeated eight times to obtain maximum extraction efficiency. Activated copper and anhydrous sodium sulfate were used to eliminate elemental sulfur and water from the extracts, which were concentrated under a stream of nitrogen prior to the addition of 10 μg/mL of internal standards.

2.3. Instrumentation

GC × GC/MS analyses were performed using an Agilent Technologies (Santa Clara, CA, USA) 6890/5975C GC/MS with Gerstel (Mülheim an der Ruhr, Germany) MPS2 autosampler and CIS6 injector. Since most sample components in coal tar are aromatic members of homologous families, instrumental conditions were chosen to maximize utilization of 2D separation space and to increase data granularity. Following the example of Arey and coworkers [8,9], two different GC × GC/MS methods were employed to evaluate if the accuracy of physical property estimates was method-dependent. These included differences in column manufacturer and size, split ratio, temperature program, flow rate, and modulation time; instrumental parameters for both