Assessing methods to estimate emissions of non-methane organic compounds from landfills

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ABSTRACT

The non-methane organic compound (NMOC) emission rate is used to assess compliance with landfill gas emission regulations by the United States Environmental Protection Agency (USEPA). A recent USEPA Report (EPA/600/R-11/033) employed a ratio method to estimate speciated NMOC emissions (i.e., individual NMOC emissions): speciated NMOC emissions = measured methane (CH4) emission multiplied by the ratio of individual NMOCs concentration relative to CH4 concentration (CNMOC/CCH4) in the landfill header gas. The objectives of this study were to (1) evaluate the efficacy of the ratio method in estimating speciated NMOC flux from landfills; (2) determine for what types of landfills the ratio method may be in error and why, using recent field data to quantify the spatial variation of (CNMOC/CCH4) in landfills; and (3) formulate alternative models for estimating NMOC emissions from landfills for cases in which the ratio method results in biased estimates. This study focuses on emissions through landfill covers measured with flux chambers and evaluates the utility of the ratio method for estimating NMOC emission through this pathway. Evaluation of the ratio method was performed using CH4 and speciated NMOC concentration and flux data from 2012/2013 field sampling of four landfills, an unpublished landfill study, and literature data from three landfills. The ratio method worked well for landfills with thin covers (<40 cm), predicting composite NMOC flux (as hexane-C) to within a factor of 10 for 13 out of 15 measurements. However, for thick covers (>40 cm) the ratio method overestimated NMOC emissions by >10 for 8 out of 10 measurements. Alternative models were explored incorporating other chemical properties into the ratio method. A molecular weight squared (MW)2-modified ratio equation was shown to best address the tendency of the current ratio method to overestimate NMOC fluxes for thick covers. While these analyses were only performed using NMOC fluxes through landfill covers measured with flux chambers, results indicate the current USEPA approach for estimating NMOC emissions may overestimate speciated NMOC emission >10 for many compounds.

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1. Introduction

With 54–69% of municipal solid waste (MSW) discarded in landfills in 2008, landfill disposal remains a major waste management option in the United States (USEPA, 2010; van Haaren et al., 2010). The decomposition of MSW organics in landfills produces landfill gas (LFG) that contains methane (55–60 vol%), carbon dioxide (40–45 vol%), and traces of non-methane organic compounds (NMOCs) at pptv to ppmv levels including alkanes, alkenes, aromatics, chlorinated ethylenes, chlorinated methanes, halocarbons, alcohols, ketones, terpenes, chlorofluoro compounds (CFCs), and siloxanes (Staley et al., 2006; Brosseau and Heitz, 1994). Gas control at MSW landfills is regulated in the United States under the Clean Air Act (section 111) New Source Performance Standards (NSPS)/Emission Guidelines (EG) (40 CFR part 60) (USEPA, 1996). Landfills with design capacity of >2.5 million Mg (or million cubic
emission rate (i.e., tracer dilution method) is the measured CH4 concentration in the LFG within landfills; and (3) formulate alternative models for estimating NMOC emissions from landfills for cases in which the ratio method results in biased estimates. Ideally, these objectives could be met by examining whole-landfill NMOC emissions, e.g., through an integrative method like the tracer dilution method (Czepiel et al., 1996). Because NMOC emission rate measurements were only available through landfill covers with flux chamber measurements, these more limited data were used in this assessment.

2. Evaluation approach

The ratio method of estimating NMOC flux (Eq. (2)) assumes that the concentrations of individual NMOCs relative to CH4 in the header gas are representative of their concentrations in LFG that escapes into the atmosphere. To quantify spatial variation of NMOCs/CH4 concentration ratios (CNMOC/CMCH4) in landfills, LFG samples for CH4 and NMOC analyses were collected in 2012–2013 from four landfills (Southeastern-US; Midwestern-US 1; Midwestern-US 2; Yolo County, CA) at various locations (header gas, vent pipe, above ground at landfill surface near active landfill face, and in gas-filled landfill pores away from gas collection wells). A description of these landfill sites including landfill cover types and thickness, sampling dates, and environmental conditions during sampling is provided in Table 1.

Pore gases in these landfills were collected using stainless steel or Teflon tubing that were installed using geopores at desired depths (0.3–2.4 m). Tubing was purged and gas samples of 25–50 mL for major gases (CH4, CO2, O2, and N2) were withdrawn with a syringe and stored in pre-evacuated glass serum bottles. All major gases were analyzed at Florida State University. Gas samples with CH4 and CO2 concentrations below 1% v/v were determined on a Shimadzu 14A gas chromatograph with a flame ionization detector and a methanizer, a 1 mL sampling loop, and a 2-m 0.32 cm diameter stainless steel column packed with Carbosphere. Methane and CO2 concentrations above 1% v/v, N2, and O2+Ar were determined on a Shimadzu 8A gas chromatograph with a thermal conductivity detector. For speciated NMOCs, gas samples were collected in 2 L stainless steel canisters and analyzed by the Blake–Rowland Laboratory at the University of California–Irvine, the same laboratory used for NMOC analyses in Scheutz et al. (2003, 2008) data sets. NMOC analyses were conducted using two separate high resolution analysis systems consisting of multi-column/detector GC (gas chromatography) and combined GC/MS (mass spectrometry). Measured concentrations of individual NMOCs and methane were used to determine speciated CNMOC/CMCH4 ratios.

In addition to the field sampling data, CH4 and speciated NMOC flux data from three published papers (Scheutz et al., 2003; Barlaz et al., 2004; Scheutz et al., 2008) and an unpublished 2005 study at Leon County landfill, FL (Chanton, 2013) were reviewed and processed. These data sets have a total of 37 landfill surface locations (i.e., 37 separate measurement points on landfill surfaces) wherein emission rates of 35–53 speciated NMOCs and CH4 were measured using static flux chambers. As shown in Table 2, the data were collected from point locations of different landfill cover systems (i.e., soil types, biocover, cover thickness), under prevailing environ-
mental conditions (ambient temperature, soil moisture content), and CH4 flux range (hotspot, lowspot). Additional data on concentrations of CH4 and speciated NMOCs at the landfill surface, within the soil profile, and in header gas or vent pipes that were measured in these studies but not provided in the previous publications were obtained from the corresponding authors. The measured CH4 and speciated NMOCs concentrations at the landfill surfaces were determined using the first gas sample collected in flux chamber measurements made at each site. While atmospheric pressure data were collected during some of these studies, e.g., Barlaz et al. (2004), knowledge of both atmospheric pressure and internal landfill gas pressure immediately beneath the landfill cover is necessary to estimate the driving force for advective gas transport through landfill covers (Jung et al., 2011). Unfortunately, these data were unavailable.

A spreadsheet database containing 71 reported NMOCs from these four data sets was developed. Various chemical properties (molecular structure, molecular weight (MW), molar volume,
Henry Law's constant \((k_H)\), aqueous solubility \((S_w)\), log octanol–water partition coefficient \((\log K_{ow})\), vapor pressure \((VP)\) and probability of biodegradability were collected from existing chemical databases (NIST Chemistry WebBook and USEPA’s Estimation Program Interface (EPI) Suite TM v. 4.1) and incorporated into the NMOC database developed for this project. The NMOC data sets were also categorized into various chemical groups including alkanes, alkenes, aromatics, chlorinated ethylenes, chlorinated methanes, halocarbons, polar nitrates, and bromides.

### 3. Results and discussion

#### 3.1. LFG concentrations from field sampling in 2012/2013

There were 79–81 NMOCs detected in landfill gas samples obtained from Southeastern-US, Midwestern-US 1, Midwestern-US 2, and Yolo County, CA landfills. Overall, 23 of 79–81 detected NMOCs had measured concentrations that were 1–3 orders of magnitude lower than the AP-42 (Compilation of Air Pollutant Emission Factors) uncontrolled default concentrations for estimating emissions from landfills when site-specific data are not available [Tables S1–S4 of the supporting information (SI)].

##### 3.1.1. Vertical variability in LFG concentrations

The concentration ratios of speciated NMOCs listed in AP-42 to \(\text{CH}_4\) are shown in Figs. 1 and 2A for Southeastern-US, Midwestern-US 1, and Yolo County landfills. \(C_{\text{NMOC}}/\text{CH}_4\) ratios vary vertically with higher ratios in gas samples obtained at shallower depths relative to deeper depths. Compare, for example, landfill surface data with samples at 0.3 m depth in Fig. 1, and geoprobe samples at 0.3 and 1.5 m depths in Fig. 2A. Similar vertical variations are observed in concentration ratios of speciated non-AP-42 NMOCs to \(\text{CH}_4\) at Southeastern-US (Fig. S1): higher \(C_{\text{NMOC}}/\text{CH}_4\) ratios are generally observed on the landfill surface versus samples with depth. In these samples the significantly higher \(\text{CH}_4\) concentrations at deeper depths reduced the concentration ratios of speciated NMOCs to \(\text{CH}_4\) below the landfill surface (>0.30 m depths). As gas neared the surface, some methane biodegradation occurred, resulting in higher ratios.

The gas data from Midwestern-US 2 landfill, however, do not show differences in the \(C_{\text{NMOC}}/\text{CH}_4\) ratios between measurements at the landfill surface and 0.55 and 2.4 m depths (Fig. 2B). Here, ratios of \(C_{\text{NMOC}}/\text{CH}_4\) are independent of sampling depth. One plausible explanation is the presence of considerable moisture in pores, which affects transport and reaction processes through this soil cover. The soil cover was wet during testing with some portions fully water saturated due to heavy rainfall prior to field sampling (Fig. S2). Excess moisture favors preferential gas flow, reduces oxygen availability and therefore aerobic biodegradation, and may slow rates of biodegradation because of the longer diffusional path from gas to microbes in water-logged soil. These are likely factors that diminished chemical and biological reactions in this soil cover, which then resulted in \(C_{\text{NMOC}}/\text{CH}_4\) ratios that remained unchanged with depth at this landfill.

##### 3.1.2. Horizontal variability in LFG concentrations

By using header gas data, the ratio method (Eq. (2)) assumes that \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the header gas represent analogous gas concentration ratios in surrounding wastes. At the Yolo County landfill, the \(C_{\text{NMOC}}/\text{CH}_4\) ratios in LFG samples taken from three geoprobe locations at 1.5 m depth (MW 1, MW 7, and MW 8, Fig. 3) and an adjacent extraction gas well are within a factor of 10 (Fig. 4A). For the probes closest to the well, using paired t-tests 58% and 53% of AP-42 speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in MW 1–1.5 m and MW 7–1.5 m, respectively, are statistically similar \((p < 0.05)\) to the speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the adjacent gas well.

Meanwhile, 95% of AP-42 speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in MW 8–1.5 m are statistically similar \((p < 0.05)\) to the speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the adjacent gas well. The speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in each probe that are significantly different from the speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios of the gas well at 95% confidence level are not systematically higher or lower than that of the gas well. Similarly, pore gas samples from three geopros at 1.5 m depth in Midwestern-US 2 landfill have comparable \(C_{\text{NMOC}}/\text{CH}_4\) ratios with samples from gas well and gas header (Fig. 4B): 86% of speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the geoproses are statistically similar \((p < 0.05)\) to the speciated \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the gas well, and there is no systematic bias between the \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the geoproses and the gas well. At least from these sites, Fig. 4 shows that off-gassing of some NMOCs due to vapor/vacuum interactions in the gas extraction process do not result in considerably higher NMOC concentrations in the gas well than in landfill pore gas surrounding the well. Therefore, header gas concentrations might reasonably represent \(C_{\text{NMOC}}/\text{CH}_4\) ratios in the surrounding waste at these two landfills. However, header gas concentrations may be significantly different from gas concentrations in cover soil, at the landfill surface, and downwind of the landfill, since \(C_{\text{NMOC}}/\text{CH}_4\) ratios vary significantly with depth from landfill surface to bottom of landfill cover (Figs. 1 and 2). The higher \(C_{\text{NMOC}}/\text{CH}_4\) ratios near landfill surfaces observed in field sampling in 2012/2013 are consistent with similar elevated \(C_{\text{NMOC}}/\text{CH}_4\) ratios observed in landfill surface data from the literature data sets, which is discussed below.
3.2. NMOC fluxes and concentrations from literature

3.2.1. Measured versus predicted speciated NMOC fluxes

Results using the ratio method to predict NMOC fluxes are summarized in Table 3 using data from four landfill sites studied in previous investigations (Scheutz et al., 2003, 2008; Barlaz et al., 2004; Chanton, 2013). The NMOC data sets are sorted according to type of landfill cover system, soil cover or biocover, thickness of the cover layer, and CH4 flux, positive or negative measured flux. Under these categories, the ratio method estimates are assessed by the percent of measured speciated NMOC data that are either overestimated or underestimated by $P_{10}/C_2$ or within a factor of $P_{10}/C_2$.

As noted in Table 2, soil covers may contain 1–2 layer of soils (e.g., sand, loam, clay, clay liner or vegetative soil) over a waste layer, while biocovers have 2–3 layers of media cover (i.e., mulch or compost layer + soil layer and possibly a highly permeable layer such as shredded tire chips) over refuse.

The ratio method does not work well for landfill covers $P_{40}$ cm with positive CH4 fluxes. For soil covers with thickness $P_{40}$–$P_{120}$ cm and CH4 flux $P_{0.3}$–$P_{49.9}$ g m$^{-2}$ d$^{-1}$ (grams per square meter per day), 49–78% of speciated NMOC flux data are overestimated by a factor $P_{10}$ or within a factor of $P_{10}$. As noted in Table 2, soil covers may contain 1–2 layer of soils (e.g., sand, loam, clay, clay liner or vegetative soil) over a waste layer, while biocovers have 2–3 layers of media cover (i.e., mulch or compost layer + soil layer and possibly a highly permeable layer such as shredded tire chips) over refuse.

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with CH₄, other NMOCs including perchloroethylene, chlorofluorocarbon (CFC) 11 and CFC 12 do not degrade under oxic conditions and so their fate and transport is not directly influenced by CH₄ oxidation in landfill covers (Kromman et al., 1998; Scheutz et al., 2004). Thus, when sufficient CH₄ oxidation occurs such that CH₄ emission rate is negative or zero, NMOC emission rate estimates are often underestimated ≥ 10⁻χ.

3.2.2. Measured versus predicted composite NMOC fluxes

USEPA operational standards described in 40 CFR 60.753 (USEPA, 1996) require estimation of composite NMOC flux using Eq. (1), where C_NMOC is expressed as an equivalent hexane concentration. Following USEPA guidance in 40 CFR 60.755 (USEPA, 1996), composite NMOC fluxes were computed from the field data, first expressing C_NMOC in g carbon for each species, summing over all species, and then dividing by six to estimate C_NMOC as hexane-C. Fig. 5 illustrates the effect of landfill cover type and thickness in predicted composite NMOC flux using the ratio method for landfill surfaces with positive CH₄ emission rates. In this figure, only positive speciated measured NMOC fluxes are used. In terms of composite NMOC flux, for thick soil or biocovers (> 40 cm) with positive CH₄ flux, 82% of ratio method estimates exceed measured NMOC flux ≥ 10⁻χ. Note that one data point for thick biocovers does not appear in Fig. 5 because the measured NMOC flux is practically zero (i.e. speciated NMOC fluxes have zero or negative values) but its predicted NMOC flux is 4.8 × 10⁻⁶ g m⁻² d⁻¹ hexane-C. For thin covers (< 40 cm, soil or biocover), though, predicted composite NMOC fluxes using the ratio method are in reasonable agreement with measured fluxes, with 87% of predictions within 10⁻χ of measurements.

3.2.3. Spatial variation in NMOCs/methane concentration ratios

The ratio method of estimating NMOC flux (Eq. (2)) assumes that the concentrations of individual NMOCs relative to CH₄ in the gas well (or vent pipe) are representative of their concentrations in LFG that escapes into the atmosphere. In thick cover data sets where the ratio method overestimated the measured individual NMOC flux at the landfill surface (Table 3 and Fig. S2), speciated C_NMOC/CH₄ ratios at the landfill surfaces were initially postulated to be lower than speciated C_NMOC/CH₄ ratios in the gas well (or vent pipe) – which would explain the overestimation of NMOC fluxes from the landfill surface. However, measured C_NMOC/CH₄ ratios at the landfill surfaces are generally higher than those of the gas well in the literature data sets analyzed here, which is consistent with data from 2012/2013 field campaigns discussed earlier. This is illustrated with data from soil covers for Lapouyade (Scheutz et al., 2003), Grand'Landes (Scheutz et al., 2008), and Leon County (Chanton, 2013) landfills (Fig. 54): select data from Grand'Landes and Leon County landfills are also shown in Fig. 6. For these data, 58–96% of NMOCs have higher C_NMOC/CH₄ ratios at landfill surface than in gas well (or vent pipe) in both thick (Scheutz et al., 2008) and thin (Chanton, 2013) soil covers. Thick soil covers tend to have more NMOCs (27–73%) that have concentration ratios ≥ 10⁻χ higher at the landfill surface compared to thin covers (17–29%) (Fig. 54).

The generally higher C_NMOC/CH₄ ratios at the landfill surfaces can be attributed to the 23–48% CH₄ oxidation (mean range of four data sets, Table 2) measured at these sites. This may have caused the 5–6 order of magnitude difference in CH₄ concentration reduction relative to NMOC concentration change between header gas and landfill surface measurements.

For biocovers the results are mixed (Fig. S5): landfill surface concentrations from Leon County landfill 30-cm thick biocovers (Chanton, 2013) have 44–75% C_NMOC/CH₄ ratios within 10⁻χ of vent pipe measurements, but 90–100% of the Outer Loop landfill data from 130-cm thick biocovers (Barlaz et al., 2004) have C_NMOC/CH₄
C\textsubscript{CH\textsubscript{4}} ratios that are \(>10\times\) lower compared to \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios in the gas well. For the Outer Loop landfill study, the lower \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios at the landfill surface compared to that of the header gas may be due to significant degradation of NMOCs in this data set, CH\textsubscript{4} generation within the biocover, and/or sub-optimal CH\textsubscript{4} oxidation. The tested biocover locations at Outer Loop landfill were found to have poor drainage and this most likely reduced CH\textsubscript{4} oxidation in biocovers (Barlaz et al., 2004). Furthermore, Barlaz et al. (2004) noted isotopic evidence that emitted CH\textsubscript{4} was generated from degrading organic matter from the biocover and not from landfilled wastes. The anaerobic decomposition in the biocovers could have contributed to the CH\textsubscript{4} concentration in the landfill surface air resulting in lower \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios than in gas well samples.

Plots depicting changes in gas concentrations and \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios of selected speciated NMOCs with soil depth for the data sets reviewed are provided in the SI (Figs. S6–S14). In general, when NMOCs like BTEXs biodegrade along with CH\textsubscript{4} in landfill covers, the \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios for these compounds did not change significantly in the soil profile. Some NMOCs including chlorinated ethylenes (e.g., tetrachloroethylene, trichloroethylene) and chlorinated methanes (e.g., chloroform, carbon tetrachloride, halo-carbons) are not degraded as much as CH\textsubscript{4} in landfill covers so their speciated \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios tend to increase near the landfill surface (0–20 cm).

### 3.3. Effect of cover thickness

Analysis of the literature data presented above indicates that the ratio method works reasonably well predicting NMOC emissions for landfills with thin soil or biocovers (<40 cm), but results in overestimation of NMOC emissions for thick covers (>40 cm) (Table 3 and Fig. 5). The only situations where this is not true are if the CH\textsubscript{4} flux is negative or near zero.

Cover thickness plays an important role in transport and reactions especially when gas diffusion is the dominant transport mechanism in the landfill cover system. The reason is that gas concentration gradients (\(\frac{\partial C}{\partial z}\)) that drive diffusion are a function of cover thickness. For example, if we assume fixed \(C_{\text{CH\textsubscript{4}}\text{atm}}\), at the atmosphere (top) and landfill (bottom) boundaries of the cover, then

\[
\frac{\Delta C_{\text{CH\textsubscript{4}}}}{\text{thickness}} \propto \frac{1}{\text{cover thickness}}
\]

Thus, thicker covers result in smaller concentration gradients and smaller diffusive fluxes, \(J_{\text{CH\textsubscript{4}}} \propto \frac{\Delta C_{\text{CH\textsubscript{4}}}}{\text{thickness}}\). Since residence time in a landfill cover \(\propto \frac{\text{thickness}}{J_{\text{CH\textsubscript{4}}}}\), residence time in the landfill cover \(\propto (\text{cover thickness})^2\). Thus, thicker covers result in longer residence times, allowing more time for biological and chemical reactions. A similar analysis conducted for advective transport would yield a similar result – if gas pressure boundary conditions on thick and thin covers were similar. Unfortunately, this assumption could not be tested, since gas pressure data at the bottom of landfill covers were not available from the field and literature studies.

The ratio method may not work in landfills with thick covers because there is sufficient time for additional reactions to modify concentrations and fluxes of CH\textsubscript{4} and NMOCs. Supporting data for this hypothesis come from \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios. The ratios of NMOCs to CH\textsubscript{4} concentrations are plotted in Figs. 6 and S4 for thick and thin soil covers, and in Fig. S5 for thick and thin biocovers. When soil covers are thick (>40 cm), \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios are systematically larger at the top of the soil than in the nearby gas well or vent pipes. These thick covers provided sufficient residence time for biological and chemical reactions to alter concentrations. However, for thin soil covers (<40 cm), the bias disappears, and concentration ratios at the top of the soil are generally within a factor of 10 of nearby gas well or vent pipes. The situation is more complex with biocovers, though. For thin biocovers (<40 cm), just as with soil covers concentration ratios at the top of the biocover are generally within a factor of 10 of nearby well or vent pipes. However, for thick covers (>40 cm) \(C_{\text{NMOCs}}/C_{\text{CH\textsubscript{4}}}\) ratios are often smaller than concentrations in nearby well or vent pipes by greater than a factor of 10. Here, the additional residence time in these biocovers may have allowed CH\textsubscript{4} generation from degrading organic matter, or NMOC degradation.

In light of analyses of the literature data, it is worth considering the field data collected in 2012/2013. Three of the four field sites

### Table 3

| LF Cover Systems | Landfill Site\textsuperscript{a} | No. of Locations Tested\textsuperscript{b} | CH\textsubscript{4} flux (g m\textsuperscript{-2} d\textsuperscript{-1}) | No. of NMOCs Detected | % of NMOC Data with <(-) or 0 flux | % NMOC Flux Data |
|------------------|--------------------------------|--------------------------------|----------------------|------------------------|--------------------------------|-----------------|
| **Soil** | | | | | | |
| 100-120 clay soil or clay/foam + sand | GL, LP | 5 | 3.2E-1 to 29.0 | 13 | 35-45 | 24-88 | 47 | 78 ± 6\textsuperscript{c} | 20 ± 5 | 2 ± 3 |
| 100-120 clay soil or clay/foam + sand | GL, LP | 2 | 8.4E-3 to 1.0E-4 | 4.3E-3 | 35-45 | 60-69 | 64 | 30 ± 42 | 34 ± 48 | 36 ± 6 |
| 100-120 clay soil or clay/foam + sand | GL, LP | 6 | -9.5E-4 to 0 | -3.0E-2 | 35-45 | 27-85 | 50 | 0 | 50 ± 28 | 50 ± 28 |
| 40 coarse sand | LP | 1 | 49.9 | 35 | 0 | 26 | 49 | 51 | 0 |
| 15 clay soil | LC | 8 | 1.9 to 165.9 | 57.0 | 53 | 4-15 | 9 | 20 ± 5 | 70 ± 4 | 11 ± 6 |
| **Biocovers** | | | | | | |
| 130 100 cm compost + 15 cm tire chips + 15 cm clay soil | OL | 3 | 2.0E-2 to 9.2 | 5.9 | 40 | 98-100 | 98 | 98 ± 1 | 2 ± 1 | 0 |
| 130 100 cm compost + 15 cm tire chips + 15 cm clay soil | OL | 4 | -8.0E-2 to -1.4E-1 | -1.2E-1 | 40 | 20-98 | 74 | 0 | 74 ± 36 | 26 ± 36 |
| 30 15 cm mulch + 15 cm clay soil | LC | 7 | 2.2E-2 to 5.6 | 2.0 | 52-53 | 19-38 | 26 | 30 ± 9 | 37 ± 22 | 33 ± 20 |
| 30 15 cm mulch + 15 cm clay soil | LC | 1 | -2.5E-1 | 53 | 36 | 0 | 36 | 64 |

\textsuperscript{a}GL (Grand'Landes Landfill, France); LP (Lapouyade Landfill, France), OL (Outer Loop Landfill, KY, USA), LC (Leon County Landfill, FL, USA).

\textsuperscript{b}Static chamber tests for both CH\textsubscript{4} and NMOCs fluxes;

\textsuperscript{c}Values represent one standard deviation.
sampled had intermediate soil covers <40 cm (see Table 1). Thus, we expect \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios to remain unchanged with sampling depth for Southeastern-US, Midwestern-US 1, and Midwestern-US 2 landfills. However, this was clearly not the case for Southeastern-US and Midwestern-US 1 landfills, as shown in Fig. 1. Here, \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios were higher at the soil cover surface than for samples with depth, which is consistent with behavior observed for thick landfill cover soils in the literature. In the very wet soil for Midwestern-US 2 landfill, though, \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios were not significantly altered with depth (Fig. 2B), consistent with the analysis of literature data for thin covers. Yolo County landfill was the single field site with a thick landfill soil cover (50–60 cm), and here \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios increased at shallower depths (Fig. 2A), consistent with literature data for thick covers. The 2012/2013 field data suggest that while significant chemical and biological reactions may be expected to alter \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios for thick covers, for thin covers results may vary and may be associated with other site-specific conditions. Thus, while the ratio methodology provided reasonable predictions of NMOC fluxes for the Leon County landfill with a thin soil cover, the same result may not be expected at other sites with similar thin landfill covers.

Finally, while the systematically higher speciated \( C_{\text{NMOC}}/C_{\text{CH}_4} \) ratios at the landfill surface than in the nearby gas well or vent pipe in thick covers could be plausibly attributed to ample residence time for additional reaction processes, the observed lower speciated NMOC flux relative to \( \text{CH}_4 \) flux (\( Q_{\text{NMOC}}/Q_{\text{CH}_4} \)), hence overestimation of the NMOC flux by the ratio method, is not expected. This paradoxical observation is a phenomenon requiring further investigation.

3.4. Modifications to ratio method

Several modifications of the ratio method (Eq. (2)) using formulations that scale emissions with other chemical properties were used to explore more appropriate models to estimate NMOC emission rates from landfills with thick covers. The data set from the Grand’Landes landfill study (Scheutz et al., 2008) was selected for model exploration because it had the largest number of low and high \( \text{CH}_4 \) emission data collected for the same sampling period and landfill cover type (Table 2). Table 4 summarizes the performance of each model using mean data set values, i.e., average speciated NMOCs and \( \text{CH}_4 \) fluxes for low and high \( \text{CH}_4 \) emission locations.

Fig. 7A shows that NMOC flux estimates using Eq. (2) (Table 4, model 1) are higher than measured fluxes of most NMOCs (60%) by \( >10 \times \). Note that since Fig. 7A is on a log scale, only positive measured speciated NMOC fluxes are shown; hence, plotted data points are fewer than 35–53 detected NMOCs (Table 3). The ratio method was first modified by incorporating Henry’s Law constant, \( k_H \) (Table 4, model 3) since this parameter describes the air–water partitioning of organic compounds. NMOCs with higher \( k_H \) (more
volatile) will likely be more equally present in the landfill gas than in the leachate or aqueous solution, and thus, will most likely contribute to overall NMOC emissions. By replacing the MW ratio with Henry’s Law constant ratio (\(k_{HNOC}/k_{Hmethane}\)), the \(k_H\)-modified Eq. (2) (Table 4, model 3a) resulted in NMOC flux estimates closer to the measured NMOC fluxes – only 16% of estimates are \(>10\times\) (Fig. S15A). Emission rates of NMOCs that have low \(k_H\) (<10\(^{-4}\)) such as ethyl nitrate (polar nitrates) are well underestimated by model 3a, though (Fig. S15A). Flux estimates for chlorinated methanes (such as tetrachloromethane (TeCM) and trichloromethane (TCM)), though relatively volatile (\(k_H = 10^{-2} – 10^{-3}\)), are also underestimated by \(>10\times\) using model 3a. Perhaps the potential for dipolar interactions by chlorinated methanes due to having electronegative Cl atoms complicates their fate and transport behavior (Schwarzenbach et al., 2003).

Aqueous solubility (\(S_a\)) is the maximum amount of a chemical that will dissolve in pure water at a specified temperature. Factors affecting the solubility of chemicals in water include the solute’s polarity and molecular size, ionic strength (presence of salts), temperature and pressure. Chemicals that have the potential to donate and/or accept electrons typically have molecular structures with O—H, —NH\(_2\), —COC, C=O, or —COOH and are classified as polar compounds. These compounds will favorably dissolve in polar solvents such as water. Larger molecules generally do not dissolve well in water compared to smaller molecules because of the higher energy requirement to create cavities between water molecules (Schwarzenbach et al., 2003). NMOCs with higher \(S_a\) will likely be more present in the landfill leachate or aqueous solution than in landfill gas. 60% of the NMOC flux estimates using the \(S_a\)-modified Eq. (2) (Table 4, model 5c) are within a factor of \(10\times\) of measured NMOC fluxes. Like the \(k_H\)-modified Eq. (2) (model 3a), \(S_a\)-modified Eq. (2) (model 5c) underestimates TeCM and TCM fluxes. The alkanes that are overestimated by 2–3 orders of magnitude are the C7–C10 hydrocarbons using experimental \(S_a\) values (EPI Suite TM v. 4.1) (Fig. S15B).

Other considered model parameters include log octanol–water partition coefficient (\(\log K_{ow}\)) and vapor pressure (VP). \(\log K_{ow}\) is linearly correlated with partition coefficient describing sorption to sorbent organic matter (OM) (Schwarzenbach and Westall, 1981). NMOCs that are more hydrophobic tend to have higher \(\log K_{ow}\) and will likely sorb to sorbent OM. The association of hydrophobic NMOCs with sorbent OM retards their transport in landfills and reduces their availability for biological and chemical degradation (Saquing et al., 2012; Sanin et al., 2000; Reinhart et al., 1991). Vapor pressure is indicative of the intermolecular attractions in chemical substances. It is dependent on the molecular size (i.e., larger molecules have lower VP) and molecular structure (i.e., specific ability to undergo van der Waals and polar

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### Table 4

NMOC emission rates estimation models.

| Model | Model equation | Bias \(\%\) | RMSE \(\%\) | Data overestimated by \(>10\times\) | Data underestimated by \(>10\times\) | Data within \(10\times\) |
|-------|----------------|-------------|-------------|-------------------------------|---------------------------------|-----------------|
| 1     | Ratio Eqtn     | Q_{NMOC} = C_{NMOC} \cdot (C_{CH4} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) | 1.7E–4 | 3.9E–4 | 60 | 7 | 33 |
| 2     | Ratio Eqtn with Conc ratio only \(k_H\)/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | 2.5E–5 | 6.0E–5 | 29 | 16 | 56 |
| 3a    | Ratio Eqtn \(* k_H\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | 2.6E–5 | 8.9E–5 | 16 | 22 | 62 |
| 3b    | Ratio Eqtn \(* k_H\) ratio/MW ratio | Exclude NMOCs with very low \(k_H\) (<10\(^{-4}\)) | 3.0E–5 | 9.4E–5 | 18 | 13 | 70 |
| 4a    | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | 7.6E–5 | 1.7E–4 | 42 | 13 | 45 |
| 4b    | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Exclude NMOCs with very low \(\log K_{ow}\) (<10) | –3.0E–6 | 1.2E–5 | 9 | 56 | 36 |
| 5b    | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | 6.5E–3 | 3.7E–2 | 27 | 16 | 58 |
| 5c    | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | 7.5E–4 | 4.2E–3 | 13 | 27 | 60 |
| 6     | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | –5.4E–6 | 1.1E–5 | 2 | 76 | 22 |
| 7     | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Q_{NMOC} = C_{NMOC} \cdot ((C_{NMOC} \cdot \text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4})) | –5.8E–6 | 1.2E–5 | 2 | 84 | 13 |
| 7a    | Ratio Eqtn \(* \log K_{ow}\) ratio/MW ratio | Exclude polar NMOCs | 7.7E–7 | 1.2E–5 | 13 | 16 | 71 |
| 8     | Two-parameter regression | Q_{NMOC} = 0.03(C_{NMOC}/C_{CH4}) + 1.57(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.5E–6 | 1.6E–7 | 1.0E–5 | 39 | 0 | 61 |
| 9     | Three-parameter regression | Q_{NMOC} = 0.03(C_{NMOC}/C_{CH4}) – 1.65(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.0E–7(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.4E–6 | 2.6E–7 | 1.0E–5 | 37 | 2 | 61 |
| 10    | Four-parameter regression | Q_{NMOC} = 0.03(C_{NMOC}/C_{CH4}) – 1.7E–7(\text{MW}_{NMOC}/\text{MW}_{CH4}) + 8.4E–8(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 5.5E–10 / (\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.5E–6 | 2.2E–7 | 1.0E–5 | 35 | 3 | 63 |
| 11    | Five-parameter regression | Q_{NMOC} = 0.03(C_{NMOC}/C_{CH4}) – 1.4E–7(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.6E–7(\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 7.5E–10 / (\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 1.95E–7(\log K_{ow}\)/\text{log}_{K_{ow}} \cdot 1.7E–6 | 2.4E–7 | 1.0E–5 | 35 | 3 | 63 |
| 12    | Three-parameter log regression | LogQ_{NMOC} = –0.95log(C_{NMOC}/C_{CH4}) – 1.95log(\text{MW}_{NMOC}/\text{MW}_{CH4}) + 3.19log(\text{MW}_{NMOC}/\text{MW}_{CH4}) / (\text{MW}_{NMOC}/\text{MW}_{CH4}) \cdot 10.86 | 3.8E–8 | 2.5E–5 | 25 | 53 | 23 |

* Bias is the arithmetic mean of the errors and RMSE is root mean squared error. Equations and explanation for bias and RMSE are provided in the SI.

* Regression model is significant (p < 0.05) but only the MW ratio is a significant contributing factor.

* Regression model is not significant (p > 0.05).
NMOCs that exhibit high VP at a given temperature do not have strong intermolecular attractions, and thus are likely to evaporate. As shown in Table 4, log $K_{ow}$-modified Eq. (2) (model 4a) overestimated 42% of NMOC fluxes by $P_{10}/C_2$, while VP-modified Eq. (2) (model 6a) underestimated 84% of NMOC fluxes by $P_{10}/C_2$. Compared to $k_H$ and $S_m$, these parameters did not provide better estimation models for NMOC fluxes (Table 4).

Fig. 7B shows that MW$_2$-modified Eq. (2) (model 7) yields NMOC flux estimates that are closest to measured NMOC fluxes: 71% of estimated NMOC fluxes are within $10 \times$, while 13% are overestimated by $10 \times$ (Table 4b). When simplified, model 7 is essentially Eq. (2) with an inverse MW ratio, i.e., MW$_{CH_4}$/MW$_{NMOC}$. The improved predictions with model 7 suggest that NMOCs with higher MW (and thus smaller MW$_{CH_4}$/MW$_{NMOC}$ ratio) likely remain in the solid and aqueous phases so their concentrations in emitted landfill gas will be lower (i.e., $C_{NMOC}/C_{CH_4}$ ratio). Molecular weight describes the size of a chemical compound. Chemicals with higher MW generally have lower $k_H$, $S_m$ and VP but higher log $K_{ow}$. Larger chemicals are generally more difficult to biodegrade than smaller molecules because they likely sorb to surrounding organic matter and become inaccessible to microbial degradation in the aqueous solutions (Shaw et al., 2000; Harms and Zehnder, 1995). Moreover, larger chemicals in the aqueous phase may not be readily available for microbial degradation due to slower or restricted transport into the cell membranes (Boethling et al., 2007). The biodegradability of larger chemicals can be enhanced by longer residence times, allowing more time for desorption from solid phases and transport in aqueous phases for biological and chemical reactions.

NMOC flux relationships involving two or more individual chemical properties were also explored through regression analysis (Table 4, models 8–12). Except for the log-transformed model (Table 4, model 12), all regression correlations are significant ($p < 0.05$) with MW$_{CH_4}$/MW$_{NMOC}$ ratio the only significant contributing factor. Moreover, regression coefficients for MW$_{CH_4}$/MW$_{NMOC}$ ratio have negative values suggesting an inverse relationship between flux ratio ($Q_{NMOC}/Q_{CH_4}$) and concentration ratio. Similar inverse relationships between concentration ratios and MW ratios were also observed in field data obtained from Southeastern-US (Fig. 1A), Midwestern-US 1 (Fig. 1B) Yolo County (Fig. 2A) and Midwestern-US 2 (Fig. 2B) landfills.

Among the alternative models, MW$_2$-modified equation 2 (ratio equation divided by MW$^2$, model 7) is best in addressing the tendency of the ratio method to overestimate NMOC flux estimates for thick covers. Application of this alternative model to Grand’Landes landfill data set reduced the speciated NMOC flux data overestimated by a factor $\geq 10 \times$ from 60% to 13%, and improved the speciated NMOC flux data that are within $10 \times$ factor from 33% to 71%. Similar results were obtained for Lapouyade landfill data set (Fig. 8): speciated NMOC fluxes overestimated by a factor $\geq 10 \times$ are reduced from 57% to 20% and the speciated NMOC flux data that are within 10× improved from 40% to 69% when model 7 is employed rather than the ratio method.

Fig. 7. Predicted average flux of speciated NMOCs including three hot spots in Grand’Landes region 25A from Scheutz et al. (2008) using (A) model 1 (Eq. (2)) and (B) model 7 (Eq. (2) with inverse MW$^2$). Data points represent flux of individual NMOCs. Solid black line indicates perfect model prediction, while dashed lines represent model predictions that are either greater than measured by a factor of 10 (upper line), or less than measured by a factor of 10 (lower line).

Fig. 8. Predicted average flux of speciated NMOCs in Lapouyade landfill from Scheutz et al. (2003) using (A) model 1 (Eq. (2)) and (B) model 7 (Eq. (2) with inverse MW$^2$). Data points represent flux of individual NMOCs. Solid black line indicates perfect model prediction, while dashed lines represent model predictions that are either greater than measured by a factor of 10 (upper line), or less than measured by a factor of 10 (lower line).
4. Conclusions

The current ratio method used in a recent USEPA Report (USEPA, 2012) uses CH₄ flux measurements and measured C_{NMOC}/C_{CH₄} ratios from landfill header gas to estimate speciated NMOC fluxes from the landfill. Header gas concentrations are in essence a composite gas sample of the landfill but may be significantly different from those gases in the cover soils, at the landfill surfaces, and downwind of the landfill as both NMOCs and CH₄ are affected by processes in the landfill cover. C_{NMOC}/C_{CH₄} ratios near landfill surfaces are generally higher than the C_{NMOC}/C_{CH₄} ratios in the header gas. Both literature data and 2012/2013 field sampling data from US landfills show systematic vertical variation of C_{NMOC}/C_{CH₄} with higher concentration ratios observed in gas samples obtained at shallower depths. One explanation for this is that CH₄ undergoes preferential biodegradation. An exception is noted for Midwestern-US 2 data, possibly due to excess moisture in pores due to prior rainfall before field sampling, this reducing CH₄ biodegradation. Moreover, field pore gas data at 1.5 m depth and thus in the waste mass show no systematic horizontal variation in C_{NMOC}/C_{CH₄} ratios (p < 0.05) relative to the adjacent gas well, suggesting that off-gassing of some NMOCs due to vapor/vacuum interactions in the gas extraction process do not result in increased NMOC concentrations in the gas well.

The ratio method worked well predicting NMOC emissions for the single landfill site with thin covers (<40 cm) and no gas collection. This scenario would result in the least opportunity for CH₄ biodegradation. However, ratio method results in overestimation of NMOC emissions for thick covers (>40 cm). The only situation where this is not true is when the CH₄ flux is negative or near zero. Among the explored alternative models incorporating other chemical properties (Henry Law’s constant, aqueous solubility, log octanol–water partition coefficient, vapor pressure, and molecular weight (MW)) into the ratio method, MW²-modified ratio equation (ratio equation divided by MW², model 7) was best in addressing the tendency of the ratio method to overestimate NMOC fluxes for thick covers. Application of this alternative model to GrandLandes and Lapouyade landfill data improved the percentage of speciated NMOC flux data estimates within 10% of actual measurements. Future work should examine the utility of the ratio method for whole-landfill NMOC emissions when such data are available.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2014.07.007.

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