

## Volatile organic compounds in pesticide formulations: Methods to estimate ozone formation potential

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### ABSTRACT

The environmental fate and toxicity of active ingredients in pesticide formulations has been investigated for many decades, but relatively little research has been conducted on the fate of pesticide co-formulants or inerts. Some co-formulants are volatile organic compounds (VOCs) and can contribute to ground-level ozone pollution. Effective product assessment methods are required to reduce emissions of the most reactive VOCs. Six emulsifiable concentrate pesticide products were characterized for percent VOC by thermogravimetric analysis (TGA) and gas chromatography–mass spectrometry (GC–MS). TGA estimates exceeded GC–MS by 10–50% in all but one product, indicating that for some products a fraction of active ingredient is released during TGA or that VOC contribution was underestimated by GC–MS. VOC profiles were examined using TGA–Fourier transform infrared (FTIR) evolved gas analysis and were compared to GC–MS results. The TGA–FTIR method worked best for products with the simplest and most volatile formulations, but could be developed into an effective product screening tool. An ozone formation potential (*OFP*) for each product was calculated using the chemical composition from GC–MS and published maximum incremental reactivity (*MIR*) values. *OFP* values ranged from 0.1 to 3.1 g ozone g<sup>-1</sup> product. A 24-h VOC emission simulation was developed for each product assuming a constant emission rate calculated from an equation relating maximum flux rate to vapor pressure. Results indicate 100% VOC loss for some products within a few hours, while other products containing less volatile components will remain in the field for several days after application. An alternate method to calculate a product *OFP* was investigated utilizing the fraction of the total mass of each chemical emitted at the end of the 24-h simulation. The ideal assessment approach will include: 1) unambiguous chemical composition information; 2) flexible simulation models to estimate emissions under different management practices; and 3) accurate reactivity predictions.

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### 1. Introduction

Large scale crop production frequently includes the use of pesticide products to reduce pest pressures or to provide protection against plant diseases. Regulatory agencies in their decision to register these products for use have largely considered only the

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toxicity and persistence of the pesticide active ingredient(s) and some of their degradation products. Transformation, transport, and toxicity of pesticide active ingredients are investigated, and several models have been developed to predict their fate in air, soils, water, and biota (Arnot and Gobas, 2003; Gamberdinger et al., 1991). However, relatively little research has been conducted to examine the environmental fate of pesticide inactive ingredients, sometimes termed co-formulants or inert ingredients.

Information on pesticide formulations for most products is limited to what is publicly available on material safety data sheets (MSDS) or on the official label documentation, such as the percentage of the active ingredient and sometimes other major or widely-used components. Detailed formulation information is confidential business information, especially when the co-formulants contribute to the effectiveness of the pesticide product in the field.

While some pesticide products contain no volatile organic compounds (VOCs), such as elemental sulfur fungicides/insecticides, a large fraction of emulsifiable concentrate (EC) formulations are frequently VOCs. EC formulations are used to solubilize the relatively non-volatile active ingredient into a concentrated form; they are also easily diluted with water for use in sprayer equipment. Although a significant body of research exists concerning fumigant (which are often gases) emissions and management practices to reduce or to mitigate these emissions (Ashworth et al., 2009; Papiernik et al., 2001); little research has been conducted to consider VOC emissions from other types of pesticides.

Emissions of VOCs associated with pesticide applications are of critical interest in the San Joaquin Valley in the State of California, USA, one of the most important and productive agricultural regions in the United States. However, this region is consistently listed as an 8-h ozone standard non-attainment area under the Federal Clean Air Act. The bowl-like geographic feature of the region combined with a hot, sunny summer climate and anthropogenic (e.g., NO<sub>x</sub>, VOCs) and biogenic (e.g., isoprene) emissions result in a perfect atmospheric reactor to create and then retain ozone pollution. Inventory reduction targets for pesticide VOC emissions have been set by the California Department of Pesticide Regulation (CDPR), and farmers are being encouraged to implement conservation practices to limit emissions (CDPR, 2010). As part of the State of California's plan to reduce ozone pollution, all pesticide products registered in the state are assigned an emission potential (*EP*) value, that fraction of the formulation which is volatile, but not including water (CDPR, 2008). The *EP* is determined using a thermogravimetric analysis (TGA) (CDPR, 2008). A yearly VOC emission inventory for pesticides is then developed by multiplying the *EP* by the total product usage and an application method adjustment factor (*AMAF*). For most pesticide products the *AMAF* is not available and is assumed to be 1, i.e., the entire volatile fraction of a product will be emitted to the atmosphere. This approach provides a worst-case scenario with respect to VOC emissions, but does not provide any information on the reactivity of the chemicals emitted, nor the amount of ozone that can potentially be produced.

In January 2010, the United States Environmental Protection Agency (US EPA) proposed to strengthen national ambient air quality standards for ground-level ozone, reducing the 8-h primary ozone standard to 0.060–0.070 ppm (US EPA, 2010a). If adopted, this change will likely increase the number of regions in non-attainment for ozone and will likely prompt other states to consider regulatory controls limiting VOC emissions from pesticides. As metropolitan areas around the world expand and as agricultural production increases to meet the needs of a growing population, air quality problems associated with urban and agricultural emissions will likely become more common (Aunan et al., 2000; Howard et al., 2010). Policy-makers will require more robust science-based tools to achieve reductions in ozone pollution levels.

The purpose of the present study was to evaluate available methods to assess pesticide products for VOC content and their ozone formation potentials (*OFP*). Six different pesticide products containing commonly-used organic solvents were characterized by TGA–Fourier Transform Infrared (FTIR) spectroscopy evolved gas analysis and by gas chromatography–mass spectrometry (GC–MS). An *OFP* of each pesticide product was estimated using chemical composition and maximum incremental reactivity (*MIR*) data. Predicted VOC emission profiles were examined using a simple regression model developed by van Wesenbeeck et al. (2008) and this data was used to calculate an *OFP* reflecting the mass of the VOCs emitted after 24 h. Results were examined with respect to the advantages and limitations of each approach and research gaps were identified.

## 2. Materials and methods

Emulsifiable concentrate pesticide product samples were obtained directly from several major pesticide manufacturers. Six products were selected for inclusion in the study: 2 herbicides, 2 fungicides, and 2 insecticides. The identity of the products is not provided as the focus of this work is not the active ingredients but rather the solvents used as co-formulants in these and many other pesticide products.

A TGA of each pesticide product was carried out in triplicate using a TA Instruments (New Castle, DE USA) model Q5000IR thermogravimetric analyzer and the method defined by the CPDR (2005). Briefly, platinum weighing pans were conditioned at 125 °C for 1 h and stored in a desiccator prior to use. After taring the platinum weighing pan, approximately 10 mg of the pesticide product was added to the pan and analyzed using the following temperature program: initial temperature of 35 °C was increased 5 °C min<sup>-1</sup> to 115 °C and held until the mass was stable (<0.5% change for 5 min) and then held for an additional 15 min. One product, H2, did not reach a stable mass at 115 °C and was re-run at 55 °C for 11 h.

Evolved gases from the TGA were then transported through a heated (200 °C) TGA–FTIR transfer line (Thermo Fisher Scientific, Inc., Waltham, MA USA) using high purity nitrogen (flow rate = 40 mL min<sup>-1</sup>) throughout the heating program and delivered to a Nicolet model 6700 (Thermo Fisher Scientific, Inc.) Fourier Transfer Infrared (FTIR) spectrometer. The FTIR gas cell was held at 210 °C, and spectra (scans = 32, resolution = 4) were collected every 30 s during the TGA temperature program. For each run, the spectra obtained were compiled into a Gram–Schmidt plot providing an indication of spectral intensity throughout the run. Using the representative spectra from each run, compound identification was achieved via OMNIC Spectra (Version 2.0, Thermo Fisher Scientific, Inc. USA) multi-component analysis software and appropriate vapor phase spectral libraries.

VOCs present in the headspace of each pesticide product were pre-screened using solid-phase microextraction (SPME) (Supelco, Inc., Bellefonte, PA USA) as a sample introduction method to GC–MS. This approach allowed for initial analysis of the pesticide formulation in the absence of any solvent to identify the chemicals components and for GC method parameter optimization. Afterward, duplicate samples of each pesticide product were diluted with toluene to 5 µg mL<sup>-1</sup>, and solutions were analyzed by GC–MS to quantify individual VOC concentrations. Chemicals in each product were initially identified using a NIST mass spectral library match of greater than 90% (Table 1) (Ambrose et al., 1975; Atkinson, 1990; Atkinson et al., 2000; Burkhard et al., 1984; Carter, 2010; Cervenkova and Boublik, 1984; Chao et al., 1983; Daubert and Danner, 1985, 1989; Karyakin et al., 1968; Macknick and Prausnitz, 1979; Meylan and Howard, 1993; Neely and Blau, 1985; Perry and Green, 1984; Phousongphouang and Arey, 2002; Ruzicka et al., 1994; US EPA, 2010b; Yaws, 1994). VOC components were verified by retention time and spectral pattern match; concentrations were determined using high purity (≥98%) analytical standards (Sigma–Aldrich, Inc., St. Louis, MO USA; Chem Service, Inc., West Chester, PA USA) and a 5-point internal standard calibration curve spanning the range of peak areas in the sample. Results were used to calculate the percent contribution of each chemical relative to the total product mass. Some compounds were present in very low concentrations and their concentrations could not be quantitatively determined.

The SPME fiber coating was Carboxen™/polydimethylsiloxane, 1.0 cm (l), 75 µm film thickness, and it was conditioned at 280 °C for 1 h prior to use. Approximately 200 µL of the pesticide product was added to a 20 mL glass headspace vial, sealed, and heated to 50 °C

**Table 1**  
Chemicals identified in six pesticide products including published vapor pressure, hydroxyl radical rate constant values, and maximum incremental reactivity (MIR) values.

| Chemical <sup>a</sup>                                  | CAS number | Molecular weight (g mol <sup>-1</sup> ) | Rate Constant ( $k \times 10^{12}$ ) (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) | Vapor pressure (Pa) <sup>b</sup> | MIR <sup>c</sup> (g O <sub>3</sub> g VOC <sup>-1</sup> ) | Identified in product |
|--|------------|---|--|----------------------------------|--|-----------------------|
| <i>Alcohols</i>  |            |   |  |                                  |  |                       |
| <b>1-Hexanol</b>                                       | 111-27-3   | 102                                     | 12.4 <sup>e</sup>  | 67 <sup>d,f</sup>                | 2.69   | I2                    |
| 1-Hexanol, 2-ethyl                                     | 104-76-7   | 130                                     | 13.2 <sup>g</sup>  | 18.1 <sup>h</sup>                | —  | H2                    |
| Propylene glycol                                       | 57-55-6    | 76                                      | 12.0 <sup>i</sup>  | 17.2 <sup>f</sup>                | 2.58   | F1                    |
| <i>Benzene derivative</i>                              |            |   |  |                                  |  |                       |
| <b>Benzene, 1,4-diethyl</b>                            | 105-05-5   | 134                                     | 8.11 <sup>g</sup>  | 141 <sup>f</sup>                 | —  | F2,I1                 |
| Benzene, 2-ethenyl-1,3,5-trimethyl                     | 769-25-5   | 146                                     | 59.32 <sup>j</sup>   | 31 <sup>j</sup>                  | —  | F2,I1                 |
| Benzene, 1-ethyl-3-methyl                              | 620-14-4   | 120                                     | 17 <sup>i</sup>  | 405 <sup>f</sup>                 | 7.39   | F2,I1                 |
| Benzene, 1-ethyl-4-methyl                              | 622-96-8   | 120                                     | 11.3 <sup>i</sup>  | 400 <sup>f</sup>                 | —  | F2,I1                 |
| Benzene, 1-ethyl-2,4,5-trimethyl                       | 17851-27-3 | 148                                     | 21.4 <sup>i</sup>  | 24.9                             | —  | F2,I1                 |
| <b>Benzene, 1-methylethyl = Cumene</b>                 | 98-82-8    | 120                                     | 7.79 <sup>j</sup>  | 1067 <sup>d</sup>                | 2.52   | F2,I1                 |
| <b>Benzene, 1-methyl-3-propyl</b>                      | 1074-43-7  | 134                                     | 19.2 <sup>i</sup>  | 405 <sup>f</sup>                 | 4.43   | F2,I1                 |
| Benzene, pentamethyl                                   | 700-12-9   | 148                                     | 52.8 <sup>g</sup>  | 4.64 <sup>d,k</sup>              | —  | H1,H2                 |
| <b>Benzene, propyl</b>                                 | 103-65-1   | 120                                     | 5.86 <sup>j</sup>  | 456 <sup>f</sup>                 | 2.03   | F2,I1                 |
| <b>Benzene, 1,2,3-trimethyl</b>                        | 526-73-8   | 120                                     | 26.4 <sup>i</sup>  | 453 <sup>l</sup>                 | 11.97  | F2,I1                 |
| <b>Benzene, 1,2,4-trimethyl</b>                        | 95-63-6    | 120                                     | 40 <sup>i</sup>  | 271 <sup>m</sup>                 | 8.87   | F2,I1                 |
| <b>Benzene, 1,3,5-trimethyl</b>                        | 108-67-8   | 120                                     | 62.4 <sup>i</sup>  | 248 <sup>d,f</sup>               | 11.76  | F2,I1                 |
| Butylated Hydroxytoluene                               | 128-37-0   | 220                                     | 18.3   | 1.9 <sup>n</sup>                 | —  | I2                    |
| <b>Ethylbenzene</b>                                    | 100-41-4   | 106                                     | 7.1 <sup>i</sup>   | 1280 <sup>h</sup>                | 3.04   | F2,I1                 |
| <b>o-Xylene</b>  | 95-47-6    | 106                                     | 13.7 <sup>i</sup>  | 881 <sup>h</sup>                 | 7.64   | F2,I1                 |
| <b>p-Xylene</b>  | 106-42-3   | 106                                     | 14.3 <sup>i</sup>  | 1179 <sup>m</sup>                | 5.84   | F2,I1                 |
| <i>Biphenyl derivative</i>                             |            |   |  |                                  |  |                       |
| Biphenyl   | 92-52-4    | 154                                     | 5.8 <sup>i</sup>   | 0.7 <sup>d,o</sup>               | —  | H1,H2                 |
| 1,1'-Biphenyl, 3,4'-dimethyl                           | 7383-90-6  | 182                                     | 13.3 <sup>i</sup>  | 0.465 <sup>l</sup>               | —  | H1,H2                 |
| 1,1'-Biphenyl, 2-methyl                                | 643-58-3   | 168                                     | 7.68 <sup>g</sup>  | 2.7 <sup>e</sup>                 | —  | H1,H2                 |
| 1,1'-Biphenyl, 4-methyl                                | 644-08-6   | 168                                     | 7.68 <sup>g</sup>  | 0.86 <sup>e</sup>                | —  | H1,H2                 |
| <i>Indane derivative</i>                               |            |   |  |                                  |  |                       |
| <b>Indane</b>  | 496-11-7   | 118                                     | 9.2 <sup>i</sup>   | 196 <sup>p</sup>                 | 3.32   | F2,I1                 |
| 1H-Indene, 2,3-dihydro-1,2-dimethyl                    | 53204-57-2 | 144                                     | 92.8 <sup>i</sup>  | 22.8 <sup>j</sup>                | —  | F2,I1                 |
| 1H-Indene, 2,3-dihydro-4,7-dimethyl                    | 6974-97-6  | 144                                     | 71.8 <sup>i</sup>  | 16 <sup>j</sup>                  | —  | F2,I1                 |
| <i>Naphthalene derivative</i>                          |            |   |  |                                  |  |                       |
| <b>Naphthalene</b>                                     | 91-20-3    | 128                                     | 18.6 <sup>i</sup>  | 12 <sup>q</sup>                  | 3.34   | H1,H2                 |
| Naphthalene, 1,3-dimethyl                              | 575-41-7   | 157                                     | 69.4 <sup>j</sup>  | 3.09 <sup>j</sup>                | —  | H1,H2                 |
| <b>Naphthalene, 1,7-dimethyl</b>                       | 575-37-1   | 157                                     | 69.4 <sup>j</sup>  | 1.71 <sup>j</sup>                | 4.99   | H1,H2                 |
| Naphthalene, 1,8-dimethyl                              | 569-41-5   | 157                                     | 69.4 <sup>j</sup>  | 0.47 <sup>j</sup>                | —  | H1,H2                 |
| <b>Naphthalene, 2,6-dimethyl</b>                       | 581-42-0   | 157                                     | 69.4 <sup>j</sup>  | 0.327 <sup>j</sup>               | 4.99   | H1,H2                 |
| Naphthalene, 1-ethyl                                   | 1127-76-0  | 157                                     | 14.6   | 3.36 <sup>r</sup>                | —  | H1,H2                 |
| <b>Naphthalene, 2-ethyl</b>                            | 939-27-5   | 157                                     | 54.8 <sup>j</sup>  | 4.21 <sup>j</sup>                | 3.76   | H1,H2                 |
| <b>Naphthalene, 1-methyl</b>                           | 90-12-0    | 142                                     | 53 <sup>i</sup>  | 8.9 <sup>s</sup>                 | 3.06   | H1,H2                 |
| <b>Naphthalene, 2-methyl</b>                           | 91-57-6    | 142                                     | 52.3 <sup>i</sup>  | 9.07 <sup>d,t</sup>              | 3.06   | H1,H2                 |
| Naphthalene, 1-(2-propenyl)                            | 2489-86-3  | 168                                     | 80.9   | 1.09 <sup>e</sup>                | —  | H1,H2                 |
| Naphthalene, 1,4,5-trimethyl                           | 2131-41-1  | 170                                     | 124  | 0.336 <sup>e</sup>               | —  | H1,H2                 |
| Naphthalene, 1,6,7-trimethyl                           | 2245-38-7  | 170                                     | 124  | 0.336 <sup>e</sup>               | —  | H1,H2                 |
| Naphthalene, 2,3,6-trimethyl                           | 829-26-5   | 170                                     | 124  | 0.336 <sup>e</sup>               | —  | H1,H2                 |
| Naphthalene, 1,4,6-trimethyl                           | 2131-42-2  | 170                                     | 124  | 0.336 <sup>e</sup>               | —  | H1,H2                 |
| <i>Ketones and others</i>                              |            |   |  |                                  |  |                       |
| <b>Acetophenone</b>                                    | 98-86-2    | 120                                     | 2.74 <sup>i</sup>  | 53 <sup>h</sup>                  | 1.05   | F1                    |
| <b>2-Heptanone</b>                                     | 110-43-0   | 114                                     | 8.67 <sup>u</sup>  | 213 <sup>q</sup>                 | 2.36   | F1                    |
| <b>N-Methyl-2-pyrrolidone</b>                          | 872-50-4   | 99                                      | 74 <sup>i</sup>  | 46.0 <sup>f</sup>                | 2.41   | H1,I2                 |
| 1,3-Dioxolane, 4-methyl-2-phenyl                       | 2568-25-4  | 164                                     | 23.1 <sup>j</sup>  | 5.97 <sup>j</sup>                | —  | F1                    |
| 1,3-Dioxolane 2-propanoic acid, 2-methyl-, ethyl-ester | 941-43-5   | 188                                     | 15.5 <sup>j</sup>  | 5.63 <sup>j</sup>                | —  | F1                    |

<sup>a</sup> Compounds listed in bold were present at levels greater than 1% of total product mass in at least one product and were quantified by GC-MS.

<sup>b</sup> All vapor pressure measured at 25 °C unless otherwise noted.

<sup>c</sup> MIR values from Carter (2010).

<sup>d</sup> Vapor pressure measured at 20 °C.

<sup>e</sup> Neely and Blau, 1985.

<sup>f</sup> Daubert and Danner, 1989.

<sup>g</sup> Meylan and Howard, 1993.

<sup>h</sup> Daubert and Danner, 1985.

<sup>i</sup> Atkinson, 1990.

<sup>j</sup> EPI Suite Software (US EPA, 2010b).

<sup>k</sup> Ruzicka et al., 1994.

<sup>l</sup> Yaws, 1994.

<sup>m</sup> Chao et al., 1983.

<sup>n</sup> Perry and Green, 1984.

<sup>o</sup> Burkhard et al., 1984.

<sup>p</sup> Cervenkova and Boublik, 1984.

<sup>q</sup> Ambrose et al., 1975.

<sup>r</sup> Phousongphouang and Arey, 2002.

<sup>s</sup> Macknick and Prausnitz, 1979.

<sup>t</sup> Karyakin et al., 1968.

<sup>u</sup> Atkinson et al., 2000.

for 10 min. A SPME fiber was then inserted into the headspace for 1 min of static extraction under dark conditions and manually injected into an Agilent Technologies, Inc (Santa Clara, CA USA) model 6890N GC coupled to a model 5973 MSD. The GC inlet was operated at 270 °C in splitless mode with a purge flow of 30 mL min<sup>-1</sup> and purge time of 1.0 min. The GC was equipped with a HP-1 (Agilent, Technologies, Inc.) (30 m, 0.32 mm i.d., 1.0 µm film thickness) column using the following temperature program: initial temperature of 70 °C was increased 5 °C min<sup>-1</sup> to an endpoint of 270 °C; ultra high purity helium was the carrier gas (1.4 mL min<sup>-1</sup>). The mass spectrometer was operated in electron impact mode under full scan from 40 to 400 *m/z*; source temp = 230 °C; quadrupole temp = 150 °C. Liquid injections were made with the same instrumentation and column but with the following GC temperature program: initial temperature of 70 °C was increased 5 °C min<sup>-1</sup> to 150 °C, hold 0.5 min, 25 °C min<sup>-1</sup> to 270 °C, hold 17 min.

### 3. Results and discussion

#### 3.1. Evaluation of analytical measurement results

All six products exhibited a high degree of volatility during TGA ranging from an average mass loss of 44.1 ± 0.4% for product I1 to 75.3 ± 0.5% for H1 (Fig. 1). Total percent VOC (non-active ingredient compounds) as determined by GC–MS were generally lower than TGA results. In three products, percent VOC results by GC–MS were approximately 50% of that measured by TGA, while the other three were comparable considering the uncertainty in the analysis. The best agreement was for product I2, where results for TGA and GC–MS were essentially the same, and for product I1 where average results differed by only 6%. For the other four products, total VOCs by GC–MS were more than 13% lower than by TGA with the greatest difference for products H1 and H2 (>50%). There are two possible reasons for the disparity; the first is that GC–MS analysis did not provide a complete VOC profile. In products H1 and H2, with similar VOC profiles, 13 and 14 compounds, respectively, were detected and identified but were not quantified because they were present in low concentrations (much less than 1% of total product mass) (Table 1). Even accounting for these un-quantified VOC components, i.e., attributing 5–10% additional VOC, the difference between the TGA and GC–MS result is still substantial. The second possible reason for the disparity between percent VOC values is that at the extreme temperature of the TGA method (115 °C) some portion of the active ingredient was volatilized. One

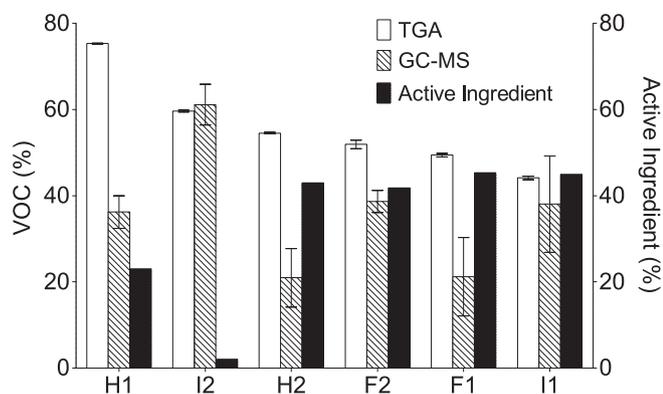


Fig. 1. Comparison % VOC as calculated from TGA with a maximum temperature of 115 °C. Also displayed is % VOC (% non-active ingredient compounds) calculated from GC–MS analysis and the % active ingredient for each product listed on the material safety data sheet.

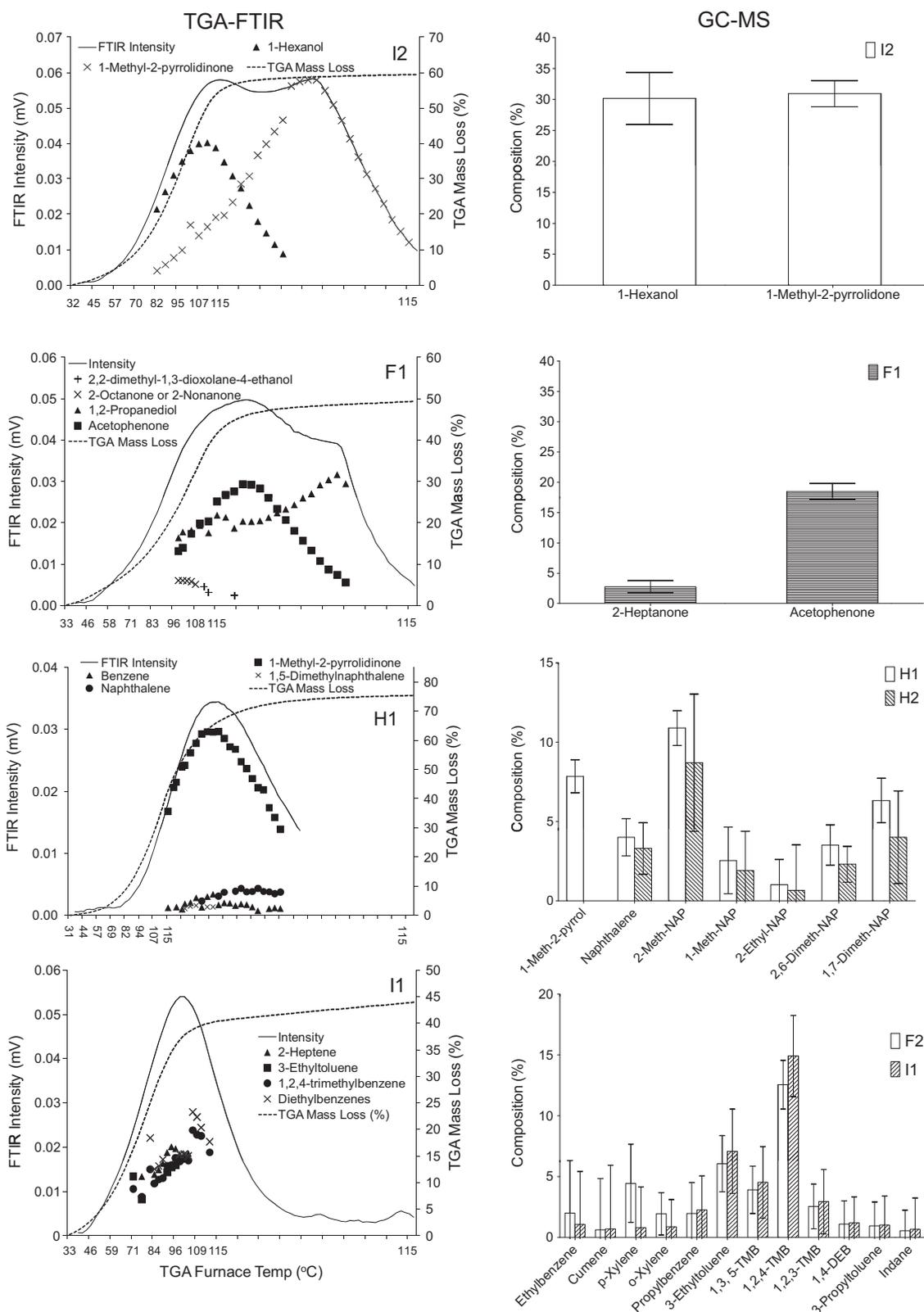
of the disadvantages of the TGA method is that no chemical emission information is collected.

Examination of the TGA–FTIR evolved gas analysis results provided some chemical-specific information on the VOCs emitted during TGA (Fig. 2). For product I2, two compounds contributed 90–95% to the observed spectral intensity; 1-hexanol contributed a greater fraction of the intensity in the beginning of the run and 1-methyl-2-pyrrolidone (1-Me-2-Pyr) dominated the latter part. This result is similar to a gas chromatograph where the most volatile compound, 1-hexanol ( $P_v = 67$  Pa) has a shorter retention time than a less volatile compound, 1-Me-2-Pyr ( $P_v = 46$  Pa). The TGA–FTIR results compared well with the GC–MS characterization (Fig. 2); both 1-hexanol and 1-Me-2-Pyr were detected by GC–MS at approximately equal concentrations, each representing around 30% of the total formulation. Thus, for product I2, TGA does provide an accurate estimate of the %VOC (approximately 60%), and the FTIR analysis provided an accurate identification of the VOCs emitted during the TGA as compared with the GC–MS analysis results.

For product F1, the TGA–FTIR analysis indicated two primary VOC components, acetophenone and 1,2-propanediol (propylene glycol) each contributing approximately 40–50% of the spectral intensity, with some minor contributions from octanone, nonanone, and from 2,2-dimethyl-1,3-dioxolane-4-ethanol (<20%). However, the GC–MS results for the same product indicated that acetophenone was the most abundant VOC at 18% and 2-heptanone was only 2.8% of the total formulation. Propylene glycol was identified along with two additional compounds, 2,4-dimethyl-ethyl ester-1,3-dioxolane-2-propionic acid and 2,4-dimethyl-2-phenyl-1,3-dioxolane, during pre-screening analysis by SPME, but none were above quantitation limits in the diluted samples. The FTIR method did not identify the 2-heptanone in the evolved gases, but did show some higher molecular weight ketones. 2-Heptanone has a very high  $P_v$  (213 Pa) and may have been emitted so rapidly from the TGA that it was missed at the 30-s interval of FTIR spectra collection. The higher molecular weight ketones may have been present as a contaminant in the 2-heptanone. Alternatively, the software may have misidentified the ketone present in the cell since concentrations were low. The FTIR results, in the case of product F1, illustrates that minor VOC components can make a significant contribution to the total spectral intensity.

Similar results were observed for product H1, where one VOC component, 1-Me-2-Pyr, contributed >75% of the spectral intensity, but was only present at 7.8% of formulation according to the GC–MS analysis. The compound 2-methylnaphthalene was present at approximately 11% of the total in this product by GC–MS, but was not identified in the FTIR analysis. This is expected since the  $P_v$  of 2-methylnaphthalene is only 9.07 Pa compared to 46 Pa for 1-Me-2-Pyr (Table 1). Benzene is a compound that was identified consistently as a minor contributor to the FTIR spectra for this product, but was not found in the GC–MS analysis. It is likely the benzene identification is just an indication of the aromaticity of the mixture. The product H2 did not contain 1-Me-2-Pyr but did contain the naphthalene components. The spectral intensity of the FTIR analysis for this product was very low throughout the run (data not shown) as would be expected from just the naphthalene compound contributions. Product H1 took approximately 20 min longer to reach a stable mass during TGA, which is likely due to the lower volatility VOC components present in these products.

The product I1 exhibited a very rapid rate of mass loss during the TGA, and the FTIR intensity also indicated a rapid release of VOCs. The FTIR intensity began to decline even before the TGA reached its maximum temperature. The FTIR spectral analysis identified alkenes, 3-ethylbenzene, diethylbenzenes, and trimethylbenzenes, all contributing approximately 30–50% of the spectral intensity at any one time. This composition was also



**Fig. 2.** Plots on the left display TGA–FTIR evolved gas analysis for individual pesticide products. Product mass loss (%) during TGA is shown as a dotted line versus furnace temperature. FTIR Gram–Schmidt Intensity (mV), shown as a solid line, was generated from spectra of the evolved gas collected every 30 s. The magnitude of the FTIR intensity is displayed for identified chemical components. Also displayed are VOC profiles determined by GC–MS in six pesticide products, displayed in order of decreasing vapor pressure. Values represent the average ( $\pm$ standard deviation) of 6 measurements of solutions prepared from pesticide products and are presented in percent composition.

reflected in the GC–MS analysis. Product F2 exhibited the same TGA–FTIR pattern (data not shown) and the VOC pattern in the GC–MS results. The observed VOC profile in products H1 and H2 were similar to each other, as were the VOC profiles of products F2 and I2. This indicates the same base solvent mixture is used in these product pairs.

### 3.2. Assessment of methods to estimate VOC emissions and ozone formation potentials

Utilizing results from TGA alone can provide an estimate of potential VOC emissions from a particular product. It does not, however, provide any information on the reactivity of the chemicals emitted or any way to estimate an ozone formation potential. Implementing reductions in the use of products based on this type of data alone may reduce overall VOC concentrations, but there is no certainty that these measures will lead to lower ozone pollution levels. Further, the TGA method fails to represent ambient atmospheric conditions observed in typical agricultural scenarios, and is thus likely to grossly overestimate potential emissions. Also, no account is made for the environmental availability, fate, and dissipation of the chemicals aside from volatility. Adsorption, absorption, degradation, etc. can play a significant role in reducing atmospheric emissions of VOCs.

A second method, proposed recently as a pilot project by CDPR includes the review of the confidential registration information and the calculation of a product-specific ozone formation potential ( $OFF_{prod}$ ) (CDPR, 2009). This approach was not designed to obtain an accurate estimate of actual ozone formed for regulatory purposes but as a means to rank products with respect to their potential contribution to ozone pollution. Ozone formation potential ( $OFF$ ) is typically given in grams of ozone formed per gram of substance and is calculated as the incremental reactivity of a VOC. The incremental reactivity method developed by Carter (1994) uses the ozone formation of a reference mixture which is compared against the reference mixture plus a small amount of test VOC. Several incremental reactivities have been developed (Carter, 1994), and  $MIR$  was proposed by CDPR for their pilot project.  $MIR$  represents a point on the ozone isopleth where  $NO_x$  concentrations are typically not limited, and this incremental reactivity has been widely used for policy-making in the United States (NRC, 1999).

Since pesticide products may contain a mixture of several VOCs of differing volatility, CDPR proposes developing a  $MIR_{prod}$  value reflecting the VOC emission profile.  $MIR_{prod}$  is defined in Eqn. (1),

$$MIR_{prod} = \sum_i f_i \times MIR_i \quad (1)$$

where  $f_i$  is the component fraction contribution to the TGA-based  $EP$  and  $MIR_i$  is the component maximum incremental reactivity (g ozone formed g  $VOC^{-1}$ ). The  $OFF_{prod}$  is then calculated as shown in Eqn. (2),

$$OFF_{prod} = mass\ prod\ applied \times EP \times AMAF \times MIR_{prod} \quad (2)$$

where  $EP$  is the volatile fraction of product as determined by the prescribed TGA method and the  $AMAF$  is the application method adjustment factor.

Part of the pilot project as proposed by CDPR (2009) was to find a model for relating product composition and its contribution to the  $EP$ . In the present study, we did not have access to the confidential registration information and therefore could not carry out the calculation of  $OFFs$  in this manner. One advantage of the method proposed by CDPR is that it does provide information on the atmospheric reactivity of the chemicals included in the formulation and would allow regulators to prioritize their efforts to reduce

usage or to mitigate emissions of particular products based on their potential contributions to ozone pollution. It also only requires one laboratory measurement per product. A limitation of this method is that there is no direct verification between the TGA-based  $EP$  and the calculation of the  $MIR_{prod}$ .

Some have argued that Equal Benefit Incremental Reactivity ( $EBIR$ ) values should be used in  $OFF$  calculations since they are more representative of the  $NO_x$  limited conditions found in agricultural settings. However, since the  $OFF$  calculations are only designed to provide a relative comparison of products, the use of  $MIR$  values is reasonable.

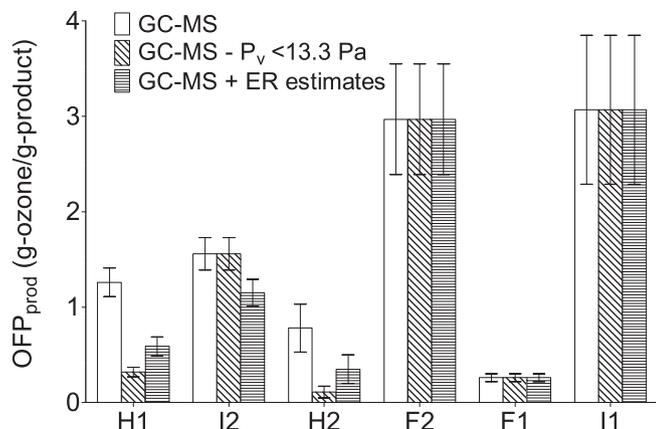
A third potential method to estimate product volatility and to develop an  $OFF_{prod}$  in the absence of confidential registration information is to utilize TGA–FTIR evolved gas analysis. This analytical approach has been successfully utilized in a number of different research applications (Dumont et al., 2010; Price and Church, 1997; Wang et al., 2010; Zhang et al., 2010) and it has the advantage of directly linking the TGA-based measurement with a chemical characterization of the VOCs emitted. As seen from results of the present study, this method works best with simple formulations with a limited number of components with strong absorbance in the infrared region (i.e., product I2 (Fig. 2)). Effective routine use of this method would require the pre-analysis of commonly-used formulation solvents and mixtures by TGA–FTIR and by more quantitative analysis methods like GC–MS. Results of the VOC profile as determined by the TGA–FTIR along with composition estimates could be used to estimate a product ozone formation potential value from mass-weighted component  $MIR$  values as shown in Eqns. (1) and (2). This approach has the advantage of providing an estimate of overall product volatility along with information on the VOC emission profile. From these experiments, it is unclear whether TGA–FTIR evolved gas analysis could be used routinely. Significantly more work would be required to develop unambiguous methods to screen for high priority ozone precursors in pesticide formulations.

A fourth potential approach is to require quantitative GC–MS analysis of a product, and the resulting data would be used directly to calculate an  $OFF_{prod}$  if a  $MIR$  value for each VOC is available.

$$OFF_{prod} = \sum_i f_i \times MIR_i \quad (3)$$

In our case study, all of the active ingredients have a  $P_v$  less than 0.01 Pa and can reasonably be excluded from the  $OFF_{prod}$  calculations;  $MIR$  values are typically not available for semi-volatile pesticides and are not available for the products included in this study. Calculated  $OFF_{prod}$  values using Eqn. (3) were highest for products F2 and I1 and were approximately equal to 3 g ozone g product<sup>-1</sup> (Fig. 3). These products contained the highly reactive VOCs *p*-xylene and 1,2,4-trimethylbenzene ( $MIR = 5.69$  and  $8.64$  g-ozone g  $VOC^{-1}$ , respectively) (Table 1) (Carter, 2010). Product F1 had the lowest  $OFF_{prod}$  as its co-formulants have the lowest  $MIR$  (<2.69 g  $O_3$  g  $VOC^{-1}$ ); the  $OFF_{prod}$  for products H1, H2, and I2 were somewhat higher reflecting the higher  $MIR$  of their co-formulants.

A variation on this method would be to exclude from the  $OFF_{prod}$  chemicals which do not meet the International Union of Pure and Applied Criteria (IUPAC) criteria for VOCs ( $P_v > 10$  Pa) (Duffus et al., 2007). This approach reduces the  $OFF$  for products H1 and H2 only, as most of the components of these products fall below this  $P_v$  value (Table 1). This potential approach has the advantage of being less ambiguous than previously described methods in that the emission profile is derived directly from chemical composition data. However, the 10 Pa criteria might eliminate from consideration some very reactive VOCs which could be emitted a low rates over many weeks after application. A safety factor of 10–1000 below the IUPAC



**Fig. 3.** Ozone formation potential ( $OFF$ ) ( $\text{g ozone g product}^{-1}$ ) calculated from composition data measured by GC–MS and mass-weighted  $MIR_{prod}$ . The second bar of each group reflects removal of any component with a vapor pressure  $< 13.3$  Pa from the  $MIR_{prod}$  calculation, and the third bar represents results of a simulation based on a maximum evaporation rate over 24 h (van Wesenbeeck et al., 2008).

standard may be more appropriate. Requirement of GC–MS analysis would likely be more expensive than TGA alone or TGA–FTIR. Alternatively, registrants could provide GC–MS analysis data of co-formulants which may be available from the manufacturer.

### 3.3. VOC emission profile simulation

One element which is missing from all the previously described approaches is a link to field-based emissions measurements. Woodrow et al. (2001) showed that vapor pressure can be used to predict the maximum evaporation rate ( $ER$ ) ( $\mu\text{g m}^{-2} \text{hr}^{-1}$ ) of semi-volatile and volatile organic compounds from plant and soil surfaces using a limited set of 13 pesticides. van Wesenbeeck et al. (2008) expanded this approach for a much larger number of

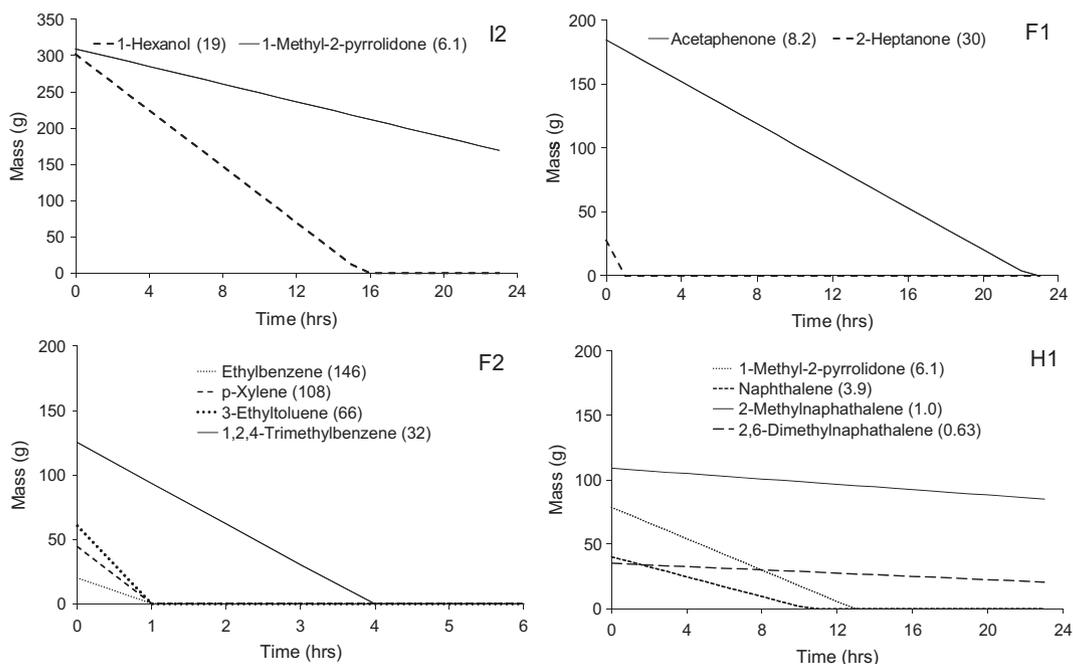
compounds, using field and laboratory measured and VOC emission rate (ASTM, 1987; Guth et al., 2004; Woodrow et al., 2001). They developed a single regression equation (Eqn. (4)) for 82 chemicals from 3 datasets with a range of vapor pressures ( $4.5 \times 10^{-5}$  to  $2.2 \times 10^4$  Pa).

$$\ln[ER] = 12.2 + 0.933\ln[P_v] \quad (4)$$

Using Eqn. (4) and the  $P_v$  data for the identified chemicals to calculate a maximum  $ER$ , a simple simulation was considered where 10 kg of product was applied to the surface of a 1 ha field. Assuming a constant evaporation rate, an emission profile was generated for each product (Fig. 4). Under these conditions, for product I2, one of the two main components (1-hexanol) will be completely emitted after 16 h, but the second less volatile component, 1-Me-2-PYR, is reduced by only 45% after 24 h. The emission rate of 1-Me-2-PYR is low ( $6.1 \text{ g m}^{-2} \text{ h}^{-1}$ ) and its fraction of the total formulation is large, therefore, approximately 2 days at this maximum flux rate would be required to achieve 100% loss. For product F1, 100% of the VOCs would be emitted in  $< 24$  h, and 100% of both product F2 and I1 (because formulations are the same) would be lost in only 4 h.

For product H1, considering 4 representative VOCs, 1-Me-2-PYR was depleted after 14 h. This result is different than product I2 above because the starting mass is much less in this formulation (309 g in I2 versus 78 g in H1). Naphthalene, another minor component with higher  $P_v$  values, is depleted in  $< 12$  h. However, the less volatile 2-methylnaphthalene and 2,6-dimethylnaphthalene, ( $P_v \approx 3\text{--}5$  Pa) are only reduced by a few percent after 24 h. Emissions of these methylated naphthalenes are likely to continue for several days after pesticide application. Similar results were observed for product H2 since its formulation is the same as product H1 (data not shown).

These simulations provide some relative comparison of emissions profiles for different products based on their composition and their volatility. Results of these simulations can then be used in the  $OFF_{prod}$  calculation as in Eqn. (5)



**Fig. 4.** Calculated volatile loss of representative VOCs over time after an application of 10 kg pesticide product to a 1 ha area. Starting mass of each chemical reflects measured product composition from the present study using GC–MS. The constant emission rate ( $ER$ ) ( $\text{g m}^{-2} \text{hr}^{-1}$ ) used for each compound is listed in parentheses after the compound name in each plot legend. The rates are derived from an equation developed by van Wesenbeeck et al. (2008) using experimental emission rate data and vapor pressure.

$$OFF_{prod} = \sum_i f_{i,sim} \times MIR_i \quad (5)$$

where  $f_{i,sim}$  is the fraction of the total mass emitted after 24 h (Fig. 3). The  $OFF_{prod}$  for products F2, F1, and I1 remain unchanged using this method because 100% of the formulation mass is emitted within 24 h. For product I2, the  $OFF_{prod}$  is decreased by 26% because only 45% of 1-Me-2-PYR is emitted in this timeframe.  $OFF_{prod}$  is also reduced for products H1 and H2 versus the GC–MS  $OFF$  approach (Eqn. (3)) because less than 30% of the mass of methylated naphthalenes is emitted in this simulation. This agrees with recent research by Kumar et al. (2010) of soil sample VOC concentrations after pesticide spray, which showed elevated concentrations (compared to pre-spray concentrations) of VOCs present in the soil as much as 60 h after spraying. The results were most pronounced for higher molecular weight hydrocarbons (such as methylated naphthalenes), which are expected because of the lower vapor pressures of these compounds. This was also shown by Warren et al. (2008) who used a fugacity model to show that 2-methylnaphthalene emissions from soil was 35% when incorporated just 1 cm into the soil and showed the impact of other dissipation processes such as biodegradation and soil sorption.

While this method used a 24 h simulation period, longer time frames could be used as well. Effective VOC  $P_v$  values adjusted for local growing season temperatures and diurnal temperature fluctuations could also be used in Eqn. (4) to calculate  $ER$  values for use in simulation runs. The final assessment approach described here brings together composition, volatility, and reactivity to estimate the potential ozone formation of pesticide products, and it provides flexibility in designing scenarios to meet the needs of different states or nations.

#### 4. Conclusions

Results of the present study reveal that TGA alone is inadequate to compose any meaningful decisions on the regulation of pesticide products to reduce ozone pollution. Results can be misleading with respect to the VOC content, and it does not provide a straightforward approach for determining  $OFF$ . Utilizing TGA–FTIR evolved gas analysis for  $OFF$  calculations provides additional useful information, but this approach should be further refined and developed with more quantitative methods and shared spectral libraries of common co-formulants.

In the absence of confidential formulation information, GC–MS analysis can provide the data needed to characterize product chemical composition, which can then be used to calculate  $OFF_{prod}$ . However, using only the GC–MS data in  $OFF_{prod}$  calculations does not consider the volatility or the emission profile of product co-formulants. Use of a simple regression model such as that by van Wesenbeeck et al. (2008) which is grounded by field measurements and chemical properties provides a more accurate assessment of formulation emission profiles. More complex models such as the fugacity based approach by Warren et al. (2008) would give a more physically based emission profile that would include mechanisms such as biodegradation and sorption, as well as the impact of incorporation into soil. Quantitative chemical characterization combined with appropriate model simulation(s) as a means to evaluate the  $OFF$  of pesticide products is the preferred assessment method, as this approach provides definitive information on chemical composition, volatility, emission profile, and atmospheric reactivity.

Detailed research efforts concerning the environmental fate of volatile pesticide co-formulants, including field studies, are needed to gain a better understanding of co-formulant contributions to ozone pollution. Improved simulation models for co-formulants,

incorporating different agronomic and conservation practices, would be most helpful in providing more realistic emissions predictions. Finally, existing pesticide emission models could be adapted to include product co-formulants with the active ingredients to obtain a more comprehensive assessment of pesticides and their potential effects on environmental quality and human health.

#### Disclaimer

Mention of specific products is for identification and does not imply endorsement by USDA to the exclusion of other suitable products or suppliers.

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