An Alternate Approach to VOC Speciation Reporting

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ABSTRACT

Emissions of volatile organic compounds (VOCs) are reported in most criteria-air-contaminant (CAC) emission inventories as a "total" value, that is, as the sum of all individual VOC species emitted from a particular source. Many chemical transport models, on the other hand, require more detailed information about the types of VOC species emitted. Consequently, an important task of emissions processing systems is to separate each reported total VOC emission value into emission values for the set of model VOC species. If VOC emissions are reported by process, then this task is usually achieved through the use of process-specific VOC speciation profiles.

In Canada, beginning with inventory year 2002, the reporting of point-source CAC emissions to air has been incorporated into the reporting to Canada's national point-source air toxics inventory, the National Pollutant Release Inventory (NPRI). One challenge related to this "one-window" reporting by facilities concerned VOC speciation. Before 2002, point-source CAC emissions in Canada were reported to the CAC inventory at the process level but NPRI-substance emissions are reported only at the facility level. If total VOC emissions were to be reported to the new NPRI only at the facility level, however, this would preclude the use of process-specific VOC speciation profiles to estimate speciated VOC emissions.

Following extensive consultations with NPRI stakeholders, the modelers's need for speciated VOC emissions was addressed by requiring larger VOC emitters (i.e., those with total VOC emissions > 10 tonnes y^{-1}, where 1 tonne = 1000 kg) to report facility emissions to air of a specified list of 60 individual VOCs, isomer groups, and other compound groups beginning in the 2003 reporting year. The specified VOC list was determined based on consideration of (a) the mass emissions of a host of VOC species from Canadian facilities, (b) the ozone and particulate-matter formation potential of these speciated emissions, and (c) speciated VOC ambient concentration levels. This paper describes in more detail the methodology to create the specified VOC list, some cross-checks carried out on the list, NPRI guidelines for speciated VOC reporting, and expected implementation issues, including the future changes required to emissions processing systems to process the NPRI VOC emissions.

INTRODUCTION

Volatile organic compounds are of interest in air-quality management for at least three reasons:

- Some individual compounds are toxic, carcinogenic, mutagenic, teratogenic, or bioaccumulative;
- VOCs are involved in the formation of ground-level ozone (directly) and acid rain (indirectly);
- VOCs contribute both directly and indirectly to the formation of organic particulate matter (PM).

Past practice in both Canada and the U.S.A. has been to collect and report environmental releases of individual VOCs identified as concerns under Reason 1 (above) in air toxics inventories: the National Pollutant Release Inventory (NPRI) in Canada and the National Toxics Inventory (NTI) in the U.S.A. On the other hand, for the criteria-air-contaminant (CAC) inventories that have been used in the management of such air issues as acid rain, ground-level ozone, and PM, VOC emissions have been reported as an aggregated or total number, although tens or hundreds of individual species may be emitted by a given facility.

CAC inventory users who require speciated VOC emissions, such as air-quality (AQ) modelers, have been able to obtain estimates of the emissions of individual VOCs or compound groups through the use of VOC speciation profiles. If the total-VOC emissions are reported at the *process* level, then process-specific VOC speciation profiles such as those contained in the U.S. EPA's SPECIATE3.2 software package (U.S. EPA, 2002) can be used to separate a reported total-VOC emission value into a set of individual VOC species emission values. In many facilities, however, where a number of different processes are present, a number of different process-specific speciation profiles may be required together with total-VOC emissions reported by process in order to obtain *facility-level* VOC speciation.

Recently, however, both Environment Canada (EC) and the U.S. Environmental Protection Agency, the government agencies in Canada and the U.S.A. responsible for producing national emission inventories, have independently undertaken to amalgamate their national air-toxics and CAC emission inventory data gathering (e.g., Government of Canada, 2001). The NPRI will now gather air emissions of 7 CAC pollutants: SO_2, NO_x, total VOC, CO, $PM_{2.5}$, PM_{10}, and TPM (NH_3 and 111 individual VOCs or isomer groups were already NPRI-listed substances). Such a data-gathering merger may require reconciliation of some different reporting practices. In Canada, one such difference arose from the reporting of point-source CAC emissions, including total VOC emissions, at the *process* or subfacility level vs. the reporting of emissions of NPRI-listed substances at the *facility* level. If the expanded EC NPRI were to adopt process-level reporting of emissions, then the VOC speciation tools used with the Canadian CAC inventory could continue to be used with the merged inventory. If, on the other hand, the existing NPRI practice of facility-level reporting were continued, then another approach would need to be found to obtain speciated VOC emissions for AQ modeling and other inventory applications.

Environment Canada was advised on a number of issues related to the NPRI/CAC-inventory data-gathering merger by the 2001-2002 NPRI Multi-stakeholder Work Group on Substances. Members of this Work Group include representatives from industry associations, environmental non-governmental organizations, and provincial environmental ministries. As part of the consultations that took place, an *ad hoc* CAC Speciation Subgroup was struck to discuss and to suggest a solution to the VOC (and PM) speciation issue to the Work Group. The two guiding principles contained in the charge to the Subgroup were that the solution proposed by the Subgroup should (1) meet the needs of inventory users, including AQ modelers, and (2) balance the need for improved information against the increased burden on facilities reporting to the NPRI due to collecting and reporting this additional information.

Two basic approaches to speciated VOC reporting were discussed by the Subgroup: (1) the *status quo* approach of process-level reporting of total VOC emissions followed by application of process-specific VOC speciation profiles; and (2) reporting of speciated VOC emissions by the facilities themselves. The second approach further required specification of some means to identify which individual VOC species needed to be reported. Arguments that were raised during Subgroup discussions <u>against</u> the *status quo* approach included the following: (a) on average, facilities should have a better knowledge of their own emissions that a distant central agency, (b) the available speciation-profile libraries are not comprehensive and contain many dated, poor quality, or unrepresentative profiles, (c) process-level reporting runs counter to previous NPRI practice and its tradition of self-reporting, and (d) process-level emissions may be considered confidential information. Arguments <u>for</u> the *status quo* approach included (a) the increased reporting burden that would fall on individual facilities required to report emissions of numerous additional VOC species, (b) the lack of emissions expertise at many facilities, especially smaller facilities, and (c) continuity with previous CAC inventory practice in Canada and internationally. There was also much discussion by the Subgroup related to possible designs and implementation of an alternate VOC speciation reporting system.

In the end, the Subgroup recommended adoption by the NPRI of an alternate approach to VOC speciation reporting based on a *specified* list of individual VOCs or groups of compounds. This recommendation was accepted by the Work Group and subsequently by Environment Canada (Environment Canada, 2002, 2003). The rest of this paper describes the design and implementation of this new VOC speciation reporting approach.

DESIGN OF A SPECIFIED-LIST VOC REPORTING SYSTEM

One of the first tasks of the Subgroup was to discuss how an alternate VOC speciation reporting approach might work. The Subgroup wrestled with the question of whether a facility required to report speciated VOC emissions to the NPRI should do so on the basis of a specified VOC list or a fixed VOC "capture fraction". In the case of a specified list, a facility would report any emissions above a specified threshold of a set of VOC species contained on a list of "priority" VOCs expected to be responsible for a large fraction of both VOC mass emissions and ozone- and PM-formation potential in Canada. This approach would be very similar to existing NPRI practice, as the pre-2002 NPRI already required releases of 111 individual VOC species and groups of species to be reported (e.g., 1,1,2-trichloroethane, aniline and its salts, chlorobenzene, isomers of xylene). In the case of a fixed VOC capture fraction, a facility would report the emissions of that set of VOC species that explained at least a specified fraction of the facility's total VOC emissions. This approach might also be called an "open" list since the set of species reported would vary from facility to facility and could not be specified beforehand.

The advantages and disadvantages of the two types of list were discussed. First, a specified-list approach permits ozone- and PM-formation potential to be considered, unlike an open-list approach, which is not able to guarantee capture of those species responsible for a specified level of ozone- and PM-formation potential. Second, some of the available VOC speciation profiles also include a large "other" or "unknown" component that might be larger than the required capture fraction for an open list. And third, an open-list approach is open-ended and would not provide an explicit "upper limit" to the effort required to report speciated VOCs. A specified-list approach, on the other hand, carries the risk that the methodology used to determine the list might itself be flawed, so that when applied the specified list of VOC species might fail to deliver the expected capture fractions for VOC mass emissions and for ozone- and PM-formation potential. It also provides no assurance that a minimum VOC capture fraction will be achieved for any particular geographic region or source sector. After weighing these strengths and weaknesses, the Subgroup opted for the specified-list approach, but it also recommended that in view of the novelty of the approach that its performance be reviewed after implementation and that modifications be made as necessary.

The two main assumptions underlying the new specified-list approach were that:

- A large fraction of the total VOC emissions from most facilities can be explained by a relatively small number of individual VOC species or groups of species; and
- Speciating a large fraction, but not all, of the total VOC mass emissions should be sufficient for AQ modeling.

In order to ensure the validity of the second assumption, three design criteria were specified:

- The VOC species reported should also capture a large fraction of the ozone- and PM-formation potential of the total VOC emissions from all regions of Canada and from all major source sectors;
- The VOC species reported should include a large number of the most common VOC species measured in ambient air in Canada;
- Any alternate VOC speciation reporting system should be at least as good as the *status quo* approach (where "good" is an indication of the completeness and accuracy of the speciation achieved).

As will be described next, a number of analyses were carried out to develop a specified list and to examine these various assumptions and criteria.

Identification Of Candidate Species For VOC Specified List

A number of lists of VOC candidates for the specified list were first prepared through a national analysis of the 1995 Canadian CAC inventory. The Residual Discharge Information System II (RDIS-II) database is used by EC to create and maintain national CAC emission inventories for different base years for point, area, mobile, and natural sources. In order to build a list of candidate VOC species for the specified list based on a ranking by mass emission, total-VOC emissions contained in the 1995 RDIS-II database were speciated using the VOC speciation-profile library and source-type/profile cross-reference file from the U.S. EPA's SPECIATE3.0 VOC and PM speciation package. (SPECIATE3.1 was also available but was not used as it does not contain a source-type/profile cross-reference file.) The SPECIATE3.0 profiles were first adjusted to remove non-VOC species based on the proposed VOC definition from the *Canada Gazette* (Government of Canada, 2001), which is very similar to the U.S. EPA definition. The percentages for the remaining species were then prorated so that they summed to 100% (allowing for round-off errors).

Speciated VOC emissions by mass were estimated for both point sources and for a select group of area sources that could potentially report to the NPRI (e.g., upstream oil & gas activities, solvent use). Note that the solvent-usage sector received special treatment since Environment Canada has reports on which types of solvents were used in Canada in 1995. Emission values for individual VOCs were extracted directly from these reports instead of applying SPECIATE3.0 profiles for solvent usage. The combined analysis using the reports on solvent usage and speciation profiles for all other source types yielded a total of 572 VOC species or groups of species emitted by point and selected area sources.

The two resulting speciated VOC emission lists, one for point sources and one for area sources, were next sorted by mass emission in descending order and cumulative total-VOC emissions were calculated. It was then possible to identify the species with the highest emissions that contributed to 80%, to 85%, and to 90% of the total VOC mass emissions. For the Canadian point sources contained in the RDIS-II database, 34, 47, and 66 VOC species or groups of species (e.g., isomers of heptane) accounted for 80%, 85%, and 90% of the total VOC emissions by mass from point sources. The corresponding numbers for the selected area sources were 16, 21, and 31. The two lists were then merged to create a third, sorted mass-emissions list in which 46, 58, and 80 VOC species accounted for 80%, 85%, and 90% of the total VOC emissions by mass from both point and area sources. Note that the species in the list were based on the SPECIATE3.0 speciation-profile library and are not always independent (e.g., methyl heptanes vs. isomers of octane).

Assessment Of Ozone-Formation And PM-Formation Potential

Mass emission values alone do not necessarily reflect the potential of a VOC species to contribute to the formation of ozone or particulate matter. For example, based on the analysis of the 1995 RDIS-II database just discussed, the VOC species with the largest overall emissions for both point and area sources is propane, but propane is neither very reactive nor likely to contribute directly to PM formation. To address this issue, three VOC physico-chemical properties were selected and then used as weighting factors to re-rank the mass-emission-ranked VOC list for ozone-formation potential and for PM-formation potential. The three properties selected were gas-phase OH reactivity (i.e., kOH), solubility in water, and condensability (defined as the reciprocal of saturation vapour pressure (SVP) with respect to pure liquid).

Reactivity is one measure of the ozone-forming potential of a VOC species. The product of kOH and a VOC concentration (in moles) gives an estimate of initial organic-radical (RO_2) production. This product is used in this case only as a relative indicator of the initial oxidation reaction of the emitted compound. In actual fact, reactive AQ models take into account many additional factors such as reaction length (includes subsequent reaction pathways), species availability, and the impact of other oxidants, temperature, and sunlight when estimating ozone levels. The reactivity weighting was performed by dividing the emitted VOC species mass by the molecular weight of the species and then multiplying it by the kOH reactivity value (molecules cm^{-3} s^{-1}).

Solubility in water and condensability were used as measures of PM-formation potential. Tropospheric PM generally contains some amount of water, and soluble VOC species can dissolve in this aerosol-bound water, thus adding to PM mass. VOC species with low saturation vapour pressures are said to be semi-volatile since they typically are present in the atmosphere in both the gas phase and condensed phase. Thus even if they are emitted in the gas phase, condensable VOCs have the potential to partition to atmospheric PM. The solubility weighting of each VOC species was performed by dividing the mass emissions of the species by its molecular weight and then multiplying by the species solubility. The condensability weighting was applied by dividing the emitted mass of each species by its molecular weight and then dividing by the SVP value.

Species-specific reactivity, condensability, and solubility values were obtained from a VOC database prepared by the Meteorological Service of Canada (MSC). OH reactivities were provided for both individual VOCs (when available) and for 81 VOC compound groups defined by MSC (see Makar et al., 2003). These compound groups are composed of VOC species that have similar chemical structures and properties. Species-specific reactivities were only available for about 35% of the 980 VOC species listed in the MSC database while surrogate values based on membership in one of the 81 groups and the representative reactivity value for that group were used for the remainder. On the other hand, individual reactivities were available for about 45% of the species in the RDIS-II database analysis, possibly because the speciation profiles used tended to include better characterized compounds. Similarly, species-specific aqueous solubilities and SVPs were used when available; for the remainder, the MSC assignment to the 81 groups of VOC compounds was used to assign a surrogate value equal to the aqueous solubility or SVP for a structurally-similar and representative compound.

Re-ranking the VOC mass emissions lists by applying each of these three weighting factors made a considerable difference. For example, for the reactivity-weighted point-source VOC list, the number of VOC species needed to explain 80%, 85%, and 90% of the reactivity-weighted mass emissions was only 18, 25, and 38 species as compared to the 34, 47, and 66 species needed to explain the same percentages of mass emissions. Propane dropped from first place on the point-source mass emissions list to 15th place while aniline rose from 19th place to second place. For the solubility-weighted and condensability-weighted point-source VOC lists, a handful of species accounted for 80%, 85%, and 90% of the weighted emissions: 3, 4, and 6 species and 3, 5, and 6 species, respectively. The area-source VOC list experienced comparable re-rankings.

Ranked-List Mergers And Reduction Of Size Of Master Species List

There is considerable commonality of species between the eight lists described above that were constructed for the two primary source types (point and area) and four weight factors (mass, reactivity, solubility, condensability). The next step was to prepare a consolidated "master" VOC species list by combining all eight tables into one. Where a species was important at the 80% level on one list but was only important at the 90% level on a second list, the higher importance rating (i.e., lower percentage value) was retained. One result is that the consolidated list of 80% species now accounts for more than 80% of the mass emissions, more than 80% of the reactivity-weighted emissions, more than 80% of the solubility-weighted emissions, and more than 80% of the condensability-weighted emissions because the consoliated 80% list contains more species than any of the lists for a single weighting factor. The consolidation was carried out in two steps: first, the four weighted lists for the point sources were combined and the four weighted lists for the area sources were combined. For the Canadian point sources contained in the RDIS-II database, 37, 52, and 76 VOC species or groups of species accounted for 80%, 85%, and 90% of the total VOC emissions from point sources for all four weightings. The corresponding numbers for the selected area sources were 23, 29, and 42. The two lists were then merged to create a third, sorted mass-emissions list, in which 58, 78, and 111 VOC species accounted for 80%, 85%, and 90% of the total VOC emissions from both point and area sources for all four weightings.

At this stage there was a need to condense the master VOC species list in order to minimize overlap and maximize consistency based on structural similarities. For example, in some cases both individual species and the isomer group for the same species were present on the list (e.g., 2,4-Dimethylpentane and Isomers of Heptane); in this case, the individual compound was subsumed into the larger isomer group. In other cases, both smaller and larger subsets of the same isomer group were present (e.g., Methylcyclopentenes and Isomers of Hexene); again, the smaller subset was subsumed into the larger one. In other cases, synonyms for the same species had been used in different speciation profiles (e.g., C5 Olefins and Isomers of Pentene); in these instances, one name was chosen. And in other cases, it was not clear from the speciation-profile species name whether an individual species or isomer group was intended (e.g., Ethyldimethylbenzene); in these cases, the isomer group was assumed. The only exceptions that were made (for backward compatibility) were for species that were already on the pre-2002 NPRI substance list. Three species fell into this category: Cyclohexane; *n*-Hexane; and 1,2,4-Trimethylbenzene; all belong to isomer groups, but both they and their isomer groups appear in Tables 1 or 2. This condensation step reduced the number of table entries from 111 to 87.

The condensed master VOC list now contained all individual VOCs or groups of compounds identified as being important up to the 90% level. The final step was to decide on which specified percentage range (80%, 85%, or 90%) to use as a cut-off for membership in the VOC specified list. Different Subgroup members advocated different range choices, and in the end, Environment Canada selected 85% as the cut-off percentage-range value.

CHARACTERISTICS OF THE SPECIFIED VOC LIST

Table 1 lists all 60 of the 80% and 85% VOC species from the master list sorted alphabetically within three primary groupings: 34 of the entries are individual VOCs, 20 are VOC isomer groups, and the remaining 6 are other compound groups and mixtures. The *second* column of the table gives the Chemical Abstracts Service (CAS) registry number, a unique identifier for a chemical compound or group of compounds. The CAS number is important because many VOC species have more than one accepted chemical name: for example, 1,3-butadiene, CAS number 106-99-0, is also known as vinyl ethylene, biethylene, and bivinyl. In fact, some facilities (e.g., automobile assembly plants, chemical production plants) employ CAS numbers as tracking numbers in their facility-level environmental accounting and reporting systems, especially for solvent and paint use. The *third* column of Table 1 indicates whether the species was one of those needed to explain either the first 80% of the total VOC mass or reactivity-weighted or solubility-weighted or condensability-weighted emission (45 species) or else the next 5% (15 species). The *fourth* column gives the chemical formula for the individual compounds and the isomer groups. The last six entries in Table 1 do not have unique chemical formulas as they are complex and variable mixtures of many VOCs. For example, the last five entries are all types of mineral spirits, which are "derived from the light distillate fractions during the crude oil refining process and are composed of C6-C11 compounds, with the majority of the relative mass composed of C9-C11" (U.S. NPS, 1997). Finally, the *last* column gives the number of members belonging to each entry. The first 34 VOCs listed in Table 1 are individual VOC species so that each is a single member and has an entry of "1" in this column. For the isomer groups, however, this column gives the number of CAS numbers corresponding to the same chemical formula. For example, butane only has two isomers, *n*-butane (CAS number 106-97-8) and isobutane (CAS number 75-28-5), but decane, the C10 alkane, has 31 CAS numbers associated with it, including *n*-Decane, Isodecane, five methylnonanes, and a variety of methylated and ethylated octanes, heptanes, and hexanes.

In total, there are 218 compounds and/or CAS numbers associated with the 20 isomer-group entries in Table 1. If all of these group members are considered, then Table 1 is made up of 258 VOC species. Note that while many of these VOC species are new to the NPRI, 20 of the 60 entries in Table 1 were also listed on the pre-2002 NPRI. As a result, implementation of this alternate VOC speciation reporting approach has added another 40 species or compound groups to the specified list of 263 NPRI substances in place before 2002, 111 of which are VOCs (Environment Canada, 2003).

Table 2 has the same format as Table 1. It contains an additional 27 species that were found from the RDIS-II database speciation analysis to account for the next 5% of the total VOC mass or reactivity-weighted or solubility-weighted or condensability-weighted emissions. Thus the 87 VOC species or species groups in Tables 1 and 2 together account for 90% of total VOC emissions from all Canadian point and selected area sources in the 1995 CAC inventory on the basis of the above analysis. Eleven of the 27 entries in Table 2 were also listed in the pre-2002 NPRI substance list.

Tables 1 and 2 also support one of the assumptions underlying the specified-list approach, that a relatively small number of VOC species or groups can explain a large fraction of total VOC mass emissions and a large fraction of ozone- and PM-formation potential. This is suggested by the larger number of species appearing in each additional increment of cumulative total VOC emissions in the ranked lists: that is, 45 VOC species or groups account for the first 80% of total VOC emissions, 15 more species account for the next 5%, 27 more species account for the next 5%, and so on, so that the last 1% of total VOC emissions is made up of hundreds or even thousands of species.

ANALYSIS OF REPORTING THRESHOLDS

One way the NPRI has balanced the information needs of inventory users with the administrative burden on facilities reporting to the NPRI is to set a reporting "trigger" or threshold for each substance. Facilities that have emissions of a substance at a lower level than the trigger are not required to report their emissions of that substance. These thresholds have two main benefits for reporters: very small emitters may be excluded from reporting; and even large facilities need not spend a large amount of effort quantifying emissions for particular substances if they have no reason to expect that their emissions of those species would be above the reporting threshold. There is clearly some loss of information reported to the NPRI, but if the reporting threshold has been set reasonably, then the magnitude of the unreported emissions is expected to be a small fraction of the reported emissions for each substance.

The reporting trigger that was set for the NPRI for total-VOC emissions to air is 10 tonnes per year (Government of Canada, 2001). The trigger value of 10 tonnes was agreed to based on an analysis of the RDIS-II database for 1995 Canadian point-source VOC emissions for a range of reporting thresholds and stakeholder consultations.

A similar analysis was carried out in the context of reporting individual VOC species or groups on the specified VOC list on the basis of the arguments above. An additional reason to consider such a reporting "*de minimus*" for individual VOCs is that the individual VOCs on the specified VOC list that were also on the pre-2002 NPRI substance list already have a *manufacture, process, or otherwise use* (MPO) reporting threshold of 10 tonnes. The possible *de-minimus* threshold values considered ranged from 0 to 10 tonnes. The RDIS-II database analysis suggested that only marginal improvements in reporting coverage were obtained for thresholds smaller than 1 tonne (see Appendix E, Environment Canada, 2003), so the Subgroup recommended a one-tonne release to air per annum as the *de minimus* for reporting individual VOC emissions under the VOC speciation requirement. If a facility chooses to, however, it may report emissions of VOCs on the specified list even if they are below the reporting threshold.

One final aspect related to speciated VOC reporting concerns the unspeciated component, that is, the difference between a facility's reported total-VOC emissions to air and the total of its reported speciated VOC emissions to air. The NPRI reporting software will ask a reporter to characterize the overall reactivity of the unspeciated VOC component: the four possible responses are expected to be "high", "medium", "low", and "insufficient information to assess".

CROSS-CHECKS

As discussed in the next section, there are a number of limitation and uncertainties associated with the methodology used to prepare Tables 1 and 2. It is thus useful to try to check the accuracy, consistency, and completeness of the results obtained via the RDIS-II database speciation analysis. Three independent data sets and one related data set were compared with Tables 1 and 2.

Comparison To Pre-2002 NPRI VOC Emissions

As summarized in Table E-3 of Environment Canada (2003), before the 2002 reporting year the NPRI specified list of substances had 263 entries, including 111 VOC species or species groups. Tables 1 and 2 include 31 of these same pre-2002 NPRI VOC species. A comparison of the NPRI emissions of these 31 species for reporting year 2000 with the speciated RDIS-II VOC emissions for 1995 shows the NPRI emission values for most of the 31 species to be 10-20% of those from the CAC inventory, although emissions of toluene, xylene, and methyl ethyl ketone are comparable (within 10%, 35%, and 10%). Two key differences between the two inventories may be partly responsible for the lower NPRI emission values: (1) fewer facilities reported to the 2000 NPRI inventory than to the 1995 CAC inventory (~2,500 vs. ~5,000); (2) substances reported to the NPRI have a 10-tonne-per-year *manufacture, process, or otherwise use* (MPO) reporting threshold vs. the previous, unofficial CAC reporting threshold of emission of 100 tonnes per year to air of any of the criteria air contaminants, including total VOCs (i.e., if emissions of one CAC species are greater than 100 tonnes y^{-1}, then emissions of all seven CAC species are reported).

Comparison To Industry-Supplied Species Lists

Five industry associations participating in the Subgroup submitted lists of VOC species thought to be emitted at one or more of their members' facilities. The lists contained VOCs emitted by petroleum refineries, chemical plants, wood-product facilities, crude-oil production from oil sands, and automobile manufacturing. These five lists, which contained 60, 144, 114, 814, and 36 species by name, respectively, were compared by eye with the 87 VOC species in Tables 1 and 2 to see how much commonality there was between the industry-specific lists and the national specified list. Individually, 23, 33, 31, 14, and 12 species matches were identified between the five industry lists and Tables 1 and 2. After combining the five lists and removing duplicates, there were found to be a total of 49 VOC species from Tables 1 and 2 that appeared on at least one of the five industry lists.

Ambient Measurements

Measurements of the abundances of VOC species in ambient air followed by identification of the most common ones can provide one independent check on the specified list of VOCs obtained from emission-inventory-based calculations (e.g., Cardelino and Chameides, 2000; Watson et al., 2001). CCME (1997) contains three tables listing the most abundant VOC species at Canadian sites in the early 1990s sorted by both "plain" mixing ratio and by propylene-equivalent-factor-weighted mixing ratio (another ozone-formation-potential weighting). The measurement sites were segregated into three groups: (1) point-source impact sites; (2) "carbonyl" sites; and (3) rural sites. For species sorting by mixing ratio, species and compound groups from Table 1 of this paper made up 25 of 29, 22 of 28, and 18 of 19 of the most abundant VOC species measured at the three groups of sites (plus 4, 5, and 0 Table 2 species and 0, 1, and 1 other pre-2002 NPRI substances not included in Tables 1 or 2). For species sorting by propylene-equivalent mixing ratio, the Table 1 species made up 24 of 30, 22 of 30, and 17 of 20 of the most abundant VOC species measured at the three groups of sites (plus 5, 5, and 0 Table 2 species and 1, 3, and 1 other pre-2002 NPRI substances). The two measured ambient species (in the propylene-equivalent table for rural-site measurements) that were not included in Tables 1 or 2 or the pre-2002 NPRI VOC species were both isomers of octene. These high inclusion rates suggest that the specified-list VOC species do represent many of the most commonly emitted VOC individual species or species groups in Canada (and likely the northern tier of U.S. states given the location of many of the measurement sites close to the Canada/U.S.A. border).

Comparison To VOC Speciation Estimates For The Windsor-Quebec City Corridor

A second RDIS-II database speciation analysis was carried out for the region of Canada known as the Windsor-Quebec City corridor (WQC). The WQC is a long, narrow area (roughly 1200 km x 200 km) of southeastern Canada extending from Windsor/Detroit in the southwest to Montreal and Quebec City in the northeast. The WQC is also the most densely populated and industrialized region of Canada. All of the species listed in Tables 1 and 2 also appeared at the 80%, 85%, or 90% level for the WQC, but nine additional VOC species were identified in this regional analysis at the 90% level (Environment Canada, 2003). Similar analyses and comparisons are needed for other Canadian regions.

IMPLEMENTATION ISSUES

The introduction of this new VOC speciation reporting system into the NPRI inventory process will require considerable effort. To begin with, although the inclusion of point-source CAC reporting in the NPRI reporting system took place for the 2002 reporting year (Government of Canada, 2001), the consultations on how to include CAC speciation in the new inventory required extra time. VOC speciation reporting is thus a new NPRI requirement beginning with the 2003 reporting year (Government of Canada, 2003). Given the NPRI reporting cycle, this means that speciated VOC emissions to air will first be reported to NPRI by June 1st the following year (2004). Before then, a guidance document will need to be developed and distributed to NPRI reporters. It might also be necessary to develop and distribute a VOC speciation "tool", which would follow the "status quo" approach of applying process-specific speciation profiles to process-level total VOC emissions and would be intended for use primarily by those facilities with less expertise.

An additional implementation issue associated with this new VOC speciation reporting system will arise when the 2003 NPRI-derived point-source inventory is processed by emission modelers. That is, how will the reported facility-level speciated VOC emissions together with the total VOC emissions be handled by current emissions processing systems (EPSs) such as CEPS and SMOKE (e.g., Moran et al., 1997; Scholtz et al., 1999; Houyoux, 2000)? Current EPSs usually have the capability to apply facility-specific temporal and speciation profiles. One possible solution, then, is to pre-process the NPRI speciated VOC emissions and total VOC emissions reported for each facility and create facility-specific VOC speciation profiles in the format used by the EPS of interest. The profiles would include an "other" or "unknown" species to account for the difference between the total VOC emissions reported by a facility and the speciated VOC emissions. These facility-specific VOC profiles could then be appended to the EPS speciation profile library and the speciation cross-reference file modified to link the Canadian point sources to these profiles. The EPS would then speciate the total VOC emissions for these facilities based on the speciated VOC emission values reported by the facilities to the NPRI.

DISCUSSION

The analyses described above most definitely have methodological limitations, but these largely reflect limitations in the current state of the science for VOC speciation, emissions processing, and AQ modeling. For example, a key component of the RDIS-II database speciation analysis was the VOC speciation profile library. The SPECIATE3.0 profile library contains 610 unique profiles, but the U.S EPA's Source Classification Code library contains more than 7,000 SCC and ASC codes for different source types. Clearly, many VOC source types lack appropriate speciation profiles. For example, the Subgroup heard that no existing speciation profiles are appropriate for crude-oil extraction from the oil sands in northern Alberta, and the few profiles that are available for pulp and paper mills are probably not representative. At the same time, some sectors may have multiple profiles (e.g., petroleum refineries), and then it is necessary to select one profile as being the most representative.

In addition, many of the existing profiles are old or of poor quality or both. One reason that the age of a profile is a concern is that formulations of some industrial products such as solvents and paints may change very quickly. In addition, many profiles, especially older profiles, do not reflect a source operating with current pollution-control equipment or Canadian-specific process variations. In terms of profile quality, one analysis carried out for the Subgroup considered the U.S. EPA quality ratings ('A' to 'E' plus 'Unknown') for the various SPECIATE3.0 speciation profiles used in the RDIS-II database speciation analysis. It was found that in speciating the 1995 VOC emissions from Canadian point sources, approximately 0% of the VOC emissions were speciated using profiles with an 'A' quality rating ("very good"), 8% using profiles with a 'B' rating ("good"), 35% using profiles with a 'C' rating ("reasonable"), 12% using profiles with a 'D' rating ("possibly unrepresentative"), 43% using profiles with an 'E' rating ("questionable"), and 3% using profiles with an 'Unknown' rating.

There is also a lack of physico-chemical data for many VOC species, including their gas-phase reactivity, aqueous solubility, and saturation vapour pressure. In the case of isomer groups, the values used for their reactivity, solubility, and condensability weights were based on the properties of one or two representative species from each group. This is of note because the properties of individual isomers can vary significantly from those of other members of the same group. On the other hand, for the 34 individual VOCs listed in Table 1, individual reactivity values were available for all but four of them (Adipic Acid, 2-Methyl-3-Hexanone, Phenyl Isocyanate, and Trimethylfluorosilane) and individual solubility and condensability values were available for all but four of them (*n*-Hexane, 2-Methyl-3-Hexanone, Myrcene, and Trimethylfluorosilane).

The fact that so few species were identified at the top of the solubility- and condensability-weighted rankings does raise the question as to whether these properties were the best surrogates to use for PM formation potential, since other VOC species might also contribute, in some cases after chemical transformation (i.e., secondary-organic-aerosol formation). On the other hand, while they may not be perfect, these lists do draw attention to some species of particular interest for primary PM formation based on their chemical and physical properties (i.e., high solubility or low volatility). Also, many of the VOCs that have been identified to date as probable secondary-organic-aerosol precursors are highly reactive compounds and will be included in the specified list for this reason if their emissions are large enough (e.g., Alpha-Pinene, Beta-Pinene, D-Limonene, Toluene, Xylene, Terpene, Trimethylbenzene: see Table 5 of Makar et al., 2003).

CONCLUSIONS

The new NPRI VOC speciation reporting requirement described in this paper was arrived at after extensive consultations with Canadian emission inventory stakeholders, including industry, environmental organizations, AQ modelers, and other levels of government. It represents a considerable departure from what has been done in the past by inventory developers to provide VOC-speciation information to AQ modelers and other inventory users. Given the premise, however, that facilities themselves are likelier to have better knowledge of their own emissions than a central agency, this new approach has the potential to provide NPRI users with better speciated VOC data.

One design goal in creating the new reporting system was that it should be at least as good as the previous process-reporting-based system in terms of the completeness and the accuracy of the resulting VOC speciation. In fact, the analyses employed to develop the VOC specified list described in this paper were themselves based on the previous VOC speciation reporting system, and it was clear from the discussions of the analysis results within the CAC Speciation Subgroup that the previous system has significant limitations, including a lack of appropriate speciation profiles for many source types and dated or poor-quality speciation profiles.

At the same time, however, these same limitations create the risk that the implementation of the new reporting system may itself be flawed, especially in the choice of the set of VOC species on the specified list. Additional uncertainties were introduced in the analysis for the specified list by the lack of physico-chemical data for many VOC species. However, a number of pre-implementation cross-checks were carried out that provide some support for the specified VOC list that has been developed.

The new VOC reporting system also adds greater complexity and imposes a greater burden both on NPRI reporters and on Environment Canada. For example, it is expected that it will take time for reporters to become familiar with the new requirements and procedures. Environment Canada also needs to make both guidance and tools available to assist reporters with the new requirements and to strengthen its quality assurance and quality control procedures for checking submitted emission reports.

The Speciation Subgroup recognized these concerns and recommended that NPRI revisit VOC speciation in subsequent years to ensure that the new framework is achieving its goals. For example, the VOC specified list will likely evolve over time as conditions change or as new information comes to light. For example, if too small a percentage of the total-VOC emissions being reported are speciated, either nationally or regionally or sectorally, then it may be necessary to increase the number of species on the VOC specified list by raising the cut-off value for the specified list from 85% to 90%. The first reporting of speciated VOC emissions to NPRI under this new system will occur for the 2003 reporting year, so it will be several years before the new system can be evaluated and its success judged. In the meantime, some aspects of the work described herein may provide useful information for any other agencies wishing to improve the treatment of VOC speciation in emission inventories.

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Table 1. Specified list for VOC speciation reporting at 85% level.

Substance Name	CAS	Percentile	Structure	# Compounds
Individual Species				
Acetylene	74-86-2	80%	C2H2	1
Adipic Acid	124-04-9	85%	C6H10O4	1
Aniline	62-53-3	80%	C6H7N	1
Benzene	71-43-2	80%	C6H6O	1
1,3-Butadiene	106-99-0	80%	C4H6	1
2-Butoxyethanol	111-76-2	80%	C6H14O2	1
***n*-Butyl Acetate**	123-86-4	80%	C6h12O2	1
Chlorobenzene	108-90-7	85%	C6H5Cl	1
p-Dichlorobenzene	106-46-7	85%	C6H4Cl2	1
Dimethylether	115-10-6	80%	C2H6O	1
Ethyl Acetate	141-78-6	85%	C4H8O2	1
Ethyl Alcohol	64-17-5	80%	C2H6O	1
Ethylene	74-85-1	80%	C2H4	1
Ethylene Dichloride	107-06-2	85%	C2H4Cl2	1
Formaldehyde	50-00-0	80%	CH2O	1
***n*-Hexane**	110-54-3	80%	C6H14	1
Isopropyl Alcohol	67-63-0	80%	C3H8O	1
D-Limonene	5989-27-5	80%	C10H16	1
Methyl Alcohol	67-56-1	80%	CH4O	1
Methyl Ethyl Ketone	78-93-3	80%	C4H8O	1
Methyl Isobutyl Ketone	108-10-1	85%	C6H12O	1
2-Methyl-3-Hexanone	7379-12-6	80%	C7H14O	1
Myrcene	123-35-3	80%	C10H16	1
Beta-Phellandrene	555-10-2	85%	C10H16	1
Phenyl Isocyanate	103-71-9	80%	C7H5NO	1
Alpha-Pinene	80-56-8	80%	C10H16	1
Beta-Pinene	127-91-3	80%	C10H16	1
Propane	74-98-6	80%	C3H8	1
Propylene	115-07-1	80%	C3H6	1
Styrene	100-42-5	80%	C8H8	1
Toluene	108-88-3	80%	C7H8	1
1,2,4-Trimethylbenzene	95-63-6	80%	C9H12	1
Trimethylfluorosilane	420-56-4	80%	C3H9FSi	1
Vinyl Acetate	108-05-4	85%	C4H6O	1
Isomer Groups				
Anthraquinone (Mixed Isomers)	*	80%	C14H8O2	3
Butane (Mixed Isomers)	*	80%	C4H10	2
Butene (Mixed Isomers)	25167-67-3	80%	C4H8	6
Cycloheptane (Mixed Isomers)	*	80%	C7H14	10
Cyclohexene (Mixed Isomers)	*	85%	C6H10	5
Cyclooctane (Mixed Isomers)	*	80%	C8H16	25
Decane (Mixed Isomers)	*	85%	C10H22	31
Dihydronapthalene (Mixed Isomers)	*	85%	C10H10	2
Dodecane (Mixed Isomers)	*	85%	C12H26	9
Heptane (Mixed Isomers)	*	80%	C7H16	13
Hexane (M. I., Excl. *n*-Hexane)	*	80%	C6H14	6
Hexene (Mixed Isomers)	25264-93-1	85%	C6H12	17
Methylindan (Mixed Isomers)	27133-93-3	85%	C10H12	2
Nonane (Mixed Isomers)	*	85%	C9H20	38

Substance Name	CAS	Percentile	Structure	# Compounds
Octane (Mixed Isomers)	*	80%	C8H18	23
Pentane (Mixed Isomers)	*	80%	C5H12	4
Pentene (Mixed Isomers)	*	80%	C5H10	10
Terpene (Mixed Isomers)	68956-56-9	80%	C10H16	1
Trimethylbenzene (M. I. Excl. 1,2,4)	25551-13-7	80%	C9H12	3
Xylene (Mixed Isomers)	1330-20-7	80%	C8H10	4
Other Compound Groups and Mixtures				
Creosote	8001-58-9	80%		1
Heavy Aromatic Solvent Naphtha	64742-94-5	80%		1
Light Aromatic Solvent Naphtha	64742-95-6	80%		1
Mineral Oil Spirits	64475-85-0	80%		1
Naphtha	8030-30-6	80%		1
Stoddard Solvent	8052-41-3	80%		1

Table 2. Additional species to bring Table 1 to 90% reporting level.

Substance Name	CAS	Percentile	Structure	# Compounds
Individual Species				
Acetaldehyde	75-07-0	90%	C2H4O	1
Acetic Acid	64-19-7	90%	C2H4O2	1
Acrolein	107-02-8	90%	C3H4O	1
n-Butyl Alcohol	71-36-3	90%	C4H10O	1
sec-Butyl Alcohol	78-92-2	90%	C4H10O	1
Cyclohexane	110-82-7	90%	C6H12	1
Dimethylamine	124-40-3	90%	C2H7N	1
Ethylbenzene	100-41-4	90%	C8H10	1
Ethylene Glycol	107-21-1	90%	C2H6O2	1
Hexafluoroethane	76-16-4	90%	C2F6	1
Hexamethylenediamine	124-09-4	90%	C6H16N2	1
Methyl Formate	107-31-3	90%	C2H4O2	1
Methylhexanal	19269-28-4	90%	C7H14O	1
Phenol	108-95-2	90%	C6H6O	1
Trichloroethylene	79-01-6	90%	C2HCl3	1
Trimethylpentadiene	756-02-5	90%	C8H14	1
Vinyl Chloride	75-01-4	90%	C2H3Cl	1
Isomer Groups				
Butylbenzene (Mixed Isomers)	68411-44-9	90%	C10H14	4
Cycloheptene (Mixed Isomers)	*	90%	C7H12	8
Cyclohexane (M.I., Excl. Cyclohexane)	*	90%	C6H12	6
Dimethylindan (Mixed Isomers)	53563-67-0	90%	C11H14	5
Ethyldimethylbenzene (M. I.)	*	90%	C10H14	6
Ethyltoluene (Mixed Isomers)	25550-14-5	90%	C9H12	4
Undecane (Mixed Isomers)	*	90%	C11H24	11
Other Compound Groups and Mixtures				
Glycolethers, Esters	*	90%		19
Solvent Naphtha Light Aliphatic	64742-89-8	90%		1
VM & P Naphtha	8032-32-4	90%		1

KEYWORDS

organic compounds
speciation
emissions processing
reactivity
condensability
solubility
VOC
organic particles
PM formation
ozone formation
isomer group
compound group
VOC mixture