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Project Summary

Methodology for Estimating Environmental Loadings from Manufacture of Synthetic Organic Chemicals

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A methodology was developed for estimating the multimedia environmental loadings for a "new" chemical, in the absence of manufacturing plant emissions data. This methodology draws on a multimedia environmental release data base (ERDB) that contains information about structurally similar compounds that undergo similar process (physical and chemical) unit operations. The ERDB is integrated with other pertinent available data on the manufacturing process of the new chemical such as (1) physical and chemical properties of process feedstock, products, and byproducts; (2) reaction stoichiometry, thermodynamics, and reaction kinetics; (3) process flow diagram and process mass balance; (4) location and composition of environmental releases and method of disposal; (5) process environmental control technology (including performance); (6) process storage and handling requirements; and (7) plant equipment components (in numbers and classes).

In practice, sufficient direct data are rarely available for estimating the environmental loadings of a compound under review. In every case where data deficiencies are likely to occur, the methodology suggests alternative means for filling the data gaps. The methodology integrates all pertinent data to enable the user to estimate controlled and uncontrolled loadings under the classifications of storage and handling, process, and fugitive emissions. An example is provided to demonstrate the applicability of the methodology.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The conduct of an exposure assessment requires reliable environmental release data, especially for new chemicals. These chemicals are frequently referred to as pre-manufacturing notice (PMN) chemicals because of the requirement that an industry must inform the U.S. Environmental Protection Agency (EPA) of its plan to manufacture a new compound.

This report presents a methodology that can be used to determine population exposure and to identify the most suitable control options. Determination of the environmental loadings associated with the production of a "new" compound is aided by classifying these loadings as storage and handling emissions, process releases, and fugitive emissions

For a precise determination of the environmental loadings associated with the production of a "new" compound, it usually is necessary to conduct a rigorous field monitoring survey. In the absence of plant data, which is usually the case for PMN chemicals, a confident estimate of plant emissions can be made by integrating data on:

- The manufacturing practices' and unit processes' multimedia environmental loadings for structurally similar compounds that undergo

analogous process (physical and chemical) unit operations.

- Physical and chemical properties of process feedstock, products, and byproducts.
- Reaction stoichiometry, thermodynamics, and reaction kinetics.
- Process flow diagram and process mass-balance.
- Location and composition of environmental releases and method of disposal.
- Process environmental control technology (including performance).
- Process storage and handling requirements.
- Plant equipment components (in numbers and classes).

In practice, available direct data on a compound under review are usually limited, and the methodology has been designed with this reality in mind (see Figure 1). In every case, where data deficiencies are likely to occur, alternative means are suggested for filling the data gaps.

Loading the ERDB

The first step in estimating the environmental release of a "new" chemical is the loading of the ERDB. This data base brings together available emissions data for the 23 major unit processes of the synthetic organic chemicals manufacturing industry (SOCMI).

The ERDB is organized into 23 categories that correspond to the 23 major large-volume SOCMI "unit process" components that carry out the fundamental synthesis reactions, e.g., alkylation, halogenation, polymerization. Conceptually, the unit process is useful in that for a given unit process, the physical or organic chemistry of the compounds within that unit process tends to be alike or similar. The significance of the process waste streams and the industrial importance of the compounds produced were also considered in the selection of the major unit processes.

Environmentally controlled and uncontrolled release data are presented for the three classes (process, storage and handling, and fugitive) in terms of the receiving medium (air, land, water). Process releases are further classified in terms of the unit operations that occasion the emissions. For each medium, the data source is identified along with an indication of whether quantified or unquantified data are available.

Reviewing the PMN

The second step of the methodology is to review the submitted PMN, which is

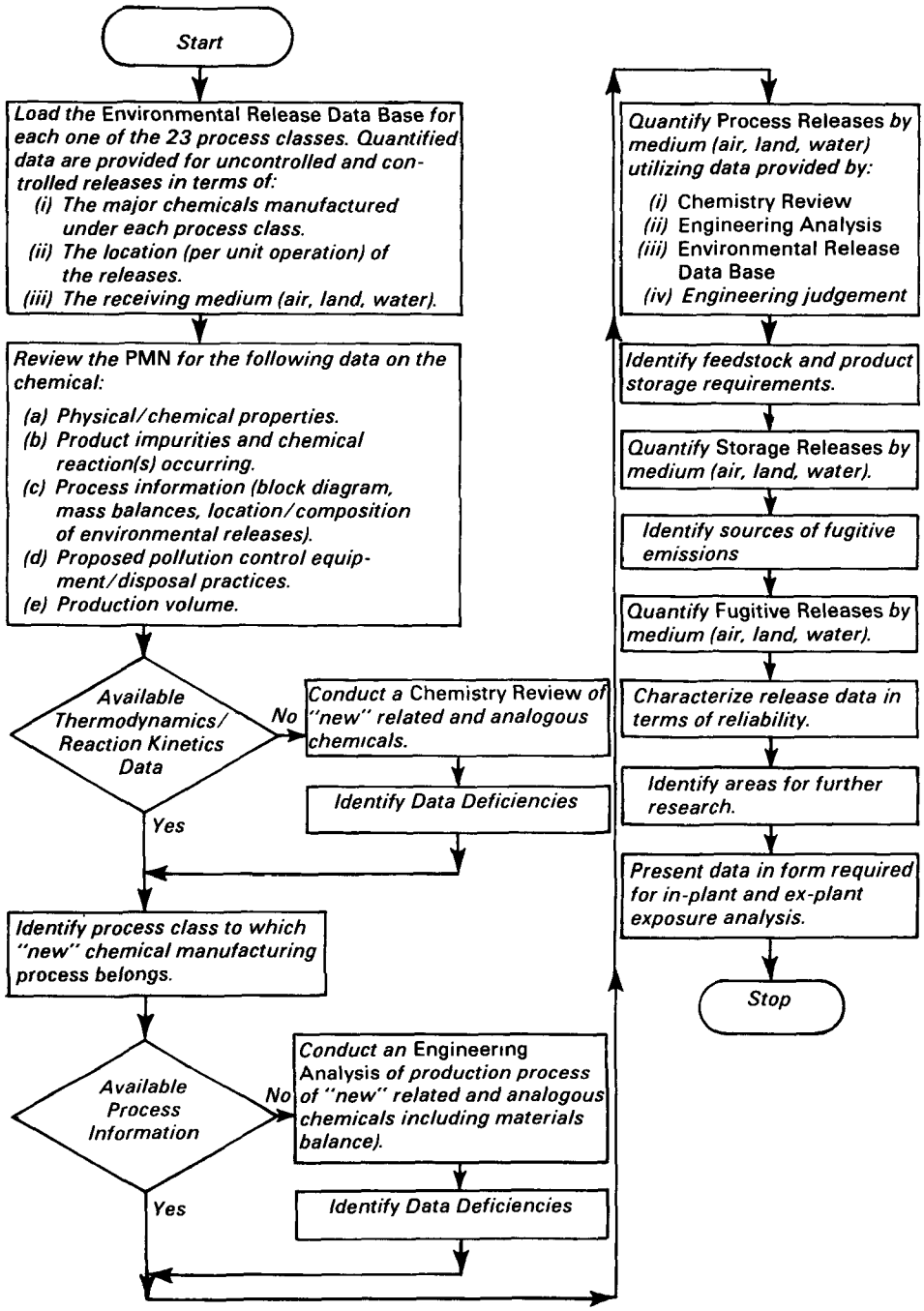

Figure 1. *Procedure for the determination of the environmental loading of a "new" chemical.*

submitted to EPA by the interested party at least 90 days before manufacturing of a new chemical is scheduled. Information supplied in PMNs varies from only enough data to fulfill the basic requirements of the Toxic Substances Control Act to data providing a total assessment of the chemical. The accuracy of estimations using the methodology will depend on the amount of information supplied. The single most important piece of data is the process flow diagram. Engineering estimates can not be expected to describe a process as accurately as the flow diagram. Information is also needed on the chemical byproducts and methods of disposal including pollution control equipment.

Conducting a Chemistry Review

Available information on the PMN chemical is reviewed as an aid in

calculating a materials balance and resultant emissions. Specific information is needed on chemical identities and structures, physical state of components at ambient conditions, vapor pressures, solubilities in water, production volume, and amounts or weights or mole percents entered or produced to yield production volume. Also required is information on chemical reaction(s) involved, side reaction(s), impurities formed, byproducts formed, percent yield of reaction, physical state of reaction, catalyst used (if any), temperature, and pressure.

The physical/chemical properties of PMN chemicals can be found in the PMN or the Consumers and Environmental Exposure Reports (CEER) prepared by the EPA's Office of Pesticides and Toxic Substance (OPTS). The physical properties, environmental fate and pathways, and health effects of PMN chemicals are estimated in these reports.

The production volume of the chemical is given in the PMN. The amounts of reactants entering can be determined from a mass balance provided with the PMN or by looking at the reaction stoichiometry. Values for the feedstock impurities, usually by weight percent, can be obtained from industry-related literature or from the feedstock producers. As much impurity information as possible should be obtained because feedstock impurities are either released or contribute to side reactions.

OPTS conducts a "chemical review" on all PMN chemicals, regardless of whether the reactions are offered in the PMN. Their results are issued in an Initial Review Chemistry (IRC) Report. For these studies, a chemist reviews related and structurally similar chemicals and their reactions, side reactions, impurities, and percent yields.

The reaction kinetics and thermodynamics, as determined by parameters such as the physical state of the reaction, its operating conditions, and the catalyst used, are usually hard to determine, but indicate the possible emission points and amounts. Generally, the phase in the reactor is not readily available information but sometimes can be deduced by looking at the physical state of the reactants and products at ambient conditions and the process flow diagram.

Conducting an Engineering Analysis

If a flow diagram is not available, an engineering analysis can produce a reasonable description of the process by reviewing patents of similar chemicals and using engineering judgement. EPA produces Engineering Review (ER) Reports as part of the PMN process. These reports review the block diagram when it is provided in the PMN and work out engineering analyses of possible flow diagrams when they are not provided with the PMN. Another flow diagram source is the construction permits that companies must submit to their State air pollution control boards before constructing or modifying a facility. These permits contain the proposed process flow construction or modification and the estimated resultant air emissions when in operation. Results using the methodology will not be as accurate without the actual flow diagram, however.

Determining Process Releases

The methodology addresses two procedures: (1) how to use the process flow diagram to identify release points from unit operations and unit processes, and (2) how to quantify the process releases once they have been identified. This produces a materials balance, an indication of where emissions might occur, and a quantification of the large process emissions. Figure 2 illustrates the procedures for quantifying process releases.

Qualitative Analysis of Releases

The environmental release points are identified by first looking at the ranking of releases of the 23 unit processes and seeing where the PMN chemical manufacturing process ranks, based on its type of unit process. This procedure is then repeated to identify the unit operations involved in the PMN process and to judge how serious their environmental releases may be. At best, process release ranking is a screening procedure to quickly eliminate processes and equipment that will have small releases. With this ranking, one knows how severe the possible air and water releases can be, based on the 23 unit processes, and also where efforts should be concentrated in estimating releases when reviewing the unit operations.

Because of the wide variation of behavior within each process class, unit operations must be analyzed in detail. The methodology presents tabular data listing the potential sources of release to air, water, and land from heating and cooling steps, reactors, product purification and separation unit operations. Fugitive emissions also occur from all unit operations as do releases when equipment is periodically cleaned.

Quantification of Releases

Releases are quantified by obtaining the material balance from which air emissions can be estimated for the large unit processes. All other releases can be found by analyzing each unit operation and applying the emission factor ranges given in the methodology. Data sources for the mass balance are the PMN and the ER and IRC reports. A mass balance is obtained for the reactor and each piece of separation equipment. Possible emission points for impurities and byproducts are also identified.

An inert-carrier gas method is used for estimating emissions from those unit processes that release the most air emissions. Emission projection by the inert-carrier gas method analyzes the feed impurities, the excess feed, and the percent yield of the reaction and multiplies these by the separation efficiency of the separation-recovery equipment.

The total gas flow rate and composition that will be emitted as a result of an inert-carrier gas process or an air-using process are estimated. These emissions are likely to occur from the reactor off-gas or its absorbers. A large amount of feedstock purity and separation efficiency data are required; if these can be provided then gaseous emissions can be quantified for this type of process.

In the absence of other methodologies for estimating emissions, one must use the ranges of releases to water and land from unit operations (emission factors) that the environmental release data base provides. These ranges are given for the unit operations for which there were data. If a unit operation does not have any release information, then either it is a small release or it has not been researched.

To quantify emissions by using these ranges, every piece of information learned in the qualitative analysis and the materials balance is used. Where high and low releases occur and where the byproducts and their amounts will be released should be noted. The materials balance will show the amounts released and the components of the release. All of these ranges of releases can then be added to obtain an overall range of releases from the PMN process for air, liquid, and solid releases.

Determining Storage and Handling Emissions

The synthetic organic chemical manufacturing industry has storage and handling requirements for feedstock, intermediate and final products, usable

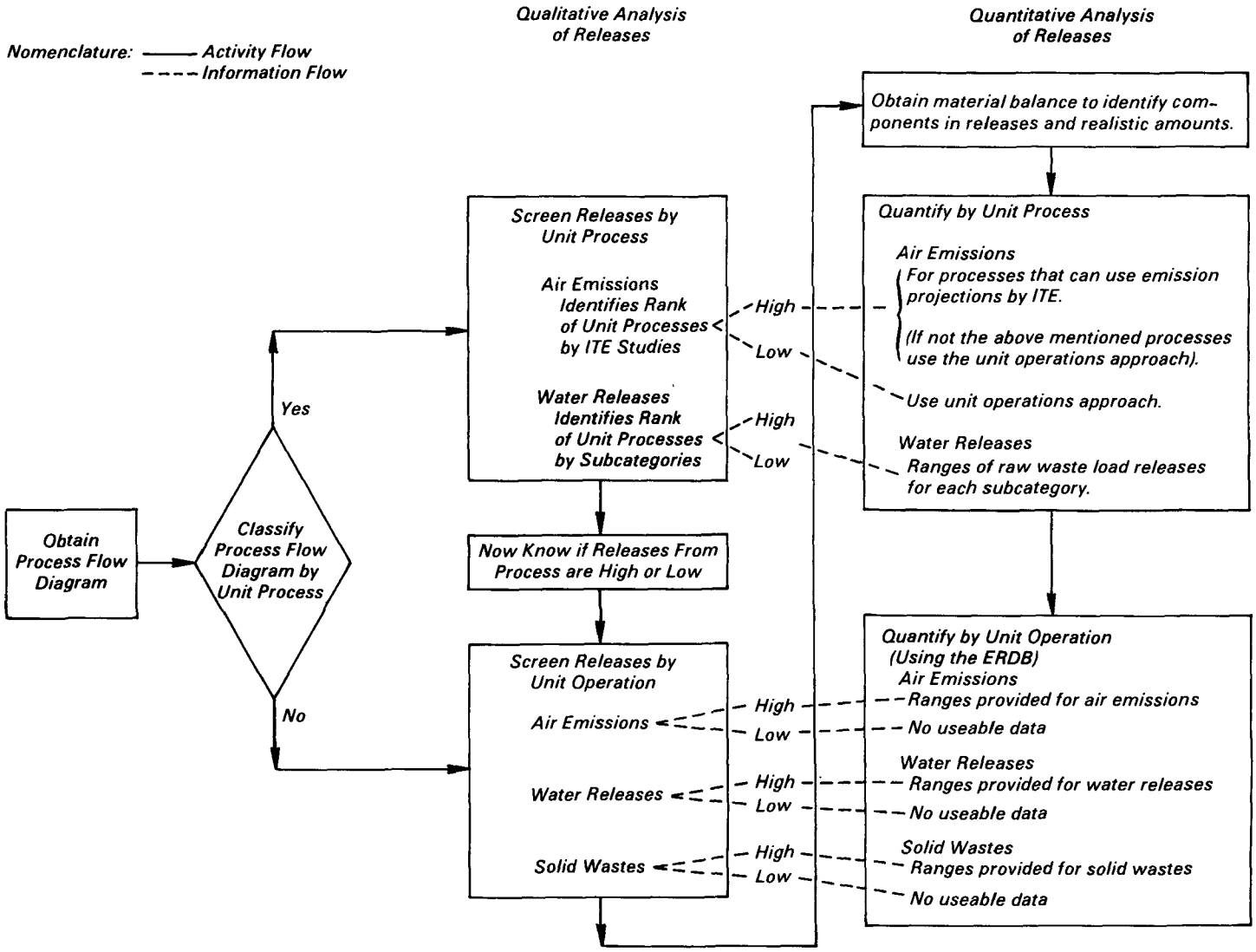

Figure 2. Quantification procedure for process releases.

byproducts, waste tars, residues and nonusable byproducts.

Storage releases depend on the kind of storage tank in use, e.g., fixed roof, floating roof, or pressure tank. The criteria used for tank selection include material stability and degrees of safety and health hazards, but primarily depend on the vapor pressure of the fluid in storage. The methodology lists the vapor pressure ranges that determine the appropriate tank class plus the use patterns for storage tanks. Formulae for calculating the uncontrolled breathing emissions and working losses for fixed roof tanks are provided which account for the effects of control technology. Formulae to calculate standing storage losses and withdrawal losses from floating roof tanks are also included.

The report also includes a formula to calculate loading losses for tank car, tank truck, and marine vessel loading.

Determining Fugitive Emissions

Pumps, valves, compressor seals, flanges, and cooling towers are the major sources of uncontrolled fugitive releases. Emissions factors for fugitive sources have been grouped depending on whether the process fluid belongs to one of these categories: vapor service, light-liquid service, and heavy-liquid service. No data are available on agitator seals or cooling tower emission factors.

Once the emission factors for the uncontrolled and controlled fugitive emissions for each source are known, it is necessary to multiply each emission factor by the number of corresponding sources to quantify the fugitive releases per plant. The methodology identifies data sources useful in determining the number of fugitive emission sources in a synthetic organic chemical manufacturing plant.

Establishing Data Reliability

The data sources used to compile the ERDB have been classified according to year of publication, basis used for reporting emissions data (plant sampling, materials balance, estimated data), relation of emissions factors to plant size, form of reported emissions, data vintage, and level of data uncertainty. The four rankings of data uncertainty are:

1. Emissions estimated from company site visits — data of reasonable accuracy.
2. Emissions estimated from data of indeterminate accuracy supplied by a company to state agencies.
3. Emissions estimated from data of indeterminate accuracy obtained from other published sources.
4. Emissions of indeterminate accuracy estimated without supporting data.

Most of the reports have a data uncertainty level of 3, indicating that most reports were at best secondary data sources, i.e., they reported data that were presented in other cited reports. Also of note are two additional factors: most of the report emissions data draw on estimates rather than observed data, and most of the reports use data that were generated more than 5 years ago.

In summary, the ERDB should be used cautiously in estimating environmental emissions from "new" synthetic organic chemicals. Special care should be taken in using those tables that contain data from different plants of possibly different sizes and even from different eras. Since the chemical industry is dynamic in its response to new technological and legislative initiatives, current plant emission levels are lower than levels reported a few years ago. Thus, more reliance may be put on recently completed studies.

Presenting Data

The format for presenting the data on environmental releases associated with the manufacture of a "new" chemical will be identical to the format used in presenting the environmental release data base. Thus, the releases associated with the functioning of each plant unit operation are readily accessible and may be combined with information on the labor practices associated with the same unit operations to conduct an in-plant employee exposure analysis.

The execution of an off-plant analysis of exposure to plant airborne emissions would take as its starting point the plant airborne emissions rate (broken down into the categories of emission type such as fugitive, process, and storage residuals) plus additional information on the physical and geographical characteristics of the emissions. These characteristics include geographic coordinates; source height (per emission type); and vent radius, vent gas temperature, ejection velocity (per emission type).

Additional information on the characteristics of plant emission sources are discussed in the methodology.

Methodology Limitations

Major limitations of the methodology and some of the assumptions on which it was based include:

- Environmental releases are estimated for steady-state, continuous processes of the synthetic organic chemical manufacturing industry.
- Releases due to accidents, spills, and process upsets are not estimated.
- No explicit procedure is provided for quantifying (unit process) solid wastes (including spent catalyst wastes).
- Releases due to the provision of utilities are not estimated (e.g., furnace emissions, boiler blowdown, etc.)
- In calculating storage, handling, and fugitive emissions, it is assumed that the equipment emissions factors are equivalent to those prevailing in petroleum refinery operations.
- The methodology tends to group the environmental releases under broad classes for air (VOC—volatile organic carbons) and water (BOD—biological oxygen demand, COD—chemical oxygen demand, TOC—total organic carbon).
- The effects of feedstock variability on the generation of environmental residuals are not allowed for explicitly.

Research Recommendations

The ERDB can be expanded in quality (by conducting an expanded plant sampling program while simultaneously observing the kinds and numbers of plant operators working at each unit operation throughout the plant) and in breadth (by measuring the emissions associated with unit operations which heretofore have not been extensively observed, e.g., filtration processes). Particular emphasis should be put on gathering data on batch manufacturing processes and on the amounts of spent catalyst sent for land disposal.

The methodology could be broadened to perform sensitivity analysis of the effects of variations in feedstock quality, process operating conditions and process upsets on the process environmental releases (in quality and quantity); to generate reliable ranges of solid waste produced for each unit process; and to estimate multimedia uncontrolled and controlled environmental releases on a compound-by-compound basis.

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***K. F. Hedden** is the EPA Project Officer (see below).*
The complete report, entitled "Methodology for Estimating Environmental Loadings from Manufacture of Synthetic Organic Chemicals," (Order No. PB 83-241 331; Cost: $41.50, subject to change) will be available only from:
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