

A computerized method for reporting SARA Title III, Section 313 emissions from a petroleum refinery

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Abstract

Recent Emergency Planning and Community Right-to-Know legislation has placed a burden on both facilities that are required to provide information to government agencies and the agencies that must manage the information and make it available to the public. The process that was used by Amoco Oil Company to respond to the reporting requirements established under the Superfund Amendments and Reauthorization Act, Title III, Section 313, is described. The methodology uses source-specific emission factors in a computerized multi-spreadsheet model that facilitates annual reporting of emissions to air, water, and land. The spreadsheet method standardizes the estimation process, is self-documenting, and easily accommodates changes.

Introduction

Under Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986, companies must provide information about listed chemicals that are present in their facilities as part of their manufacturing, storage, or processing activities. Section 313 of the Act requires owners and operators of facilities that meet certain criteria to file a form annually, called Form R, that provides information about chemical releases to the environment.

A facility must first determine whether it meets the threshold reporting level. Threshold levels were established to determine whether reports were required to be filed for the listed chemicals. For a chemical that appears on the Section 313 list and is "manufactured" or "processed," the first year (calendar year 1987) reporting level was 75,000 pounds per year, which was reduced to 50,000 per year for reports due for calendar year 1988, and is further reduced to 25,000 pounds per year for reports due in 1990 for calendar year 1989 and thereafter. A chemical that is "otherwise used" by a facility must exceed a threshold of 10,000 pounds per year before reporting is required. Any facility that meets the

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established criteria must file a Form R for each chemical that exceeds the threshold level.

A facility that converts a purchased chemical into another chemical product must count the total chemical in the raw materials and finished products to determine whether it meets the established threshold levels for every listed chemical. For a chemical facility that handles a few of the listed chemicals (probably in relatively pure form), the procedure requires reviewing the inventory lists to determine if quantities of raw materials purchased and products generated exceed the threshold amount and then secondarily estimating the emissions of those chemicals. However, the process becomes very complex for a petroleum refinery, because the raw materials and products generated are complex mixtures that vary daily in composition. The compositional variations of hydrocarbons are dependent upon many factors such as crude sources, seasonal requirements, and process operating conditions.

Given the many variables in calculating both the threshold levels and the emissions, from a petroleum refinery, a computerized spreadsheet methodology was developed for use by Amoco Oil refineries to facilitate the reporting process.

Emissions estimation

Among the most widely used techniques reported in the literature for estimating fugitive hydrocarbon emissions from various point sources are those based on the "emission factor" concept. An emission factor expresses the emission rate for a specific type of emitting source, often as a function of some throughput parameter. By multiplying the emission factor by the number of corresponding sources and summing over the entire source population, total emissions for a given operating facility can be estimated.

Emission factors have been developed and published for various hydrocarbon sources found in petroleum refineries and chemical plants [1]. These include pump and compressor seals, valves, drains, flanges, and other connections. Hydrocarbon emission models have been developed for entire refineries by representing each of the various process units as a collection of emitting sources and associated emission factors [2,3]. An example of this kind of representation is shown in Table 1 for a typical atmospheric crude distillation unit in a hypothetical 250,000 bbl/day refinery and shows an estimated hydrocarbon emission rate of 996.8 lb/day of fugitive volatile organic compounds, VOCs. By including the appropriate number and types of process units, a refinery emissions model of any configuration can be simulated. But, because available hydrocarbon emission factors are not compound specific, only total VOC estimates can be made by using these factors. A modification to this method was developed to provide estimates for emissions of specific chemical species required annually by Section 313.

TABLE 1

Estimated fugitive emissions for an atmospheric crude distillation unit

Source type	Service	Number of sources	Emission factor (lb/day)/source	VOC emissions (lb/day)
Pump seals	Light liquid	13	6	78.0
	Heavy liquid	21	1.1	23.1
Compressor seals	Hydrocarbon gas	0	34	0.0
	Hydrogen gas	0	2.6	0.0
Valves	Hydrocarbon gas	139	1.4	194.6
	Hydrogen gas	0	0.43	0.0
	Light liquids	480	0.58	278.4
	Heavy liquids	775	0.012	9.3
Connections	All	4879	0.013	63.4
Relief valves	Gas	23	8.6	197.8
	Liquid	3	0.37	1.1
Open end lines	All	105	0.12	12.6
Process drains	All	61	1.7	103.7
Sampling taps	All	44	0.79	34.8
Total fugitive VOC emissions, lb/day:				996.8

The approach

The estimation of compound-specific emission rates requires knowledge of hydrocarbon composition as well as the VOC emission rate. However, refinery hydrocarbons are present as exceedingly complex mixtures and their composition varies greatly not only among different process units, but also among the various streams within the same unit. A simple VOC estimate obtained for an entire process unit as described above is too imprecise to be of value in estimating the emissions of individual compounds for that unit. A more useful VOC estimate would be one that is stream-based, since the stream is the largest entity for which the VOC estimate represents a single composition. Mathematically, the VOC emission rate for any stream j is expressed as

$$\text{VOC}_j = \sum_k (\text{source}_{jk} \times f_k) \quad (1)$$

where source_{jk} = k th emission source in stream j ; f_k = emission factor for k th source. Then, for each stream, the emission rate for each chemical species, E_{ij} , may be calculated as the product of its stream concentration, C_{ij} (expressed as a mass fraction) and its stream VOC emission rate, VOC_j ,

$$E_{ij} = C_{ij} \times \text{VOC}_j \quad (2)$$

An obvious simplifying assumption here is the lack of distinction between stream vapor and liquid phases and any partitioning between phases that might

occur. For fugitive emissions from streams under pressure (most process streams), this is a good approximation.

The overall emission rate, E_i , for each chemical species can be obtained by summing eq. (2) over all streams:

$$E_i = \sum_j (C_{ij} \times \text{VOC}_j) \quad (3)$$

Because it is convenient and useful to express emissions on a process unit basis, the summation in eq. (3) may be grouped by the streams of a specific unit. That is, each process unit can be regarded as a collection of specific inlet and outlet streams, each having its own composition and a VOC emission rate that is estimated from eq. (1). Schematically, this is shown in Fig. 1.

While stream composition data are available for many refinery streams, they are often incomplete and only include compounds having economic impor-

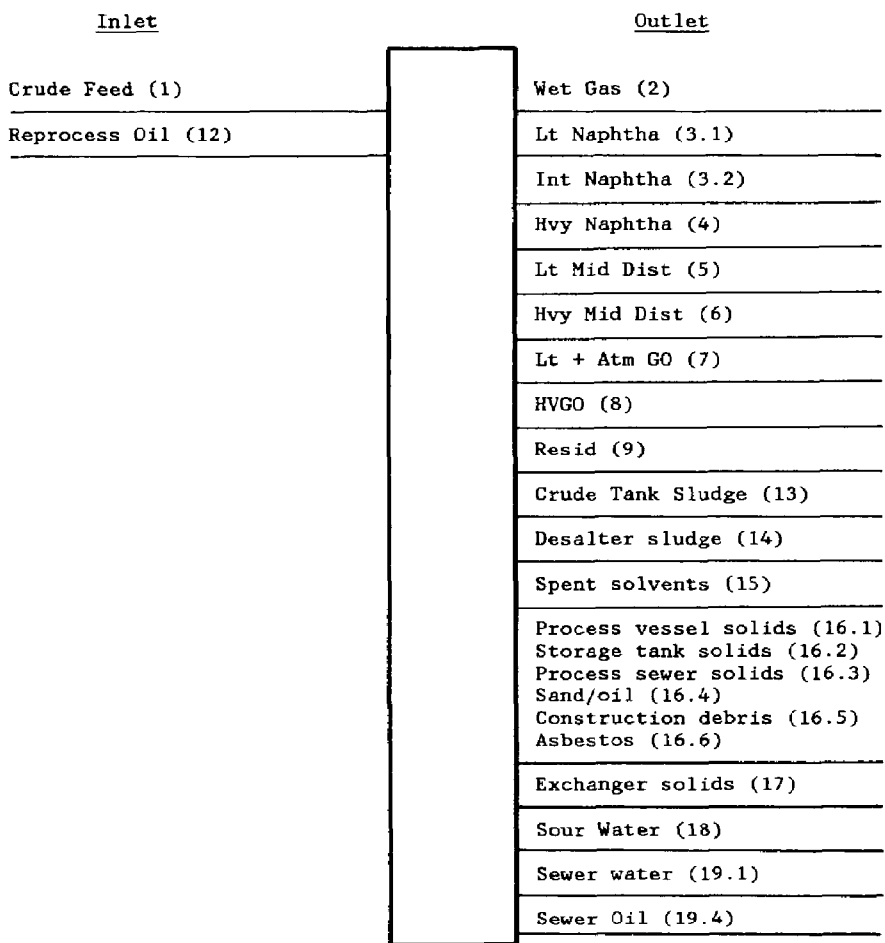


Fig. 1. Example of process unit inlet and outlet streams.

tance to the operation or final products. The requirements of Section 313 specify the reporting of emissions for many compounds whose concentrations in refinery streams are not known. Though not required, chemical analysis of these streams is often the only practical way to obtain this information. Therefore, in the development of this emissions model, over 100 refinery streams were sampled and analyzed to determine composition data for the specific list of Section 313 compounds.

Although the group of analyzed streams was extensive, it was only a fraction of the total number of streams that exist in a refinery. For reasons of simplicity and economy, the compositions of similar streams were represented by a single analyzed stream. For example, the analyzed composition for a heavy naphtha stream from one crude unit might also be used to represent heavy naphtha streams not only from other crude units, but from other process units, such as reformers, wherever a similar composition was expected to occur.

The spreadsheet model

The above calculational procedure and associated composition data were incorporated in a spreadsheet emissions model for an entire petroleum refinery. Each process unit or operation was represented as a single "page" in a multi-page DynaPlan¹ spreadsheet model [4]. The motivation for choosing a spreadsheet approach was the need for a generalized tool that could be applied quickly and consistently by each of the refinery locations. Also, the repetitive computations and bookkeeping nature of the estimation procedure are well suited to spreadsheet-programming. Finally, the results are in a form that is easy to analyze, consolidate, and document for reporting purposes.

Table 2 is a portion of a single page of the multi-page spreadsheet model, in this case, for a typical crude unit. The function of this process unit in the refinery is to fractionate crude oil by distillation into different boiling range stocks for processing by other downstream units. The streams associated with the crude unit are represented as individual columns in the spreadsheet beginning in column L. They are identified by a unique stream number and name in rows 10-13 of their respective columns. The upper half of the spreadsheet is used to estimate the VOC emission rate for each stream with the results tabulated in row 51. The lower half of the spreadsheet contains the composition data which, when multiplied by the VOC estimate, will give emission rates for individual species in each stream. For the data shown here, the *de minimis*

¹DynaPlan is a general spreadsheet program for use with mainframe computers that allows a three-dimensional worksheet representation. While this is a convenient feature of DynaPlan, other spreadsheet software, including those commonly available for personal computers, could also be adapted.

rule² specified by the regulation has already been applied. That is, only concentration values equal to or greater than 1 weight percent (0.1 for carcinogens) have been included.

To illustrate the emission estimation logic, we will examine a few areas of the worksheet in detail. The upper left-hand corner of the spreadsheet (columns A-E, rows 18-47) contains information about the population of emission sources for the crude unit. It contains the same information shown previously in Table 1. It simply lists the various emission sources, the type of hydrocarbon service in which they are used, the number of each source, and the corresponding emission factor. Where more than one type of service is shown for a source, the percent of sources in each type of service, as well as the actual number, is listed. These percentages are based on published source counts for "average" refinery VOC emission models. The user is required to input the number of sources. In the absence of complete actual source count information, the user could rely on the published source counts as a default or input only the totals and allow the program to compute the number of sources based on the published percentages. In any case, the more closely the input source distribution is to the actual unit being modelled, the better the chances are for a more accurate emissions estimate.

In the fourth column of Table 1 are the emission factors for each source. Each factor depends upon the source type and the schedule of inspection and maintenance established by the refinery's leak detection and repair program (LDRP). LDRPs reduce fugitive emissions through routine inspection and repair of leaking sources. The effectiveness of emissions reduction depends on the frequency of inspection and the repair response time. The type of LDRP varies with each facility depending on local air regulations but, more recently, many facilities have instituted such programs on a voluntary basis. Categories of various LDRPs are described in Table 3, where Category 0 represents no LDRP being used and Category 3 is the most stringent and having the greatest emission reduction potential. The LDRP category is a required input by the user (column B, row 18) and automatically selects the appropriate set of emission factors to be used in the calculations. The emission factors shown in the example of Table 2 are for an LDRP category of 2 (i.e., quarterly monitoring, repair action required at 10,000 ppm or greater, and response within 15 days), for which published emission reduction data were conveniently available.

The emission factor, multiplied by the number of corresponding sources, gives the VOC emissions for that source. In this example (Table 2), 13 "pump seals in light liquid service" times an emission factor of 1.4 lb/day per source

²The *de minimis* rule specifies that non-carcinogenic components of process streams with concentrations less than 1 weight percent and carcinogenic components less than 0.1 weight percent are not required to be included in the estimates. The rule cannot be applied to components in waste streams.

TABLE 3

Leak detection and repair (LDRP) categories for VOC emission sources [2]

LDRP Category	0	1	2	3
Monitoring frequency	(No LDRP)	Yearly	Quarterly	Monthly
Action level, ppm		100,000	10,000	1,000
Repair lag, days		15	5	1
	Emission factors	% Reduction vs. LDRP=0		
<i>Pumps</i>				
Light liquid	6.0	47	77	82
Heavy liquid	1.1	0	31	71
<i>Compressors</i>				
Unvented	34.0	37	80	90
Vented/control		98	98	98
<i>Valves</i>				
Gas	1.4	70	87	93
Light liquid	0.58	41	74	85
Heavy liquid	0.012	0	0	32
Hydrogen	0.43	70	87	93

results in 18.2 lb/day of VOC associated with all "pump seals in light liquid service" for the crude unit. The VOC emissions from the other sources are computed accordingly and, when added together, result in an estimate of 425 lb/day of total VOC from the crude unit. But, the stream VOC emission rate, not the total VOC, as pointed out earlier, is the desired result. Still needed is a means of apportioning the VOC emissions from each source type among the contributing streams. In this example, 18.2 lb/day of VOC from "pump seals in light liquid service" needs to be divided among the contributing streams. The only possible streams, of course, are those involving light liquids, and their VOC contributions should be proportional to the number of such sources that they contain. In similar fashion, the VOC emissions from the other source types can be apportioned among contributing streams according to the relative number of such sources in each stream.

In the spreadsheet model (Table 2), source counts for each stream are represented as a *relative* distribution in rows 23 through 47, columns L through W. In our example, a uniform distribution (all 1's) of the various emission sources among contributing streams is assumed as the default. Obtaining actual source counts for each stream would, of course, give a more accurate representation. The actual spreadsheet computation multiplies the product of columns D and E (the source VOC) times the fraction of those sources in a given stream and sums over all source types. In Table 2 the VOC result for each stream is tabulated in row 51.

Another simplifying assumption used in this model is that emissions from

multiple process units of the same type may be represented by a simple multiplicative factor times the emissions from one of the units. In our example, there are three crude units in this model refinery, as input in row 6, column B (i.e. cell B6). Row 52 contains the stream VOC emission estimate for all three crude units.

Once the stream VOC estimate is made (row 52), the total emission rate for each species can be estimated using eq. (3). In the spreadsheet model, this is obtained as the scalar, or "dot," product of row 52 and each of the composition data rows (rows 59 and greater). The result, the total emission rate for each compound from all crude units, is listed in column AB of the spreadsheet. In our example, the toluene emissions are calculated as

$$(41.2 \times 1.36 + 120.5 \times 5.11 + 311.1 \times 0.0005) / 100 = 6.72 \text{ lb/day}$$

In addition to these fugitive air emissions, a relatively minor contribution of VOC comes from combustion sources and other point (non-tank)³ sources. These are calculated in a separate area of the spreadsheet and are illustrated in Table 4. Combustion emissions are determined from the furnace heat duty and the type of fuel. The heat duty, if unknown, can be estimated from refinery throughput [2,3] VOC concentrations in combustion flue gas are extremely low and, since the concentration of individual reportable compounds is only a very small fraction of the total VOC, their reportable emissions from combustion sources are negligible. In fact, combustion and point sources (non-tank) were estimated to contribute less than 3% of the total refinery VOC. However, reportable compounds present in the fuel do contribute to the threshold quantities in the "otherwise used" category discussed below and have been counted as such. The stream composition data for the fuel are contained in column AK of the spreadsheet.

Threshold calculations

Chemical quantities are tabulated by the spreadsheet model according to their threshold category using the same stream composition data along with an appropriate stream quantity and category designator input by the user in rows 16 and 17 (Table 2). The following categories are denoted: P=process; M=manufactured; U=otherwise used; A=article; I=intermediate stream. Wherever a stream quantity is entered (in row 17), it is multiplied by the stream's composition to calculate quantities for individual chemical components; component quantities are then summed according to their threshold category and tabulated in columns AC-AF next to the emission totals in column AB. The absence of a user-input quantity in row 17 indicates that the

³Tank sources are estimated separately, and these calculations are explained in the discussion on other units.

stream is not relevant to a specific threshold category (such as an intermediate stream) or that it is being counted more appropriately on another spreadsheet for a different unit. The "sewer water" stream in the crude unit spreadsheet is an example of a waste, or "manufactured," category whose stream quantity is more appropriately counted in the wastewater treatment unit in combination with wastewater streams from all other units. It is omitted from the crude unit worksheet to avoid being counted twice. Both the threshold category quantities and the emission rates represent totals for the specific unit, but are actually subtotals in relation to the overall refinery estimates.

Other units

The crude unit example discussed thus far illustrates a spreadsheet model for estimating air emissions under SARA III. Similar spreadsheets can be made for the other process units and operations in the refinery to estimate emissions to air and other environmental media. Other spreadsheet unit models that have been included in the general refinery model are listed in Table 5. These

TABLE 5

Spreadsheet unit models

Module	Process/Operations	Module	Process/operations
AIR 1	Crude Reformer Alkylation FCU Coker Vapor recovery Naphtha Hydrogenation Distillate Hyd (2) Sulfur recovery Fuels treating Product blending (Combustion/furnaces by process)	AIR3	Wastewater treatment Water treatment (Cooling towers) Power Station Production loading/Transfer Blowdown/Flares Maintenance
		TANK	Feed/product storage
		WATER	Wastewater treatment
		SOLIDS	Solid/liquid wastes
AIR2	Cat feed Hyd Isomerization Aromatics extraction Hydrocracking Resid hydroprocessing Hydrogen production Lune oils Asphalt (Combustion furnaces by process)		

TABLE 7

W	C	P	Q	R	S	T	U	V	W	X	Y
23											
24											
25											
26											
27											
28		Avg Vap		Turnovers		Seal	Adj Factr		Turnover	Brth Loss	Stand Loss
29	Tank No.	Space	Est	per Yr	FSFAC	Factor	for small	TFAC0	Factor	Product	Product
30		Height	Tank	TURN0	(Type 2 Only)	SFAC	Tanks		TFAC	Factor	Factor
31		VAPHT	Capacity				DFAC			PRFACA	PRFACB
32		(ft)	(Mbb1)								
33	3030	21.26	20.10	1.00	5.94	0.20	1.00	1.00	1.00	1.00	1.00
34	3153	26.89	55.50	0.00	6.35	0.00	1.00	1.00	1.00	1.00	1.00
35	3154	22.19	44.80	8.93	6.35	0.00	1.00	1.00	1.00	1.00	1.00
36	3155	22.19	44.80	0.00	6.35	0.00	1.00	1.00	1.00	1.00	1.00
37	3157	21.89	55.50	90.09	6.35	13.05	1.00	0.20	0.49	1.00	1.00
38	3165	21.09	8.70	9.77	6.29	0.00	1.00	1.00	1.00	1.00	1.00
39	3166	21.09	8.80	9.66	6.29	0.00	1.00	1.00	1.00	1.00	1.00
40	3167	22.86	72.70	82.53	7.04	0.00	1.00	0.31	0.51	1.00	1.00
41	3168	21.89	43.60	6.88	6.35	0.00	1.00	1.00	1.00	1.00	1.00
42	3169	22.66	77.50	34.84	7.04	0.00	1.00	1.00	1.00	1.00	1.00
43	3174	26.89	55.50	18.02	6.35	0.00	1.00	1.00	1.00	1.00	1.00
44	3201	21.05	13.60	0.00	6.00	0.00	1.00	1.00	1.00	1.00	1.00
45	3213	21.05	13.60	20.22	6.00	0.00	1.00	1.00	1.00	1.00	1.00
46	3228	21.05	13.70	0.51	6.00	0.00	1.00	1.00	1.00	1.00	1.00
47	3234	21.56	19.60	14.03	5.94	0.00	1.00	1.00	1.00	1.00	1.00
48	3259	21.26	13.70	20.07	5.94	0.00	1.00	1.00	1.00	1.00	1.00
49	3260	20.99	8.70	5.98	6.29	0.00	1.00	1.00	1.00	1.00	1.00
50	3265	24.84	10.50	26.19	6.29	0.00	1.00	1.00	1.00	1.00	1.00
51	3509	5.17	0.10	30.00	18.48	0.00	0.45	1.00	1.00	1.00	1.00
52	3573	15.74	5.10	33.33	6.57	0.00	1.00	1.00	1.00	1.00	1.00
53	3574	15.74	5.10	33.33	6.57	0.00	1.00	1.00	1.00	1.00	1.00
54	3377	18.03	3.00	20.00	7.72	0.00	0.95	1.00	1.00	1.00	1.00
217	3919	25.62	273.40	25.60	10.47	0.20	1.00	1.00	1.00	0.65	0.40
218	3920	25.62	294.10	81.93	10.47	0.20	1.00	0.32	0.51	0.65	0.40
219	6248	27.36	166.90	0.96	8.39	0.00	1.00	1.00	1.00	1.00	1.00
220	6249	27.36	166.90	1.44	8.39	0.00	1.00	1.00	1.00	1.00	1.00
221	6250	27.36	166.20	1.35	8.39	0.00	1.00	1.00	1.00	1.00	1.00
222	6251	27.36	166.90	1.35	8.39	0.00	1.00	1.00	1.00	1.00	1.00
223	6252	27.36	166.80	1.35	8.39	0.00	1.00	1.00	1.00	1.00	1.00
224	6253	27.36	166.80	21.22	8.39	0.00	1.00	1.00	1.00	1.00	1.00
225											
226											
W	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	
23											
24											
25											
26											
27	Work Loss	Shell	Wind	Breathing	Working	Vap Pres	Standing	Withdrawal	Total VOC	Total	
28	Product	Clingspe	Speed	Loss	Loss	Function	Loss	Loss	Emissions	VOC	
29	Factor	Factor	Exponent	BRL	WORKL	FPRES	STANDL	WITHDL	TOTAL	(lb/Day)	
30	PRFACC	CFAC	EFAC	(T/Yr)	(T/Yr)		(T/Yr)	(T/Yr)	(T/Yr)		
31											
32											
33	1.00	0.0015	1.00	0.12	0.01	0.0001	0.00	0.00	0.00	0.01	
34	1.00	0.0015	0.00	0.36	0.00	0.0001	0.00	0.00	0.36	1.99	
35	1.00	0.0015	0.00	0.80	0.27	0.0002	0.00	0.00	0.77	4.24	
36	1.00	0.0015	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	
37	1.00	0.0015	0.00	8.31	128.34	0.0231	1.09	0.28	1.37	7.51	
38	1.00	0.0015	0.00	0.07	0.03	0.0001	0.00	0.00	0.09	0.52	
39	1.00	0.0015	0.00	3.68	9.90	0.0657	0.00	0.00	13.58	74.43	
40	1.00	0.0015	0.00	0.08	0.06	0.0000	0.00	0.00	0.14	0.74	
41	1.00	0.0015	0.00	0.05	0.01	0.0000	0.00	0.00	0.06	0.31	
42	1.00	0.0015	0.00	0.08	0.05	0.0000	0.00	0.00	0.13	0.73	
43	1.00	0.0015	0.00	0.05	0.02	0.0000	0.00	0.00	0.07	0.39	
44	1.00	0.0015	0.00	0.09	0.00	0.0001	0.00	0.00	0.09	0.48	
45	1.00	0.0015	0.00	0.02	0.01	0.0000	0.00	0.00	0.02	0.12	
46	1.00	0.0015	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	
47	1.00	0.0015	0.00	0.12	0.07	0.0001	0.00	0.00	0.19	1.06	
48	1.00	0.0015	0.00	0.02	0.01	0.0000	0.00	0.00	0.03	0.16	
49	1.00	0.0015	0.00	0.06	0.01	0.0001	0.00	0.00	0.07	0.40	
50	1.00	0.0015	0.00	0.10	0.08	0.0001	0.00	0.00	0.18	0.99	
51	1.00	0.0015	0.00	0.01	0.06	0.0231	0.00	0.00	0.07	0.41	
52	1.00	0.0015	0.00	0.01	0.00	0.0000	0.00	0.00	0.01	0.06	
53	1.00	0.0015	0.00	0.01	0.00	0.0000	0.00	0.00	0.01	0.06	
54	1.00	0.0015	0.00	0.00	0.00	0.0000	0.00	0.00	0.01	0.03	
217	0.84	0.0060	1.00	33.25	414.89	0.0528	0.24	0.64	0.86	4.61	
218	0.84	0.0060	1.00	33.25	610.42	0.0528	0.24	1.82	2.06	11.30	
219	1.00	0.0015	0.00	1.45	0.09	0.0001	0.00	0.00	1.54	8.45	
220	1.00	0.0015	0.00	0.14	0.00	0.0000	0.00	0.00	0.15	0.81	
221	1.00	0.0015	0.00	0.14	0.00	0.0000	0.00	0.00	0.15	0.81	
222	1.00	0.0015	0.00	0.14	0.00	0.0000	0.00	0.00	0.15	0.81	
223	1.00	0.0015	0.00	0.14	0.00	0.0000	0.00	0.00	0.15	0.81	
224	1.00	0.0015	0.00	0.14	0.07	0.0000	0.00	0.00	0.21	1.16	
225											
226									375.48	2,057.45	

TABLE 8

W	A	B	C	D	E	F	G	H
228								
229								
230								
231		Product Code:	1	2	3	4	5	6
232		TOTAL VOC BY PRODUCT (lb/Day):	62.5	0.0	0.0	0.0	0.0	1.7
233		(% of TOTAL Tank VOC):	(3.2)	0.0	0.0	0.0	0.0	(0.1)
234								
235		Stream No.:	1	126	127	128	421	3.1
236								
237		Stream Name:	FEED	LPG	BB	SAT C4	C5/C6 FEED	LIGHT NA PHTHA
238								
239								
240		Stream Type:	HL	LL	LL	LL	LL	LL
241		Threshold Category:	F	P	P	I	I	I
242		Quantity (Mlb/yr):		440,000	1,375,000			
243	CAS NO	COMPOUND						
244								
245	74-85-1	ETHYLENE						
246	115-07-1	PROPYLENE		1.19	2.19			
247	106-99-0	1,3-BUTADIENE*			0.45			
248	110-82-7	CYCLOHEXANE	1.45					
249	71-43-2	BENZENE*	0.71					
250	108-88-3	TOLUENE	1.81					
251	100-41-4	ETHYLBENZENE						
252	106-42-3	P-XYLENE						
253	108-38-3	M-XYLENE	1.12					
254	1330-20-7	XYLENE	3.25					
255	95-47-6	O-XYLENE	1.67					
256	98-82-8	CUMENE						
257	95-63-6	1,2,4-TRIMETHYLBENZENE						
258	91-20-3	NAPHTHALENE						
259	120-12-7	ANTHRACENE						
260	108-95-2	PHENOL						
261	95-48-7	O-CRESOL						
262	106-46-5	P-CRESOL						
263	108-39-4	M-CRESOL						
264	1319-77-3	CRESOL						

W	I	J	K	L	M	N	O	P	Q	R	S
228											
229											
230											
231	7	8	9	10	11	12	13	14	15	16	17
232	48.0	58.3	451.9	296.9	238.6	38.7	0.0	126.1	287.6	35.3	22.4
233	(2.4)	(3.0)	(21.9)	(15.1)	(12.1)	(2.0)	0.0	(6.4)	(14.6)	(1.8)	(1.1)
234											
235	4	184.1	184.2	184.3	184.4	185	45	41.00	22.00	5.00	186.10
236											
237	HEAVY	LEADED	GASOLINE	GASOLINE	GASOLINE	XYLENE	C5-C4 FE	ALKYLATE	TOTAL RE	LIGHT HI	MOI FURN
238	NAPHTHA	GASOLINE	No. 1	No.2	No.3		ED		FORMATE	D DISTIL	ACE OIL
239											
240	LL	LL	LL	LL	LL	LL	LL	LL	LL	HL	HL
241	I	P	P	P	P	P	I	I	I	I	P
242		2,000,000	7,500,000	2,000,000	4,000,000	1,000,000					3,000,000
243											
244											
245											
246							6.82				
247							0.42				
248											
249	1.14			2.46	0.96				6.20		
250	1.17	3.92		8.71	8.19			12.00	19.20		
251	4.62	13.5	11.3	1.25	1.44	18.9			3.80		
252	4.52			1.12	1.31	16.3			3.70		
253				2.87	3.23	39.4			8.70		
254	2.46	2.38	1.87	5.54	6.31	75.2			17.80	1.14	1.04
255	4.52	4.4	3.2	1.55	1.77	19.5			4.60		
256	1.23	1.16									
257											
258		1.53		4.18	4.9				5.00		
259											
260											
261											
262											
263											
264											

have been grouped into seven multi-worksheet DynaPlan modules: AIR1, AIR2, AIR3, TANK, WATER, SOLIDS, and SUMMARY.

The first four modules are used to test both fugitive and point source air emissions from process units or operations and storage tanks. The WATER module calculates emissions to water bodies from wastewater discharges. The

TABLE 8 (continued)

W	T	U	V	W	X	Y	Z	AA	AB	AC	AD
228											
229											
230											
231	18	19	20	21	22	23	24	25	26	27	28
232	99.2	29.3	84.0	84.7	17.1	5.0	0.0	0.0	3.2	0.0	0.0
233	(5.0)	(1.5)	(4.3)	(4.3)	(0.9)	(0.3)	0.0	0.0	(0.2)	0.0	0.0
234											
235	186.20	187.20	187.20	7.00	9.00	71.00	293.00	12.0000	352.00	189.00	161.00
236											
237	NO2 FURN	JP-4 JET	TYPE A J	PRIMARY	RESID	DCO	NO 7 SEP	REPROCESS	NO 3 OXI	LUBES	MEK
238	ACE OIL	FUEL	ET FUEL	GAS OIL			OIL	OIL	DIZER AS		
239											
240	HL	LL	HL	HL	HL	HL	HL	HL	HL	HL	LL
241	P	P	P	I	P	I	I	I	P	P	U
242	4,000,000	1,000,000	1,000,000		400,000				2,000,000	660,000	
243											
244											
245											
246											
247											
248		9.69									
249		4.05				0.16	0.28				
250		5.82					3.30				34.10
251							1.06				
252							1.03				
253							2.48				
254			1.55			1.67	4.58				
255							1.15				
256											
257							1.93				
258	1.15										
259											
260											
261											
262											
263											
264											

W	AE	AF	AG	AH
228				
229			TOTAL	TOTAL
230			VOC	VOC
231	29	30	(lb/Day)	(T/Yr)
232	0.0	0.0	1,970.6	359.6
233	0.0	0.0		
234				
235				
236				
237	METHAN	ADDI		
238	OL	TIVES		
239				
240	LL	LL	TOTAL	TOTAL
241	U	U	EMISSIONS	EMISSIONS
242				
243			(lb/Day)	(T/Yr)
244				
245			0.0	0.00
246			0.0	0.00
247			0.0	0.00
248			4.3	0.78
249			44.4	8.11
250			177.5	32.39
251			27.6	5.03
252			23.4	4.27
253			67.8	12.38
254			132.1	24.10
255			31.9	5.82
256			0.0	0.00
257			39.4	7.19
258			1.1	0.21
259			0.0	0.00
260			0.0	0.00
261			0.0	0.00
262			0.0	0.00
263			0.0	0.00
264			0.0	0.00

SOLIDS module accounts for chemical emissions from the various types of onsite and offsite disposal of solid wastes.

The TANK module estimates fugitive air emissions from storage tanks using published (AP-42) correlations. An example of the TANK spreadsheet is shown in Tables 6-9.

In Table 6, the facility's average ambient diurnal temperature change and

TABLE 9

W	A	B	AT	AJ	AK	AL	
238							
239							
240							
241							
242							
243	CAS NO	COMPOUND	Stream Type: Threshold Category: Quantity (Mlb/yr):	Chemical Quantities by Threshold Category (Mlb/yr) (All streams in TANK)			Article
244			Mfr	Process	Used		
245	74-85-1	ETHYLENE	0	0	0	0	
246	115-07-1	PROPYLENE	0	35,349	0	0	
247	106-99-0	1,3-BUTADIENE*	0	5,913	0	0	
248	110-82-7	CYCLOHEXANE	0	96,900	0	0	
249	71-43-2	BENZENE*	0	424,000	0	0	
250	108-88-3	TOLUENE	0	1,677,500	0	0	
251	100-41-4	ETHYLBENZENE	0	271,600	0	0	
252	106-42-3	P-XYLENE	0	237,800	0	0	
253	108-38-3	M-XYLENE	0	768,450	0	0	
254	1330-20-7	XYLENE	0	1,489,990	0	0	
255	95-47-6	O-XYLENE	0	320,000	0	0	
256	98-82-8	CUMENE	0	0	0	0	
257	95-63-6	1,2,4-TRIMETHYLBENZENE	0	310,200	0	0	
258	91-20-3	NAPHTHALENE	0	46,000	0	0	
259	120-12-7	ANTHRACENE	0	0	0	0	
260	108-95-2	PHENOL	0	0	0	0	
261	95-48-7	O-CRESOL	0	0	0	0	
262	106-44-5	P-CRESOL	0	0	0	0	
263	108-39-4	M-CRESOL	0	0	0	0	
264	1319-77-3	CRESOL	0	0	0	0	

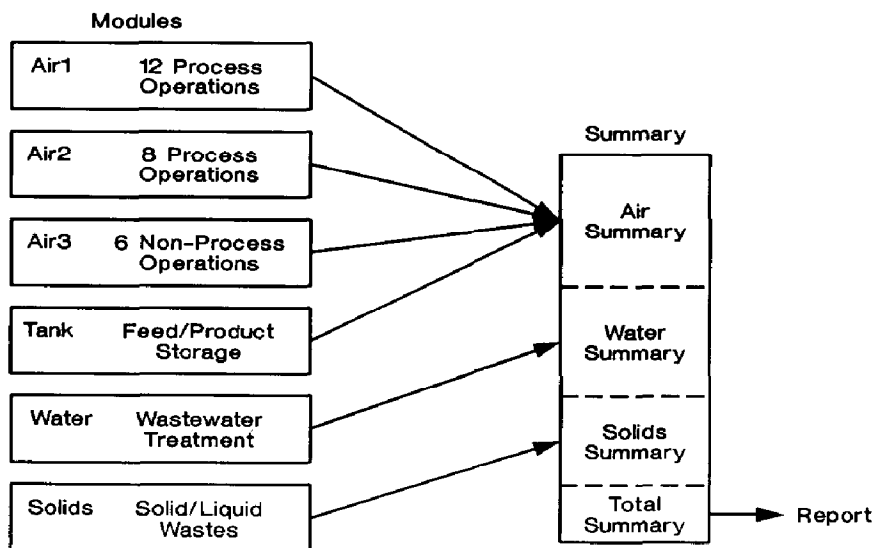


Fig. 2. Relationship of modules.

the average wind speed are entered in cells D13 and D14. A list of the facility's tank parameters is entered in columns C through O beginning in row 33. These input parameters specify the physical characteristics of each tank along with some technical data on the contained material. The contents of each tank is further identified by a "product code" in column F which serves to group tanks containing similar material.

Table 7 lists columns P through AI of the TANK spreadsheet which contain calculated factors based on the AP-42 methodology from which each tank's

TABLE 10

SARA III emissions estimation summary

A		B	C	D	E	F	H	J	K	L	
TOTAL EMISSIONS SUMMARY			EMISSIONS TO AIR	EMISSIONS TO WATER	EMISSIONS TO LAND	TOTAL	Threshold:	Mfr	Process	Used	Article
			6,955,624	94,976	N/A	7,050,600		75	75	10	
1	TOTAL VOC, lb/yr										
2	Refinery: XYZ										
3	Capacity, BCD: 250,000										
4											
5											
6											
7											
8											
9											
10											
11	TOTAL VOC, lb/yr		6,955,624	94,976	N/A	7,050,600					
12											
13											
14	EMISSIONS BY CONSTITUENT, lb/yr										
15	CAS NO	COMPOUND					Threshold:	Mfr	Process	Used	Article
16								75	75	10	
17	74-85-1	ETHYLENE	20,292			20,292	<==	0.0	0.0	339,026.5	0.0
18	115-07-1	PROPYLENE	69,777			69,777	<==	0.0	71,059.1	229,499.3	0.0
19	110-82-7	1,3-BUTADIENE*	523			523	<==	0.0	69,618.9	0.0	0.0
20	110-82-7	CYCLOHEXANE	8,614		1,847	10,461	<==	2.4	532,331.6	0.0	0.0
21	110-82-7	BENZENE*	30,157		80,943	111,101	<==	103.5	346,425.1	4.1	0.0
22	71-43-2	TOLUENE	179,846		206,879	386,725	<==	30.8	871,315.2	1,568.6	0.0
23	108-88-3	ETHYLBENZENE	27,853		32,115	59,968	<==	35.8	11,406.1	0.0	0.0
24	100-41-4	P-XYLENE	22,736		19,631	42,367	<==	27.3	10,371.6	0.0	0.0
25	106-42-3	M-XYLENE	65,679		77,229	142,907	<==	68.6	409,795.0	16.8	0.0
26	108-38-3	O-XYLENE	29,348		28,749	58,097	<==	26.0	550,443.6	10.4	0.0
27	95-47-6	CUMENE	40,667			40,667	<==	0.0	0.0	0.0	0.0
28	98-82-8	1,2,4-TRIMETHYLBENZENE	1,339		48,330	49,669	<==	9.3	43,235.0	42.9	0.0
29	95-63-6	METHYLENE CHLORIDE			24,618	24,618	<==	4.5	23,284.8	21.0	0.0
30	91-20-3	ANTHRACENE			16	16	<==	0.0	0.0	0.0	0.0
31	120-15-7	PHENOL	1			1	<==	0.0	0.0	0.0	0.0
32	108-95-2	O-CRESOL	1			1	<==	0.0	0.0	0.0	0.0
33	95-48-7	P-CRESOL	0			0	<==	0.0	0.0	0.0	0.0
34	106-44-5	M-CRESOL	1			1	<==	0.0	0.0	0.0	0.0
35	108-39-4	DIMETHYLPHENOL	0			0	<==	0.0	0.0	0.0	0.0
36	105-67-9										
61	1344-28-1	ALUMINUM OXIDE	997,189		13,797,331	14,794,521	<==	99.9	0.0	14,218.2	0.0
62	7440-62-2	VANADIUM PENTOXIDE			9,264	9,264	<==	12.0	0.0	0.0	0.0
63	7664-41-7	AMMONIA	391		23,285	23,676	<==	1.1	0.0	0.0	0.0
64	7723-14-0	PHOSPHORUS	2		15,468	15,470	<==	28.9	0.0	0.0	0.0
65	7664-93-9	SULFURIC ACID	15,468		1,372	16,840	<==	0.0	0.0	0.0	0.0
66	7782-49-2	SELENIUM	0		418,000	418,000	<==	2.0	0.0	0.0	0.0
67	1310-73-2	SODIUM HYDROXIDE	1,392			1,392	<==	41.6	0.0	418.0	0.0
68	7664-39-3	HYDROGEN FLUORIDE						0.0	0.0	0.0	0.0
69	7757-82-6	SODIUM SULFATE						1,260.3	0.0	0.0	0.0
70											
71	TOTAL REPORTABLE EMISSIONS (lb/yr):		1,718,749	7,561,544	14,763,153	24,043,447					
72	(% of TOTAL REPORTABLE EMISSIONS):		(7.1)	(31.4)	(61.4)						

TABLE 11

Source contributions to total estimated XYZ refinery VOC emissions

Process/Area	VOC Emissions	
	(lb/day)	(%)
Process units	10,917	57.3
Storage tanks	1,971	10.3
Wastewater treating	4,621	24.2
Combustion/point (non-tanks)	605	3.2
Other non-process	943	5.0
Total	19,057	100.0

total VOCs are calculated in columns AH and AI. These calculated VOCs are then summed by product code and appear in row 232 (Table 8) as the VOC emission rate for the streams listed in columns C through AF, identified by their respective product codes in row 231. The total emission rate for each chemical species is obtained as the scalar product of the VOC emission rate (row 232) and each of the composition data rows (row 245 and greater), in the same manner illustrated previously for the crude unit.

Threshold quantity subtotals for the TANK spreadsheet are also tabulated by category (designated in row 241) using the stream composition data and an appropriate stream quantity input by the user in row 242. The threshold quantities calculated for this example are shown in Table 9.

Each of the seven worksheet modules can be user-modified to represent any refinery configuration by including only those unit models that exist in the actual refinery. Entering "0" for the "number of units" in cell B6 excludes the emissions and threshold quantities calculated for that unit from the refinery totals. Further specification of source counts and stream composition data for each unit enables the user to tailor the model to represent his own specific refinery. The quantities used of non-hydrocarbon chemicals, such as those that could be used as catalysts or specific treatment chemicals (e.g., acids), are obtained from inventory lists.

The purpose of the SUMMARY module is to accumulate totals for emissions and threshold quantities in a form useful for reporting. Its function and relation to the other modules is shown in Fig. 2. An example of the final page of the SUMMARY module is shown in Table 10. Chemical species that are flagged with an arrow (\leftarrow) have met or exceeded the threshold requirements and are thus subject to reporting.

The SUMMARY module also summarizes emission estimates by unit so that an analysis of the results can be made among units and among different refineries. For example, each unit's contribution to the total plant VOC emis-

sions is summarized and expressed as a percentage. The air emissions for XYZ refinery are summarized in Table 11 and show that over half the VOC emissions occur from fugitive sources on process units in this example. Emissions to air from "Wastewater Treating" operations are also significant.

Improvements and other uses

A default system has been incorporated into the spreadsheet to provide average numbers of sources if actual counts are not available. Inventory lists have been used to derive the actual number of sources for each process unit at each refinery. The actual counts are verified by each refinery, and spare equipment items are distinguished from those in use to more accurately represent the emission sources.

AP-42 factors have been used in most cases; other factors will be evaluated for improving the accuracy of emission estimates. The spreadsheet can easily accommodate different factors by simply changing the values in a single column.

The spreadsheet can be used to evaluate the effects on estimated emissions of more stringent monitoring programs, that is, beyond what is required by state and local regulations. The effects can be assessed on an individual unit basis. For example, the impact of a leak detection and repair program on a crude unit is illustrated in Table 12. The estimated emissions from a unit without an LDRP are shown in the first row. Estimated emissions from the same unit with increasingly more stringent monitoring and repair frequencies are shown in subsequent rows. Obviously, significant reductions in emission estimates can be achieved with the use of a monitoring program. For this hypothetical example, the most stringent program shows a reduction in VOC of over 60% and a reduction in 313 reportable compounds of nearly 75% compared with unit emissions with no monitoring program. The spreadsheet model can also be used to identify those units for which a more stringent monitoring program will have the greatest benefit in reduced emissions.

In 1989, EPA allowed the submission of Form R's by an electronic method

TABLE 12

Effect of LDRP category on estimated emissions from refinery crude unit

LDRP category	Emissions, lbs/day			
	VOCs	(%Red'n)	313 Reportables	(%Red'n)
0	1073	(0)	45.4	(0)
1	736	(31)	28.3	(38)
2	501	(53)	15.2	(67)
3	401	(63)	11.3	(75)

such as a floppy disk or tape. The spreadsheet method was easily modified to generate a facsimile of the Form R, thereby eliminating the need for transferring estimates by hand to a hard copy.

Plans for additional work include further improvement in the precision of the estimation procedures and use of the spreadsheet method as an evaluation tool. Each refinery is tailoring the methods that have been developed to its specific needs. The stream analyses used in the 1988 report (for calendar year 1987) were derived from samples taken at one refinery. Those refineries that process crudes different from those processed at the selected refinery can sample process and product streams to evaluate the effects of stream composition on emission estimates.

Conclusions/recommendations

The spreadsheet model provides a general framework for estimating refinery emissions that can be tailored to individual facilities and yet maintain a high degree of consistency and standardization among users. The spreadsheet model and the Form R facsimile program were developed exclusively for use by Amoco Oil facilities. The bookkeeping features of spreadsheet programming provide access to data and intermediate results (e.g., VOCs, unit subtotals) in a natural format. Because spreadsheets are change-oriented, the model is easily modified to accommodate new data or to predict the effects of new emissions control strategies. We also found that during the course of development, "bugs" in the spreadsheet model were easily and quickly corrected via computer links to all remote locations and using simple spreadsheet LOAD commands. Finally, the spreadsheet format is convenient for analyzing, documenting, and reporting the results.

Based on published or user-developed emission factors, the spreadsheet emissions model provides a convenient, generalized tool that can be tailored quickly and in a consistent manner to specific refinery configurations for estimating and reporting chemical releases under SARA Title III.

References

- 1 *Compilation of Air Pollutant Emission Factors. Volume 1. Stationary Point and Area Sources, 4th edn.*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Washington, DC, September 1985; PB86-124906.
- 2 *Model for Evaluation of Refinery and Synfuels VOC Emission Data Volume 1. Technical Report and Appendix A*, prepared by R.G. Wetherold, G.E. Harris, F.D. Skinner, L.P. Provost. Radian Corp., Austin, TX for U.S. Environment Protection Agency, Air and Energy Eng. Res. Lab., Washington, DC, May 1985, Report PB85-215713.

- 3 Model for Evaluation of Refinery and Synfuels VOC Emission Data. Volume 2. Appendices B and C. Prepared by R.G. Wetherold, F.D. Skinner, G.E. Harris, L.P. Provost. Radian Corp., Austin, TX, for U.S. Environment Protection Agency, Air and Energy Eng. Res. Lab., Washington, DC, May 1985, Report PB85-215721.
- 4 DynaPlan is a proprietary software product developed and licensed by Dynasoft Corp., Rosemont, Illinois.